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Conformity assessment of the measurement accuracy in testing laboratories using a software application*

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Abstract. This article presents a method for assessing the accuracy of the measurements obtained at different tests conducted in laboratories by implementing the interlaboratory comparison method (organization, performance and evaluation of measurements of tests on the same or similar items by two or more laboratories under predetermined conditions). The program (independent software application), realised by the author and described in this paper, analyses the measurement accuracy and performance of testing laboratory by comparing the results obtained from different tests, using the modify Youden diagram, helping identify different types of errors that can occur in measurement, according to ISO 13528:2015, Statistical methods for use in proficiency testing by interlaboratory comparison. A case study is presented in the article by determining the chemical composition of identical samples from five different laboratories. The Youden diagram obtained from this study case was used to identify errors in the laboratory testing equipment.

1. Introduction

In recent years, interlaboratory comparisons (***ILC***) have gained a special importance both as a tool for verification of traceability in the process of quality assurance, as well as validation tool for working procedures of related testing laboratories accredited or pending accreditation activities.

The need for reliable continuous performance of a laboratory is not only essential for laboratories and their customers, but also for other entities such as regulators, laboratory accreditation institute and other organizations that specify requirements for laboratories. The correct operation of testing laboratories requires an internal or external quality control. Internal quality control is provided by calibration set by different standards and assessment of uncertainty, while external quality control can be established through a modern method – ***ILC*** [1,2].

Interlaboratory comparisons are reliable and efficient mechanisms to certify the competence of laboratories because they allow ensuring quality of results delivered by the laboratory and helps demonstrate its competence as a mechanism for progress. An interlaboratory comparison is designed to answer one of the following objectives: 1. to assess the skills laboratories, 2. to evaluate the characteristics of a material, 3. to evaluate the characteristics of a method of analysis, testing or calibration. Participation in proficiency testing is an appropriate way to train the laboratory and risk management. For technical and metrological level alignment of national and references standards with the performance of European metrology institutes, is needed extension and integration of research

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activities carried out within an institutional framework at national and European level through involvement in inter-laboratory comparisons [7,8].

2. Organizing interlaboratory comparison tests

In ISO/IEC 17025, participation in interlaboratory comparison tests ***ILC***, also known as proficiency testing is explicitly required for the accreditation of testing and calibration laboratories. ISO/IEC 17043 standard provides general requirements for conducting the proficiency tests. The results of tests obtained based on ISO/IEC 17043 protocols are usually analysed by statistical methods laid down in ISO 13528. In many cases Youden diagram is used to evaluate the test results provided by ***ILC***. Scheme comparison test specifies that two samples (with slightly different properties) are distributed to a participant in a scheme of interlaboratory comparison [5].

Accuracy (truth value and precision) of measurement should be determined in a series of tests or measurement results reported by laboratories participating in the study organized for this purpose. To avoid any discrepancy and to reduce dispersion, all participants must have the same detailed measurement or test method which describes how the measurement should be performed and how the specimens should be obtained or prepared. Measurement method under investigation should be an optimized method in terms of procedure used, such a method should be robust (for example: small variations in procedure should not produce major changes in the final results).

The document specifies the method of measurement should be clearly and completely. All essential operations related to working environment, equipment and metrological traceability of test and specimen preparation method must be included in the ***ILC*** procedure [3,4].

3. Youden diagram - model for comparing the test results of *ILC*

Youden diagram is a graphical method to analyse the experimental data provides by different participants in ***ILC***. Chart view variability in laboratory testing and interlaboratory variability. In this graphical method for the analysis of inter-laboratory experimental data, all laboratories analysed two samples. Youden diagram with two variables is a useful method for certain types of interlaboratory comparisons and test results. For Youden diagram, the two samples may be similar and have measurement values close to the average of measurements taken, but may have differences from the average, in this case is used the standard deviation for framing values on the two axes. Axes in this chart are drawn to the same scale: a unit on the x axis has the same length as a unit on the y axis. Each point on the chart corresponds to the results of one laboratory tests and is defined by a variable on the horizontal axis and a second response variable on the vertical axis [6].

The diagram can be drawn using three types of models that take into account the laws of normal distribution, whereby a standard deviation, or sigma (1σ), define a region that evaluates 68% of all data points (measured values), two sigma (2σ) will comprise 95% percent of data and three sigma (3σ) will comprise 97.7%. The most common types of Youden diagram are:

- diagram using framing squares, as shown in figure 1;
- diagram using framing circles, as shown in figure 2;
- diagram using framing ellipse, as shown in figure 3.

