Interlaboratory comparisons to demonstrate the competence of two similar mobile laboratories

Marius Kovacs[1*], Angelica-Nicoleta Găman[1], *Lorand Toth*[1], and *Romeo Hrișcan*[1]

[1] National Institute for Research and Development in Mine Safety and Protection to Explosion – INSEMEX Petroşani

Abstract. In order to maintain the RENAR (Romanian Accreditation Association) accreditation, each accredited laboratory must periodically participate in interlaboratory testing programs carried out with specialized providers or similar laboratories. In December 2021, an interlaboratory comparison in the field of environmental protection was organized by INCD ISEMEX PETROȘANI. The current paper examines the similarity of results of two auto-laboratories, in similar sampling points to demonstrate the competence of accredited laboratories. During the interlaboratory test session, immission measurements (nitrogen dioxide, nitrogen monoxide, carbon monoxide and sulphur dioxide), ambient noise measurements and determination of suspended dust concentration were performed. The main objective of the interlaboratory tests is to comply with limits established by the bilateral testing protocol, and all these results can be processed and achieved in situ due to systems endowing the auto-laboratories, which integrate all the measurements performed in situ. Results of the study indicate very close values found by the two mobile laboratories, which leads to the performance requirement for all components analysed, namely coefficients of variation below 20%.

1 Generalities

The mobile laboratory offers the possibility to determine a large number of indicators that can be determined in-situ for air environment components. The laboratory is aligned with the most modern and new techniques in the field, equipped with facilities such as: gas analysers, dust sampler (PM2.5, PM10), weather station, high precision GPS for field location, multicomponent cylinder for calibrating equipment. Endowment of the mobile laboratory ensures the facilities for fast measurement / monitoring of physical-chemical indicators and fast forecasting of accidental pollution situations.

The Environmental Testing Laboratories Group (GLI) within INCD INSEMEX Petrosani has organized interlaboratory tests with the Environmental Laboratory of ROMPETROL - Quality Control Navodari. Both environmental testing laboratories within the mentioned institutions are accredited by RENAR (Romanian Accreditation Association) according to SR EN ISO / CEI 17025:2005, have their own policies and procedures, as well as qualified and competent personnel. According to scientific papers carried out in other countries, the mobile laboratory are a precious tool for project manager, can manage the priorities,

* Corresponding author: marius.kovacs@insemex.ro

© The Authors, published by EDP Sciences. This is an open access article distributed under the terms of the Creative Commons Attribution License 4.0 (http://creativecommons.org/licenses/by/4.0/).

and take quicker decisions. Thanks to the feedback of the accredited stationary laboratory, project manager ensures that technicians are trained and skilled, and to that air poluant expertise can be accurate [1].

2 Materials and methods

The notion of proficiency testing is defined by SR EN ISO / IEC 17043:2010 - Conformity assessment. General requirements for proficiency testing, a standard that specifies general requirements for the development and implementation of proficiency testing schemes, which can be used as a basis for intercomparison of tests specific to any field of application. [2]
Proficiency testing by interlaboratory comparisons is used to determine the performance of individual laboratories for specific tests or measurements and to monitor the ongoing performance of laboratories. The introduction to ISO / IEC Guide 43-1:1997 should be consulted for a full exposition of proficiency testing purposes. In statistical language, the performance of laboratories can be described by three properties: laboratory bias, stability and repeatability. The stability of laboratory results is measured by precision as defined in ISO 5725-3.
The purpose of the interlaboratory tests is provided by the need of the GLI-INSEMEX Petrosani and the LM ROMPETROL Quality Control Navodari laboratories to verify and prove performance of their equipment and also to verify the accuracy of test results, for each analysis method used.

There are a multitude of advantaged for using mobile laboratories, namely: more efficient in situ measurement, increased protection of equipment, ensures a comfortable and safe working environment for operators, ensures the facilities of fast measurement / monitoring of physical-chemical indicators and fast forecast of accidental pollution situations.

