REPEATABILITY AND REPRODUCIBILITY-TESTS FOR EVALUATION AND VALIDITY OF THE ANALYTICAL DATA

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Abstract: In this study the identification of the non-conformities that influence the analytic determinations is proposed, by utilising repeatability and reproducibility tests. The case-study consists in the application of these tests to five laboratories, where determinations for the methylic alcohol, aldehydes, acidity and extract in ethylic alcohol were made. In this way the causes that generated errors in the results of the quality determinations were identified.

Keywords: repeatability, reproducibility, analytical data

INTRODUCTION

At the world level, millions of analytical measurements are made daily. One example is the support for the health insurance for evaluating the merchandises for marketing. The cost of these measurements is high, fact that justifies the researches to determine the correct result and to prove it (Lewis, 1991).

It is considered that an analysis laboratory has a high degree of knowledge which cannot be obtained by the clients alone. When talking about the results, the clients expect that the laboratory gives the correct answer for the analytical part of the analysis. The validity of the method allows the researchers to prove that a method corresponds to the purpose (**, 1997).

The performance parameters are: selectivity-specification, detection limit, quantifications limit, work and geometrical domain, accuracy (confidence-truth, precision-the precision repeatability and the reproducibility precision), sensibility, recovery, the uncertainty measurement (***, 2003).

A collaborative study, realised in order to validate a published method, for example, according to the A OAC/IUPAC protocol or the ISO 5 725 standard, is a valuable source of data in order to support the uncertainty estimation. The data typically included estimations of the reproducibility of

the standard deviation s_R, for different levels of answer, a geometrical estimation of the dependence on the answer level and it can also include a bias estimation according to the CRM studies (***, 2003).
It is necessary to identify any uncertainty sources which are not covered by the data from the study realised in collaboration, as the samples evaluation, pre-treatment, the method bias, the conditions variations, the changes in the sample matrix. Any significant source of uncertainty, uncovered by the data from the study in collaboration, must be evaluated according to a standard uncertainty and combined with the reproducibility of the standard deviation s_R in a common way.
Such a study is proposed in this work, implying five laboratories where the refined ethylic alcohol was subjected to analysis.

MATERIALS AND METHODS

A comparative test was realised, where 5 laboratories, noted as: A, B, C, D and E participated. The analysed product was the refined ethylic alcohol. The analyses were:

- The methylic alcohol content - according to STAS 184/10-90, point 4 (the litigation method)
- The aldehydes concentration - according to STAS 184/7-85, point 3 (the litigation method)
- The acidity - according to SR 184-5:1997, point 4 (a method established through the specific working instruction, ISL no.001/10.04.2002)
- The extract content – according to STAS 184/3-70, point 2 (a variant chosen according to the content of extract from the product).

In all the laboratories, the analysis was done on assays originating from the same samples of refined ethylic alcohol, through the same methods and with the same reagents. During the attempts the following parameters varied:

- the executing staff,
- the measurements and attempts equipments
- the graduated and/or quoted glasses.

Each analysis was performed five times and the limit results (maximal and minimal) were not considered in calculations.

In all laboratories, the good functioning of the analytical balances was checked. In all laboratories (except A laboratory which is equipped with a SPEKOL 10 spectrometer) the maximum absorption of the colour

components was checked and the observations made can be found in Table 1.

Table 1. Maximum absorption of the colour components in the tested laboratories

Laboratory	Methylic alcohol determination λ=570nm	Aldehydes determination λ=560nm
A	570*	560*
B	572	560
C	573	563
D	570	569
E	570	568

The analysis of the obtained results was made according to the calculation method from the general proceeding COD: PG-013 "Interlaboratory comparative attempts" (Curie, 1995).

RESULTS AND DISCUSSIONS

Determination of the methylic alcohol

The obtained results are presented in Figure 1, which presents the acceptance interval of the results for a confidence level of 95%. Absurd results after the analysis were obtained by the laboratory A and B, and they were eliminated.
The explication of the causes of the absurd results in the case of the laboratory B could be the lack of a micro-burette for dosing the substances when tracing the sample curve and the imprecision of the measurements equipments in the case of B laboratory. The cause is the SECOMAM S750 spectrophometer which got blocked during the tracing of the sample curve and it did not noticed any different concentrations, although the intensity of the colours was different and it could be visible.
For laboratory A, the cause is the SPEKOL 10 photocolorimeter: the machine could not be stabilized (0 and 100) only at a sensibility of 10 which is the limit of the good functioning of the machine.