Youden diagram is applied to identify laboratories with large systematic errors and high random errors. Interpretation of data obtained from experimental tests from the perspective of integrating them in a Youden diagram, can be made as follows [9,10]:

a. experimental values pairs obtained from experimental tests, conducted in ***ILC,*** focus on arithmetic - *small random and systematic error*;

b. the pairs of values determined by experimental tests are scattered along the line of 45° in the upper right quadrant and the lower left quadrant – *small random error and large systematic error*;

c. the pairs of values determined by experimental tests are located away from the line of 45^0 in the upper left quadrant and lower right quadrant – *large random error and small systematic error*;

d. the pairs of values determined by experimental tests are situated outside diagram (rectangle, circle or ellipse) - *large systematic and random errors*.

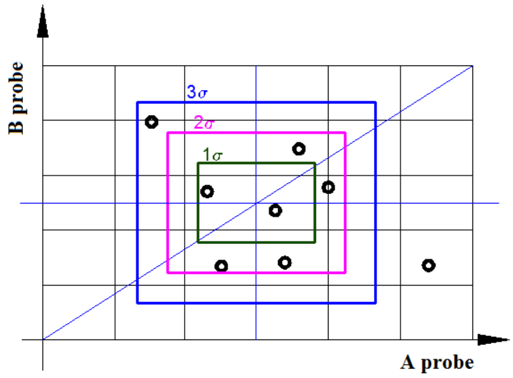


Figure 1. Youden diagram using the model with squares.

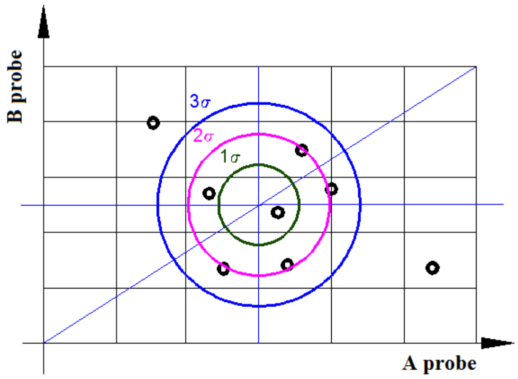


Figure 2. Youden diagram using the model with circles.

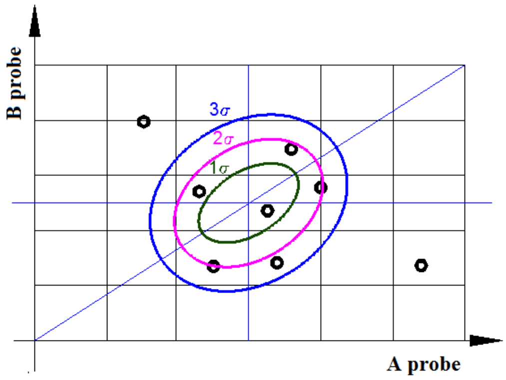


Figure 3. Youden diagram using the model with ellipse.

For the analysis of experimental data, in this research, will be used Youden diagram using ellipses framing type (*1σ, 2σ, 3σ*). To determine parametric equations of the ellipse (*ellipse is the locus of points in the Euclidean plane whose sum of distances from two fixed points is constant*) is used the following parametric equations, considered model is shown in figure 4 [4,5]:

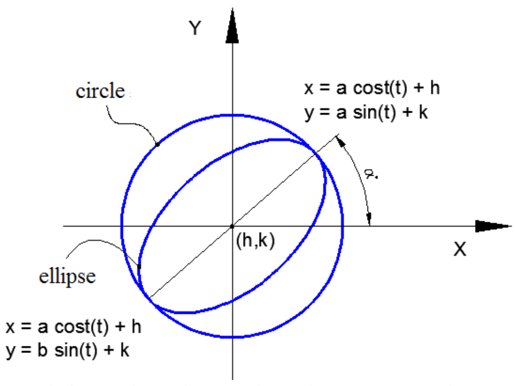


Figure 4. Analysis model used to determine the parametric equations of an ellipse.

- parametric equation of a circle:

$$\begin{cases} x = a \cdot \cos(t) + h \\ y = a \cdot \sin(t) + k \end{cases} \tag{1}$$

Coordinates point (*h, k*) is the centre of the circle, *a* is the circle radius, and $t = 0 \ldots 2\pi(360^0)$ is a parametric variable, being geometrically interpreted as the angle formed by the circle radius with x axis.

