

OIV-MA-AS1-07 Collaborative study

The purpose of the collaborative study is to give a quantified indication of the precision of method of analysis, expressed as its repeatability r and reproducibility R .

Repeatability: the value below which the absolute difference between two single test results obtained using the same method on identical test material, under the same conditions (same operator, same apparatus, same laboratory and a short period of time) may be expected to lie within a specified probability.

Reproducibility: the value below which the absolute difference between two single test results obtained using the same method on identical test material, under different conditions (different operators, different apparatus and/or different laboratories and/or different time) may be expected to lie within a specified probability.

The term "individual result" is the value obtained when the standardized trial method is applied, once and fully, to a single sample. Unless otherwise stated, the probability is 95%.

General Principles

- The method subjected to trial must be standardized, that is, chosen from the existing methods as the method best suited for subsequent general use.
- The protocol must be clear and precise.
- The number of laboratories participating must be at least ten.
- The samples used in the trials must be taken from homogeneous batches of material.
- The levels of the analyte to be determined must cover the concentrations generally encountered.
- Those taking part must have a good experience of the technique employed.
- For each participant, all analyses must be conducted within the same laboratory by the same analyst.
- The method must be followed as strictly as possible. Any departure from the method described must be documented.
- The experimental values must be determined under strictly identical conditions:

on the same type of apparatus, etc.

- They must be determined independently of each other and immediately after each other.
- The results must be expressed by all laboratories in the same units, to the same number of decimal places.
- Five replicate experimental values must be determined, free from outliers. If an experimental value is an outlier according to the Grubbs test, three additional measurements must be taken.

Statistical Model

The statistical methods set out in this document are given for one level (concentration, sample). If there are a number of levels, the statistical evaluation must be made separately for each. If a linear relationship is found ($y = bx$ or $y = a + bx$) as between the repeatability (r) or reproducibility (R) and the concentration (\bar{x}), a regression of r (or R) may be run as a function of \bar{x} .

The statistical methods given below suppose normally distributed random values.

The steps to be followed are as follows:

A/ Elimination of outliers within a single laboratory by Grubbs test. Outliers are values which depart so far from the other experimental values that these deviations cannot be regarded as random, assuming the causes of such deviations are not known.

B/ Examine whether all laboratories are working to the same precision, by comparing variances by the Bartlett test and Cochran test. Eliminate those laboratories for which statistically deviant values are obtained.

C/ Track down the systematic errors from the remaining laboratories by a variance analysis and by a Dixon test identify the extreme outlier values. Eliminate those laboratories for which the outlier values are significant.

D/ From the remaining figures, calculate standard deviation of repeatability S_r , and repeatability r standard deviation of reproducibility S_R and reproducibility R .

Notation:

The following designations have been chosen:

m Number of laboratories

i ($i = 1, 2, \dots, m$) Index (No. of the laboratory)

n_i Number of individual values from the i th laboratory

$N = \sum_{i=1}^m n_i$ Total number of individual values

x ($i = 1, 2, \dots, n_i$) Individual value of the i th laboratory

$$\bar{x}_i = \frac{1}{n_i} \sum_{i=1}^{n_i} x_i \text{ Mean value of the } i\text{th laboratory}$$

$$\bar{x} = \frac{1}{N} \sum_{i=1}^m \sum_{i=1}^{n_i} x_i \text{ Total mean value}$$

$$s_i = \sqrt{\frac{1}{n_i - 1} \sum_{i=1}^{n_i} (x_i - \bar{x}_i)^2} \text{ Standard deviation of the } i\text{th laboratory}$$

A/ Verification of outlier values within one laborator

After determining five individual values x_i , a Grubbs test is performed at the laboratory, to identify the outliers' values.

Test the null hypothesis whereby the experimental value with the greatest absolute deviation from the mean is not an outlier observation.

Calculate $PG = \frac{|x_i^* - \bar{x}_i|}{s_i}$

x_i^* = suspect value

Compare PG with the corresponding value shown in Table 1 for P = 95%.

If $PG < \text{value as read}$, value x_i^* is not an outlier and s_i can be calculated.

If $PG > \text{value as read}$, value x_i^* probably is an outlier therefore make a further three determinations.

Calculate the Grubbs test for x_j^* with the eight determinations.

If $PG > \text{corresponding value for } P = 99\%$, regard x_i^* as a deviant value and calculate s_i without x_i^* .

B/ Comparison of variances among laboratories

Bartlett Test

The Bartlett test allows us to examine both major and minor variances. It serves to test the null hypothesis of the equality of variances in all laboratories, as against the alternative hypothesis whereby the variances are not equal in the case of some laboratories.

At least five individual values are required per laboratory.

