INSTRUCTION

CONCERNING THE REPORT OF A CECALAIT

PHYSICO-CHEMICAL PROFICIENCY TESTING

GENERAL PRINCIPLE OF THE DATA TREATMENT:

The general principle consists in an evaluation of the accuracy performances of the laboratory on the basis of the results obtained on the samples sent.

The shaded parts are data for information only and do not fall within the criteria for evaluating the performance of the proficiency test

➢ The repeatability treatment contains the edition of the deviations between duplicates per sample and the calculation of the standard deviation of repeatability of the laboratory, SL **(Table I).**

➢ The accuracy treatment is divided up as follows:

- Calculation of the means of duplicates sent by the laboratory.

- Calculation of the assigned values as follows:

1) Selection of the laboratories which have performed the tests before deadline (defined for each proficiency test),
2) Selection of the laboratories according to the method used (according to the criteria) and/or to the responses obtained on pure solutions (optional according to the criteria),
3) Calculation, with selected laboratories, of an assigned value per sample with the algorythm A of the ISO 13528 standard (robust mean).

- Edition, per sample, of the means of duplicates, of the calculated assigned values and the « laboratory mean-assigned value » deviation. Calculation of the statistics of performances: the mean deviation ($\overline{d}$) and the standard deviation of differences (Sd) **(Table II).**

- Evaluation of the laboratory's global accuracy on a target of conformity (positioning of each laboratory according to the $\overline{d}$ and Sd calculated performance statistics), **corresponding to the evaluation of the laboratory's performance (Figure I).**

- **For information**, a z score calculation per sample **(Table III)** and a graph of the values obtained **(Figure II)** are realised.

A) TREATMENT OF THE LABORATORY'S REPEATABILITY (For your information):

1) Definition:

The repeatability measures the accordance between the successive results obtained with the same method and in the same conditions. They can be expressed, either by the standard deviation of repeatability, Sr, of the method (95% of the results are divided between $\pm$ 2.Sr around the rates mean), or by r, the absolute deviation between duplicates in 95% of cases (r = 2.77.Sr).

2) Presentation of the results: Table of the deviations between duplicates (Table I)

The first line of the table corresponds to the identification of the test samples.
The second line concerns **the deviations between duplicates per sample of your laboratory.**
The deviation between duplicates must be compared to the absolute deviation between duplicates of the standardised method r mentioned below the table.
At the end of the line, you will find the standard deviation of repeatability of your laboratory, **SL,** and the number of the results taken into account for this calculation, **NL.**

$SL = \sqrt{\frac{\sum W_i^2}{2n}}$; W_i : deviation between duplicates and n: number of samples

This value must be compared to permissible absolute limit (Lim SL). Indeed, as the SL value is estimation from n samples, a tolerance linked to the confidence interval of the calculation SL (according to a law of χ^2 with an unilateral risk α = 5%) and calculated from Sr (normative): **Lim SL**, is allowed.
For example: 10 samples: Lim SL = 1.35 x Sr.

