New approach of classification for the competence of spectrochemical analysis laboratories based on obtained results in a Round Robin scheme

I. PENCEA[*], C. E. SFAT, M. PENCEA[a]
*BIOMAT Department, „POLITEHNICA" University of Bucharest, Romania,
Splaiul Independentei 313, 060042, Romania*
[a]*"Viaceslav Harnaj" High School of Bucharest, Romania, Sect 1, Bd. Ficusului 3, CP 010045, Romania*

The paper addresses mainly an advanced way of statistical data processing applied to a Round Robin spectrochemical laboratory scheme. This may be applied with adequate modification to the proficiency testing scheme or to other interlaboratories comparisons. BIOMAT and ICEM organized a six laboratories Round Robin scheme designed to demonstrate the competence of the three laboratories that candidate to RENAR accreditation to perform OES-SDAR analysis. The other accredited ones are interested in this scheme to demonstrate that their spectrochemical analysis proficiency is improved or are at the level they were accredited. There were analyzed two MRCs (medium alloyed steel and Al-Cu-Zn alloy) and were dozed simultaneously 10 and 8 elements, respectively. Because of the different Z scores obtained by the laboratories for the same sample it is quite impossible to classify the laboratories competence. In this regard, the authors introduced a new way of classification of the laboratory's analytical competence based on the mean Z score and its associated dispersion.

1. Introduction

In this paper we address only to optical emission spectrometry (OES) elemental analysis using spark discharge in argon (SDAR) that is a widely used technique in metallurgy and related fields. The OES-SDAR is preferred due to its best efficiency – cost ratio, rapidity and robustness. In spite of a long history of theoretically and technically development of OES –SDAR, it remains somehow an empirical test method that needs calibration and recalibrations for each grade using CRMs (certified reference materials) [1-4].

Thus, the spectrochemical methods were standardized according to grades and any new spectrochemical method must be confirmed before being used [9-12]. On the other hand, even though the method is standardized, the Romanian accreditation body RENAR imposes to any accreditation candidate laboratory to demonstrate its capacity to perform spectrochemical analysis at a certain accuracy level. In the case of standardized method the Round Robin Scheme (RRS) is an optimal test for the participating laboratories to prove their spectrochemical analysis proficiencies [9]. In this regard, BIOMAT and ICEM organized a RRS in order to demonstrate the proficiency of the accreditation candidate laboratories as providers of spectrochemical analysis.

The RRS encompassed six laboratories; among those three are accredited by RENAR and the others candidate.

According to the RRS protocol, laboratory names and organization identifications will be kept anonymously in every report related to the RRS spectrochemical results. Thus, in this paper the laboratories are identified by L1 ÷ L6. The labs L1, L2 and L3 are those accredited and L4, L5, L6 are the candidate ones.

The RRS was organized in accordance with the in force regulations of RENAR and other international recognized rules [9-13]. The RRS manager was a third part person that had no interest related to RRS participants and he has the necessary competence recognized by RENAR.

The RRS addresses the competence of the participants to perform spectrochemical analysis on mild steel and Cu-Si-Zn aluminum base grade using OES-SDAR standardized methods and adequate spectrometers and sample preparation machines. As RRS attendant, the non accredited laboratory will be considered as competent to perform spectrochemical analysis if it obtains analytical results comparable with those of the accredited ones and complying Z score criterion [9].

2. Experimental

According to RRS practice two CRM were chosen to undertake round analysis, sample Fe_1 is a mild steel grade (BRML certificate of analysis no: MA 4/30.01.2006) and sample Al_1 is an aluminum /silicon/copper grade (MBH certificate of analyses no. 55XG 02 D10).

The chemical composition of the samples was unknown for RRS attendants; but known by RRS manager.

To get a more anonymity of the Fe1 and Al1 target samples, supplementary second samples Fe2 and Al2 were introduced – and those are low alloyed iron and aluminum alloys. In this paper we address only the analytical results obtained for samples Fe_1 and Al_1 while those for Fe_2 and Al_2 will be the topic of another RRS analysis.

The RRS attendants were informed that the qualification criterion is the Z score:

$$Z = \left| \bar{c} - c_0 \right| / \sigma_m \qquad (1)$$

where: $\bar{c}$ - average concentration of an element; c_0 – true value considered of the element's concentration specified in CRM certificate; σ_m- standard deviation of c_o

The Z score criterion is applied to the following elements: C, Si, Mn, P, S, Cr, Ni, Mo, Al, Cu dosed in Fe_1 sample and to: Si, Fe, Cu, Mn, Cr, Ni, Zn, Sn, dosed in Al_1 sample.