Calculate the statistics of the test:

$$PB = \frac{1}{C} \left[(N - m) \ln S_r^2 - \sum_{i=1}^m f_i \ln S_i^2 \right]$$

$$C = \frac{\sum_{i=1}^m \frac{1}{f_i} - \frac{1}{N-m}}{3(m-1)} + 1$$

$$S_r^2 = \frac{\sum_{i=1}^m f_i S_i^2}{N-m}$$

$f_i = n_i - 1$ degrees of freedom of s_i

Compare PB with the value x^2 indicated in table 2 at $m - 1$ degrees of freedom.

If $PB >$ the value in the table, there are differences among the variances.

The Cochran test is used to confirm that the variance from one laboratory is greater than that from other laboratories.

Calculate the test statistics:

$$PC = \frac{s_i^2 \max}{\sum_{i=1}^m s_i^2}$$

Compare PC with the value shown in table 3 for m and n_i at $P = 99\%$.

If $PC >$ the table value, the variance is significantly greater than the others.

If there is a significant result from the Bartlett or Cochran tests, eliminate the outlier variance and calculate the statistical test again.

In the absence of a statistical method appropriate to a simultaneous test of several outlier values, the repeated application of the tests is permitted, but should be used with caution.

If the laboratories produce variances that differ sharply from each other, an investigation must be made to find the causes and to decide whether the experimental values found by those laboratories are to be eliminated or not. If they are, the coordinator will have to consider how representative the remaining laboratories are.

If statistical analysis shows that there are differing variances, this shows that the laboratories have operated the methods at varying precisions. This may be due to inadequate practice or to lack of clarity or inadequate description in the method.

C/ Systematic errors

Systematic errors made by laboratories are identified using either Fischer's method or Dixon's test.

R.A. Fischer variance analysis

This test is applied to the remaining experimental values from the laboratories with an identical variance.

The test is used to identify whether the spread of the mean values from the laboratories is very much greater than that for the individual values expressed by the variance among the laboratories (s_z^2) or the variance within the laboratories (s_I^2).

Calculate the test statistics :

$$PF = \frac{s_z^2}{s_I^2}$$

$$s_z^2 = \frac{1}{m-1} \sum_{i=1}^m n_i (\bar{x}_i - \bar{x})^2$$

$$s_I^2 = \frac{1}{N-m} \sum_{i=1}^m \sum_{j=1}^{n_i} (x_{ij} - \bar{x}_i)^2$$

Compare PF with the corresponding value shown in table 4 (distribution of F) where $f_1 = f_z = m - 1$ and $f_2 = f_I = N - m$ degrees of freedom.

If $PF >$ the table value, it can be concluded that there are differences among the means, that is, there are systematic errors.

Dixon test

This test enables us to confirm that the mean from one laboratory is greater or smaller than that from the other laboratories.

Take a data series $Z(h)$, $h = 1, 2, 3, \dots, H$, ranged in increasing order.

Calculate the statistics for the test:

| | |
|--|--|
| 3 to 7 $Q_{10} = \frac{Z(2) - Z(1)}{Z(H) - Z(1)}$ | Or $\frac{Z(H) - Z(H-1)}{Z(H) - Z(1)}$ |
| 8 to 12 $Q_{11} = \frac{Z(2) - Z(1)}{Z(H-1) - Z(1)}$ | Or $\frac{Z(H) - Z(H-1)}{Z(H) - Z(2)}$ |
| 13 plus $Q_{22} = \frac{Z(3) - Z(1)}{Z(H-2) - Z(1)}$ | Or $\frac{Z(H) - Z(H-2)}{Z(H) - Z(3)}$ |

Compare the greatest value of Q with the critical values shown in table 5.

If the test statistic is > the table value at P = 95%, the mean in question can be regarded as an outlier.

If there is a significant result in the R A Fischer variance analysis or the Dixon test, eliminate one of the extreme values and calculate the test statistics again with the remaining values. As regards repeated application of the tests, see the explanations in paragraph (B).

If the systematic errors are found, the corresponding experimental values concerned must not be included in subsequent computations; the cause of the systematic error must be investigated.

D/ Calculating repeatability (r) and reproducibility (R).

From the results remaining after elimination of outliers, calculate the standard deviation of repeatability s_r and repeatability r , and the standard deviation of reproducibility s_R and reproducibility R , which are shown as characteristic values of the method of analysis.

$$s_r = \sqrt{\frac{1}{N-m} \sum_{i=1}^m f_i S_i^2} \qquad r = s_r \cdot 2\sqrt{2}$$

$$s_R = \sqrt{\frac{1}{a} [s_z^2 + (a-1)s_f^2]} \qquad R = s_R 2\sqrt{2}$$

$$a = \frac{1}{m-1} \left[(N - \sum_{i=1}^m \frac{n_i^2}{N}) \right]$$

If there is no difference between the means from the laboratories, then there is no difference between s_r and s_R or between r and R . But, if we find differences among the laboratory means, although these may be tolerated for practical considerations, we have to show s_r and s_R and r and R .