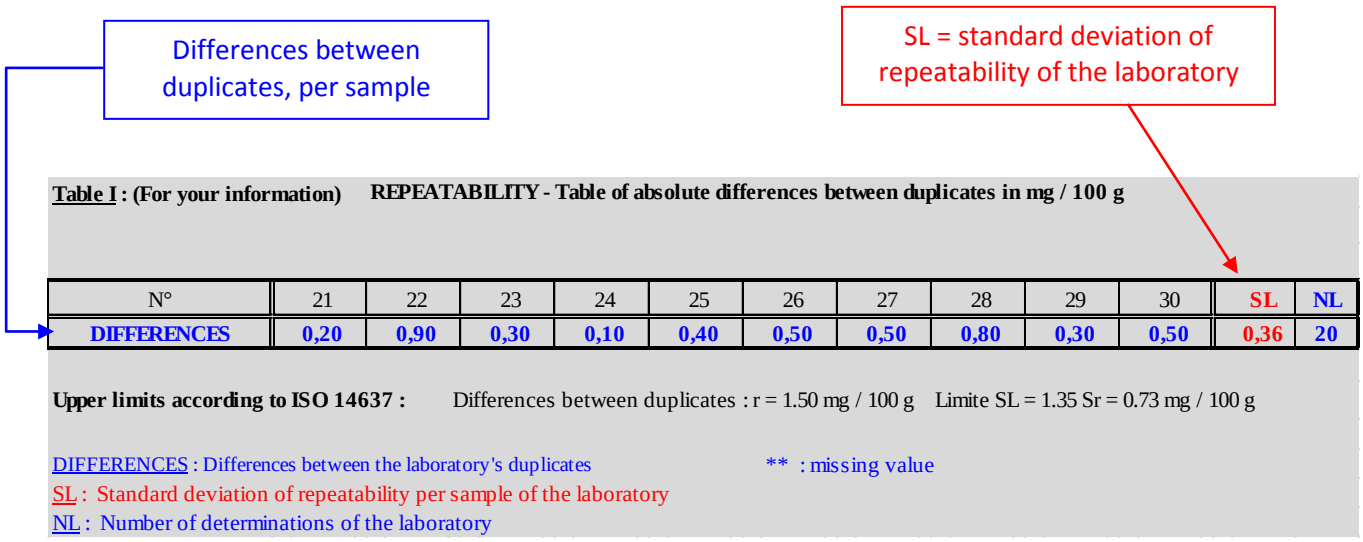


Table I : (For your information) **REPEATABILITY - Table of absolute differences between duplicates in mg / 100 g**

N°	21	22	23	24	25	26	27	28	29	30	SL	NL
DIFFERENCES	0,20	0,90	0,30	0,10	0,40	0,50	0,50	0,80	0,30	0,50	0,36	20

Upper limits according to ISO 14637 : Differences between duplicates : r = 1.50 mg / 100 g Limite SL = 1.35 Sr = 0.73 mg / 100 g

DIFFERENCES : Differences between the laboratory's duplicates ** : missing value
SL : Standard deviation of repeatability per sample of the laboratory
NL : Number of determinations of the laboratory

B) TREATMENT OF THE LABORATORY'S ACCURACY:

1) Definition:

Accuracy measures the accordance between the true value and the mean value that could be obtained applying the experimental proceeding a large number of time.

2) Presentation of the results:

2.1) ACCURACY table (Table II):

- The first line of the table (N°) corresponds to the identification of the test samples.
- The second line of the table **MOY** presents **the means of duplicates** obtained by your laboratory. The results with an asterisk have been identified as abnormal according to the Grubbs test at 5%.
- The 3rd, 4th and 5th lines present **the assigned values of the test (REF), number of values retained and the standard deviation S* of determination of this value** per sample.
- The 6th line **DEVIATIONS (MOY – REF)** presents **the deviations of your laboratory's results in relation to the assigned values for each sample**. At the end of the line, you will find the performance statistics: **the mean $\bar{d}$ and the standard deviation Sd of the deviations « mean of results - assigned value ».**
  These calculated values must be compared to the fixed limits, which are calculated, either from the repeatability (r) and the reproducibility (R) values given in the standards or taken from the bibliography, or correspond to the limits already established (within the context of the control of interprofessional laboratories, for example).
  The value of the Student t test indicates the pertinence of any given judgement: if the value is higher than the threshold value (respectively 2.26; 2.57 ; 2.78 and 4.30 for 10; 6; 5 and 3 samples with n-1 degree of freedom), then the deviations mean of the laboratory is statistically different from 0 (at a threshold of 5 %), indicating a systematic analytical bias. This test enables also to conclude to systematic bias with $\bar{d}$ value lower than the limit (tendencies).

