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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Chemical analysis of light metals and their alloys — Statistical interpretation of inter-laboratory trials

Analyse chimique des métaux et des alliages légers — Interprétation statistique des circuits interlaboratoires

Technical Report 7242 was drawn up by Technical Committee ISO/TC 79, *Light metals and their alloys*, and has been approved by the majority of its members.

Sub-committee ISO/TC 79/SC 1 considered it preferable to publish this document in the form of a Technical Report, as its purpose is to provide information which could not be considered as a suitable subject for standardization but which is useful for users of standards confronted with the complex problems encountered during statistical studies resulting from round-robin, comparative analytical trials.

0 Introduction

The purpose of inter-laboratory trials is to compare the results obtained in terms of two parameters : the methods and the laboratories.

The following combinations can therefore be considered :

— a method tested by several laboratories;

— several methods tested within one laboratory;

— two or more methods tested by several laboratories.

As an example, see tables 1, 2 and 3 relating to the determination of chromium.

Whichever combination is selected for the trial, interpretation of the results seeks to establish whether the recorded numerical differences are mainly due to the influence of the parameter studied (laboratory, method) or whether they can be explained by the dispersion observed between individual results (repeatability or experimental error). In all cases, the results of the statistical examination should be interpreted from an analytical viewpoint. The repeatability of a method can be sufficiently good for the small inter-laboratory differences to be significant from the statistical point of view, although they can be considered negligible in practice. Conversely, poor repeatability does not imply that differences considered important by the user are significant.

Statistical interpretation, even when using very sophisticated calculation methods, has never corrected the failures of a method, nor has it improved the results from a laboratory.

It is a tool leading very often to conclusions, the essential merit of which is objectivity.

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1 Scope and field of application

This Technical Report constitutes an attempt to explain the numerical results of a statistical examination in the simplest possible way and to show how statistical results can be used in laboratory practice.

This simplified method is applicable when the number of laboratories is not more than 20 and when the number of results per laboratory is not more than 10.

2 Symbols

$\bar{x}_n$: arithmetic mean of n results;

S_n : estimated standard deviation of n results;

$S_{\bar{x}_n}$: estimated standard deviation of the mean of n results : $S_n/\sqrt{n}$;

$S_n/\bar{x}_n$: relative standard deviation or coefficient of variation, as a percentage.

NOTE — To add or subtract two standard deviations, determine the sum or difference of their squares and take the square root.

3 Example of interpretation of statistical parameters — Determination of chromium

Results of an inter-laboratory trial of two methods, A and B, for the determination of chromium are given. It is not intended to give a complete interpretation of the results, but to show the possibilities of interpretation from the parameters established.

Individual results are given in tables 1 and 2.

The statistical parameters relating to the comparison of both methods are given in table 3. These parameters can be explained, or at least translated into, more practical formulae without requiring recourse to basic statistical documents. Reference may be made to a standardized method of calculating these parameters.

Table 4 summarizes explanations relative to the parameters given in table 3.