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Table 1 - Critical values for the Grubbs test

| | | |
|-------|---------|-------|
| n_i | P = 95% | P 99% |
|-------|---------|-------|

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| | | |
|----|--------------|--------------|
| 3 | 1,155 | 1,155 |
| 4 | 1,481 | |
| 5 | <u>1,715</u> | 1,496 |
| 6 | 1,887 | |
| 7 | 2,020 | 1,764 |
| 8 | 2,126 | |
| 9 | 2,215 | 1,973 |
| 10 | 2,290 | |
| 11 | 2,355 | 2,139 |
| 12 | 2,412 | |
| | | <u>2,274</u> |
| | | 2,387 |
| | | 2,482 |
| | | 2,564 |
| | | 2,636 |

Table 2 - Critical values for the Bartlett test (P = 95%)

| $f(m - 1)$ | X^2 | $f(m - 1)$ | X^2 |
|------------|-------|------------|-------|
|------------|-------|------------|-------|

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| | | | |
|----|-------|-----|-------|
| 1 | 3,84 | 21 | 32,7 |
| | 5,99 | 22 | 33,9 |
| 2 | 7,81 | 23 | 35,2 |
| | 9,49 | 24 | 36,4 |
| 3 | 11,07 | 25 | 37,7 |
| | 12,59 | 26 | 38,9 |
| 4 | 14,07 | 27 | 40,1 |
| | 15,51 | 28 | 41,3 |
| 5 | 16,92 | 29 | 42,6 |
| | 18,31 | 30 | 43,8 |
| 6 | 19,68 | 35 | 49,8 |
| | 21,03 | 40 | 55,8 |
| 7 | 22,36 | 50 | 67,5 |
| | 23,69 | 60 | 79,1 |
| 8 | 25,00 | 70 | 90,5 |
| | 26,30 | 80 | 101,9 |
| 9 | 27,59 | 90 | 113,1 |
| | 28,87 | 100 | 124,3 |
| 10 | 30,14 | | |
| | 31,41 | | |
| 11 | | | |
| 12 | | | |
| 13 | | | |
| 14 | | | |
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Table 3 – Critical values for the Cochran test

| <i>m</i> | $n_i = 2$ | | $n_i = 3$ | | $n_i = 4$ | | $n_i = 5$ | | $n_i = 6$ | |
|----------|-----------|-------|-----------|-------|-----------|-------|-----------|-------|-----------|-------|
| | 99% | 95% | 99% | 95% | 99% | 95% | 99% | 95% | 99% | 95% |
| 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 | 0.445 |
| 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 | 0.246 |
| 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 |

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|----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 25 | 0.413 | 0.334 | 0.278 | 0.228 | 0.222 | 0.185 | 0.190 | 0.160 | 0.170 | 0.144 |
| 26 | 0.402 | 0.325 | 0.270 | 0.221 | 0.215 | 0.179 | 0.184 | 0.155 | 0.164 | 0.140 |
| 27 | 0.391 | 0.316 | 0.262 | 0.215 | 0.209 | 0.173 | 0.179 | 0.150 | 0.159 | 0.135 |
| 28 | 0.382 | 0.308 | 0.255 | 0.209 | 0.202 | 0.168 | 0.173 | 0.146 | 0.154 | 0.131 |
| 29 | 0.372 | 0.300 | 0.248 | 0.203 | 0.196 | 0.164 | 0.168 | 0.142 | 0.150 | 0.127 |
| 30 | 0.363 | 0.293 | 0.241 | 0.198 | 0.191 | 0.159 | 0.164 | 0.138 | 0.145 | 0.124 |
| 31 | 0.355 | 0.286 | 0.235 | 0.193 | 0.186 | 0.155 | 0.159 | 0.134 | 0.141 | 0.120 |
| 32 | 0.347 | 0.280 | 0.229 | 0.188 | 0.181 | 0.151 | 0.155 | 0.131 | 0.138 | 0.117 |
| 33 | 0.339 | 0.273 | 0.224 | 0.184 | 0.177 | 0.147 | 0.151 | 0.127 | 0.134 | 0.114 |
| 34 | 0.332 | 0.267 | 0.218 | 0.179 | 0.172 | 0.144 | 0.147 | 0.124 | 0.131 | 0.111 |
| 35 | 0.325 | 0.262 | 0.213 | 0.175 | 0.168 | 0.140 | 0.144 | 0.121 | 0.127 | 0.108 |
| 36 | 0.318 | 0.256 | 0.208 | 0.172 | 0.165 | 0.137 | 0.140 | 0.119 | 0.124 | 0.106 |
| 37 | 0.312 | 0.251 | 0.204 | 0.168 | 0.161 | 0.134 | 0.137 | 0.116 | 0.121 | 0.103 |
| 38 | 0.306 | 0.246 | 0.200 | 0.164 | 0.157 | 0.131 | 0.134 | 0.113 | 0.119 | 0.101 |
| 39 | 0.300 | 0.242 | 0.196 | 0.161 | 0.154 | 0.129 | 0.131 | 0.111 | 0.116 | 0.099 |
| 40 | 0.294 | 0.237 | 0.192 | 0.158 | 0.151 | 0.126 | 0.128 | 0.108 | 0.114 | 0.097 |