Thus, if a Z score is less than 2 the result is acceptable, if $2 \leq Z \leq 3$ the result is questionable and if Z > 3 the result is unacceptable. A laboratory is qualified as competent to analyze mild steel and/or aluminum alloys if it obtains Z scores less than 2 for all elements specified in the RRS protocol except two or three critical elements in each sample.

The four sample set was submitted by the RRS manager to each RRS attendant laboratory with associated documentation; subsequently the laboratory returned the samples, documentation and their analytical results to the manager. It was in charge of each laboratory to apply its own analytical procedure to get ten replicated results on each sample e.g. to perform ten sparks on each sample.

The results were specified in previous agreed analytical reports together with values of laboratory temperature and humidity during the tests.

The accredited laboratories L1 ÷ L3 performed the tests using SpectroMaxx (2005); G.N.R. (2005) and ARL (1990) spectrometers while L4÷L6 laboratories used SpectromaxM (2006); Foundry Master (2000) and SpectromaxM (2007), respectively.

The reported results, considered as primary data, were analyzed by the manager and subsequently by the RRS board to assess their conformity with the RRS protocol to detect data lacks or redundant data.

3. Results and discussions

In order to be statistical processed the obtained results (data) on each sample (Fe_1, Al_1) were grouped according to the dozed elements. Mean concentration (c_m) and experimental standard dispersion (S_e) of each element for each laboratory were calculated as given in Table 1 and Table 2.

A Fisher–Snedecor test [13-15] was performed for each dosed element to appraise if the data belongs to the same statistical population with respect to factors F.

If factors F (see Table 1 and Table 2) are less than F (0,05;9;5) =3.48 [14], then the data belongs to the same statistical population e.g. (c_m, S_e) with 0.95 confidence level. Otherwise the data must be supplementary checked to remove the incongruent data.

All the data reported by the RRS attendant laboratories succeeded the F test thus the RRS board advised the application of Z score criterion to the mean concentrations of each element using $\sigma_m = U / 2$, where U – the extended uncertainty given in the CRM's certificates of analysis (ex. for Si in Fe: c_m =1.15; U=0.03; for Cu in Al1: c_m =4.68; U = 0.09).

The Z scores obtained by the laboratories for the elements analyzed in sample Fe_1 are given in Table 3.

Table 1. The Si concentrations measured by labs for the sample Fe_1 and the associated statistical parameters.

Lab's code	The replicate test number										c_m*	S^{2**}	F***
	1	2	3	4	5	6	7	8	9	10			
L1	1.16	1.14	1.16	1.14	1.15	1.16	1.14	1.14	1.15	1.16	**1.15**	**0.009**	**0.54**
L2	1.16	1.18	0.96	0.88	1.2	1.16	1.12	0.87	1.12	1.16	**1.08**	**0.127**	**0.99**
L3	1.15	1.14	1.13	1.13	1.15	1.14	1.16	1.16	1.16	1.16	**1.15**	**0.012**	**0.03**
L4	1.21	1.22	1.21	1.2	1.19	1.19	1.19	1.2	1.19	1.2	**1.20**	**0.011**	**2.04**
L5	1.15	1.14	1.22	1.14	1.16	1.14	1.15	1.15	1.15	1.14	**1.15**	**0.024**	**1.73**
L6	1.15	1.16	1.15	1.15	1.14	1.14	1.14	1.15	1.15	1.15	**1.15**	**0.006**	**1.82**

* c_m- mean concentration;**S_e^2-the experimental standard dispersion; ***F-Fisher factor

Table 2. The Cu concentrations measured by labs for the sample Al_1 and the associated statistical parameter.

Lab's code	The replicate test number										c_m*	S^2**	F***
	1	2	3	4	5	6	7	8	9	10			
L1	4.93	4.86	4.86	4.67	4.78	4.81	4.68	4.66	4.68	4.58	**4.75**	**0.013**	**0.45**
L2	4.55	4.61	4.48	4.94	4.87	4.76	4.56	4.68	4.84	4.69	**4.70**	**0.023**	**0.83**
L3	4.69	4.65	4.68	4.73	4.74	4.67	4.68	4.69	4.7	4.68	**4.69**	**0.001**	**0.03**
L4	4.56	4.6	4.92	4.86	4.56	5.15	4.83	4.66	5	4.5	**4.76**	**0.048**	**1.71**
L5	4.54	4.59	4.99	4.74	5.06	4.77	4.81	4.56	4.52	4.98	**4.76**	**0.041**	**1.45**
L6	4.68	4.49	5.03	4.67	4.56	5.04	5.04	4.61	4.7	4.8	**4.76**	**0.043**	**1.53**

* c_m- mean concentration;**S^2-the experimental standard dispersion; ***F-Fisher factor

Table 3. The Z scores obtained by the laboratories for the elements dosed in sample Fe1.