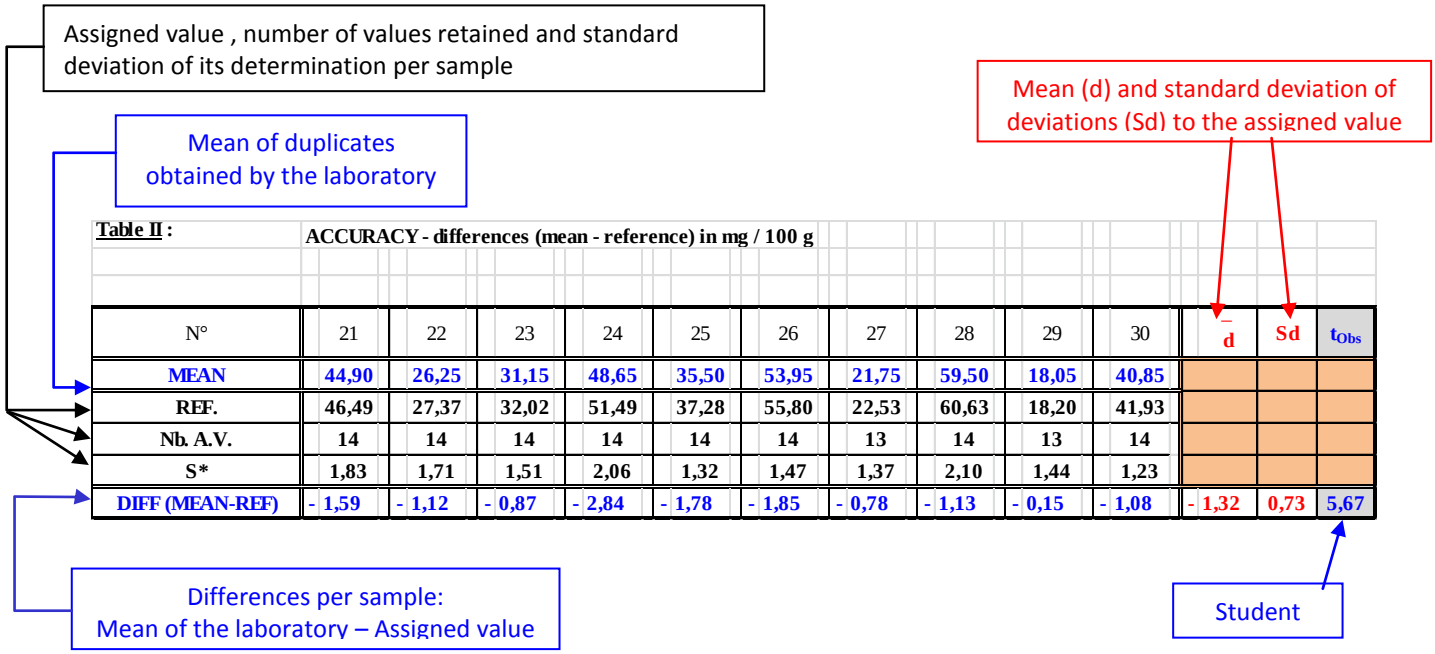


Table II : ACCURACY - differences (mean - reference) in mg / 100 g

N°	21	22	23	24	25	26	27	28	29	30	$\bar{d}$	Sd	t_{Obs}
MEAN	44,90	26,25	31,15	48,65	35,50	53,95	21,75	59,50	18,05	40,85			
REF.	46,49	27,37	32,02	51,49	37,28	55,80	22,53	60,63	18,20	41,93			
Nb. A.V.	14	14	14	14	14	14	13	14	13	14			
S*	1,83	1,71	1,51	2,06	1,32	1,47	1,37	2,10	1,44	1,23			
DIFF (MEAN-REF)	- 1,59	- 1,12	- 0,87	- 2,84	- 1,78	- 1,85	- 0,78	- 1,13	- 0,15	- 1,08	- 1,32	0,73	5,67

Performance indicator

Individual performance :	For this evaluation, the goal has been reached	☺

You will find below the accuracy table how the assigned values were calculated (number of laboratories, analytical method taken into account…).

A performance indicator informs you if the values of $\bar{d}$ and Sd obtained by the participant are within the tolerance specified by evaluation.

2.2) *z* scores table (Table III) (For your information):

- The first line of the table (N°) corresponds to the identification of the test samples.
- The second line of the **SCORE *Z*** table presents the z score values, per sample, obtained by your laboratory. The values are calculated as follows:

$$\text{z score} = \frac{(MOY - REF)}{S*}$$

The z score calculation enables an individual evaluation sample by sample of the performances of the laboratory in comparison with the global dispersion of the participating laboratories. This evaluation is strictly given for information and does not correspond to the evaluation of the laboratory's performance.

Table III : (For your information) *Z* SCORE - Table of *Z* SCORE value

N°	21	22	23	24	25	26	27	28	29	30
Z SCORE	- 0,87	- 0,65	- 0,58	- 1,38	- 1,36	- 1,25	- 0,57	- 0,54	- 0,11	- 0,87

Z SCORE = (MEAN - REF) / S* N.C. = z score value Not Calculated

2.3) Table of the linear regression (Table IV) according to the proficiency tests and/or criteria (For your information):

The table presents the results of the simple linear regression between the laboratory and the assigned values:

- Regression equation Y = b.X + a (b = slope and a = intercept point of the regression).
- t Test of the slope, which, if is higher than the limit value of the table (at the threshold of 5 %), indicates that the slope is different from 1.00 (t > 2.26 for n = 10 samples)
- Sx-y: Standard deviation of differences
- Sy,x: Residual standard deviation of regression
- d mean: Mean deviations of the laboratory's values in relation to the assigned value
- d to xxx: Mean deviation at the level of the given concentration

Table IV : (For your information) TABLE OF CALIBRATION EVALUATION using the SIMPLE LINEAR REGRESSION (Y = reference, X = laboratory) Evaluation of the instrument calibration