Table 4 – Critical values for the F-Test (P=99%)

| f_1 f_2 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|----------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 1 | 4052 | 4999 | 5403 | 5625 | 5764 | 5859 | 5928 | 5981 | 6023 | 6056 | 6083 | 6106 | 6126 | 6143 | 6157 |
| 2 | 98.5 | 99.0 | 99.2 | 99.3 | 99.3 | 99.3 | 99.4 | 99.4 | 99.4 | 99.4 | 99.4 | 99.4 | 99.4 | 99.4 | 99.4 |
| 3 | 34.1 | 30.8 | 29.4 | 28.7 | 28.2 | 27.9 | 27.7 | 27.5 | 27.3 | 27.2 | 27.1 | 27.1 | 27.0 | 26.9 | 26.9 |
| 4 | 21.2 | 18.0 | 16.7 | 16.0 | 15.5 | 15.2 | 15.0 | 14.8 | 14.7 | 14.5 | 14.5 | 14.4 | 14.3 | 14.2 | 14.2 |
| 5 | 16.3 | 13.3 | 12.1 | 11.4 | 11.0 | 10.7 | 10.5 | 10.3 | 10.2 | 10.1 | 9.96 | 9.89 | 9.82 | 9.77 | 9.72 |
| 6 | 13.7 | 10.9 | 9.78 | 9.15 | 8.75 | 8.47 | 8.26 | 8.10 | 7.98 | 7.87 | 7.79 | 7.72 | 7.66 | 7.60 | 7.56 |
| 7 | 12.2 | 9.55 | 8.45 | 7.85 | 7.46 | 7.19 | 6.99 | 6.84 | 6.72 | 6.62 | 6.54 | 6.47 | 6.41 | 6.36 | 6.31 |