Table 1 — Photometric determination of chromium — Method A — Results

ISO *n*	IT A	IT B	IT C	IT D	IT E	GB B	GB E	GB F	GB N	ES A	ES B	ES C	HU	US A	US B	US C	US D	DE A	DE B
	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %
10 = 0,	151	151	157	159	161	170	156	158	142	140	150		16(0)	156	17(0)			134	130
	153	153	161	163	153	170	154	160	142	150	150		17(0)	156	15(0)			137	130
	153	154	158	162	161	170	156	159	156	150			17(0)	159	14(0)			137	138
	151	151	159	158	158	168	157	160	154	160			16(0)	159				131	132
	153	151	158	159	158	169	155	160	156	150			16(0)	158				131	136
													16(0)						
13 = 0,	340	344	347	360	371	36(0)	348	362	336	330	345		35(0)					325	324
	338	342	350	362	357	36(0)	348	358	340	340	350		36(0)					315	327
	340	346	341	362	359	36(0)	349	353	334	350			36(0)					338	337
	336	344	352	359	364	37(0)	349	360	340	340			37(0)					339	318
	337	346	345	363	357	36(0)	350	365	352	350			35(0)					337	322
													36(0)						
15 = 0,0	161	160	142	170	179	20(0)	170	18(0)	169	145	14(0)	140	15(0)	16(0)	16(0)	17(0)		167	171
	165	163	138	173	179	18(0)	172	19(0)	166	145	14(0)	145	14(0)	16(0)	16(0)	16(0)		168	158
	163	163	138	171	171	19(0)	174	18(0)	169	15(0)		145	15(0)	16(0)	14(0)	16(0)		155	158
	165	163	140	168	176	19(0)	176	16(0)	166	16(0)		140	15(0)	16(0)	12(0)	16(0)		164	167
	161	161	142	174	181	19(0)	178	17(0)	171	15(0)		150	14(0)	17(0)	15(0)			158	165
													16(0)	17(0)	15(0)				
25 = 0,0			31	31	31	30	36	32	42	29	30			33	28	34	4(0)		27
			30	31	31	31	36	34	38	29	30			33	31	34	4(0)		25
			30	31	30	31	35	30	45	30	31			33	30	35	4(0)		27
			31	32	30	31	36	33	40	30	31			33	32	34	3(0)		27
			31	33	30	32	34	28	36	32	32			33	29	33			30
																34			

Table 2 — Photometric determination of chromium — Method B — Results

ISO *n*	IT	IT	IT	ES	US	US	DE	GB	GB	GB	GB	HU	DE	ES
	A	B	C		A	B		F	M	B	E			
	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %
10	0,154	0,172	0,158		0,163	0,163	0,162	0,160	0,156			0,170	0,165	0,162
	0,155	0,172	0,157		0,161	0,163	0,163	0,158	0,158			0,170	0,168	0,165
	0,155	0,171	0,160		0,162	0,164	0,161	0,158	0,158			0,170	0,166	0,167
	0,155	0,172	0,157		0,165	0,163	0,160	0,161	0,161			0,170	0,161	0,167
	0,156	—	0,158		0,164	0,163	0,163	0,160	0,158			0,170	0,160	0,167
13	0,349	0,364	0,360	0,350	0,357	0,362	0,360	0,370				0,368	0,340	0,365
	0,348	0,363	0,360	0,340	0,363	0,359	0,358	0,350				0,367	0,340	0,365
	0,346	0,363	0,364	0,340	0,361	0,360	0,352	0,350				0,367	0,370	0,365
	0,353	0,361	0,370	0,350	0,364	0,359	0,363	0,360				0,370	0,365	0,370
	0,353	—	0,370	—	0,366	0,360	0,362	0,360				0,370	0,370	0,372
15	0,017 4	0,017 7	0,015 5	0,016 0	0,017 8	0,017 0	0,017 3		0,018 0	0,017 0		0,018 0	0,017 3	0,017 0
	0,017 3	0,017 6	0,016 5	0,016 0	0,018 2	0,017 0	0,016 8		0,018 3	0,017 0		0,018 0	0,017 3	0,017 5
	0,017 0	0,017 5	0,017 0	0,015 5	0,017 8	0,016 3	0,017 0		0,018 0	0,017 0		0,018 0	0,017 3	0,018 0
	0,017 1	0,017 3	0,017 5	—	0,018 5	0,017 1	0,017 4		0,018 3	0,017 0		0,018 0	0,018 0	0,018 0
	0,017 4	—	0,017 5	—	0,017 4	0,016 8	0,017 0		0,018 0	0,017 0		0,018 0	0,017 8	0,018 2
25	0,003 1	0,002 8	0,003 5	0,003 1	0,003 2	0,002 9	0,003 3				0,003 0	0,003 4	0,003 5	0,002 8
	0,003 1	0,002 8	0,003 5	0,003 1	0,003 0	0,002 8	0,003 5				0,003 0	0,003 4	0,003 5	0,002 7
	0,003 1	0,002 6	0,003 0	0,003 1	0,003 5	0,002 8	0,003 3				0,003 0	0,003 3	0,003 3	0,002 7
	0,003 1	0,002 9	0,003 5	0,003 1	0,003 2	0,002 7	0,003 4				0,003 0	0,003 4	0,003 3	0,003 0
	0,003 1	—	0,003 5	—	0,003 7	0,002 8	0,003 2				0,003 0	0,003 4	0,003 5	0,003 0