Lab's code	C	Si	Mn	S	P	Ni	Mo	Cr	Al	Cu
L1	1.71	0.00	0.52	0.32	2.73	1.97	1.43	1.97	0.84	0.55
L2	1.66	2.30	0.98	2.40	0.10	1.88	1.49	1.47	1.98	0.41
L3	0.00	0.07	0.90	1.50	0.27	0.80	0.64	0.87	0.84	1.00
L4	2.69	1.67	0.57	1.90	1.13	1.35	0.13	1.63	1.19	1.35
L5	1.72	0.13	0.65	1.60	0.67	1.89	0.16	1.20	0.81	1.00
L6	1.04	0.07	0.92	2.70	2.80	0.80	0.06	1.93	0.31	0.11

As it results from Table 3 and Table 4 all the RRS attendant laboratories passed the Z score test but each laboratory obtained different Z score for different dozed element.

From the Z score point of view the laboratories got comparable results and one can consider that they have comparable competence so that the candidate laboratories have demonstrated their competence in performing spectrochemical analysis on mild steel grade.

Table 4. RRS laboratories classification according with Z scores obtained for each dosed element in sample Fe_1.

	Z<2 (satisfactory)	2<Z<3 (questionably)	Z>3 (unsatisfactory)
Element	Labs' code numbers	Labs' code numbers	Labs' code numbers
C	1, 2, 3 ,5,6	4	*
Si	1, 3, 4, 5 ,6	2	*
Mn	1, 2, 3, 4, 5, 6	*	*
S	1,3,4,5	2, 6	*
P	2, 3, 4, 5	1, 6	*
Ni	1, 2, 3, 4, 5, 6	*	*
Mo	1, 2, 3, 4, 5, 6	*	*
Cr	1, 2, 3, 4, 5, 6	*	*
Al	1, 2, 3, 4, 5, 6	*	*
Cu	1, 2, 3, 4, 5 , 6	*	*

In an analogue manner, the Z scores based on the results given by the laboratories on sample Al_1 were checked, tested and calculated. In Table 5 there are given the Z scores obtained by the laboratories on sample Al_1 and in Table 6 the classification of the laboratories performances according to Table 5

Considering the RRS practice, Table 4 and Table 6 all the RRS attendant laboratories demonstrated their competence to perform spectrochemical analysis

On the other hand, RRS was generally used to demonstrate the competence of the laboratories to perform a single type of measurement e.g. to dose a single element.

Table 5. The Z scores obtained by the laboratories for the elements dosed in sample Al_1

Lab's code	Cu	Si	Fe	Mn	Ni	Zn	Sn	Cr
L1	1.58	1.23	0.50	1.80	0.59	1.10	1.88	1.10
L2	0.42	0.75	2.68	1.80	2.39	1.91	1.68	1.50
L3	0.24	1.72	1.80	2.20	1.76	0.10	1.64	1.83
L4	1.87	1.37	2.62	0.40	1.76	1.83	1.12	2.53
L5	1.69	1.65	1.26	1.62	1.76	1.83	1.84	1.57
L6	1.82	1.20	0.00	1.60	2.47	1.90	0.72	0.90

Table 6. RRS laboratories classification according with Z scores obtained for each dosed element in sample Al_1

Element	Z<2 (satisfactory) Labs' code numbers	2<Z<3 (questionably) Labs' code numbers	Z>3 (unsatisfactory) Labs' code numbers
Cu	1, 2, 3, 4, 5, 6	*	*
Si	1, 2, 3, 4, 5, 6	*	*
Fe	1, 3, 5, 6	2, 4	*
Mn	1, 2, 4, 5, 6	3	*
Ni	1, 3, 4, 5	2, 6	*
Zn	1, 2, 3, 4, 5, 6	*	*
Sn	1, 2, 3, 4, 5, 6	*	*
Cu	1, 2, 3, 4, 5 , 6	*	*

In the case of RRS we addressed there were ten elements dosed in sample Fe_1 and eight elements in sample Al_1 and the Z score given by each laboratory varies from element to element as can be seen in Table 3 and Table 4. Thus, it is difficult to arrange the RRS laboratories after their testing proficiency. In this regard we propose a classification based on average Z_m score and the standard deviation of the Z scores obtained for each sample.

