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# PROFICIENCY TESTING FOR AIR POLLUTION TEST LABORATORIES BY INTER-LABORATORY COMPARISON SCHEMES

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**Abstract.** The quantification of transboundary atmospheric pollutants involves measurements which, after sampling, consist in quantitative chemical analyses. In the environmental Romanian legislation there are maximum value concentration for over 100 pollutants for the atmospheric stationary emission sources and for 29 pollutants for air quality. The prove of the traceability and of the accuracy of the analyses results is made by certified reference material (CRM) use or by the inter-laboratory analysis. This issue presents the activity of Air Pollution Laboratory from INCD ECOIND concerning organisation and the co-ordination of a proficiency testing scheme for five pollutants of the atmosphere: $NO_2$, $Cl^-$, $CN^-$, Co and Ni with the participation of nine laboratories. There are presented the inter-laboratory analyses results performed in nine laboratories for the certified reference materials or synthetic reference solutions prepared by INCD ECOIND followed by the statistical interpretation of the results. Calculation of 'Z-score' and the elaboration of 'The Proficiency Testing Report' which represent, for our clients and for the National Accreditation Organism in accordance with SR EN ISO/CEI 17.25:2001, the prove of the participation to this kind of activity.

*Keywords*: accreditation, proficiency testing, emission, imission (air quality), Z-score.

## AIMS AND BACKGROUND

EN ISO CEI 17025:1999 – reference standard for accreditation of test and calibration laboratories requires:

– Existence of methods for quantitative analyses of air quality and flue/exit – EG – gases with high level of reproducibility and repeatability;

– Measurements traceability and results quality assurance by CRM use;

– Laboratories participation in proficiency testing (PT) schemes by inter-laboratory comparison according with ISO / CEI Guide 43.

The quantification of transboundary atmospheric pollutants involves measurements made by automatic methods or classical/wet methods. The classical methods, after sampling, involve quantitative chemical analyses.

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The prove of the traceability and of the accuracy of the analyses results is made by CRM use or by the inter-laboratory analysis.

Because CRMs are expensive, sometimes their concentrations are not in the range of calibration curves or CRMs do not exist for all the pollutants. The use of PT schemes by inter-laboratory comparison is the best solution which solves one of the Romanian National Accreditation Body (RENAR) and EN ISO CEI 17025:1999 requirement.

The Romanian National Accreditation Body signed in March 2004 the MLA (Mutual Laboratory Agreement) with the European Co-operation for Accreditation.

The Order No 462/1993 of the Waters, Forests and Environmental Protection Ministry makes limitations for over 150 organic or/and inorganic pollutants into the atmosphere like: cyanides ($CN^-$), nitrogen dioxide ($NO_2$), chloride ($Cl^-$), nickel (Ni) and cobalt (Co).

STAS 12574/87 'Air from protected areas. Quality conditions' does not contain limitations for all these pollutants but contains for nitrogen dioxide, hydrogen chloride and other metals with daily limits very low.

INCD ECOIND and other laboratories are interested in maintenance and improvement of the quality/accuracy of their analysis results.

One of the accredited test laboratories from INCD ECOIND is Air Pollution Laboratory.

## EXPERIMENTAL

Taking into account the RENAR and SR EN ISO/CEI 17025:2001 requirements, Air Pollution Laboratory from INCD ECOIND, with INFRAS program financial support, organised and co-ordinated, with the participation of eight test laboratories, two proficiency testing schemes: 'AIR & INFRAS C2/2002 – split samples' and 'AIR & INFRAS C2 / 2003 – unique samples', for five pollutants of the atmosphere: $NO_2$, $Cl^-$, $CN^-$, Co and Ni.

The participants (021 to 029 codes in 2002 and 031 to 039 codes in 2003, without link with the order below, for confidentiality reason) were:

1. S.C. CAST S.A. Bucharest;
2. S.C. LACECA S.A. Bucharest;
3. INCD – I.C.I.M. Bucharest;
4. S.C. ICECHIM S.A. Bucharest;
5. INSTITUTUL de CERCETĂRI pentru PROTECȚIA MUNCII Bucharest;
6. INSPECTORATUL DE PROTECȚIA MEDIULUI Ploiesti;
7. ROMPETROL RAFINARE – COMPLEXUL PETROMIDIA SA Navodari;
8. S.C. REPUBLICA S.A Bucharest;
9. INCD ECOIND Bucharest.