Table 3 — Statistical parameters — Comparison of methods A and B

Sample	ISO 10		ISO 13		ISO 15		ISO 25	
	R 2298	440	R 2298	440	R 2298	440	R 2298	440
N Number of observations	77	54	68	53	89	57	70	53
K Number of laboratories	16	11	14	11	18	12	14	11
$\bar{x}$ Arithmetic mean	0,153 89	0,162 5	0,347 83	0,359 7	0,016 17	0,017 17	0,003 231	0,003 141
Standard deviation								
S_w (within laboratories)	0,004 45	0,001 614	0,005 83	0,006 340	0,000 205 9	0,000 368	0,000 185	0,000 136
S_b (between laboratories)	0,009 44	0,004 916	0,011 73	0,006 249	0,001 335	0,000 573	0,000 325	0,000 244
S_t (total)	0,0104 5	0,005 174	0,013 1	0,008 902	0,001 485	0,000 680	0,000 374	0,000 280
S_n (one pool)	0,010 15	0,004 998	0,012 78	0,008 737	0,001 457	0,000 664	0,000 365	0,000 271
Confidence level 99 %								
$S_t \cdot tN-1$ ±	0,027 69	0,013 84	0,034 8	0,023 84	0,003 93	0,001 81	0,000 992	0,000 749
$S_t \cdot tK-1$ ±	0,030 80	0,016 40	0,039 5	0,028 21	0,004 30	0,002 11	0,001 126	0,000 887
Confidence level 95 %								
$S_t \cdot tN-1$ ±	0,020 85	0,010 38	0,026 2	0,017 88	0,002 96	0,001 36	0,000 747	0,000 562
$S_t \cdot tK-1$ ±	0,022 27	0,011 53	0,028 3	0,019 83	0,003 13	0,001 50	0,000 808	0,000 624

Table 4 — Explanation of the statistical parameters figuring in table 3

Parameter	Significance	Use
S_w	Estimate of the dispersion within laboratories (i.e. the repeatability).	Basic term for evaluation of "laboratory effects" and "method effects".
S_b	Estimate of the effect of the factor studied (laboratory or method). Prior to this estimation, the observed dispersion between means has to be calculated, from which the contribution of S_w to the observed dispersion has to be subtracted. It is independent of the number of measurements carried out in each laboratory.	If it has a significant value, it is important in the estimation of the two parameters [(S_t and $S_{t\alpha}\,(K-1)$].
S_t	Only has meaning if S_b is significant. It estimates the reproducibility related to a single measurement in one laboratory $S_t^2 = S_b^2 + S_w^2$	Very often, it is not physically different from S_b. Practically it does not decrease when the number of determinations n increases.
S_n (S_N would be more logical)	Estimate of the standard deviation of N measurements. Only has meaning if S_b is not significant and then is not significantly different from S_w which has already been computed.	S_w is more often used in this case.
$S_t \cdot t_\alpha\,(N-1)$ α = risk $N-1$ = number of degrees of freedom	Confidence interval of the true value (at risk α) when S_b is not significant and when only a single determination has been made. $S_N \cdot t_\alpha\,(N-1)$ would be more logical.	Confidence interval of a single determination. $(N-1)$ is sufficiently high that $t = 2{,}0$ when $\alpha = 0{,}05$.
$S_t \cdot t_\alpha\,(K-1)$ α = risk $K-1$ = number of degrees of freedom	Confidence interval of the true value (at risk α) when S_b is significant and only a single determination has been made.	Provides a confidence interval to be used in practice, and to compare data; t is given by Student's table and is a function of $(K-1)$.