- parametric equation of an ellipse rotated at an angle *α*, having semi-major axis equal to *a* and semi-minor axis equal to *b*:

$$[X \quad Z] = \begin{bmatrix} \cos(\alpha) & \sin(\alpha) \\ -\sin(\alpha) & \cos(\alpha) \end{bmatrix} \begin{bmatrix} X^{'} & Y^{'} \end{bmatrix} \tag{2}$$

In which $\begin{bmatrix} \cos(\alpha) & \sin(\alpha) \\ -\sin(\alpha) & \cos(\alpha) \end{bmatrix}$ it is rotation matrix.

- parametric equations of an ellipse centred on the point (*h, k*) and rotated at an angle *α* are obtained from the developing equation 2:

$$\begin{cases} x = h + a \cdot \cos(t) \cdot \cos(\alpha) - b\sin(t)\sin(\alpha) \\ y = k + a \cdot \cos(t) \cdot \sin(\alpha) + b\sin(t)\cos(\alpha) \end{cases} \tag{3}$$

Parametric equations of an ellipse rotated at an specific angle used to the analyses results of experimental tests carried out during ILC involves using the arithmetic average of the two series of experimentally determined values as the origin of the ellipse and the standard deviation for **A probe** is considered semi-major axis of the ellipse and standard deviation calculated for the **B probe** is semi-minor axis of the ellipse.

Custom equations used as a tool in evaluating ***ICL*** by the implementation of Youden diagram are:

- *Case I*. The standard deviation (*1σ*) is used to define a region which includes 68% of all the values determined by experimental tests

$$\begin{cases} x = \bar{x} + 1\sigma_{A\,probe} \cdot \cos(t) \cdot \cos(\alpha) - 1\sigma_{B\,probe}\sin(t)\sin(\alpha) \\ y = \bar{y} + 1\sigma_{A\,probe} \cdot \cos(t) \cdot \sin(\alpha) + 1\sigma_{B\,probe}\sin(t)\cos(\alpha) \end{cases} \tag{4}$$

- *Case II*. The standard deviation (*2σ*) is used to define a region which includes 95% of all the values determined by experimental tests

$$\begin{cases} x = \bar{x} + 2\sigma_{A\,probe} \cdot \cos(t) \cdot \cos(\alpha) - 2\sigma_{B\,probe}\sin(t)\sin(\alpha) \\ y = \bar{y} + 2\sigma_{A\,probe} \cdot \cos(t) \cdot \sin(\alpha) + 2\sigma_{B\,probe}\sin(t)\cos(\alpha) \end{cases} \tag{5}$$

- *Case III*. The standard deviation (*2σ*) is used to define a region which includes 97.7% of all the values determined by experimental tests

$$\begin{cases} x = \bar{x} + 3\sigma_{A\,probe} \cdot \cos(t) \cdot \cos(\alpha) - 3\sigma_{B\,probe}\sin(t)\sin(\alpha) \\ y = \bar{y} + 3\sigma_{A\,probe} \cdot \cos(t) \cdot \sin(\alpha) + 3\sigma_{B\,probe}\sin(t)\cos(\alpha) \end{cases} \tag{6}$$

$\bar{x}$, $\bar{y}$ - average values for **A probe** and respectively for **B probe**.

- the rotation angle of the ellipse corresponding to Youden diagram

$$\alpha = atan\frac{\sum_{i=1}^{n}\left(x_i-\overline{x}\right)^2-\sum_{i=1}^{n}\left(y_i-\overline{y}\right)^2+\sqrt{\left(\sum_{i=1}^{n}\left(x_i-\overline{x}\right)^2-\sum_{i=1}^{n}\left(y_i-\overline{y}\right)^2\right)^2+4\cdot\left(\sum_{i=1}^{n}\left(x_i-\overline{x}\right)\cdot\left(y_i-\overline{y}\right)\right)^2}}{2\cdot\sum_{i=1}^{n}\left(x_i-\overline{x}\right)\cdot\left(y_i-\overline{y}\right)^2} \quad (7)$$