3 Description of analysis methods and equipment used

There is specialized measuring equipment for measuring emissions of nitrogen dioxide, nitrogen monoxide, carbon monoxide, sulphur dioxide, built in accordance with reference standards. Thus, standards used for each parameter are showed in table no. 1.

The mobile laboratory offers the possibility to determine a large number of indicators that can be determined in-situ for air environment components. The laboratory is aligned with the most modern and new techniques in the field, with equipment such as: gas analysers, dust sampler (PM2.5, PM10), weather station, high precision GPS for field location, multicomponent cylinder for equipment calibration.

Table 1. Test methods used as well as related standards

Measured parameter	Standard
Nitrogen dioxide (NO_2) and nitrogen monoxide (NO)	SR EN 14211: 2012 Ambient air. Standardized method for measuring the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence
Carbon monoxide (CO)	SR EN 14626: 2012 Ambient air. Standardized method for measuring the concentration of carbon monoxide by non-dispersive infrared spectroscopy
Sulfur dioxide (SO_2)	SR EN 14212: 2012 Ambient air. Standardized method for measuring the concentration of sulfur dioxide by ultraviolet fluorescence

Measured parameter	Standard
Suspended dust concentration	SR EN 482: 2016 Workplace atmosphere. General requirements for the performance of chemical measurement procedures
Ambient noise	SR 6161-3: 2020 - Acoustics in construction. Part 3: Determination of noise levels in urban areas. Method of determination.

Sampling differs depending on the type of compound analysed in the sample collected, thus equipment used complies with the reference standards and European directives for each component analysed. The following is the equipment integrated in the INCD INSEMEX Petrosani mobile-laboratory, used in the interlaboratory comparisons. The equipment used by ROMPETROL Quality Control Navodari Environmental Laboratory has the same measurement principles but is built by a different manufacturer.

3.1 FIDAS 200 Dust Analyzer: PM10, PM4, PM2.5 and Total Powders (TSP)

Determination of PM 10, PM 4 and PM 2.5 dusts consists of aspirating a volume of air through a laser beam, the sample produces a flash of light and the intensity of the scattered light is a complex function of the diameter, shape and refractive index of particles, as well as light wavelength and geometry of the optical detector, so the light is reflected on the material particles and a photoelectric cell measures the amount of light scattered on each particle and records the optical measurement of particle size by particle size classes (fig. 1).

Fig. 1. Mobile laboratory- view from behind

3.2 Carbon monoxide (CO) analyser - HORIBA APMA 370

Determination of carbon monoxide (CO) is performed by attenuating the infrared light passing through a sampling cell, measuring CO concentration in the cell, according to Lambert-Beer law. Not only CO, but most heteroatomic molecules absorb infrared light; in particular, water and CO_2 have wide bands that can interfere with CO measurement. The analyzer eliminates cross-sensitivity, instability and drift, so the monitoring system continues to have the following performance requirements:

- measurement of IR absorption at a specific wavelength (4.7 μm for CO)
- dual cell analyzers, which use a reference cell filled with pure air (drift compensation);
- gas-filter correlation, which measures on a wavelength range.

Fig. 2. Carbon monoxide analyzer

3.3 Nitrogen oxide (NOx) analyser - ECOTECH - SERINUS 40

Determination of nitrogen oxides (NO, NO_2, NOx) is based on the reaction of nitrogen monoxide with ozone (chemiluminescence reaction). Thus, in a chemiluminescence analyser, the air is taken through a filter (to prevent contamination of the gas transport system, especially the analyser's optical components) and fed at a constant flow into the reaction chamber of the analyser, where it is mixed with an excess of ozone for the determination of nitrogen monoxide only (fig. 3). The emitted radiation (chemiluminescence) is proportional to the number of molecules of nitrogen monoxide in the detection volume and thus proportional to the concentration of nitrogen monoxide. The emitted radiation is filtered through a selective optical filter and converted into an electrical signal by a photomultiplier tube or photodiode.