3.1 Such inter-laboratory trials enable objective answers to be given to a number of questions which may be raised by analysts, among which are :

a) Can it be considered that, for a given method, all laboratories have supplied the same result?

b) Are the average results for each method the same?

c) When these questions have been answered, which confidence interval should be allocated to a result? Can this interval be improved by repeating the determination?

3.2 **Effect of factor studied** (laboratory effect)

To try to give an objective answer to the questions posed in 3.1, the statistical method relies on the following principle : comparison of the dispersion of the mean results characterizing the factor studied with the experimental dispersion observed within the series of results.

3.2.1 If the dispersion ratio is not sufficiently high, i.e. if it does not exceed a determined threshold given in a table[1], it cannot be said that an additional dispersion has been introduced by the factor studied.

3.2.2 Conversely, if the dispersion ratio exceeds the determined threshold for the selected risk (significance level), the experimental dispersion may be estimated from the observed dispersion of the mean values, and this can be subtracted in order to evaluate the specific effect of the factor studied.

3.2.3 Referring to table 3, — sample ISO 13 — column A (case of a method used by several laboratories) :

S_w is the standard deviation allowing characterization of the dispersion within laboratories; it is the common experimental standard deviation[2] : it is 58 ppm for an average content of 3 480 ppm, i.e. 1,7 % as a relative value.

Each of the means of five values obtained by a laboratory for this sample will have an experimental dispersion characterized by a standard deviation of :

$$\frac{58}{\sqrt{5}} = 26 \text{ ppm}$$

But the standard deviation characterizing the observed dispersion of mean values is 123 ppm (this does not appear in table 3).

The ratio of the two dispersions is $\left(\frac{123}{26}\right)^2 = 22$, which is greater than the threshold given in the Snedecor table, at a risk $\alpha = 0{,}05$ and for the appropriate number of degrees of freedom.

3.2.4 It can therefore be stated, at the risk selected, that the results differ from one laboratory to another with respect to the experimental dispersion. A laboratory effect can be observed. This effect is characterized in table 3 by S_b, such that :

$$S_b^2 = S^2_{\text{observed between means}} - \frac{S_w^2}{5}$$

The mean of n results obtained subsequently by one single laboratory is characterized by a standard deviation $S_{t_{(n)}}$ (called the standard deviation of the reproducibility) such that :

$$S^2_{t_{(n)}} = S_b^2 + \frac{S_w^2}{n}$$

If S_b is proportionately larger than S_w, as is very often the case, it is useless to repeat measurements several times in order to improve the accuracy. S_t is never less than S_b.

NOTE — It should be noted that $S^2_{\text{observed between means}}$ equals $S^2_{t_{(n)}}$ when $n = 5$.

1) Snedecor table.

2) To be exact, a preliminary homogeneity test should be applied to the dispersion within laboratories.

3.2.5 In the case where statistical testing does not allow the affirmation that the observed mean dispersion is significantly greater than the experimental dispersion, the laboratory effect cannot be calculated, and the dispersion affecting a subsequent result has to be estimated from S_n which is not significantly different from S_w.

It is in fact considered that all individual results belong to one same population, the dispersion of which is due only to experimental error. The dispersion should then decrease with an increasing number of determinations.

3.3 Confidence intervals of results

Two confidence limits are thus obtained according to whether there is a laboratory effect or not.

For a selected level α, the following cases can be considered.

3.3.1 Case where there is no laboratory effect

The term $S_t\ [t_{\alpha,\ (N-1)}]$[1] in table 3 represents the confidence interval affecting one single result obtained by one laboratory (S_t is not significantly different from S_n or S_w; these are three different estimates of the same dispersion). This interval decreases in the proportion $1/\sqrt{n}$ in the case of n determinations. In the example, this limit cannot be used because a laboratory effect exists.

3.3.2 Case where there is evidence of a laboratory effect

The term $S_t\ [t_{\alpha,\ (k-1)}]$ of table 3 represents the confidence interval affecting one single result obtained by one laboratory; this interval decreases in the case of n repetitions according to the formula

$$S_t^2 = S_b^2 + \frac{S_w^2}{n}$$

In the example, this interval is practically independent of n since S_b (laboratory effect) is large with respect to S_w.