Air Pollution Laboratory from INCD ECOIND prepared the samples analysed in the two PT schemes.

These samples were:

– CRM obtained by Air Pollution Laboratory in 2000 and 2002 for $NO_2$, $Cl^-$, $CN^-$, Co and Ni, or

– Reference Standard Solutions prepared using salt or/and metal powder or wire.

In Table 1 are indicated the samples analysed.

**Table 1.** Samples analysed

| Pollutant | 2002 | 2003 |
|---|---|---|
| Chloride | P1: CRM 4 – Cl / 2000<br>P2: CRM 5 – Cl / 2000 | P11: CRM 4 – Cl / 2000<br>P12: CRM 5 – Cl / 2000 |
| Nitrogen dioxide | P3: CRM 6 – $NO_2$ / 2000<br>P4: CRM 7 – $NO_2$ / 2000 | P13: CRM 6 – $NO_2$ / 2000<br>P14: CRM 7 – $NO_2$ / 2000 |
| Cyanides | P5 and P6 (prepared using potassium cyanide) | P19 and P20 (prepared using potassium cyanide) |
| Co | P7 and P8 for Co (prepared using cobalt chloride hexahydrated) | P15: CRM 16 – Co / 2002<br>P16 (prepared using cobalt powder) |
| Ni | P9 and P10 for Ni (prepared using nickel sulphate hexahydrated) | P17: CRM 17 – Ni / 2002<br>P18 (prepared using nickel wire) |

In 2002, each solution of P1-P10 was divided in 15 bottles and distributed to each participant.

In 2003 10 bottles containing P11-P20 were transported to the first participant and after the analyses the bottles was transported to the next participant and so on.

Informative and certified and calculated concentrations of the sample P1-P20 are shown in Table 2.

After the verification of their working conditions, the laboratories performed the analysis of P1-P20 applying:

– VIS spectrophotometric methods: $Cl^-$, $NO_2$, $CN^-$, Co and Ni;

– ICP – AES: Co and Ni;

– AAS: Co and Ni;

– volumetric: $Cl^-$.

The results were transmitted to INCD ECOIND.

For the statistical interpretation of the inter-laboratory results were applied Cochran and Grubbs tests (for the within and inter-laboratory variance study and outliers identification) and were calculated (Table 3 for 2002 and Table 4 for 2003):

**Table 2.** Informative, certified and calculated concentrations

| 2002 | | | 2003 | | |
|---|---|---|---|---|---|
| Sample codes | Informative concentrations | 'Real concentrations' | Sample codes | Informative concentrations | 'Real concentrations' |
| SSR – P1 | 6-12 μg $Cl^-$/ml | 9.06 μg $Cl^-$/ml | SSR – P11 | 6-12 μg $Cl^-$/ml | 9.06 μg $Cl^-$/ml |
| SSR – P2 | 450-550 μg $Cl^-$/ml | 504.84 μg $Cl^-$/ml | SSR – P12 | 450-550 μg $Cl^-$/ml | 504.84 μg $Cl^-$/ml |
| SSR – P3 | 1-3 μg $NO_2$/ml | 2.03 μg $NO_2$/ml | SSR – P13 | 1-3 μg $NO_2$/ml | 2.03 μg $NO_2$/ml |
| SSR – P4 | 14-18 μg $NO_2$/ml | 16.30 μg $NO_2$/ml | SSR – P14 | 14-18 μg $NO_2$/ml | 16.30 μg $NO_2$/ml |
| SSR – P5 | 1-3 μg $CN^-$/ml | 2.15 μg $CN^-$/ml | SSR – P15 | 10-14 μg Co/ml | 11.47 μg Co/ml |
| SSR – P6 | 6-10 μg $CN^-$/ml | 8.62 μg $CN^-$/ml | SSR – P16 | 8-10 μg Co/ml | 9.06 μg Co/ml |
| SSR – P7 | 3-5 μg Co/ml | 5.70 μg Co/ml | SSR – P17 | 8-10 μg Ni/ml | 8.56 μg Ni/ml |
| SSR – P8 | 10-14 μg Co/ml | 17.25 μg Co/ml | SSR – P18 | 2-4 μg Ni/ml | 2.80 μg Ni/ml |
| SSR – P9 | 3-5 μg Ni/ml | 4.30 μg Ni/ml | SSR – P19 | 0.06-0.08 μg $CN^-$/ml | 0.076 μg CN/ml |
| SSR – P10 | 12-18 μg Ni/ml | 16.40 μg Ni/ml | SSR – P20 | 0.14-0.18 μg $CN^-$/ml | 0.167 μg CN/ml |