For the determination of nitrogen dioxide, the sampled air is fed through a converter where the nitrogen dioxide is reduced to nitrogen monoxide and analysed in the same way as described above. The electrical signal obtained from the photomultiplier tube or photodiode is proportional to the sum of nitrogen dioxide and nitrogen monoxide concentrations. The amount of nitrogen dioxide is calculated from the difference between this concentration and that obtained only for nitrogen monoxide (when the sampled air did not pass through the converter).

Fig. 3. Nitrogen oxide analyzer

Chemiluminescence is the emission of light during a chemical reaction. During the gas phase of the NO and ozone reaction, light is produced with an intensity proportional to the NO concentration when the electrons of the activated NO_2 molecules disintegrate at lower energy states.

3.4 Sulphur dioxide (SO_2) analyser - ECOTECH SERINUS 50

Determination of sulfur dioxide (SO_2) is a phenomenon of photoluminescence (fluorescence) which involves the generation of an initial absorption phenomenon. The luminescent molecules excited by certain quantum states (in this case ultraviolet irradiation), remain in this state for at least 10-9 sec, after which they return to the ground state, by luminescent emission. This secondary emission is proportional to molecules of sulfur dioxide SO_2 in the sample and captured, transformed and transmitted as an electrical signal by the device's photomultiplier tube (PMT) (fig. 4).

Fig. 4. Sulfur dioxide analyzer

The fluorescence phenomenon occurs when the molecule, which is at a certain energy level, has at least two distinct electronic states whose level of rotation-vibration intersects in such a way that there is at least one level of rotation-vibration of the same value of energy, in each state.

3.5 Integrating sound level meter BRUEL & KJAER Type 2250

This integrating sound level meter is used to determine the level of environmental noise and is used along with the acoustic calibrator type 4231 and the determination visualization software BZ 5503 (fig. 5).
Tests performed with this equipment comply with SR ISO 1996 / 1-2016, description, measurement and assessment of ambient noise. The test method consists in the instrumental determination of noise level with the help of the integrating sound level meter type 2250, with microphone type 4189 and A, C and Z weighting networks.

Fig. 5. Integrating sound level meter

It is a portable device powered by a rechargeable source (batteries) with a minimum standby time of 8 hours with the possibility of powering from an external source (220 V / ac or 8-24 Vcc).

3.6 Weather station

Determination of environmental conditions (temperature, pressure, relative humidity, global radiation, speed and direction of air currents) is performed with electronic sensors by picking-up an electrical signal by a sensitive element that has a variation of a physical quantity in relation to the variation of temperature, humidity, pressure, speed of air currents which is transformed into a quantity whose variation can be observed and measured with the help of a transducer accompanied by an amplifier (fig. 6).

Fig. 6. Weather station and common sampling system

Sampling from the ambient air is performed through a single common collector and the sampling of the collected assay is done through individual sampling lines to which gas chromatographs and analyzers endowment of mobile laboratory, are attached.

The common sampling system consists of:

- main collector;
- sampling lines for all equipment endowment of the mobile laboratory, analyzers for CO, SO_2, NO_2, NO, NOx, dusts from the ambient air;
- sampling / assaying pumps.

The main collector is made up of a device to protect against precipitation in such a way that prevents rain from entering the sampling line. The inlet of the main collector as well as the sampling line is made of polytetrafluoroethylene (PTFE) so it doesn't influence the composition of the sample.

The connections are made in such a way that the influence of the pressure drop along the inlet and sampling line is less than 1,0%.

The final results reported by each laboratory represent the average of measurements performed each second for 30 minutes. Each laboratory calculated and declared the measurement uncertainty, and in order to assess the uncertainty, it was necessary to take into account the uncertainty propagated throughout the measurement traceability system. The budget for calibration uncertainty assessment was in line with national and international guidelines and standards [5].

The location chosen by mutual agreement for the interlaboratory measurements was the Super Trans Com S.R.L fuel distribution station, located in Hunedoara County, Petroșani City, December 1918 Street(fig. 7).

In order to perform parallel measurements, the mobile laboratories were placed next to each other, in the perimeter of the fuel distribution station, so as not to influence the activity of Super Trans Com S.R.L company and results to be conclusive.

