

### **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  $Sr$ , and repeatability  $r$  standard deviation of reproducibility  $SR$  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  $PG <$  value as read, value  $x_i^*$  is not an outlier and  $s_i$  can be calculated.

If  $PG >$  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  $PG >$  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.

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

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

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

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  $R$ .

**Bibliography**

- AFNOR, norme NFX06041, *Fidélité des méthodes d'essai. Détermination de la répétabilité et de la reproductibilité par essais interlaboratoires.*
- DAVIES O. L., GOLDSMITH P.L., *Statistical Methods in Research and Production*, Oliver and Boyd, Edinburgh, 1972.
- GOETSCH F. H., KRÖNERT W., OLSCHIMKE D., OTTO U., VIERKÖTTER S., *Meth. An.*, 1978, No 667.

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- GOTTSCHALK G., KAISER K. E., *Einführung in die Varianzanalyse und Ringversuche*, B-1 Hoschultaschenbücher, Band 775, 1976.
- GRAF, HENNING, WILRICH, *Statistische Methoden bei textilen Untersuchungen*, Springer Verlag, Berlin, Heidelberg, New York, 1974.
- GRUBBS F. E., *Sample Criteria for Testing Outlying Observations*, The Annals of Mathematical Statistics, 1950, vol. 21, p 27-58.
- GRUBBS F. E., *Procedures for Detecting Outlying Observations in Samples*, Technometrics, 1969, vol. 11, No 1, p 1-21.
- GRUBBS F. E. and BECK G., *Extension of Sample Sizes and Percentage Points for Significance Tests of Outlying Observations*, Technometrics, 1972, vol. 14, No 4, p 847-854.
- ISO, norme 5725.
- KAISER R., GOTTSCHALK G., *Elementare Tests zur Beurteilung von Messdaten*, B-I Hochschultaschenbücher, Band 774, 1972.
- LIENERT G. A., *Verteilungsfreie Verfahren in der Biostatistik*, Band I, Verlag Anton Hain, Meisenheim am Glan, 1973.
- NALIMOV V. V., *The Application of Mathematical Statistics to Chemical Analysis*, Pergamon Press, Oxford, London, Paris, Frankfurt, 1963.
- SACHS L., *Statistische Auswertungsmethoden*, Springer Verlag, Berlin, Heidelberg, New York, 1968

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

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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		
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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%;  $f_1 = 7$ ;  $f_2 = 34$ )