16th International Research/Expert Conference
"Trends in the Development of Machinery and Associated Technology"
TMT 2012, Dubai, UAE, 10-12 September 2012

INTERLABORATORY RESULTS COMPARISON OF ANALYTICAL DETERMINATION OF LEAD (Pb) IN PETROL AND SULPHUR (S) IN DIESEL

Munir Mehović[1]
University "Džemal Bijedić"
Faculty of Education
Sjeverni Logor bb. Mostar

Sejit Bobar, Sanela Konjarić

ABSTRACT
Aim of this work was to perform interlaboratory comparison of analytical results of tests to estimate proficiency for laboratories accredited according to EN ISO / IEC 17025: 2006. To make officially acceptable comparison results, provider must meet the requirements of relevant international documents such as ILAC G-13: 2000 (at the time of implementation, in the meantime has issued ISO / IEC 17043:2010). In this sense, it was necessary to do the following: Establish a quality system for provider who will plan, organize, implement PT-sheme, perform statistical processing of data and create reports on the results of PT-scheme; perform statistical analysis of results obtained from laboratories participating in the PT-scheme; make a report, comments and conclusions of the analyzed results of PT-scheme. There were participate six laboratories that analyse engine fuels. It was tested content of lead (Pb) in petrol and sulphur (S) in diesel. Statistical analysis of results obtained from the participants was done in accordance with ISO 5725-1: 1994 and ISO 5725-2: 1994. Proficiency of participants were estimated by z-score calculation, as the most frequently used parameter for results assessing.
Keywords: acreditation, quality management, PT-sheme, repeatability, statistical analysis

1. INTRODUCTION

According to the requirements of 5..9 b)[1] of the Standard EN ISO 17025: 2006, the laboratory shall have quality control procedures for monitoring the validity of tests and calibrations undertaken. The obtained data can be written in such a way that they can monitor trends and, where applicable, must be used statistical techniques to review the results. Participation in PT increase security in own laboratory results. There are several types of PT's, which is mainly based on the comparison of measurement results from two or more laboratories. The main benefit of the participating laboratories in the PT is proficiency performance evaluation for testing. The evaluation may include a laboratory, a customer or accreditation body. Enforcement of external measurements (comparison) complements own laboratory control. For users of laboratory services (customer) the most important is confidence in the accuracy of measurements. Users can evaluate the recieved services himself or use the services of other subjects. Some accreditation bodies use their own PT, a significant number use PT developed by other subjects.

1 b) participation in the programs of interlaboratory comparisons or proficiency testing programs

2. RESEARCH AIMS

The objectives set in this research can be defined in the following tasks:

- Establish a quality system for providers who will plan, organize, implement the PT-sheme, carried out statistical processing of data and create reports on the results of PT-sheme.
- Implement PT-sheme.
- Perform statistical analysis of results obtained from laboratories participating in the PT-sheme.
- Create reports, comments and conclusions of the analyzed results of PT-scheme.

3. EXPERIMENTAL WORK

In accordance with established Quality Management System and operational procedures, after the intention polling list confirmation by the participants, we started with the preparations for the implementation of sheme. Samples are taken at retail refueling gas stations so as to directly fill in plastic containers. Samples were labeled on the spot. Primary amount is divided in small canisters and labeled in such a way to avoid an agreement among the participants. Under the previous agreement, the participants were required to organize assumption and transport of test items. Test items nalysis should be done in requirements of repeatability and as routine analysis of ordinary samples. All participants were informed how to submit results of analysis.

First step of statistical analysis was identification of outliers for each level severally and after that outliers inside results of laboratory. Outliers were identified by the Cochran's and Grubss's statistics, according ISO 5725-1-4: 1994. After outliers idntification was calculated z-score for each level to estimate laboratory proficiency for specified parameters analysis.

4. RESULTS

Participants submitted results presented in Table 1. All results expressed as mg kg^{-1}.

Table 1. Results of participants

LEVEL	LABORATORY						LEVEL	LABORATORY					
	1	2	3	4	5	6		1	2	3	4	5	6
	113	127	141	122	123	136		7,86	7,58	8,00	5,72	3,00	7,00
	112	129	139	121	119	136		7,68	6,57	8,00	5,85	1,00	8,00
	111	130	141	122	120	138		7,99	7,84	13,00	6,36	2,00	9,00
	112	130	140	123	119	138		7,39	6,86	14,00	6,56	7,00	7,00
1	114	130	138	123	119	140	2	7,86	6,27	14,00	5,72	5,00	11,00
	112	130	137	123	120	140		7,62	7,55	9,00	4,97	4,00	14,00
	112	131	140	123	120	138		7,92	6,73	8,00	5,35	5,00	8,00
	113	129	141	122	119	138		7,49	6,72	14,00	4,76	4,00	8,00
	111	130	137	123	120	138		7,81	6,33	7,00	4,68	1,00	14,00
	111	131	138	122	119	142		7,42	7,33	7,00	4,47	1,00	14,00

Level 1 – Results of lead (Pb) level in petrol
Level 2 – Results of sulphur (S) level in diesel

4.1. Intralaboratory outliers – Cochran's statistics

Cochran's factor was calculated according to:

$$C = \frac{s_{\max}^2}{\sum_{i=1}^{p} s_i^2} \qquad ...(1)$$

Calculated values of C were $C_{level\ 1}$ = 0,327 and $C_{level\ 2}$ = 0,410. For number of participants and appropriate degree of freedom, 1% critical value of Cochran's factor is α(0,01)=0,4229 and 5% critical value of Cochran's factor is α(0,05)=0,3682.