In the preceding formulae

t_α is the Student-Fischer variable;

$k-1$ is the number of degrees of freedom of S_t when S_b is significant.

3.4 There is a standardized method for calculating all the parameters mentioned and used in table 3. This method is rather time consuming and requires experience.

An extremely simplified method, requiring only elementary calculations but which leads to the same conclusions as the so-called "orthodox" method, is proposed.

This rapid method is applicable when the number of laboratories does not exceed 20 and when the number of results per laboratory does not exceed 10.

Three statistical tables have been established for this purpose; from one single parameter, called the range[1], they allow ascertainment :

— that the population is suitable for such tests (previous checking tests),

— of whether there is a laboratory effect,

— of the magnitude of such an effect, if any,

— of the confidence interval which characterizes a result or the mean of n results.

The procedure and tables are given later.

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1) The formula given in table 3 is not clear. The letter t in S_t means "total"; the second usage is the t Student-Fischer variable which should be followed by the sign α; $(N-1)$ is the number of degrees of freedom of S_t in this case.

1) The range of a series of measurements is the difference between the highest and the lowest results in the series.

4 Examples of rapid interpretation of the results of inter-laboratory trials

All laboratories should have supplied the same number of individual results, each to a given number of significant figures.

The method is valid for k laboratories ($k \leqslant 20$), each supplying n results ($n \leqslant 10$).

The procedure is given below; an example of application of the method using the results in table 1 is given in table 5.

4.1 Applicability of a statistical examination to the whole range of results

4.1.1 Examination of mean values — aberrant laboratories (extreme values) : see table 7 in the annex. The Dixon test allows elimination of a laboratory giving results which are "too high" or "too low".

4.1.2 Homogeneity of experimental internal dispersions; see table 8 in the annex.

Calculation of ranges : w_o for each laboratory. Test to be used : $w_{o\,max.}/\Sigma w_o$.

4.2 Estimation of the common experimental dispersion : (see table 9 in the annex)

Mean range $\overline{w}_o$ divided by an appropriate coefficient $C_{n,\,k}$. Table 9 gives the number of degrees of freedom v' characterizing the standard deviation

$$\overline{w}_o / C_{n,\,k} = S_w.$$

4.3 Existence of a laboratory effect

It is necessary to determine whether the dispersion of the means supplied by the laboratories are significantly larger than those which could be explained by the experimental dispersion (S_w).

Let $w_{\bar{x}}$ be the range of mean values $\bar{x}$ (i.e. the difference between the highest and the lowest mean values).

Test :

Compare the equation $q'_{calculated} = w_{\bar{x}}/\overline{w}_o$ with the value of $q'_{theoretical}$ given in table 10 (at the risk chosen)

k = number of laboratories;

n = number of measurements in each laboratory.

4.3.1 If $q'_{calculated} < q'_{theoretical}$, there is no laboratory effect. The uncertainty is characterized by S_w and decreases at the rate $1/\sqrt{n}$. The confidence interval of one result obtained in one laboratory is thus subject to an interval of $\pm\ 2\ S_w$; if there were four determinations, this interval will be $\pm\ 2\ S_w/2$.

4.3.2 If $q'_{calculated} > q'_{theoretical}$, at a risk of error α, a laboratory effect exists and the observed numerical dispersions are not due only to the experimental dispersion.

4.3.2.1 It is therefore necessary to calculate the standard deviation which characterizes the observed dispersion of the means :

$$w_{\bar{x}}/C_k = S_{\bar{x}}$$

(C_k is given in table 11 in the annex.)

4.3.2.2 The laboratory effect S_b is such that :

$$S_b^2 = S_{\bar{x}}^2 - \frac{S_w^2}{n}$$

This effect is independent of the number of measurements performed in each laboratory.