**Table 3**. 2002 inter-laboratory results

| Laboratory | P1-Cl | P2-Cl | P3-$NO_2$ | P4-$NO_2$ | P5-Co | P6-Co | P7-Ni | P8-Ni | P9-CN | P10-CN |
|---|---|---|---|---|---|---|---|---|---|---|
| 021 | 9.33 | 515.00 | 1.97 | 16.30 | 2.20 | 8.40 | 6.00 | 17.60 | 4.39 | 16.58/15.90 |
| 022 | 9.40 | 520.00 | 2.00 | 16.18 | 2.36 | 8.66 | 5.70 | 17.33 | 4.24 | 16.13 |
| 023 | 9.53 | 487.00/480.75 | 2.68 | 15.58 | 1.92 | 7.94 | 5.45 | 17.67 | 4.25 | 16.10 |
| 024 | 9.06 | 504.22 | 2.06 | 16.12 | 2.06 | 8.15 | 5.84 | 17.44 | 4.20 | 16.41 |
| 025 | 8.99 | 500.27 | 2.00 | 16.17 | 1.99 | 8.52 | 5.61 | 17.18 | 4.30 | 16.25 |
| 026 | 9.06 | 509.63 | 1.98 | 16.19 | 2.10 | 9.02 | 5.74 | 17.22 | 4.29 | 16.40/16.28 |
| 027 | 9.13 | 501.62 | 2.01 | 16.32 | 2.02 | 9.09 | 5.83 | 17.41 | 4.40 | 16.25 |
| 028 | 9.06 | 500.06 | 2.02 | 16.28 | 2.00 | 9.09 | 5.80 | 17.27 | 4.38 | 16.63 |
| 029 | 8.99 | 501.25 | 1.97 | 16.44 | 2.08 | 8.86 | 5.71 | 17.08 | 4.28 | 16.25 |
| 'Real concentrations' | 9.06 | 504.84 | 2.03 | 16.30 | 2.15 | 8.62 | 5.70 | 17.25 | 4.30 | 16.40 |
| Mean (reference consensus value) | 9.17 | 504.34 | 2.08 | 16.18 | 2.08 | 8.64 | 5.74 | 17.36 | 4.30 | 16.33 / 16.24 |
| $s$* | 0.197 | 9.614/11.129 | 0.228 | 0.244 | 0.131 | 0.418 | 0.155 | 0.194 | 0.072 | 0.186/0.203 |

* Standard deviation.

**Table 4.** 2003 inter-laboratory results

| Laboratory | P11-Cl | P12-Cl | P13-$NO_2$ | P14-$NO_2$ | P15-Co | P16-Co | P17-Ni | P18-Ni | P19-CN | P20-CN |
|---|---|---|---|---|---|---|---|---|---|---|
| 031 | 9.14 | 512.78 | 1.97 | 16.05 | 11.49 | 9.04 | 8.45 | 2.73 | 0.076 | 0.166 |
| 032 | 10.88 | 538.25 | 2.39 | 15.15 | 10.22 | 8.69 | 8.44 | 2.34 | 0.076 | 0.166 |
| 033 | 9.12 | 499.36 | 2.03 | 16.30 | 12.52 | 8.93 | 8.79 | 2.84 | 0.073 | 0.156 |
| 035 | 10.50 | 475.72 | 2.38 | 19.20 | 12.28 | 9.38 / 9.46 | 8.88 | 2.80 | 0.095 | 0.205 |
| 036 | 9.03 | 504.88 | 2.01 | 16.25 | 11.43 | 9.04 | 8.62 | 2.81 | 0.076 | 0.167 |
| 037 | 9.05 | 510.00 | 2.03 | 15.97 | 11.45 | 9.02 | 8.42 | 2.61 | 0.073 | 0.165 |
| 038 | 7.90 | 452.04 | 2.53 | 18.49 | 11.52 | 9.75 | 9.51 | 3.00 | 0.059 | 0.183 |
| 039 | 9.06 | 504.55 | 2.03 | 16.30 | 11.42 | 9.00 | 8.52 | 2.81 | 0.073 | 0.162 |
| 'Real concentrations' | 9.06 | 504.84 | 2.03 | 16.30 | 11.47 | 9.06 | 8.56 | 2.80 | 0.076 | 0.167 |
| Mean (reference consensus value) | 9.18 | 501.40 | 2.15 | 16.66 | 11.59 | 9.05/9.06 | 8.66 | 2.72/2.72 | 0.075/0.075 | 0.170 |
| $s$* | 0.998 | 24.669 | 0.221 | 1.300 | 0.659 | 0.344/0.355 | 0.369 | 0.192/0.200 | 0.009/0.009 | 0.015 |