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|----|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 8 | 11.3 | 8.65 | 7.59 | 7.01 | 6.63 | 6.37 | 6.18 | 6.03 | 5.91 | 5.81 | 5.73 | 5.67 | 5.61 | 5.56 | 5.52 |
| 9 | 10.6 | 8.02 | 6.99 | 6.42 | 6.06 | 5.80 | 5.61 | 5.47 | 5.35 | 5.26 | 5.18 | 5.11 | 5.05 | 5.01 | 4.96 |
| 10 | 10.0 | 7.56 | 6.55 | 5.99 | 5.64 | 5.39 | 5.20 | 5.06 | 4.94 | 4.85 | 4.77 | 4.71 | 4.65 | 4.60 | 4.56 |
| 11 | 9.64 | 7.20 | 6.21 | 5.67 | 5.31 | 5.07 | 4.88 | 4.74 | 4.63 | 4.54 | 4.46 | 4.39 | 4.34 | 4.29 | 4.25 |
| 12 | 9.33 | 6.93 | 5.95 | 5.41 | 5.06 | 4.82 | 4.64 | 4.50 | 4.39 | 4.30 | 4.22 | 4.16 | 4.10 | 4.05 | 4.01 |
| 13 | 9.07 | 6.70 | 5.74 | 5.21 | 4.86 | 4.62 | 4.44 | 4.30 | 4.19 | 4.10 | 4.02 | 3.96 | 3.90 | 3.86 | 3.82 |
| 14 | 8.86 | 6.51 | 5.56 | 5.04 | 4.69 | 4.46 | 4.28 | 4.14 | 4.03 | 3.94 | 3.86 | 3.80 | 3.75 | 3.70 | 3.66 |
| 15 | 8.68 | 6.36 | 5.42 | 4.89 | 4.56 | 4.32 | 4.14 | 4.00 | 3.89 | 3.80 | 3.73 | 3.67 | 3.61 | 3.56 | 3.52 |
| 16 | 8.53 | 6.23 | 5.29 | 4.77 | 4.44 | 4.20 | 4.03 | 3.89 | 3.78 | 3.69 | 3.62 | 3.55 | 3.50 | 3.45 | 3.41 |
| 17 | 8.40 | 6.11 | 5.18 | 4.67 | 4.34 | 4.10 | 3.93 | 3.79 | 3.68 | 3.59 | 3.52 | 3.46 | 3.40 | 3.35 | 3.31 |
| 18 | 8.29 | 6.01 | 5.09 | 4.58 | 4.25 | 4.01 | 3.84 | 3.71 | 3.60 | 3.51 | 3.43 | 3.37 | 3.32 | 3.27 | 3.23 |
| 19 | 8.18 | 5.93 | 5.01 | 4.50 | 4.17 | 3.94 | 3.77 | 3.63 | 3.52 | 3.43 | 3.36 | 3.30 | 3.24 | 3.19 | 3.15 |
| 20 | 8.10 | 5.85 | 4.94 | 4.43 | 4.10 | 3.87 | 3.70 | 3.56 | 3.46 | 3.37 | 3.29 | 3.23 | 3.18 | 3.13 | 3.09 |
| 21 | 8.02 | 5.78 | 4.87 | 4.37 | 4.04 | 3.81 | 3.64 | 3.51 | 3.40 | 3.31 | 3.24 | 3.17 | 3.12 | 3.07 | 3.03 |
| 22 | 7.95 | 5.72 | 4.82 | 4.31 | 3.99 | 3.76 | 3.59 | 3.45 | 3.35 | 3.26 | 3.18 | 3.12 | 3.07 | 3.02 | 2.98 |
| 23 | 7.88 | 5.66 | 4.76 | 4.26 | 3.94 | 3.71 | 3.54 | 3.41 | 3.30 | 3.21 | 3.14 | 3.07 | 3.02 | 2.97 | 2.93 |
| 24 | 7.82 | 5.61 | 4.72 | 4.22 | 3.90 | 3.67 | 3.50 | 3.36 | 3.26 | 3.17 | 3.09 | 3.03 | 2.98 | 2.93 | 2.89 |
| 25 | 7.77 | 5.57 | 4.68 | 4.18 | 3.85 | 3.63 | 3.46 | 3.32 | 3.22 | 3.13 | 3.06 | 2.99 | 2.94 | 2.89 | 2.85 |
| 26 | 7.72 | 5.53 | 4.64 | 4.14 | 3.82 | 3.59 | 3.42 | 3.29 | 3.18 | 3.09 | 3.02 | 2.96 | 2.90 | 2.86 | 2.81 |
| 27 | 7.68 | 5.49 | 4.60 | 4.11 | 3.78 | 3.56 | 3.39 | 3.26 | 3.15 | 3.06 | 2.99 | 2.93 | 2.87 | 2.82 | 2.78 |
| 28 | 7.64 | 5.45 | 4.57 | 4.07 | 3.75 | 3.53 | 3.36 | 3.23 | 3.12 | 3.03 | 2.96 | 2.90 | 2.84 | 2.79 | 2.75 |
| 29 | 7.60 | 5.42 | 4.54 | 4.04 | 3.73 | 3.50 | 3.33 | 3.20 | 3.09 | 3.00 | 2.93 | 2.87 | 2.81 | 2.77 | 2.73 |
| 30 | 7.56 | 5.39 | 4.51 | 4.02 | 3.70 | 3.47 | 3.30 | 3.17 | 3.07 | 2.98 | 2.91 | 2.84 | 2.79 | 2.74 | 2.70 |
| 40 | 7.31 | 5.18 | 4.31 | 3.83 | 3.51 | 3.29 | 3.12 | 2.99 | 2.89 | 2.80 | 2.73 | 2.66 | 2.61 | 2.56 | 2.52 |
| 50 | 7.17 | 5.06 | 4.20 | 3.72 | 3.41 | 3.19 | 3.02 | 2.89 | 2.78 | 2.70 | 2.62 | 2.56 | 2.51 | 2.46 | 2.42 |
| 60 | 7.07 | 4.98 | 4.13 | 3.65 | 3.34 | 3.12 | 2.95 | 2.82 | 2.72 | 2.63 | 2.56 | 2.50 | 2.44 | 2.39 | 2.35 |

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| | | | | | | | | | | | | | | | |
|-----|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 70 | 7.01 | 4.92 | 4.07 | 3.60 | 3.29 | 3.07 | 2.91 | 2.78 | 2.67 | 2.59 | 2.51 | 2.45 | 2.40 | 2.35 | 2.31 |
| 80 | 6.96 | 4.88 | 4.04 | 3.56 | 3.25 | 3.04 | 2.87 | 2.74 | 2.64 | 2.55 | 2.48 | 2.42 | 2.36 | 2.31 | 2.27 |
| 90 | 6.92 | 4.85 | 4.01 | 3.53 | 3.23 | 3.01 | 2.84 | 2.72 | 2.61 | 2.52 | 2.45 | 2.39 | 2.33 | 2.29 | 2.24 |
| 100 | 6.89 | 4.82 | 3.98 | 3.51 | 3.21 | 2.99 | 2.82 | 2.69 | 2.59 | 2.50 | 2.43 | 2.37 | 2.31 | 2.27 | 2.22 |
| 200 | 6.75 | 4.71 | 3.88 | 3.41 | 3.11 | 2.89 | 2.73 | 2.60 | 2.50 | 2.41 | 2.34 | 2.27 | 2.22 | 2.17 | 2.13 |
| 500 | 6.69 | 4.65 | 3.82 | 3.36 | 3.05 | 2.84 | 2.68 | 2.55 | 2.44 | 2.36 | 2.29 | 2.22 | 2.17 | 2.12 | 2.07 |
| ∞ | 6.63 | 4.61 | 3.78 | 3.32 | 3.02 | 2.80 | 2.64 | 2.51 | 2.41 | 2.32 | 2.25 | 2.18 | 2.13 | 2.08 | 2.04 |

