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**PROFICIENCY TESTING SCHEME**

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**Abstract**

Our institute, INCD ECOIND Bucharest, with the activity domain environmental research (pollution control, pollution assessment, environmental technologies, environment and quality management, trainings, expertise, consultancy, technical assistance) by its Pollution Control Department organized during years some National and International Proficiency testing schemes on different pollutants and environment factors. Further will present the statistical treatment and the results of an international PT organized in 2005-2006. Participating laboratories analyzed the samples as part of their normal routine, and reported the results to the scheme organizers. After the statistical treatment done by the organizers the participating laboratories were provided with a report showing how closely their results agree with the accepted value.

**Keywords**

*Proficiency Testing Scheme, air pollutants, emission, ambient air*

**1 INTRODUCTION**

Regular participation in a proficiency-testing scheme provides independent verification of the analytical competence of a laboratory and shows a commitment to the maintenance and improvement of performance. It demonstrates to the public, customers, accreditation bodies, regulators, and management that analytical procedures are under control and gives analysts confidence that the service which they provide will withstand scrutiny. The cost of participation in a proficiency testing scheme gives good value for money compared with the consequences of producing inaccurate results which might put workers' health at risk, damage a company's reputation or contravene national regulations.

## 2 PROFICIENCY TESTING SCHEME for AIR EMISSION [1-10]

In the PT were involved 16 laboratories from different European countries: Poland, Greece, Serbia and Montenegro, Slovenia and Romania. The scheme consisted in some pollutants analysis from aqueous media and was organized in two rounds: in the first round were analyzed three heavy metals: Cd, Pb and Ni and in the second round were analyzed some inorganic compounds:  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ . The concentrations of the solutions containing these pollutants characterized both low and high concentrations which correspond to air emission and ambient air.

The Proficiency testing scheme operated by providing participating laboratories with reference standard solution (RSS) containing specified material but the actual quantity of the substance was known only to the organizers. For all RSS preparation were used Reference Standard Materials produced in INCD-ECOIND in 2001-2002. After preparation, first step was to check the concentration of the obtained solutions by multiple analyzes. The results showed the validity of the certified values for concentration and uncertainties.

Second, the homogeneity and stability tests were performed using ten samples from the solutions to be sent to the participating laboratories. The results demonstrated the homogeneity and stability of the solutions. The participating laboratories analyzed the samples as part of their normal routine, and reported the results to the scheme organizers.

Figures 1, 2, 3 and 4 presents the type of the methods used to analyze the RSS.