4.3.2.3 The confidence interval of the results obtained by a laboratory having made n measurements may be obtained from the standard deviation of reproducibility S_R :

— if $n = 1$, $S_R^2 = S_b^2 + S_w^2$

— if $n = 4$, $S_R^2 = S_b^2 + S_w^2/4$

— if $n = 9$, $S_R^2 = S_b^2 + S_w^2/9$

For a confidence interval of 95 %, the value 2 S_R is generally taken to characterize the results obtained by a laboratory and 2,8 S_R for the smallest significant difference between two values (2,8 = 2 × $\sqrt{2}$).

This is true when the number of laboratories is high, but if $4 < k < 20$, tS_R is used instead of 2 S_R, the values of t being given in the Student-Fischer table for the appropriate number of degrees of freedom.

Values of t at the 95 % confidence level are given in table 11 in the annex.

5 Photometric determination of chromium — Method A

Table 5 — Rapid analysis of dispersion : example 1 (sample ISO 13)

ISO 13	IT	IT	IT	IT	IT	GB	GB	GB	GB	ES	ES	HU	DE	DE
	A	B	C	D	E	B	E	F	N	A	B	—	A	B
	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %	Cr %
	10^{-3}													
	340	344	347	360	371	36(0)	348	362	336	330	345	35(0)	325	324
$n = 5$	338	342	350	362	357	36(0)	348	358	340	340	350	36(0)	315	327
	340	346	341	362	359	36(0)	349	353	334	350		36(0)	338	337
$k = 13$	336	344	352	359	364	37(0)	349	360	340	340		37(0)	339	318
	337	346	345	363	357	36(0)	350	365	352	350		35(0)	337	322
$\overline{x}_5$	338	344	347	361	**362**	**362**	349	359	340	342		358	331	**326**
w_5	4	4	11	4	14	10	2	12	18	20		20	24	19

5.1 Homogeneity tests

5.1.1 There is no obviously aberrant mean value. In case of doubt, the Dixon test can be applied (see table 7 in the annex).

5.1.2 Examination for homogeneity of dispersions within laboratories :

$w_{max.}/\Sigma w_o = 24/162 = 0,15$

Table 8 (see the annex) gives 0,162.

It may be concluded, therefore, that there is a common standard deviation, which can be used to characterize the experimental dispersions inside the laboratories.

5.2 Examination for a laboratory effect

5.2.1 Estimation of the experimental standard deviation common to all laboratories :

$S_{w_o} = \overline{w}_o/C_{(n,\,k)}$ with $n = 5$; $k = 13$

$\overline{w}_o = \Sigma w_o/13 = 162/13 = 12,5$

Table 9 gives $C_{(5,13)} = 2,33$ with 58,5 degrees of freedom :

$S_{w_o} = 12,5/2,33 = 5,35$ (the standard method gives 5,8).

5.2.2 Test for significance (see table 10 in the annex)

Dispersion observed on mean values : difference between greatest and least mean values :

$w_{\bar{x}} = 362 - 326 = 36$; $\overline{w}_o = 12{,}5$

$q'_{\text{calculated}} = 36/12{,}5 = 2{,}88$ (highly significant).

(Table 10 of the annex gives $q'_{\text{theoretical}} = 1{,}11$ for $\alpha = 0{,}01$; $k = 13$; $n = 5$.)

Standard deviation of means :

$S_{\bar{x}} = w_{\bar{x}}/C_k$; $k = 13$; $C = 3{,}3$ (see table 11 of the annex)

$S_{\bar{x}} = 36/3{,}3 = 10{,}9$

5.2.3 Standard deviation characterizing the laboratory effect

$$S_b = \sqrt{S_{\bar{x}}^2 - \frac{S_w^2}{5}}$$

$$S_b = \sqrt{(10{,}9)^2 - \frac{(5{,}35)^2}{5}} = 10{,}6$$

(The standard method gives 11,8.)