Fig. 7. Location of measurements

4. Results and statistical analysis

Mainly methods described in ISO 13528 but also additional methodologies described in reference literature were used for analysing results obtained from the inter-laboratory tests.

In the case of this exercise, several statistical tests were used, including the Cochran test, adequacy of the model by the Fisher test (test F - ANOVA methodology), dispersibility of reproducibility, dispersion between samples, SAP test for analytical accuracy, ABSV test for verification of samples variation's acceptance, Z score and En score, Grubb test.

Obviously, not all the above could be applied to all tests.[7] Repeatability of experiments was verified using the Cochran test, by estimating the experimental error and dispersion of the dependent variable. Estimation of reproducibility's dispersion of san2 was performed with the help of several measurements replicated in the center of the experimental field [4].

With the help of reproducibility dispersion, the dispersion of regression coefficients' estimation (repeatability of experiments) was calculated. For this purpose, the Cochran test was applied, according to which the number of repeated experiments is considered sufficient when condition (1) is satisfied:

$$G_{calc} < G_{tabel} \qquad \text{where Cochran criterion: } G = \frac{D^2{}_{\max}}{\sum D^2{}_i} \tag{1}$$

D_{max} –the biggest difference between duplicate attempts
D_i – the difference between each pair of duplicate attempts

The suitability test is performed using the Fischer test ("F-test"). The determined polynomial is considered appropriate if for the test variables by the ANOVA analysis of variance procedure, several tests are passed. In this exercise, the ANOVA technique was applied due to research design and because ANOVA includes the error of comparisons sets within the calculation of statistical errors (which is impossible with the "t" test). The analytical technique thus used is fully consistent with the one-factor ANOVA analysis.

Thus, the following are calculated:

- analytical variation

$$s^2{}_{an} = MS_{within} \tag{2}$$

- variation between samples

$$s^2{}_{an} = \frac{MS_{between} - MS_{within}}{2} \tag{3}$$

where: $MS_{between} = \frac{SS_{between}}{J-1}$, $MS_{within} = \frac{SS_{within}}{(N-J)}$, $MS_{total} = \frac{SS_{total}}{N-1}$ (4)

J – number of groups / equipment used in duplicate tests
N – total number of tests performed

- test for analytical accuracy (SAP test - Sufficient Analytical Precision)

$\sigma = \chi \cdot CV$ with which the value of the criterion is calculated $SAP = \frac{s_{an}}{\sigma}$ (5)

$CV = 2^{(1-0.5 \cdot \log C)}$ –inter-laboratory coefficient of variation and C is the power factor of the measured concentration (e.g., 1 ppm = 10^{-6} thus C = -6)

$$\chi = \sum_{i=1}^{n} \frac{(x_i - y_i)}{n} \tag{6}$$

x_i, y_i – duplicate individual values obtained by each laboratory in the *n* tests.

- test of variation between samples (ABSV test - Acceptable Between Sample Variance)

$$\sigma^2_{all} = (0.3 \cdot \sigma)^2 \tag{7}$$

the critical value to be compared is calculated with the relation:

$$c = F_1 \cdot \sigma^2_{all} + F_2 \cdot \sigma^2_{all} \tag{8}$$

Factors F_1 and F_2 are dependent on the number of duplicate tests performed being defined in the references, in the case of our exercise $F_1 = 1.88$ and $F_2 = 1.01$. the value of σ^2_{sam} must be less than *c* for the test to be passed.

To facilitate the analytical effort, equations are calculated:

$$eq1 = \frac{(\sum y_{ij})^2}{N}, \quad eq2 = \sum y_{ij}{}^2, \quad eq3 = \sum \frac{T_{Aj}{}^2}{N_{Aj}} \tag{9}$$

where y_{ij} –concentration obtained after each individual test; T_{Aj}, N_{Aj} –sum of results and number of tests for each laboratory

thus:

$$SS_{total} = eq2 - eq1, \; SS_{between} = eq3 - eq1, \qquad SS_{within} = eq2 - eq3 \;\; F = \frac{MS_{between}}{MS_{within}} \tag{10}$$

The standard deviation of the s_{erf} reference value is calculated using the limits of the range in which the standard is certified.

$$s_{ref} = \frac{(a_+ - a_-)^2}{12} \tag{11}$$

where a_+ is the concentration value of the incertitude and a_- is the value of the standard concentration minus the uncertainty associated with it.