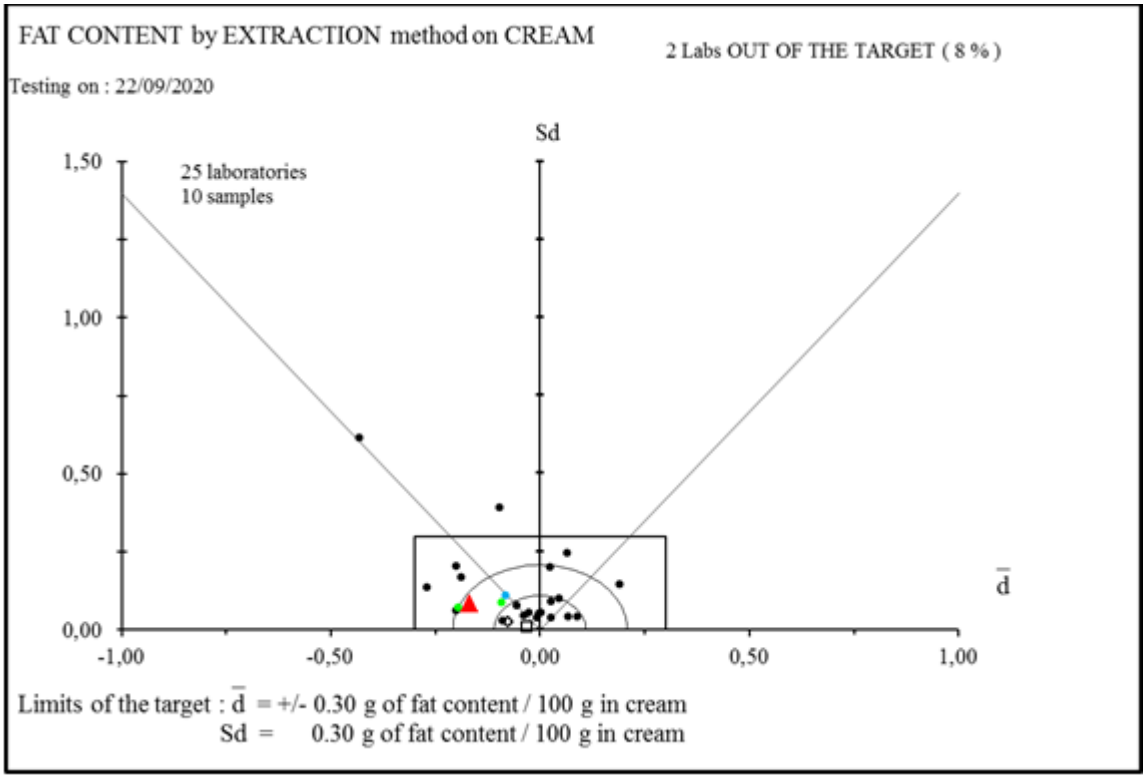
REGRESSION	linear regression equation	t slope	d.f.	Sx-y	Sy,x	d mean	d 20.0	d 50.0
	Y = 1,0333 x X + 0,05	2,30	8	0,73	0,61	- 1,32	- 0,7	- 1,7

d mean : mean of differences x-y; d 20.0 and d 50.0: estimated biase at levels 20.0 and 50.0
Sx-y: standard deviation of differences; Sy,x: residual standard deviation of the regression
t slope: test of Student of the slope vs. 1

2.4) Personalised target of conformity (Figure 1 associated to table II):

The figure represents a general target of conformity, in which all the participating laboratories are represented from their $\bar{d}$ and Sd values obtained on the test. Your laboratory is represented on this graph by a **red triangle**. In this figure, $\bar{d}$ is on the x axis and Sd on the y axis. A target (black rectangle) indicates the quality objective to be reached. Two symmetrical lines represent the significant limits of $\bar{d}$ (according to Sd) following the Student test at 5%: significant differences between the line and the x axis, and no significant differences between the both lines.
In the case of different methods used by the laboratory, identification is realised by the form and/or the colour of the marker (the correspondence marker - method is indicated below the target of conformity). .

This target corresponds to the evaluation of your laboratory's performance.



Positioning, as an additional laboratory, of the reference values of the groups of French and foreign laboratories. However, these data can only be provided if there are at least 5 French and 5 foreign laboratories.