4.2. Interlaboratory outliers – Grubss's statistics

Determination of outliers at one level was done as Grubss examining of outlying observations (one maximum or one minimum value) and Grubss's factor calculation of this factor to the equation:

$$G_p = \frac{\left(x_p - \bar{x}\right)}{s} \qquad ...(2)$$

and

$$G_l = \frac{\left(\bar{x} - x_l\right)}{s} \qquad ...(3)$$

Grubss's factors had values of 1,138 and 1,376 for level 1 and values 1,101 and 1,492 for level 2.

4.3. Accuracy testing within a single cell

For the determination of cell-outlier was used Grubss-this is a test outlying observations (one maximum or one minimum value). Computed on the Grubss's G statistic for each cell within a single laboratory.
For maximum observation Grubss's data was calculated as:

$$G_h = \frac{\left(x_h - \bar{y}_{ij}\right)}{s} \qquad ...(4)$$

For minimum observation Grubss's data was calculated as:

$$G_l = \frac{\left(\bar{y}_{ij} - x_l\right)}{s} \qquad ...(5)$$

For one outlying observation, 1% of critical value of Grubss's parameter and appropriate number of laboratories and series of results within cells is 2,482 and 5% of critical value of Grubss's parameter is 2,290.

Table 2. G_h and G_l values for each cell

			LABORATORY					
			1	**2**	**3**	**4**	**5**	**6**
LEVEL	**1**	**G_h**	1,9106	1,1212	1,1116	0,8581	2,6032*	1,9588
		G_l	1,1062	2,3286*	1,3586	2,0023	0,6508	1,3059
	2	**G_h**	1,3223	1,5493	1,2180	1,5550	1,7983	1,3416
		G_l	1,4517	1,2725	1,0257	1,3572	1,1179	1,0062

4.4. z-score

After outliers determination, z-score was calculated by equation:

$$z_i = \frac{\left|\bar{x}_i - X\right|}{s} \qquad ...(6)$$

Satisfactorily values of z-scores are from -2 to 2 (acceptable results). The values of z-scores between -2 and -3 and between 2 and 3 are doubtful (suspicious results), while the value of z-scores lower than -3 and greater than 3 are unsatisfactory (unacceptable results).

Table 3. zscores by laboratories and levels

z_i	LEVEL	
	1	**2**
z_1	-11,306	0,218
z_2	2,109	-0,147
z_3	9,350	1,47
z_4	-3,455	-0,919
z_5	-5,437	-1,996
z_6	8,740	1,372

5. CONCLUSION

Applying Grubss's tests by one outlying observation for interlaboratory outliers were not determine the existence of outliers. Grubss's tests for results within a single cell by one outlying observation established that the highest score of laboratory 5, level 1 is outlier and the smallest result of laboratory 2, level 1 is stragler, while other results are satisfactory. Calculated z-scores indicates that result of laboratory 2 for level 1 is suspicious result and results of laboratories 1, 3, 4, 5 and 6 for level 1 are unacceptable results. Interlaboratory testing of samples organized by clearly defined procedures in the framework of quality system, is the best tool for checking the proficiency level of analytical testing laboratories for defined determination.

6. REFERENCES

[1] ILAC – G13: 2000, Guidelines for the Requirements for the Competence of Providers of Proficiency Testing Shemes.,

[2] ISO GUIDE 43 – 1: 1997, Proficiency testing by interlaboratory comparisons – Part 1: Development and operation of proficiency testing shemes.,

[3] ISO GUIDE 43 – 2: 1997, Proficiency testing by interlaboratory comparisons – Part 2: Selection and use of proficiency testing shemes by laboratory accreditation bodies.,

[4] ISO 5725 – 1:1994, Tačnost (istinitost i preciznost) mjernih metoda i rezultata – Dio 1: Opšti principi i definicije.,

[5] ISO 5725 – 2:1994, Tačnost (istinitost i preciznost) mjernih metoda i rezultata – Dio 2: Osnovna metoda za određivanje ponovljivosti i reproduktivnosti standardne mjerne metode.,

[6] BAS EN ISO / IEC 17025:2006, Opći zahtjevi za kompetentnost ispitnih i kalibracionih laboratorija.,

[7] ISO 13528: (Draft 1998), Statistical methods for use in proficiency testing by interlaboratory comparison.,

[8] ISO 4259: 1992, Naftni proizvodi: Odreñivanje i primjena tačnih podataka u odnosu na ispitne metode.,

[9] EURACHEM GUIDE ON SELECTION, USE AND INTERPRETATION OF PT SCHEMES, 2000, Edition 1.0., http://www.eurachem.org

[10] Vatrenjak – Velagić, V.,:Analitička kontrola kvaliteta, Studentska štamparija Univerziteta Sarajevo, 1997.,

[11] Lawn, R.E., Tomphson, M., Walker, R.F., :Proficiency testing in Analytical Chemistry, Royal Society of Chemistry, London, 1997.