Table 4 – Critical values for the F-Test (P=99%) [Continued]

| f_1 f_2 | 16 | 17 | 18 | 19 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 100 | 200 | 500 | ∞ |
|----------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 1 | 6169 | 6182 | 6192 | 6201 | 6209 | 6261 | 6287 | 6303 | 6313 | 6320 | 6326 | 6335 | 6350 | 6361 | 6366 |
| 2 | 99.4 | 99.4 | 99.4 | 99.4 | 99.5 | 99.5 | 99.5 | 99.5 | 99.5 | 99.5 | 99.5 | 99.5 | 99.3 | 99.5 | 99.5 |
| 3 | 26.8 | 26.8 | 26.8 | 26.7 | 26.7 | 26.5 | 26.4 | 26.4 | 26.3 | 26.3 | 26.3 | 26.2 | 26.2 | 26.1 | 26.1 |
| 4 | 14.2 | 14.1 | 14.1 | 14.0 | 14.0 | 13.8 | 13.7 | 13.7 | 13.7 | 13.6 | 13.6 | 13.6 | 13.5 | 13.5 | 13.5 |
| 5 | 9.68 | 9.64 | 9.61 | 9.58 | 9.55 | 9.38 | 9.29 | 9.24 | 9.20 | 9.18 | 9.16 | 9.13 | 9.08 | 9.04 | 9.02 |
| 6 | 7.52 | 7.48 | 7.45 | 7.42 | 7.40 | 7.23 | 7.14 | 7.09 | 7.06 | 7.03 | 7.01 | 6.99 | 6.93 | 6.90 | 6.88 |
| 7 | 6.28 | 6.24 | 6.21 | 6.18 | 6.16 | 5.99 | 5.91 | 5.86 | 5.82 | 5.80 | 5.78 | 5.75 | 5.70 | 5.67 | 5.65 |
| 8 | 5.48 | 5.44 | 5.41 | 5.38 | 5.36 | 5.20 | 5.12 | 5.07 | 5.03 | 5.01 | 4.99 | 4.96 | 4.91 | 4.88 | 4.86 |
| 9 | 4.92 | 4.89 | 4.86 | 4.83 | 4.81 | 4.65 | 4.57 | 4.52 | 4.48 | 4.46 | 4.44 | 4.41 | 4.36 | 4.33 | 4.31 |
| 10 | 4.52 | 4.49 | 4.46 | 4.43 | 4.41 | 4.25 | 4.17 | 4.12 | 4.08 | 4.06 | 4.04 | 4.01 | 3.96 | 3.93 | 3.91 |
| 11 | 4.21 | 4.18 | 4.15 | 4.12 | 4.10 | 3.94 | 3.86 | 3.81 | 3.77 | 3.75 | 3.73 | 3.70 | 3.65 | 3.62 | 3.60 |
| 12 | 3.97 | 3.94 | 3.91 | 3.88 | 3.86 | 3.70 | 3.62 | 3.57 | 3.54 | 3.51 | 3.49 | 3.47 | 3.41 | 3.38 | 3.36 |
| 13 | 3.78 | 3.74 | 3.72 | 3.69 | 3.66 | 3.51 | 3.42 | 3.37 | 3.34 | 3.32 | 3.30 | 3.27 | 3.22 | 3.19 | 3.17 |
| 14 | 3.62 | 3.59 | 3.56 | 3.53 | 3.51 | 3.35 | 3.27 | 3.22 | 3.18 | 3.16 | 3.14 | 3.11 | 3.06 | 3.03 | 3.00 |
| 15 | 3.49 | 3.45 | 3.42 | 3.40 | 3.37 | 3.21 | 3.13 | 3.08 | 3.05 | 3.02 | 3.00 | 2.98 | 2.92 | 2.89 | 2.87 |
| 16 | 3.37 | 3.34 | 3.31 | 3.28 | 3.26 | 3.10 | 3.02 | 2.97 | 2.93 | 2.91 | 2.89 | 2.86 | 2.81 | 2.78 | 2.75 |