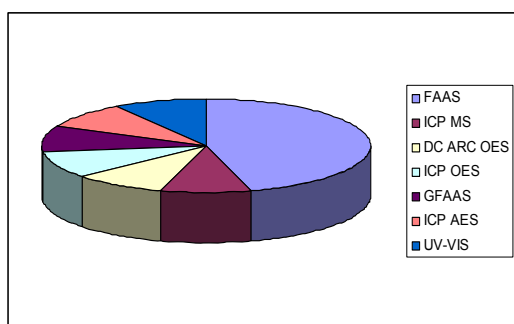


Figure 1 - Methods used for Round I

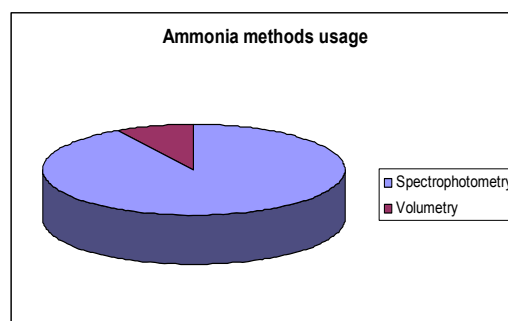


Figure 2 - Methods for ammonia

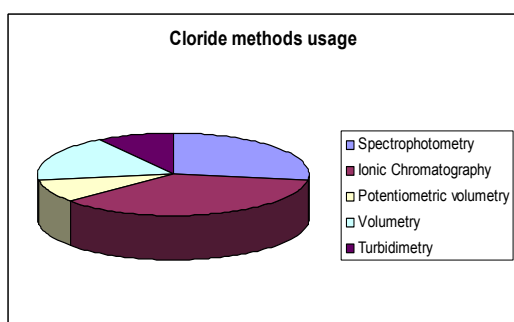


Figure 3 - Methods for chloride

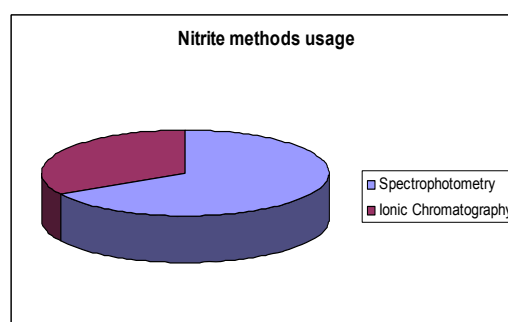


Figure 4 - Methods for nitrite

### 3 RESULTS

Tables 1 to 4 presents the values obtained by the participating laboratories, the mean value of the results, calculated standard deviation as well as the obtained “Z” score.

Pictures 5 to 12 present the difference between “Z” scores obtained by the participating laboratories and the difference between the mean values and the assigned values of individual RSS for each laboratory.

Table 1 - RSS-Ni

LAB	X1	X2	X3	mean	Std.dev	min.	max.	Z score
L 4	2.990	2.880	2.853	2.908	0.073	2.880	2.990	-7.12
L 7	9.042	8.910	9.156	9.036	0.123	8.910	9.156	0.97
L 8	5.150	5.050	5.080	5.093	0.051	5.050	5.150	-4.24
L 9	8.940	8.950	9.100	8.997	0.090	8.940	9.100	0.92
L 11	8.489	8.571	8.489	8.516	0.047	8.489	8.571	0.28
L 12	7.020	7.020	7.020	7.020	0.000	7.020	7.020	-1.69
L 13	8.368	8.282	8.274	8.308	0.052	8.274	8.368	0.01
L 13*	7.885	7.926	7.918	7.910	0.022	7.885	7.926	-0.52
L 15	7.325	7.222	7.257	7.268	0.052	7.222	7.325	-1.36
L 16	9.093	9.116	8.945	9.051	0.093	8.945	9.116	0.99
L 16*	9.030	8.332	8.438	8.600	0.376	8.332	9.030	0.39
<b>Assigned value</b>								<b>8.301</b>
<b>Assigned deviation</b>								<b>0.757</b>

\* - second method used

Table 2 - RSS-Pb

LAB	X1	X2	X3	mean	Std.dev.	min.	max.	Z score
L 4	5.427	5.470	5.443	5.447	0.022	5.427	5.470	0.27
L 7	6.661	5.583	5.633	5.626	0.040	5.583	6.661	0.78
L 8	4.000	4.010	3.980	3.997	0.015	4.010	5.150	-3.86
L 9	5.680	5.720	5.670	5.690	0.026	5.670	5.720	0.96
L 11	5.433	5.433	5.472	5.446	0.023	5.433	5.472	0.27
L 12	5.220	5.220	5.220	5.220	0.000	5.220	5.220	-0.38
L 13	4.799	4.836	4.816	4.817	0.019	4.799	4.836	-1.52
L 13*	4.685	4.665	4.615	4.655	0.036	4.615	4.685	-1.99
L 15	5.515	5.512	5.512	5.513	0.002	5.512	5.515	0.46
L 16	5.538	5.558	5.610	5.579	0.054	5.538	5.610	0.65
L 16*	5.100	6.033	5.460	5.531	0.471	5.100	6.033	0.51
<b>Assigned value</b>								<b>5.35</b>
<b>Assigned deviation</b>								<b>0.351</b>

\* - second method used

Table 3 - RSS – Cl<sup>-</sup>

LAB	X1	X2	X3	mean	Std.dev.	min.	max.	Z score
L 1	8.170	8.540	8.310	8.340	0.187	8.170	8.540	-0.28
L 2	6.090	7.160	6.930	6.730	0.563	6.090	7.160	-1.65
L 4	9.281	9.419	9.541	9.410	0.130	9.281	9.541	0.78
L 5	10.030	10.360	10.100	10.160	0.174	10.030	10.360	1.46
L 7	16.000	15.500	16.500	16.000	0.500	15.500	16.500	6.74
L 8	40.000	40.050	39.950	40.000	0.050	39.950	40.050	28.44
L 11	8.871	8.944	8.382	8.730	0.306	8.382	8.944	0.16
L 12	8.670	8.650	8.550	8.620	0.064	8.550	8.670	0.06
L 15	7.246	7.453	7.224	7.310	0.016	7.224	7.453	-1.12
L 16	9.360	9.200	8.750	9.100	0.100	8.750	9.360	0.5
<b>Assigned value</b>								<b>8.55</b>
<b>Assigned deviation</b>								<b>1.106</b>