Standard deviation for each laboratory was calculated with the relation:

$$s = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (x_i - \bar{x})} \tag{12}$$

where *x* – individual values şi $\bar{x}$ - average individual values

- the "z" score is the ratio between the difference of the average x_{mas} value of an individual laboratory from the X_{ref} reference value and the standard deviation of the s_{ref} reference value.

$$z = \frac{x_{mas} - X_{ref}}{s_{ref}} \tag{13}$$

If $|z| \leq 2$ 2 laboratory performance is satisfactory, if $|z| \leq 3$ laboratory performance is

debatable and if $|z| > 3$ laboratory performance is unsatisfactory. [3]

- the score "En" represents the ratio between the difference of the average x_{mas} value of an individual laboratory compared to the reference value X_{ref} and the radical of the sum between the extended standard uncertainty of the individual laboratory at square U^2_x and the extended standard uncertainty of the reference value at square U^2_X.

$$E_n = \frac{x_{mas} - X_{ref}}{\sqrt{U^2_x + U^2_X}} \tag{14}$$

In order to perform interlaboratory comparisons, on 18.12.2021, parallel measurements and test reports for each parameter analyzed were performed.
The values determined by each laboratory represent the average of the measurements made in the same time interval, under the same environmental conditions, over a period of 30 minutes recorded each second.
The average results obtained for each component are shown in table 2.

Table 2. Average values of intercomparison results

Measured parameter	Measuring unit	Value found by INSEMEX Petrosani	Value found by RQC Navodari	Average of measured values
NO_2 - imissions	µg/m³	99,48	96,07	97,78
NO - imissions	µg/m³	51,37	53,22	52,30
CO - imissions	mg/m³	0,67	0,71	0,69
SO_2 - imissions	µg/m³	1,127	1,313	1,22
Total dusts	mg/m³	0,87	0,93	0,90
Noise	dB(A)	64,70	63,50	64,10

Analysis of results (table 2 and fig. 8) shows that the average of measured values is close to the value determined by each mobile laboratory.

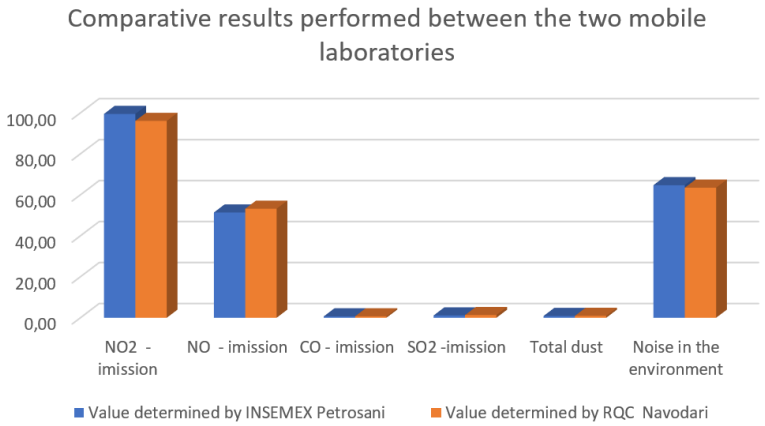

Fig. 8. Graphical representation of comparative results

Replacing formulas no. 1 ÷ 14 (presented above) for all the indicators analyzed, shows that the score "z" is lower than 3, which indicates that laboratories' performance was

satisfactory and the score "En" is in all cases less than 1, which indicates that laboratories' performance is also satisfactory.

Table 3. Calculation of the "z" score for each parameter.