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| | | | | | | | | | | | | | | | |
|-----|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 17 | 3.27 | 3.24 | 3.21 | 3.19 | 3.16 | 3.00 | 2.92 | 2.87 | 2.83 | 2.81 | 2.79 | 2.76 | 2.71 | 2.68 | 2.65 |
| 18 | 3.19 | 3.16 | 3.13 | 3.10 | 3.08 | 2.92 | 2.84 | 2.78 | 2.75 | 2.72 | 2.70 | 2.68 | 2.62 | 2.59 | 2.57 |
| 19 | 3.12 | 3.08 | 3.05 | 3.03 | 3.00 | 2.84 | 2.76 | 2.71 | 2.67 | 2.65 | 2.63 | 2.60 | 2.55 | 2.51 | 2.49 |
| 20 | 3.05 | 3.02 | 2.99 | 2.96 | 2.94 | 2.78 | 2.69 | 2.64 | 2.61 | 2.58 | 2.56 | 2.54 | 2.48 | 2.44 | 2.42 |
| 21 | 2.99 | 2.96 | 2.93 | 2.90 | 2.88 | 2.72 | 2.64 | 2.58 | 2.55 | 2.52 | 2.50 | 2.48 | 2.42 | 2.38 | 2.36 |
| 22 | 2.94 | 2.91 | 2.88 | 2.85 | 2.83 | 2.67 | 2.58 | 2.53 | 2.50 | 2.47 | 2.45 | 2.42 | 2.36 | 2.33 | 2.31 |
| 23 | 2.89 | 2.86 | 2.83 | 2.80 | 2.78 | 2.62 | 2.54 | 2.48 | 2.45 | 2.42 | 2.40 | 2.37 | 2.32 | 2.28 | 2.26 |
| 24 | 2.85 | 2.82 | 2.79 | 2.76 | 2.74 | 2.58 | 2.49 | 2.44 | 2.40 | 2.38 | 2.36 | 2.33 | 2.27 | 2.24 | 2.21 |
| 25 | 2.81 | 2.78 | 2.75 | 2.72 | 2.70 | 2.54 | 2.45 | 2.40 | 2.36 | 2.34 | 2.32 | 2.29 | 2.23 | 2.19 | 2.17 |
| 26 | 2.78 | 2.75 | 2.72 | 2.69 | 2.66 | 2.50 | 2.42 | 2.36 | 2.33 | 2.30 | 2.28 | 2.25 | 2.19 | 2.16 | 2.13 |
| 27 | 2.75 | 2.71 | 2.68 | 2.66 | 2.63 | 2.47 | 2.38 | 2.33 | 2.29 | 2.27 | 2.25 | 2.22 | 2.16 | 2.12 | 2.10 |
| 28 | 2.72 | 2.68 | 2.65 | 2.63 | 2.60 | 2.44 | 2.35 | 2.30 | 2.26 | 2.24 | 2.22 | 2.19 | 2.13 | 2.09 | 2.06 |
| 29 | 2.69 | 2.66 | 2.63 | 2.60 | 2.57 | 2.41 | 2.33 | 2.27 | 2.23 | 2.21 | 2.19 | 2.16 | 2.10 | 2.06 | 2.03 |
| 30 | 2.66 | 2.63 | 2.60 | 2.57 | 2.55 | 2.39 | 2.30 | 2.25 | 2.21 | 2.18 | 2.16 | 2.13 | 2.07 | 2.03 | 2.01 |
| 40 | 2.48 | 2.45 | 2.42 | 2.39 | 2.37 | 2.20 | 2.11 | 2.06 | 2.02 | 1.99 | 1.97 | 1.94 | 1.87 | 1.85 | 1.80 |
| 50 | 2.38 | 2.35 | 2.32 | 2.29 | 2.27 | 2.10 | 2.01 | 1.95 | 1.91 | 1.88 | 1.86 | 1.82 | 1.76 | 1.71 | 1.68 |
| 60 | 2.31 | 2.28 | 2.25 | 2.22 | 2.20 | 2.03 | 1.94 | 1.88 | 1.84 | 1.81 | 1.78 | 1.75 | 1.68 | 1.63 | 1.60 |
| 70 | 2.27 | 2.23 | 2.20 | 2.18 | 2.15 | 1.98 | 1.89 | 1.83 | 1.78 | 1.75 | 1.73 | 1.70 | 1.62 | 1.57 | 1.54 |
| 80 | 2.23 | 2.20 | 2.17 | 2.14 | 2.12 | 1.94 | 1.85 | 1.79 | 1.75 | 1.71 | 1.69 | 1.65 | 1.58 | 1.53 | 1.49 |
| 90 | 2.21 | 2.17 | 2.14 | 2.11 | 2.09 | 1.92 | 1.82 | 1.76 | 1.72 | 1.68 | 1.66 | 1.62 | 1.55 | 1.50 | 1.46 |
| 100 | 2.19 | 2.15 | 2.12 | 2.09 | 2.07 | 1.89 | 1.80 | 1.74 | 1.69 | 1.66 | 1.63 | 1.60 | 1.52 | 1.47 | 1.43 |
| 200 | 2.09 | 2.06 | 2.03 | 2.00 | 1.97 | 1.79 | 1.69 | 1.63 | 1.58 | 1.55 | 1.52 | 1.48 | 1.39 | 1.33 | 1.28 |
| 500 | 2.04 | 2.00 | 1.97 | 1.94 | 1.92 | 1.74 | 1.63 | 1.56 | 1.52 | 1.48 | 1.45 | 1.41 | 1.31 | 1.23 | 1.16 |
| ∞ | 2.00 | 1.97 | 1.93 | 1.90 | 1.88 | 1.70 | 1.59 | 1.52 | 1.47 | 1.43 | 1.40 | 1.36 | 1.25 | 1.15 | 1.00 |