Table 4 - RSS – NO<sub>2</sub><sup>-</sup>

LAB	X1	X2	X3	mean	Std.dev.	min.	max.	Z score
L 1	13.560	11.230	12.070	12.290	1.180	11.230	13.560	-1.9
L 2	14.630	12.910	13.800	13.780	0.860	12.910	14.630	-0.92
L 4	16.081	16.262	16.406	16.250	0.164	16.081	16.406	0.71
L 5	15.602	15.700	15.700	15.670	0.057	15.602	15.700	0.33
L 7	17.500	17.250	16.670	17.140	0.426	16.670	17.500	1.3
L 8	12.910	12.960	12.860	12.910	0.050	12.860	12.960	-1.49
L 11	16.157	15.987	15.764	15.970	0.197	16.157	15.987	0.53
L 12	15.200	15.230	15.140	15.190	0.046	15.140	15.230	0.01
L 14	15.740	15.640	15.720	15.700	0.053	15.640	15.740	0.35
L 15	15.814	15.688	15.694	15.730	0.071	15.688	15.814	0.13
L 16	16.050	16.500	16.200	16.250	0.229	16.050	16.500	0.71
<b>Assigned value</b>								<b>15.171</b>
<b>Assigned deviation</b>								<b>1.518</b>

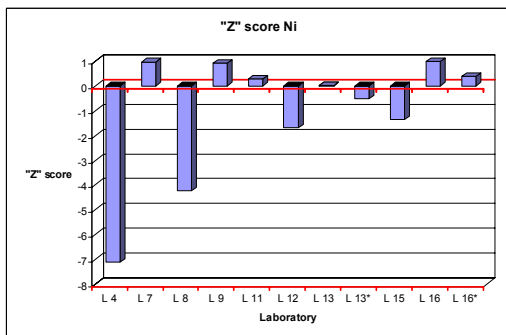


Figure 5 - "Z" score Ni

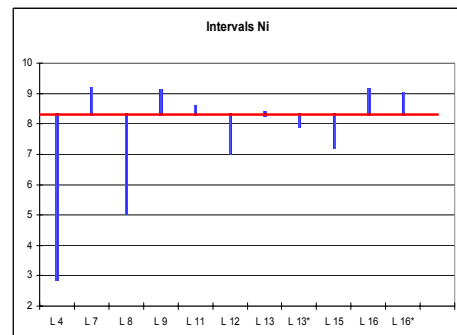


Figure 6 - Intervals Ni

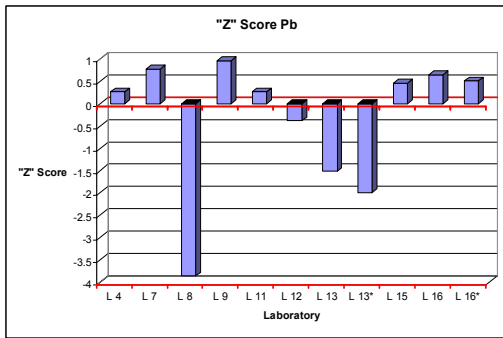


Figure 7 - "Z" score Pb

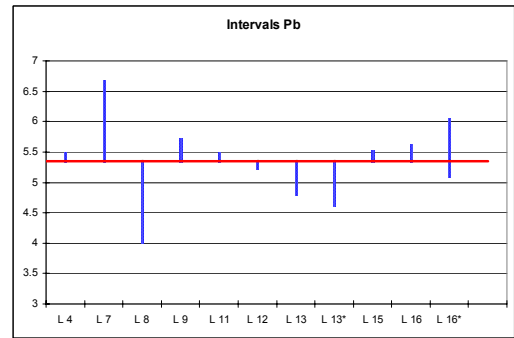


Figure 8 - Intervals Pb

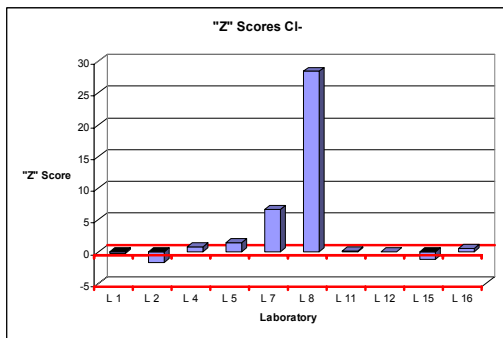


Figure 9 - "Z" score Cl-

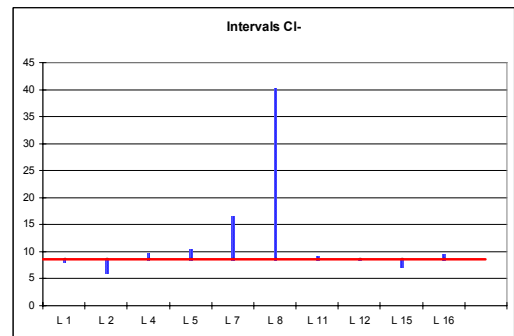


Figure 10 - Intervals Cl-

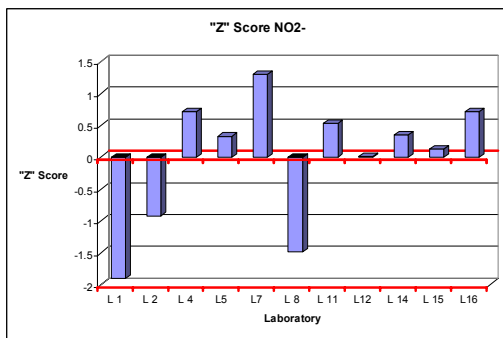


Figure 11 - "Z" score NO<sub>2</sub><sup>-</sup>

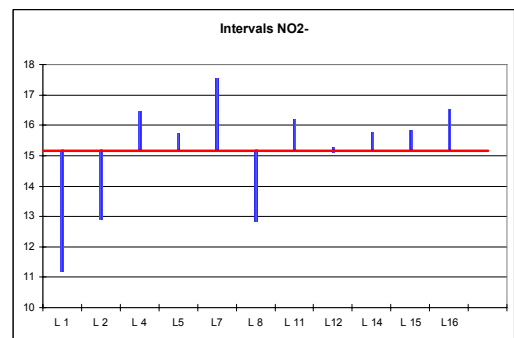


Figure 12 - Intervals NO<sub>2</sub><sup>-</sup>

#### 4 STATISTICAL TREATMENT [11-20]

##### Assigned values and their uncertainties

There are more methods to calculate the assigned values and them uncertainties:

- Mixture of known components
- Certified reference values
- Reference values
- Consensus values

For this scheme the consensus values method was used. The assigned value was calculated using the results received from the participating laboratories as a mean