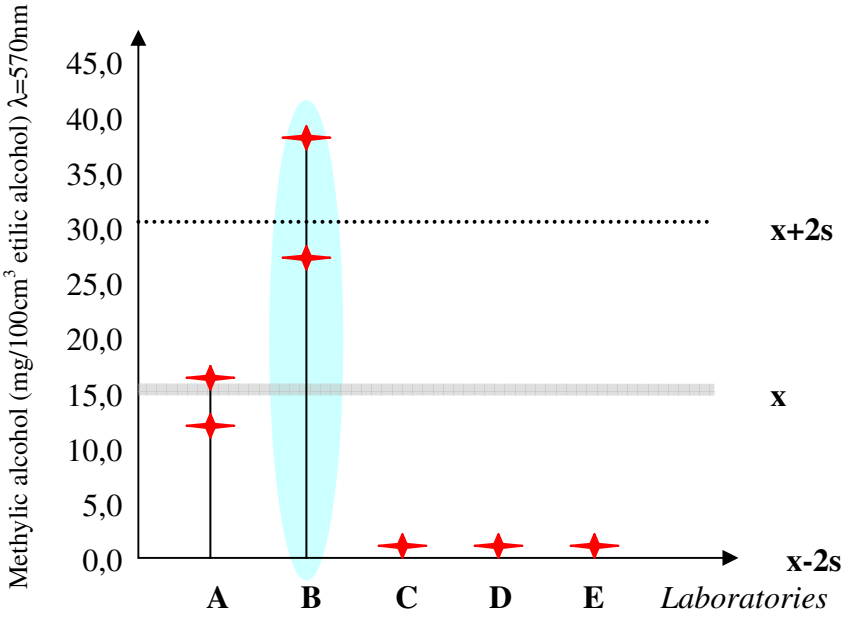

Figure 1: Values registered at the determination of the methylic alcohol from ethylic alcohol in the five laboratories. The acceptance interval of the results is for a confidence level of 95 %.

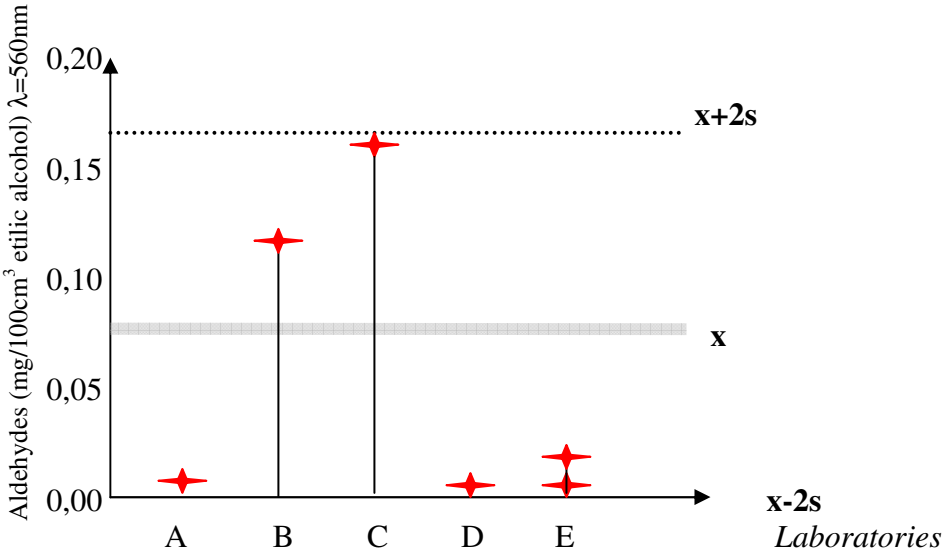

Figure 2: Values registered at the determination of the content in aldehydes from ethylic alcohol in the five laboratories

Determination of the aldehydes

The obtained results are plotted in Figure 2, for a confidence level of 95 % is presented. All the results are considered as accepted.

Determination of the acidity

The obtained results are presented in Figure 3. The acceptance domains of the results for a confidence level of 95 % are indicated.

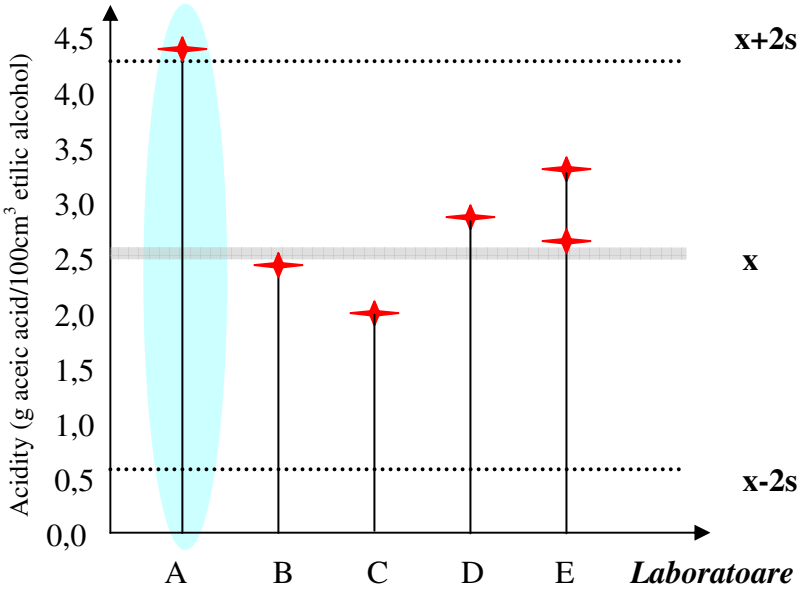

Figure 3: Values registered at the determination of the acidity from ethylic alcohol in the five laboratories