Table 5 – Critical values for the Dixon test

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| Test criteria | Critical values | | |
|--|-----------------|-------|-------|
| | <i>m</i> | 95% | 99% |
| $Q_{10} \frac{Z(2) - Z(1)}{Z(H) - Z(H-1)}$ $\frac{Z(H) - Z(1)}{Z(H) - Z(1)}$ The greater of the two values | 3 | 0,970 | 0,994 |
| | 4 | 0,829 | 0,926 |
| | 5 | 0,710 | 0,821 |
| | 6 | 0,628 | 0,740 |
| | 7 | 0,569 | 0,680 |
| | 8 | 0,608 | 0,717 |
| | 9 | 0,564 | 0,672 |
| $Q_{11} \frac{Z(2) - Z(1)}{Z(H) - Z(H-1)}$ $\frac{Z(H-1) - Z(1)}{Z(H) - Z(2)}$ The greater of the two values | 10 | 0,530 | 0,635 |
| | 11 | 0,502 | 0,605 |
| | 12 | 0,479 | 0,579 |
| | 13 | 0,611 | 0,697 |
| $Q_{22} \frac{Z(3) - Z(1)}{Z(H) - Z(H-2)}$ $\frac{Z(H-2) - Z(1)}{Z(H) - Z(3)}$ The greater of the two values | 14 | 0,586 | 0,670 |
| | 15 | 0,565 | 0,647 |
| | 16 | 0,546 | 0,627 |
| | 17 | 0,529 | 0,610 |
| | 18 | 0,514 | 0,594 |
| | 19 | 0,501 | 0,580 |
| | 20 | 0,489 | 0,567 |
| | 21 | 0,478 | 0,555 |
| | 22 | 0,468 | 0,544 |
| | 23 | 0,459 | 0,535 |

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| | | | |
|--|----|-------|-------|
| | 24 | 0,451 | 0,526 |
| | 25 | 0,443 | 0,517 |
| | 26 | 0,436 | 0,510 |
| | 27 | 0,429 | 0,502 |
| | 28 | 0,423 | 0,495 |
| | 29 | 0,417 | 0,489 |
| | 30 | 0,412 | 0,483 |
| | 31 | 0,407 | 0,477 |
| | 32 | 0,402 | 0,472 |
| | 33 | 0,397 | 0,467 |
| | 34 | 0,393 | 0,462 |
| | 35 | 0,388 | 0,458 |
| | 36 | 0,384 | 0,454 |
| | 37 | 0,381 | 0,450 |
| | 38 | 0,377 | 0,446 |
| | 39 | 0,374 | 0,442 |
| | 40 | 0,371 | 0,438 |

Table 6 – Results of the collaborative study

| Analysis | | | | | | | | | Sample | | | | |
|-----------|-------------------------|-----|-----|------|-----|-----|-----|-----|--------|-------------|-------|---------|-----------|
| Lab n° | Individual values x_i | | | | | | | | n_1 | \bar{x}_1 | s_1 | s_1^2 | |
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | | | | | |
| 1 | 548 | 556 | 558 | 553 | 542 | | | | 5 | 551 | 6,47 | 41,8 | |
| 2 | 300 | 299 | 304 | 308 | 300 | | | | 5 | 302 | 3,83 | 14,7 | $x_1 < x$ |
| 3 | 567 | 558 | 563 | 532* | 560 | 560 | 563 | 567 | 7 | 563 | 3,51 | 12,3 | |

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| | | | | | | | | | | | | | |
|----|-----|-----|-----|-----|-----|-----|-----|-----|---|-----|-------|-------|-------------|
| 4 | 557 | 550 | 555 | 560 | 551 | | | | 5 | 555 | 4,16 | 17,3 | |
| 5 | 569 | 575 | 565 | 560 | 572 | | | | 5 | 568 | 5,89 | 34,7 | |
| 6 | 550 | 546 | 549 | 557 | 588 | 570 | 576 | 568 | 8 | 563 | 14,92 | 222,6 | $s_1 > s_1$ |
| 7 | 557 | 560 | 560 | 552 | 547 | | | | 5 | 555 | 5,63 | 31,7 | |
| 8 | 548 | 543 | 560 | 551 | 548 | | | | 5 | 550 | 6,28 | 39,5 | |
| 9 | 558 | 563 | 551 | 555 | 560 | | | | 5 | 556 | 5,63 | 31,7 | |
| 10 | 554 | 559 | 551 | 545 | 557 | | | | 5 | 553 | 5,5 | 30,2 | |

Statistical Figures:

Bartlett Test:

Within laboratory: $s_1 = \pm 5.37$ $f_{i=34}$

PB = 3.16 < 15.51 (95%; $f = 8$)

Between laboratory: $s_z = \pm 13.97$ $f_z = 7$

Analysis of variance:

$s_r = \pm 5.37$

$r = 15$

$s_R = \pm 7.78$

$R = 22$

PF = 6.76 > 3.21 (99%; $f_1 = 7$; $f_2 = 34$)