value of means from each laboratory. Before doing that the outlier values were eliminated by use of Grubbs and Cochran tests.

*Cochran Test* was applied for all values received from the participating laboratories to verify the fidelity within- and between - laboratories.

First, the mean values were calculated (Eq. 1) and second, the dispersion (Eq. 2):

$$\bar{y}_n = \frac{1}{n} \sum_{i=1}^n y_{ni} \quad (1)$$

$$s_p^2 = \sum_{i=1}^n (y_{pi} - \bar{y}_p)^2 \quad (2)$$

For the laboratory with the highest dispersion  $s_{2max}$  will be calculated Cochran Test value (Eq. 3):

$$C = \frac{s_{max}^2}{\sum_k^p s_k^2} \quad (3)$$

The obtained value will be compared with critical values  $C1\%$  and  $C5\%$ . [18] In the case of an unacceptable value, the laboratory with highest dispersion is eliminated and the test will be repeated.

In the case of our scheme all laboratories had good fidelity, after Cochran Test none of the laboratories being eliminated.

*Grubbs Test* was applied on the mean values from each laboratory to eliminate de extreme values.

First de mean values were calculated (Eq. 4) and then standard deviation (Eq. 5):

$$\bar{y} = \frac{1}{n} \sum_{i=1}^n y_i \quad (4)$$

$$S = \sqrt{\frac{1}{n-1} \sum_{n-1}^n (y_n - \bar{y})^2} \quad (5)$$

Further the following rapport is calculated (Eq. 6):

$$G_n = \frac{y_n - \bar{y}}{S} \quad (6)$$

The obtained value from the above rapport will be compared with Grubbs statistics:  $G1\%$  (1) and  $G5\%$  (1). [18]

In the same way the value will be compared for the minim values (Eq. 7).

$$G_1 = \frac{\bar{y} - y_1}{S} \quad (7)$$

After Grubbs test, in our scheme, there were eliminated values for all the metals in the first round and for chloride determination in the second round.