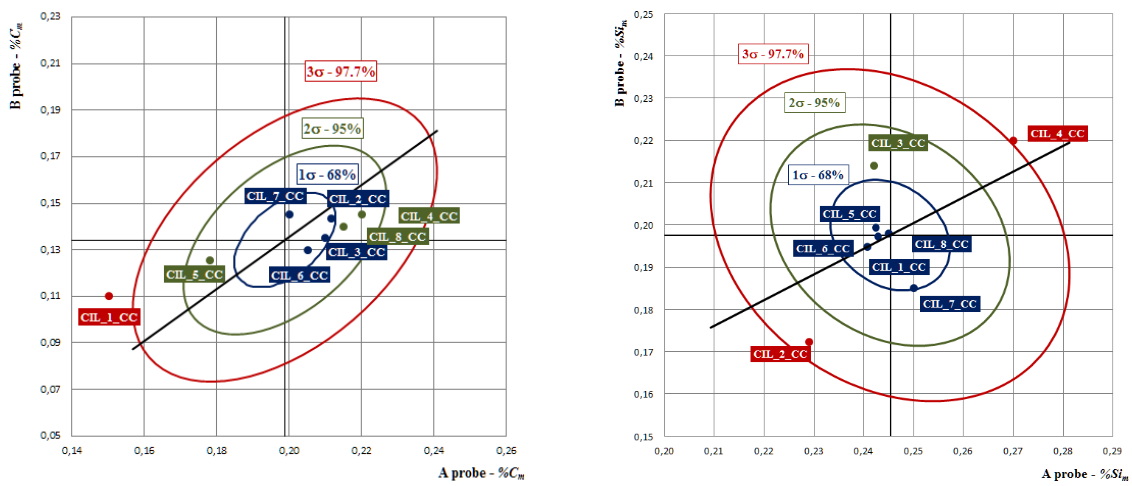
4. Case study on interlaboratory comparison

Verification of research developed in this paper was realized for a proficiency test - ***chemical composition analysis / identification code CC*** - using optical emission spectrometer to determine quantitative analysis of chemical elements in solid samples of specify alloy, taking into considering only masic concentration of carbon and silicon. Analysis of ***CC*** proficiency test was started by submitting an ***ILC*** invitation to 8 companies (laboratories) which are equipped with optical emission spectrometer, due to copyright the company names are replaced with the following codes: ***ILC_1…8_CC***. After receipt confirmation of acceptance for participating in ***ILC***, each laboratory received two samples marked as **A probe** and respectively **B probe**. Mass concentrations of $\%C_m$ and $\%Si_m$ provided by participating laboratories to ***ILC*** are summarized in table 1.

Table 1. The values obtained by laboratory test.

Laboratory code	A probe		B probe	
	$\%C_m$	$\%Si_m$	$\%C_m$	$\%Si_m$
ILC_1_CC	0.150	0.243	0.105	0.197
ILC_2_CC	0.212	0.229	0.138	0.172
ILC_3_CC	0.210	0.242	0.130	0.214
ILC_4_CC	0.220	0.270	0.140	0.220
ILC_5_CC	0.178	0.242	0.120	0.199
ILC_6_CC	0.205	0.241	0.125	0.195
ILC_7_CC	0.200	0.250	0.140	0.185
ILC_8_CC	0.215	0.245	0.135	0.198

The calculation results of parameters used to analyse the data received from participating laboratories are presented in figure 5. The final report was submitted to the 8 participating laboratories in interlaboratory comparison to take in consideration some measures for corrections of systematic errors as well as random errors.



(*a*) (*b*)

Figure 5. Youden diagram applied for a ***CC*** proficiency test considered, **A probe** (*a*); **B probe** (*b*).

The results obtained and the need to use a program that is not limited by the installation of specialized software required the development of a executable software (*Interlaboratory Comparison software was developed using Matlab*) on any computer with minimal technical specifications, the working interface of the program created by the author is shown in figure 6. The software developed by the author was created using MATLAB (Matrix Laboratory), which is a development environment for numerical analysis and statistical analysis, the programming language that contains the same name, created by MathWorks. MATLAB allows the manipulation of matrices, visualization functions, implementation of algorithms, and creation of interfaces and can interact with other applications. The procedure for the realization of interlaboratory comparisons, using the software, includes the following steps: *a. Organizing interlaboratory comparison*: Establish frequency and data of ***ILC***; selection of participants; protocol development and documentation; sending documents to participants; *b. Preparation of samples used in* ***ILC***: manufacture or acquisition of samples; calibration / testing and assigning the reference value of sample; handling and storage of samples; *c. Running round* ***ILC***: preparation and distribution / sending of samples; monitoring activities of participants; data collection and processing; *d. Analysis and Decision:* Comparison of the results obtained by well-established and documented methods; performance evaluation of participants; issue views and interpretations; development and approval of competence test reports; publication of reports.