Average Z scores of each laboratory (Z_m) and the associated standard deviations (SD-Z) for sample Fe_1 are shown in Figure 1.

Based on Z_m scores the laboratories can be arranged as follows: L3; L5; L6; L1; L4; L2 while based on SD-Z those could be arranged as follows: L3; L5; L4; L2; L1; L6.

Because Z score is the definite parameter of proficiency testing assessing and SD-Z reflects the stability of performance, we consider that the total score T, $T=Z_m + \frac{1}{2} * SD-Z$ is a good parameter for a final classification of laboratories based on their global analytical performance as shown in Figure 2.
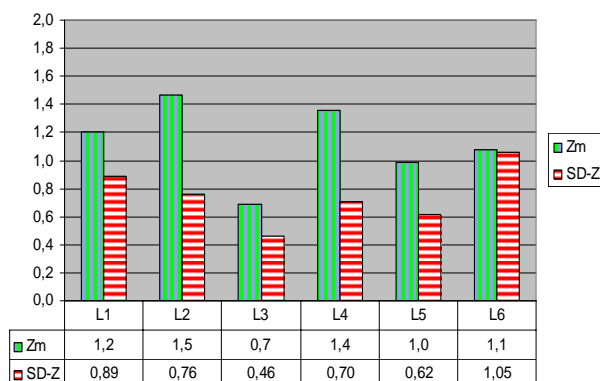
Based on T parameter the analytical performances of the RRS laboratories, demonstrated for Fe_1 sample, could be arranged from the best to the worst: L3, L5, L6, L1, L4 and L2.

Z_m, SD-Z and T scores for Al_1 sample were calculated in the same way. A comparative representation of the Z_m scores and their associated SD-Zs is given in Figure 3. A classification based on T scores for sample Fe_1 could be done using the data in Figure 4, respectively: L1, L6, L5, L3, L2 and L4.

The way the laboratories' analytical performances were distinguished based on T score is far away from an infallible one but offers an acceptable vision about the laboratories classification from the analytical competence point of view.

Without denying the preferred Z score in assessing the RRS performances we consider that in the case of OES-HEPS RRS it is useful to introduce the null hypothesis test of the mean concentration among the laboratories.
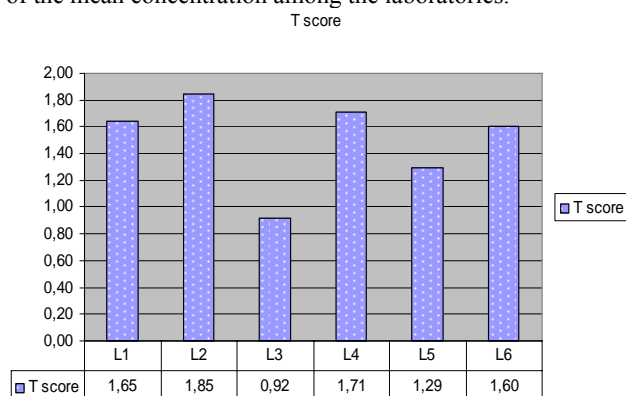

T score	L1	L2	L3	L4	L5	L6
T score	1,65	1,85	0,92	1,71	1,29	1,60

Fig 2. The RRS labs' T scores for sample Fe_1

	L1	L2	L3	L4	L5	L6
Zm	1,2	1,6	1,4	1,7	1,7	1,3
SD-Z	0,51	0,76	0,78	0,73	0,19	0,78

Fig 3. The RRS labs' Z_m scores and standard deviations (SD-Z) for Al_1 sample

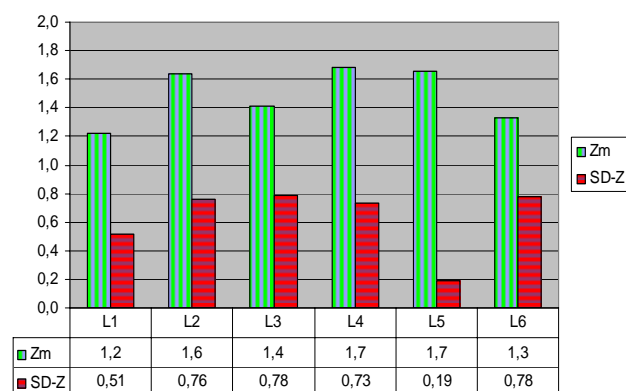|	L1	L2	L3	L4	L5	L6
Zm	1,2	1,5	0,7	1,4	1,0	1,1
SD-Z	0,89	0,76	0,46	0,70	0,62	1,05