The accepted results are from laboratories B, C, D and E.
The absurd results were obtained by laboratory A. The explication of the absurd results for A laboratory was that because of the lack of an ascending refrigerant according to the attempt method, Soxhlet extractors were used, which impurified the sample.
After the exclusion of laboratory A, the confidence domain of 95 % for the other four laboratories was recalculated. All the laboratories were accepted.

Determination of the extract

The obtained results are presented in Figure 4. The acceptance level of the results for a confidence level of 95 % are indicated.

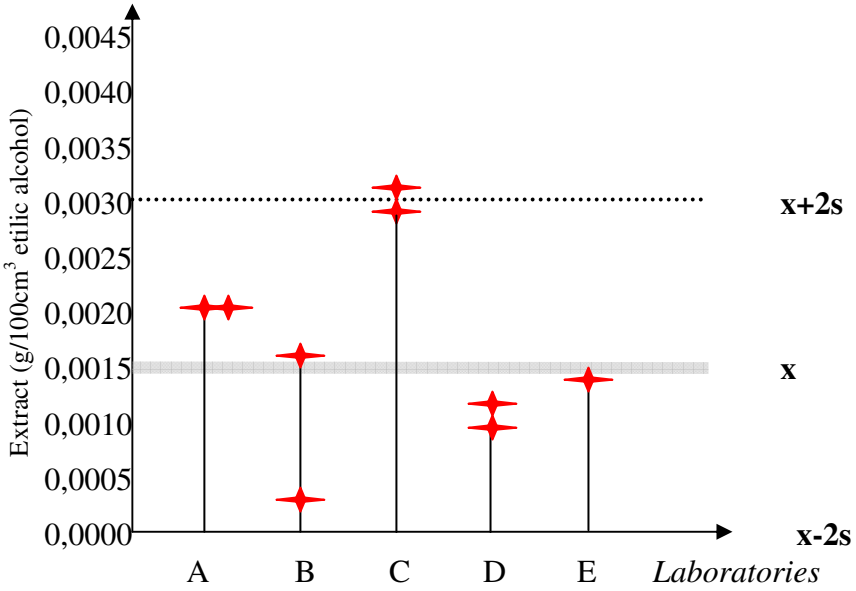

Figure 4: Values registered at the determination of extract from ethylic alcohol in the five laboratories

The results are accepted for all the laboratories, excepting laboratory C. The explication can be the use of Berzelius glasses of 250 ml because of the lack of some capsules for a liquid volume of 100 ml and it is possible that the glass cooling was not uniform.

CONCLUSIONS

After the comparative interlaboratory test, some conclusions are important:

1. In the laboratories included in the study, the working staffs have a good laboratory practise, this being proved by the repeatability of the results in most of the cases.
2. It is necessary to equip the laboratory with graduated and/or quoted glasses: a micro-burette for laboratories A, B C and E and two vats of

glass of 10 mm for A and C laboratories and two burettes of 25 ml for laboratory B, 10 quoted balloons of 25 ml with sample certificates for all five laboratories, an ascending refrigerant for laboratory A, two capsules of stain, porcelain, quartz or thermoresistant glass having a capacity of 100ml, for laboratories C and D, two cylinders colorimetric of 50 ml with a run in stopper mad from the same type of glass (the same colour), for laboratories C and E.

3. It is necessary a method for checking in the good functioning of the SECOMAM S750 spectrophotometers for the visible domain for λ between 550 and 600 nm.
4. It is necessary to equip the 5 laboratories with thermostat bath.
5. It is necessary a study for the forming conditions of the colour complex in order to determine the methylic alcohol and the aldehydes. Suggestions are necessary.
6. It is necessary to make two specific ISL work instructions, in order to determine the aldehydes and the methylic alcohol.
7. It is necessary for the laboratories to define a SMC according to ISO 17025 for that the supply with reference substance to demand correctly the reagents demanded by the attempt method.
8. Reagents witch are graduated-release or with the validity date out of term should not be used. For the following reagents: disodic salts of the chromothropic acid, of the potassium permanganate or the sodium sulphite or the potassium it is recommended a special attention concerning the storage conditions (some are photo sensible), the validity term and also the date of the opening of the packing (they can degrade under the air action if the vessel is not airtight).
9. It is necessary to spread the guide of good practise in the laboratories included in the study.

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