Measured parameter	Cochran C test	Analytical variation S_{an}^2	Variation between samples S_{am}^2	SAP (test for Sufficient Analytical Precision) S_{an}/σ	ABSV (test for Acceptable Between Sample Variance) σ^2all	Score „z"	Score „E_n"
NO_2 - imissions	0,16	0,45	3,89	0,07	64,1	1,2	0,7
NO - imissions	0,31	0,45	3,8	0,14	17,7	0,69	0,41
CO - imissions	0,20	0,01	0,06	0,27	0,07	0,014	0,09
SO_2 - imissions	0,100	0,001	0,003	0,048	0,131	0,056	0034
Total dusts	0,181	0,001	0,003	0,078	0,046	0,032	0,019
Noise	0,14	0,08	0,65	0,07	13,31	0,465	0,260

To compare these results, the standard deviations, reproducibility and coefficient of variation for each type of test were calculated (Table 4).

Tabel 4. Calculation of standard deviation and reproducibility.

Measured parameter	Measuring unit	Value found by INSEMEX Petrosani	Value found by RQC Navodari	Average measured values	Standard deviationd	Repeatability	CVR found (%)	Acceptability criterion
NO_2 - imissions	µg/m³	99,48	96,07	97,78	2,41	10,8	2,47	CVR ≤ 20%
NO - imissions	µg/m³	51,37	53,22	52,30	1,31	5,86	2,50	
CO - imissions	mg/m³	0,67	0,71	0,69	0,03	0,13	4,10	
SO_2 - imissions	µg/m³	1,127	1,313	1,22	0,13	0,59	10,78	
Total dusts	mg/m³	0,87	0,93	0,90	0,04	0,19	4,71	
Noise	dB(A)	64,70	63,50	64,10	0,85	3,80	1,32	

According to the collaboration agreement between the two institutions, the acceptability criterion of results must be less than or equal to 20% of the measurement, which is fulfilled for absolutely all tests performed.

The coefficient of variation has values in the range of 1.32 ÷ 10.78%, shown in fig.9, and is below 20%.

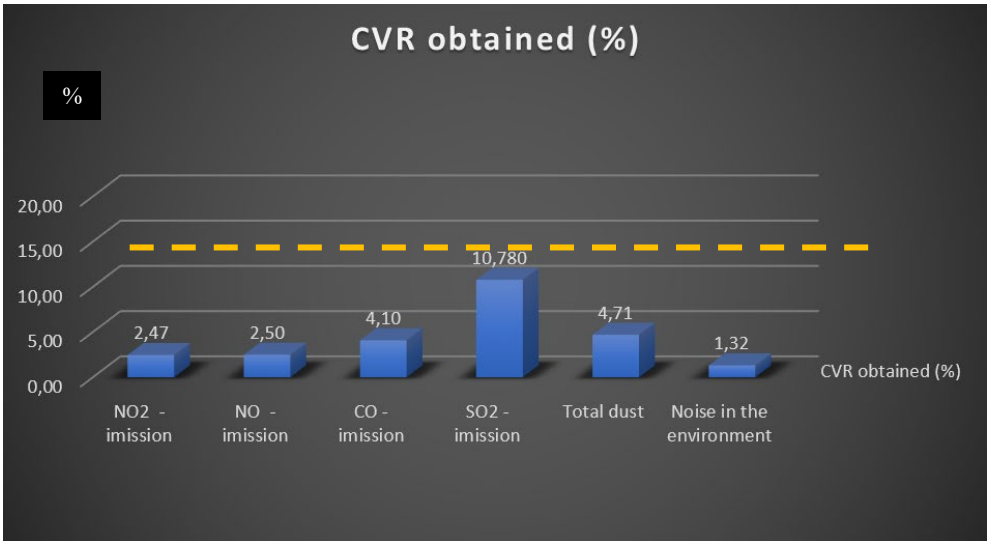

Fig. 9. Graphical representation of the coefficient of variation calculated for the two mobile laboratories.

