



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	IT	IT	IT	IT	GB	GB	GB	GB	ES	ES	ES	HU	US	US	US	US	DE	DE
	A	B	C	D	E	B	E	F	N	A	B	C		A	B	C	D	A	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
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
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
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

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

ISO <i>n</i>	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 %								
$S_t \cdot t_{N-1} \pm$	0,027 69	0,013 84	0,034 8	0,023 84	0,003 93	0,001 81	0,000 992	0,000 749
$S_t \cdot t_{K-1} \pm$	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 %								
$S_t \cdot t_{N-1} \pm$	0,020 85	0,010 38	0,026 2	0,017 88	0,002 96	0,001 36	0,000 747	0,000 562
$S_t \cdot t_{K-1} \pm$	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 $(K-1)$.