5.3 Characterization of a result obtained in one laboratory

— Single result :

$$\pm\, 2\sqrt{(10{,}6)^2 + (5{,}35)^2} = 24\ (\pm\ 7\ \%)$$

— Mean of four determinations :

$$\pm\, 2\sqrt{(10{,}6)^2 + \frac{(5{,}35)^2}{4}} = 20\ (\pm\ 6\ \%)$$

Repeat determinations do not significantly reduce the accuracy.

6 Determination of chromium — Method B

Table 6 — Rapid analysis of dispersion : example 2 (sample ISO 13)

$n = 5$ $k = 9$ $\overline{\overline{x}} = 361$

Laboratories	1	2	3	4	5	6	7	8	9
$\bar{x}_5$	**350**	365	362	360	359	358	**368**	357	367
w_5	7	10	9	3	11	20	3	30	7

6.1 Homogeneity tests

6.1.1 There are no apparently aberrant mean values — Dixon test — $k = 9$, $r(11) = 357 - 350/367 - 350 = 7/17 = 0,41$

Table 7 (see the annex) for $\alpha = 0,05$, gives 0,512 : homogeneity checked.

6.1.2 Examination for homogeneity of dispersions :

$$w_{max.}/\Sigma w_o = 30/100 = 0,30$$

Table 8 (see the annex) gives 0,22 : homogeneity unchecked.

Laboratory 8, which gives results with too large a dispersion, should be eliminated.

Considering the 8 remaining laboratories :

$$w_{max.}/\Sigma w_o = 20/70 = 0,28$$

Table 8 (see the annex) gives 0,25 (see notes at the end of the clause).

Laboratory 6 should now be eliminated and only the 7 laboratories for which the dispersion is homogeneous are considered.

$$w_{max.}/\Sigma w_o = 11/50 = 0,22$$

Table 8 (see the annex) gives 0,278.

6.2 Examination for a laboratory effect

6.2.1 Estimation of the experimental standard deviation common to all laboratories :

$$S_w = \overline{w}_o/C_{(5,7)}$$

Table 9 (see the annex) gives $C_{(5,7)} = 2,35$ with 25,6 degrees of freedom :

$$S_w = 7,15/2,35 = 3,04$$

6.2.2 Test for significance (see table 10 of the annex)

Observed dispersion of mean values :

$$w_{\overline{x}} = 368 - 350 = 18$$

$$\overline{w}_o = 7,15$$

$q'_{calculated} = 18/7,15 = 2,51$ (highly significant).

(Table 10 of the annex gives $q'_{theoretical} = 1,05$ for $\alpha = 0,01$; $k = 7$; $n = 5$).

Observed standard deviation on mean values :

$S_{\overline{x}} = w_{\overline{x}}/C_7$ with $C_7 = 2,82$ (table 11)

$$S_{\overline{x}} = 18/2,82 = 6,4$$

6.2.3 Standard deviation S_b characterizing the laboratory effect

$$S_b = \sqrt{S_{\overline{x}}^2 - \frac{S_w^2}{5}}$$

$$S_b = \sqrt{(6,4)^2 - \frac{(3,04)^2}{5}} = 6,25$$

6.3 Characterization of a result obtained in one laboratory

— Single result :

$$\pm 2\sqrt{(6{,}25)^2 + (3{,}04)^2} = \pm 14\ (4\ \%)$$

— Mean of four determinations :

$$\pm 2\sqrt{(6{,}25)^2 + \frac{(3{,}04)^2}{4}} = \pm 13\ (3{,}5\ \%)$$

NOTES

1 If all laboratories had been considered in the case of method B, the results would have been :

$\overline{w}_0 = 100/9 = 11{,}1$ and

$S_{w_0} = 11{,}1/2{,}34$

$S_{w_0} = 4{,}74$ with 25 degrees of freedom.

Laboratory effect :

$q'_{\text{calculated}} = 18/11{,}1 = 1{,}62$ remains significant (see table 10 in the annex).

The interpretations for the example studied would have remained the same.

2 In fact, the large dispersion observed for laboratories 6 and 8 is explained by the fact that results are given to two significant figures only. The results obtained within these laboratories cover the whole range obtained for the 9 laboratories. Hence the need for uniformity in data presentation.