5. Conclusions

In order to ensure the quality of test results and to prevent / detect possible errors in testing, RENAR accredited laboratories must periodically participate in interlaboratory testing programs. According to RENAR requirements, each accredited laboratory must carry out and comply with an interlaboratory test plan. Due to the fact that at present in Romania there are only a few mobile laboratories, until now these tests have not been performed and there are no external providers to perform tests.

The main advantages of using these mobile laboratories (auto-laboratories) are that they make in situ measurements more efficient, achieve an increased protection of equipment and ensure a comfortable and safe working environment for operators. Equipment of the mobile laboratory provides the facilities for fast measurement / monitoring of physical-chemical indicators and fast forecasting of accidental pollution situations. [5]

The current paper aims to statistically compare results found by two similar mobile laboratories in order to confirm their competence [6]. Results of the interlaboratory comparison can be further used to assess the competence of the participating laboratories in the approached field.

In December 2021, the Group of Environmental Testing Laboratories (GLI) within INCD INSEMEX Petroşani organized interlaboratory tests with the Environmental Laboratory of ROMPETROL Quality Control Navodari. Both environmental testing laboratories within the mentioned institutions are RENAR accredited according to SR EN ISO / CEI 17025:2005, have their own policies and procedures, as well as qualified and competent personnel. These tests were performed within a fuel distribution station located in the city of Petroșani.

During interlaboratory testsing, immission measurements (nitrogen dioxide, nitrogen monoxide, carbon monoxide, sulfur dioxide), ambient noise measurements and determination of suspended dust concentration were performed.

To compare these results, standard deviations, reproducibility and coefficient of variation were calculated for each individual test, and the criterion of results acceptability must be less than or equal to 20% of measurements. Alalysis of results showed that the coefficient of variation has values in the range of 1.32 ÷ 10.78% and is below the value of 20%, thus performance requirement was met for absolutely all tests performed.

Importance of these interlaboratory tests results from the fact that supporting documents as well as statistical calculations will be presented to the RENAR audit team, being an essential element in maintaining the laboratories acredited for tests performed.

Laboratories participating in the comparison demonstrated compatibility of the results, having different measurement capabilities in the analyzed field. The experiment can also be extended to make comparisons with other multinational laboratories which have accredited mobile laboratories.

The knowledge gained during the interlaboratory comparison will be used for similar actions, developing the field of measurement and widening the area of participation.

This paper was developed within the Nucleu-Programme, carried out with the support of MCI, Program Nucleu EXTOX 2, entitled "Modernization of the research infrastructure for complete investigation of both physical and chemical parameters of environmental components' quality in situ within landfills as well as in work environments in order to increase the degree of safety and health".

References

1. V. Goudeau , B. Daniel, D. Dubot *"Mobile laboratories: An innovative and efficient solution for radiological characterization of sites under or after decommissioning"*
2. J. McGlade, director executiv al Agenției Europene de Mediu, *SR EN ISO/CEI 17043:2010 - Evaluarea conformităţii. Cerinţe generale pentru încercările de competenţă*
3. A. Drăghici (Găman), F. Popescu, G. Gheţie, L. Toth, M. Kovacs, „*Analiza statistică a rezultatelor obţinute în urma încercărilor interlaboratoare*"
4. V. Goudeau, B. Daniel, D. Dubot "Mobile laboratories: *An innovative and efficient solution for radiological characterization of sites under or after decommissioning" Journal of Environmental Radioactivity journal homepage: www.elsevier.com/locate/jenvrad*
5. A. Gherasimov „*Interlaboratory comparisons organized by BRML: calibration of static uniaxial testing machines*" ROMANIAN BUREAU OF LEGAL METROLOGY – Force and Hardness Laboratory, Timişoara
6. X. Zhang, J. Xu, W. Zhao, L. Zhai, and others, *"High-spatial-resolution distributions of aerosol chemical characteristics in urban Lanzhou, western China, during wintertime: Insights from an on-road mobile aerosol mass spectrometry measurement experiment"*
7. H. Wang , YeWua, K. Max Zhang , and others *"Evaluating mobile monitoring of on-road emission factors by comparing concurrent PEMS measurements"* Science of the Total Environment 2020