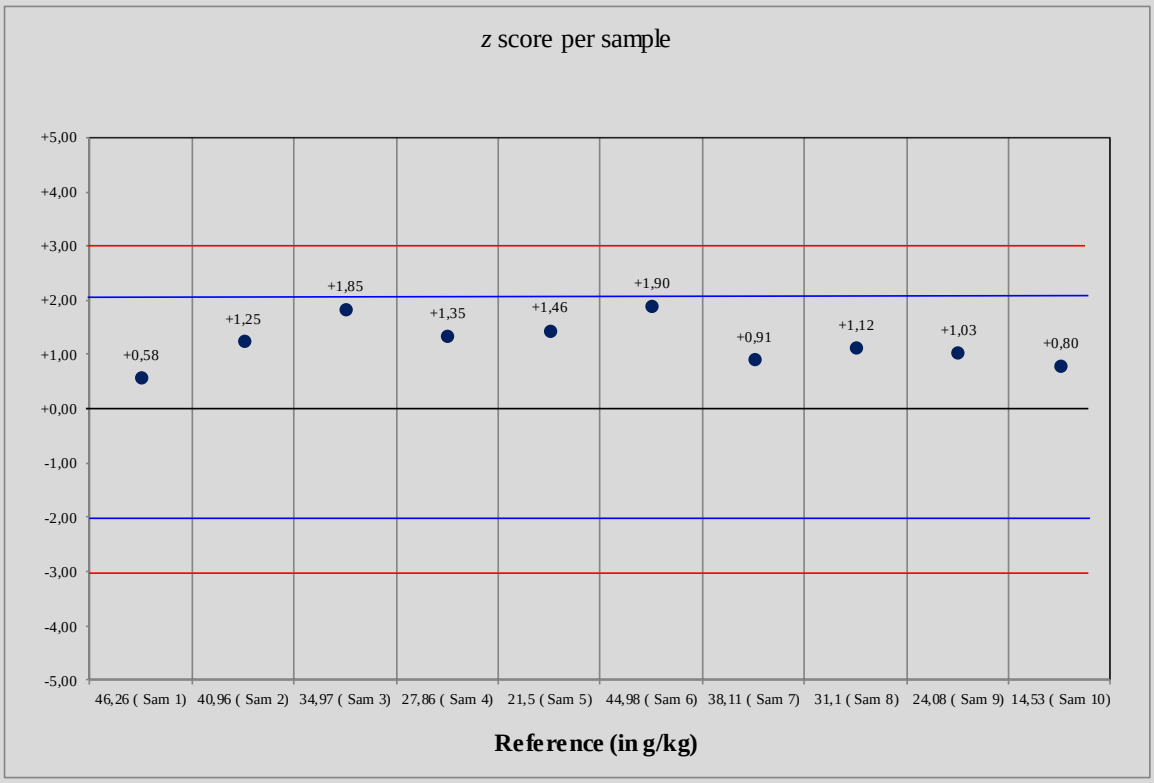
These two data are represented graphically on the compliance target by the following symbols :

□ "robust average values" of the xx french laboratories (according to ISO 13 528)
◊ "robust average values" of the x foreign laboratories (according to ISO 13 528)

2.5) z scores graph (figure 2 associated to table II):

The figure represents a graphical positioning of the z scores obtained for the n samples of the test. No relation between the scores obtained on each sample to evaluate the global performance of the laboratory (on all the samples) is possible.
At best, this graph enables to visualise the positioning of each sample in relation to the statistical limits (± 2 and ± 3 corresponding to the alert and action limits) and to orientate the reflexion of the laboratory on its performance on one or many samples.

Figure 2 : (For your information) **ACCURACY - Evaluation of the individual performances according to z score**



$-2 \leq z \leq +2$: satisfactory $-3 < z < -2$ ou $+2 < z < +3$: warning signal $-3 \geq z \geq +3$: signal for action

C) EXPLOITATION OF THE PERFORMANCE STATISTICS:

1) Case of exceeding of the $\bar{d}$ tolerance limit:

The deviations mean is an element indicating "the mean accuracy" of the participating laboratory.
First, it is necessary to observe the Sd value:

1.1) Low Sd value and t test value higher than the threshold value:

Case of a quasi constant deviation at all the levels indicating a systematic accuracy bias. In this case, the search of causes could be oriented towards a drift in the analytical procedure or to accuracy anomalies in the measurement.

1.2) High Sd value and t test value lower than the threshold value:

Case of a non systematic bias indicating a random deviation according to the samples. In this case, a more precise investigation may have to be carried out to refine the diagnostic:

- Search of outliers and recalculation of $\overline{d}$ and Sd without the sample(s) to do again the diagnostic at the first step.
- Influence of the measured analyte rate (level effect)
- Abnormally high repeatability on one or several samples (SL > Lim SL or deviation between duplicates > r).

2) <u>Case of exceeding of the Sd tolerance limit</u>

Follow the procedure described §1.2

Following the diagnostic of the "default" type met, a search will be carried out to identify the components of the method used (chosen process, material, reagents…), which can produce the problem in the considered test.