Fig 1. The RRS labs' Z_m scores and standard deviations (SD- Z) for Fe_1 sample.
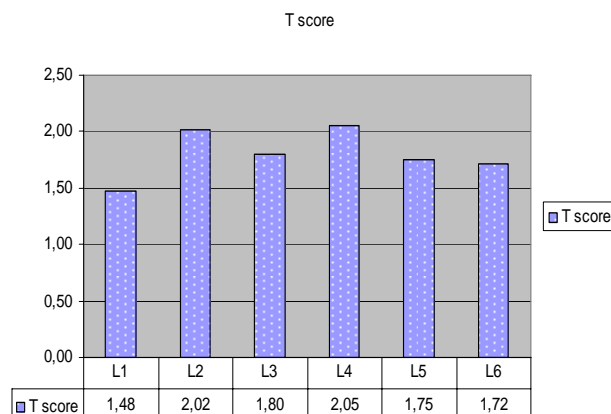
T score

Fig. 4. The RRS labs' T scores for Al_1 sample

In this sense, we consider the parameter:

$$t_{mij} = (c_{mi} - c_{mj})/S_{mij} \qquad (2)$$

where: c_{mi}, c_{mj} – the mean concentration reported by the L_i and L_j laboratories; S_{mij} – the pooled standard deviation of the mean concentration.

$$S_{mij} = \sqrt{\left[\frac{(n_i - 1)S_i^2}{n_i} + \frac{(n_j - 1)S_j^2}{n_j}\right]/(n_i + n_j - 2)} \qquad (3)$$

where: n_i, n_j – the numbers of replicated measurements done by L_i, respectively L_j laboratories; S_i^2, S_j^2 –the experimental dispersion of the concentrations dosed by the laboratories L_i and L_j, respectively.

Because the t_{mij} could be expressed as:

$$t_{mij} = \left(\frac{c_{mi} - c_0}{\sigma_m} - \frac{c_{mj} - c_0}{\sigma_m}\right)\left(\frac{\sigma_m}{S_{mij}}\right) \qquad (4)$$

where: c_0 –the certified concentration of the element; $\sigma_m = U/k$, with U certified extended uncertainty and k – the certified extension coefficient.

It could be shown that t_{mij} has a Student distribution.
Based on relation (3) one can consider that the number of the degrees of freedom (ν_{ij}) associated with t_{mij} is ($n_i + n_j$ -2) but it is questionable. Anyhow, $\nu_{ij} \geq (n_i + n_j$ -2)/2. Taking $\nu_{ij} = (n_i + n_j$ -2)/2 is a smart thing because it is the best precaution hypothesis.
The RRS practice highly recommends that the number of replicated measurements to be the same. In our case $n_i = n_j$ =10;   i = j = 1÷ 6 and t_{mij} is:

$$t_{mij} = \frac{(c_{mi} - c_{mj})\cdot\sqrt{20}}{\sqrt{S_i^2 + S_j^2}} \qquad (5)$$

Based on relation (5) we calculated the r_{mij} = factors to be:

$$r_{mij} = t_{mij}/t(0,05;9) \qquad (6)$$

where: t (0,05; 9) – the critical Student factor associated to the 0,05 significance level and 9 degrees of freedom[14-15].

In accordance with the statistical inference the two means c_{mi} and c_{mj} belong to the same population if $r_{mij} \leq 1$, otherwise they are different with a 0.95 confidence level.
The **t** test seems to be more powerful than the Z test because for Fe_1 sample it identified mismatches between results as it is shown in Table 7 while Z did not(see Table 3). The data in Table 7 and Table 8 exemplify the results given by applying t test in the case of Si element for Fe_1 sample and Cu in Al_1, respectively.
For most dosed elements the t test was succeeded by all laboratories (see Table 8) but, as it results from Table 7, some results reported by L2 do not belong to the same population of data while the others are congruent.

Table 7. The r_{mij} factors related to Si concentration dosed for Fe_1 sample.