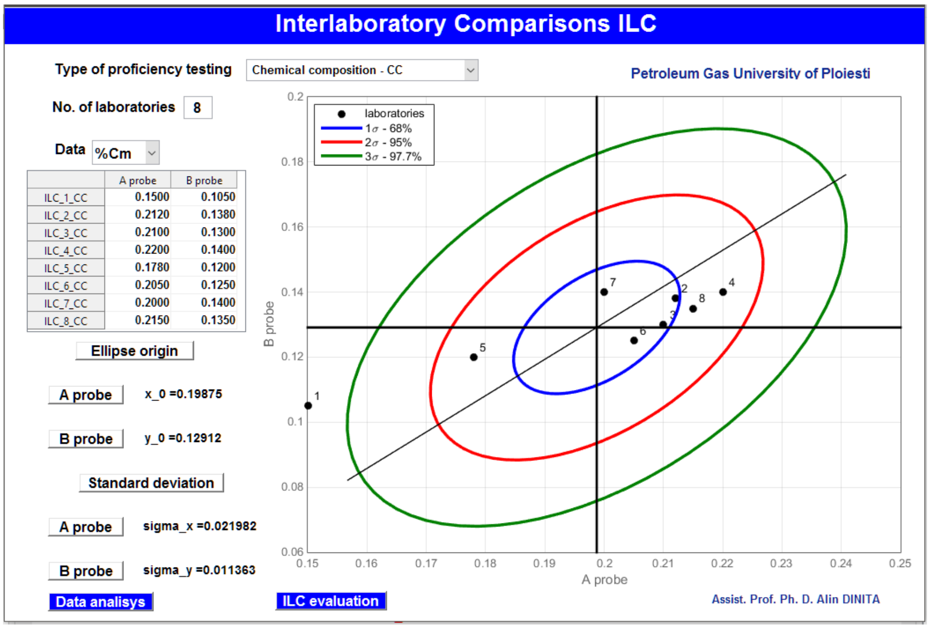


Figure 6. Specialized software for ***ILC*** data evaluation.

Analysing the Youden diagram, obtained by processing the data obtained from 8 participating laboratories in ***ILC,*** provides useful information to eliminate possible errors appeared in the experimental tests. Using the application, the processed data from laboratory no. 1 is situated outside from diagram, which indicates a *large systematic and random errors*, which may drastically influence the measurement process. After delivering results to all laboratories involved in the study, the laboratory no. 1 made a recalibration of equipment used to determine the chemical composition and provided second set of values that were within the allowable limits, confirming the usefulness of this software application created.

The main aim of the research was conducted to develop a standalone application that can be used in the performance evaluation laboratories. The application was verified by conducting a comparison scheme involving 8 laboratories in Romania, using as the reference test, determining the chemical composition for two samples provided by the author researches. The study is valuable for laboratories doing quantitative studies.

5. Conclusions

Proficiency testing ***ILC*** is used to determine the performance of individual laboratories for some tests or measurements, to monitor the continuing performance and quality of laboratories and the confidence provided by a laboratory evaluation. The software developed in this paper can be used as a simple numerical and graphical criterion to identify warning signals provided by systematic and random errors.

Proficiency testing is gaining increasing importance in many laboratories from different countries and becomes extremely important for quality assurance when used in relation with certified reference materials, validated methods.

ILC schemes and programs are organized primarily for the benefit of laboratories, the results obtained in these schemes are used by third-party organizations, including national accreditation organizations, national and international regulators and customer's laboratories. This is reflected in the quality of services provided by ILC schemes and confirmation of fulfilment of technical requirements and quality assurance specified in the applicable referential is objectively necessary

Software created can easily be used for many types of proficiency tests. It is a necessary tool for laboratories to check the compliance of the test results. The software application can be used to improve the analytical performance of the interlaboratory comparisons and it is a useful tool for getting quick results achieved by different laboratories in laboratories schemes. The results of the intercomparison conducted in this paper improve confidence in the equipment and procedures used to perform various tests and measurements.

The main objective of a software developed is to help the participating laboratory to assess the accuracy of its test results. Intercomparison of measurements obtained from different tests are one of the main method of proving realistic estimates of measurement uncertainty.

6. References

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