* Standard deviation.

**Table 5**. 2002 Z-score

| Laboratory | $Cl^-$ | | $NO_2$ | | $CN^-$ | | Co | | Ni | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $Z_t$ | $Z_m$ | $Z_t$ | $Z_m$ | $Z_t$ | $Z_m$ | $Z_t$ | $Z_m$ | $Z_t$ | $Z_m$ |
| 021 | 1.921/0.795 | 0.961/0.398 | 0.974 | 0.487 | 1.490 | 0.745 | 2.914 | 1.457 | 2.594/2.925 | 1.297/1.463 |
| 022 | 2.797/2.638 | 1.399/1.319 | 0.351 | 0.176 | 2.185 | 1.092 | 0.413 | 0.206 | 1.908/1.375 | 0.954/0.688 |
| 023 | 3.631/3.884 | 1.816/1.942 | 5.091 | 2.546 | 2.896 | 1.448 | 3.469 | 1.734 | 1.931/1.384 | 0.965/0.692 |
| 024 | 0.570/0.610 | 0.285/0.305 | 0.334 | 0.167 | 1.325 | 0.663 | 1.057 | 0.529 | 1.819 | 0.910 |
| 025 | 1.337/1.217 | 0.669/0.609 | 0.392 | 0.196 | 0.974 | 0.487 | 1.767 | 0.883 | 0.430/0.049 | 0.215/0.025 |
| 026 | 1.108/1.096 | 0.554/0.548 | 0.480 | 0.240 | 1.062 | 0.531 | 0.722 | 0.361 | 0.515/0.336 | 0.258/0.168 |
| 027 | 0.486/0.385 | 0.243/0.193 | 0.881 | 0.441 | 1.535 | 0.767 | 0.839 | 0.420 | 1.819/1.438 | 0.910/0.719 |
| 028 | 1.003/0.880 | 0.502/0.440 | 0.673 | 0.337 | 1.688 | 0.844 | 0.851 | 0.425 | 2.724/3.032 | 1.362/1.516 |
| 029 | 1.235/1.129 | 0.618/0.565 | 1.548 | 0.774 | 0.526 | 0.263 | 1.637 | 0.819 | 0.708/0.327 | 0.354/0.164 |

Legend: before and after elimination of outliers by the Cochran test.

**Table 6**. 2003 Z-score

| Laboratory | $Cl^-$ | | $NO_2$ | | $CN^-$ | | Co | | Ni | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $Z_t$ | $Z_m$ | $Z_t$ | $Z_m$ | $Z_t$ | $Z_m$ | $Z_t$ | $Z_m$ | $Z_t$ | $Z_m$ |
| 031 | 0.501 | 0.251 | 1.283 | 0.642 | 0.378 | 0.189 | 0.181/0.208 | 0.091/0.104 | 0.621/0.619 | 0.311/0.310 |
| 032 | 3.197 | 1.599 | 2.248 | 1.124 | 0.378 | 0.189 | 3.126/3.121 | 1.563/1.561 | 2.575/2.496 | 1.288/1.248 |
| 033 | 0.143 | 0.072 | 0.820 | 0.410 | 1.155 | 0.578 | 1.760/1.777 | 0.880/0.889 | 0.977/0.952 | 0.489/0.476 |
| 034 | 1.830 | 0.915 | 1.220 | 0.610 | 1.223/0.889 | 0.612/0.445 | 1.930/1.918 | 0.965/0.959 | 1.757/2.076 | 0.879/1.038 |
| 035 | 2.364 | 1.182 | 2.995 | 1.498 | 4.555 | 2.278 | 2.006/2.174 | 1.003/1.087 | 1.008/0.996 | 0.504/0.498 |
| 036 | 0.291 | 0.146 | 0.948 | 0.474 | 0.311 | 0.156 | 0.272/0.299 | 0.136/0.150 | 0.577/0.558 | 0.289/0.279 |
| 037 | 0.479 | 0.240 | 1.074 | 0.537 | 0.555 | 0.278 | 0.299/0.325 | 0.150/0.163 | 1.223/1.200 | 0.612/0.600 |
| 038 | 3.284 | 1.642 | 3.127 | 1.564 | 2.645 | 1.323 | 2.141/2.046 | 1.070/1.023 | 3.762/3.704 | 1.881/1.852 |
| 039 | 0.248 | 0.124 | 0.820 | 0.410 | 0.755 | 0.378 | 0.403/0.427 | 0.202/0.214 | 0.848/0.829 | 0.424/0.415 |