Lab	L1	L2	L3	L4	L5	L6
L1	0.00	0.78	0.31	2.40	0.21	0.33
L2	0.78	0.00	0.72	1.28	0.75	0.73
L3	0.31	0.72	0.00	4.40	0.18	0.00
L4	2.40	1.28	4.40	0.00	4.84	5.71
L5	0.21	0.75	0.18	4.84	0.00	0.25
L6	0.33	0.73	0.00	5.71	0.25	0.00

Table 8. The r_{mij} factors related to Cu concentration dosed for Al_1 sample.

Lab	L1	L2	L3	L4	L5	L6
L1	0.00	0.33	0.47	0.00	0.06	0.00
L2	0.33	0.00	0.09	0.31	0.36	0.32
L3	0.47	0.09	0.00	0.44	0.71	0.46
L4	0.00	0.31	0.44	0.00	0.06	0.00
L5	0.06	0.36	0.71	0.06	0.00	0.06
L6	0.00	0.32	0.46	0.00	0.06	0.00

Based on our experience in applying the t test to the whole volume of the RRS data we forward the idea of introducing the F and t tests prior to applying the Z score calculation.

4. Conclusions

The paper addresses the optimal way of the OES-SDAR laboratories to demonstrate their competence in performing standardized tests e.g. to participate in a RRS.

An OES-SDAR RRS has some specificity caused by: a large number of elements that are simultaneously dosed, large uncertainty budget of OES-SDAR test, spreading of laboratories performances depending on elements dosed etc. Thus, making clear distinctions among the laboratories from the proficiency testing point of view is quite a difficult task.

In the paper we address a more carefully statistical testing of the laboratories results and promote the idea of introducing a total score (parameter) T to make distinction among analytical performances of the RRS attendant laboratories as it was shown in Fig. 2 and Fig. 4.

The t test we applied shows a greater capacity to detect data incongruence (see Table 7). The authors point out a lack of knowledge in assessing the number of the degrees of freedom of the t test but they argued that they done a valuable compromise in applying this test.

Finally, the authors consider that the problem of improving the procedure of assessing the competence of the laboratories participating in OES-SRAD RRS makes sense because OES-SDAR technique includes stochastic processes. This is why OES-SRAD RRS needs powerful statistical methods to increase their analytical performances.

Acknowledgment

References

[1] K. Slickers, "Automatic Atomic Emission Spectroscopy," Bruhler Drukarei, 1993

[2] I. Pencea, Ed Printech 2007, ISBN 978-973-718-657-7

[3] N. Popescu, R. Şaban, D. Bunea, I. Pencea. "Materials Science" Ed.. Fair Partners, ISBN 973 - 98724 - 4 – 1.

[4] I. Pencea, "Materials' structure analysis basics", Ed. Printech, 2001, ISBN 973-652-462-0

[5] I. Pencea, M. Branzei, F. Miculescu, M. Pencea, O. Trante, M. Miculescu, J. Optoelectron. Adv. Mater. **9**(11), 3411 (2007).

[6] ***, SR EN 14726:2006 –„Aluminum and aluminum alloys. Chemical analysis" Guide to optical emission spectrometry

[7] ****, SR CR 10316:2002 "Optical emission analysis of low alloy steels (routine method)" - Guidelines for the preparation of standard routine method for optical emission spectrometry.

[8] ****, SR EN 15079:2007 "Copper and copper alloys – Analysis by spark source optical emission spectrometry (S-OES)"

[9] ***, SR EN ISO/IEC 17025: 2005(E)-"General requirements for the competence of testing and calibration laboratories."

[10] ***, Eurachem "Guide on selection, use and interpretation of PT scheme", Edition 1.0 , 2000

[11] ***, ISO 5725-1. "Accuracy (trueness and precision) of measurement methods and results"-Part 1: General principles and definitions. ISO: Geneva, Switzerland.

[12] ***, ISO 43-1995 (E), "Part 1: Selection and use of proficiency testing scheme by laboratory accreditation bodies" and "Part 2: Development and operation of proficiency testing programs"

[13] ***, ASTM Guide E1301-96 (1196), "Standard guide for the development and operating of laboratory proficiency testing programs", American Society for Testing and Materials, West Conshohocken, Part 1

[14] D. Taloi, E. Florian, C.Bratu C, E Berceanu, "Optimization of the metallurgical processes", Ed. Didactica si pedagogica, Bucharest, 1983.

[15] W. J. Youden, "Statistical Techniques for Collaborative Tests", 1975

_____
*Corresponding person: ipencea@yahoo.com