Another approach to calculate the assigned value and its uncertainty is represented by the application of principles of robust statistic according with ISO 13528:2005.

- Assigned value:

$$X^* = \text{median of } (x_1, x_2, \dots, x_i, \dots, x_p)$$

- Uncertainty (Eq. 8)

$$s^* = 1,483 \times \text{median } (|x_1 - x^*|, |x_2 - x^*|, \dots, |x_p - x^*|) \quad (8)$$

where  $x_i$  are de mean values from participating laboratories

- With  $x^*$  and  $s^*$  will be calculate:

$$d = j = 1,5 s^*$$

- Then we construct the equivalent input data row, by the following role:

$$x_i^* = \begin{cases} x^* - \varphi & , \text{ for } x_i < x^* - \varphi \\ x^* + \varphi & , \text{ for } x_i > x^* + \varphi \\ x^* & , \text{ for } x^* - \varphi \leq x_i \leq x^* + \varphi \end{cases}$$

- The new values for  $x^*$  and  $s^*$  are (Eq. 9, Eq. 10):

$$x^* = \frac{1}{p} \sum_{i=1}^p x_i^* \quad (9)$$

$$s^* = 1,134 \sqrt{\frac{1}{p-1} \sum_{i=1}^p (x_i^* - x^*)^2} \quad (10)$$

- The calculus will be performed again with the new values until the  $x^*$  and  $s^*$  values are stabilized.

In the statistic treatment of the results received for our scheme we applied both methods.

For the evaluation of the performance level of each participating laboratories "Z" score were calculate, the same, using both methods.

From the Figure 13 which presents the value for "Z" score calculated according with ISO 5725-1994 compared with the value for "Z" score calculated according with ISO 13528:2005, we can see that the differences between "Z" scores are insignificant.

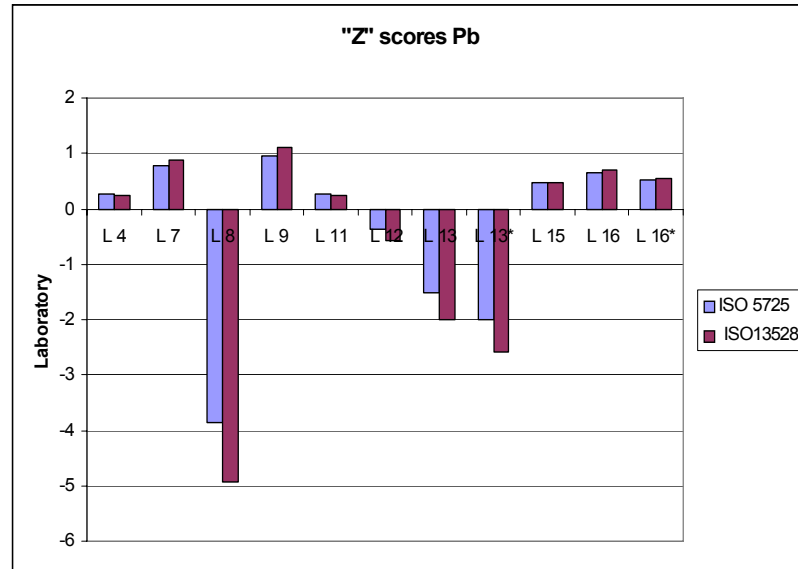


Figure 13 - Comparison between “Z” scores calculated using different standards

“Z” score is calculate according with Equation 11:

$$Z = \frac{x - \bar{x}}{s} \quad (11)$$

where:

- $x$  = individual result;  $\bar{x}$  = mean of all results;  $s$  = standard deviation of  $x$

The following ratings for Z score are usually employed:

- $|Z| \leq 2$ : satisfactory
- $2 < |Z| < 3$ : questionable
- $|Z| \geq 3$ : unsatisfactory

After statistical treatment and “Z” score calculation the participating laboratories were provided with a report showing how closely their results agree with the accepted value.

## 5 CONCLUSIONS

One unsatisfactory result in any round does not make a laboratory poor, neither does the achievement of 100% satisfactory results in any round make a laboratory necessarily good.

The way in which a laboratory responds to an unsatisfactory result will usually give more information about that laboratory than the occurrence of the unsatisfactory result.

The participating laboratories receive very useful information, which help its personnel and the management to evaluate and compare its technical capability and to diagnose and cure causes in the case of deviating results.



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