Legend: before and after elimination of outliers by the Cochran test.

**Table 7.** 2002 and 2003 mean Z-score

| Laboratory | $Cl^-$ | | $NO_2$ | | $CN^-$ | | Co | | Ni | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 2002 | 2003 | 2002 | 2003 | 2002 | 2003 | 2002 | 2003 | 2002 | 2003 |
| 029, 031 | 0.565 | 0.251 | 0.774 | 0.642 | 0.263 | 0.189 | 0.819 | 0.104 | 0.164 | 0.310 |
| 022, 032 | 1.319 | 1.599 | 0.176 | 1.124 | 1.092 | 0.189 | 0.206 | 1.561 | 0.688 | 1.248 |
| 024, 033 | 0.305 | 0.072 | 0.167 | 0.410 | 0.663 | 0.578 | 0.529 | 0.889 | 0.910 | 0.476 |
| 021, 034 | 0.398 | 0.915 | 0.487 | 0.610 | 0.745 | 0.445 | 1.457 | 0.959 | 1.463 | 1.038 |
| 023, 035 | 1.942 | 1.182 | 2.546 | 1.498 | 1.448 | 2.278 | 1.734 | 1.087 | 0.692 | 0.498 |
| 025, 036 | 0.609 | 0.146 | 0.196 | 0.474 | 0.487 | 0.156 | 0.883 | 0.150 | 0.025 | 0.279 |
| 027, 037 | 0.193 | 0.240 | 0.441 | 0.537 | 0.767 | 0.278 | 0.420 | 0.163 | 0.719 | 0.600 |
| 026, 038 | 0.548 | 1.642 | 0.240 | 1.564 | 0.531 | 1.323 | 0.361 | 1.023 | 0.168 | 1.852 |
| 028, 039 | 0.440 | 0.124 | 0.337 | 0.410 | 0.844 | 0.378 | 0.425 | 0.214 | 1.516 | 0.415 |

– The mean value of the inter-laboratory results – $X_p$ / considered as reference consensus value.

– The standard deviation of the inter-laboratory results – S.

## CONCLUSIONS

For laboratory performance (Tables 4 and 5) were calculated, for each pollutant and each laboratory:

– The individual Z-score – $Z_i$: $Z_i = (x_n - X_p) / s$;

– Total Z-score – $Z_t$: $Z_t = (Z_1 + Z_2)$;

– Mean Z-score – $Z_m$: $Z_m = (Z_1 + Z_2) / 2$.

The Z-score has the following signification (according with ISO/CEI Guide 43):

$$|Z| \leq 2 \text{ satisfactory}$$

$$2 < |Z| < 3 \text{ questionable}$$

$$|Z| \geq 3 \text{ unsatisfactory}$$

All laboratories obtained in 2002 a $Z_m$-score < 2 which represents very good performance, excepting lab. 023 for $NO_2$.

All laboratories obtained in 2003 a $Z_m$-score < 2 which represents very good performance, excepting lab. 035 for cyanide.

A part of the laboratories performed their performances in 2003 obtaining lower mean Z-score, part of those had obtained higher mean Z-score (Table 7) but the variability within laboratory was better.

The results were used for method validation in a CALIST National R&D project.

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