Evaluation of the essence of sampling based on the first in Poland proficiency testing for liquefied petroleum gas (LPG) sampling

Paweł BUKREJEWSKI, Marta SKOLNIAK, Jarosław FRYDRYCH – Automotive Industry Institute, Warsaw, Poland

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Introduction

Sampling is a estabilished procedure for sampling to test a portion of a substance, material or product in order to ensure a representative sample of the whole set. According to PN- EN ISO 3534–1:2009 [1] sample is called one or more units of sampling from a population and intended to provide information about the population. Thus, sampling is a key step in providing information about the set of material. If the sample is properly sampled can obtain unreliable information about the material.

To be able to meet customer espectation laboratory (at the stage of understanding with client) should specify the purpose of research and define the measured quantity, the measurement method and a possible method of sampling. At this stage, it is necessary to decide whether the test result relates only to the samples received to the laboratory or will apply to the whole part.

In the first case, the laboratory is responsible only for the supplied sample. If the laboratory does not receive the same sample test report should include information who sampled for testing and possible implications of the possibility of using the results of such due to not considering the uncertainty associated with sampling. These requirements are included in the document Polish Centre for Accreditation DAB-07 [2]. In addition, the report should contain information that the results relate only to the tested object, not a whole (PN-EN ISO / IEC 17025:2005 see 5.10.2) [3].

In the latter case, the laboratory must ensure that the delivered test portion of the material is represented by the object (set) and thereby reflect representative characteristics of the test object.

In order to properly sampling laboratory should have developed an apropriate method to obtain a sample representative of the whole part. This can be own method that has previously been validated, or the method described in the standard, the correctness of the use of laboratory confirmed.

When the laboratory sampling it must ensure that the impact of human factors that may affect the representativeness of the sample is minimized. This is accomplished through specialized training and adequate selection of personnel.

Another important issue is sampling using the appropriate equipment and instrumentation properly selected for the sample type and sampling method. In the case of own methods information about the suitability of equipment laboratory received during method validation. In the case of standard methods necessary equipment to sampling is described in detail in a standard, so it can be concluded that it is appropriate for the application.

According to the document DAB-07 which defines the specific requirements of the Polish Centre for Accreditation for the accreditation of testing laboratories, PCA accredits sampling without test of the sample in laboratory and research including sampling. Accreditation for sampling not to be tested in the laboratory is granted in special cases (e.g. where a legislative provision that requires), and the laboratory has been accredited to perform testing or requests for accreditation for testing and sampling. According to this document, the laboratory should provide objective evidence of its competencies to sampling. One of the first to demonstrate the competence of the laboratory's participation in proficiency testing [4]. Through the proficiency testing is meant to assess the results of a lab, the predetermined criterion by interlaboratory comparisons. However, interlaboratory comparisons is organization, performance and evaluation of measurements or tests with the same or similar objects by two or more laboratories in accordance with predetermined conditions. Before getting accreditation laboratory is required to participate with a positive result in at least one proficiency testing program for certain sub-disciplines (the technical competence defined by at least one technique measurement property (test feature) and the product (object, group of objects) that are linked). After getting accreditation laboratory is required to determine a plan to participate in proficiency testing covering all the sub-disciplines and time in accreditation cycle length (four years) and provide evidence of successful participation in these studies.

Therefore, the competences of the sampling should also be confirmed by proficiency testing.

Background and assumptions of proficiency testing

The team of authors organized the first Polish proficiency testing of liquefied petroleum gas (LPG) sampling. Sampling method is specified in PN-EN ISO 4257:2004 [5]. Sampling LPG from cistern was held on 26 April 2012 in one of the transshipment terminals in Poland. In the proficiency testing participate 10 laboratories – seven laboratories accredited by Polish Accreditation Centre for LPG sampling.

Proficiency testing was carried out according to PN-EN ISO / IEC 17043:2011 [6] and organized under the auspices of the Club of Polish Research Laboratories POLLAB.

The main assumptions of the proficiency testing was the sampling of LPG by all participants and performing analysis of samples taken in one selected laboratory. Therefore, the organizer laboratory has done the necessary analysis. This approach allowed us to assess the competence of a laboratory for only sampling of LPG. If participants sampled and analyzed in their lab competences have been defined for both sampling and testing methods. Thus, determining the laboratory performance guarantee for sampling only was the way described above.

Prior to proficiency testing should prepare their own probes with a capacity of more than 1 dm3 with the transmission line (according to PN-EN 4257:2004) and final part to allow connection to a hose in the cistern from which the LPG sample was sampled. Each participant in isolation took a sample of LPG from the tank in previously prepared own probes, according to PN-EN ISO 4257:2004. Sampling procedure has also been described in the above standard.

For liquefied petroleum gas (LPG) sampling is specified in a regulation of the Minister of Economy [7], which in 4th section refers to PN-EN ISO 4257:2004 standard ("Liquefied petroleum gases. The sampling method"). Scope specifies the procedure to be followed when sampling of non-refrigerated liquefied gases (LPG). It is suitable for sampling from tanks, to provide samples for laboratory tests.

Required equipment: probes (sample containers) made of stainless steel equipped with two overflow valves and tubing in the upper set (probe can fill 80%) of the metal quick-line transmission cable made of wire steel braided Teflon and resistant for LPG and able to withstand the pressure min. 25 bar, equipped with a control valve and pressure relief valve and a pressure relief valve that carries away excess gas. Pressure relief valve can perform the functions of relief valve. For safety reasons, the equipment you need: leak tester, gloves and eye protection, protective clothing, antistatic and vehicle for the transport of LPG samples.

Before LPG sampling the laboratory should properly prepared the sample container and a transmission line in the following way: empty sample container from the liquid, then clean the container using volatile (low-boiling) solvent (use first acetone, and secondly pentane). In the same way, clean the transmission line. Drain the transmission line and a container under vacuum. Fill a clean, dry, gaseous propane.

Set of fuel, from which the samples was sampled was approximately 5000 l (80% of the liquid in the tank). Research material, located in the tank was homogenized by stirring.

30 minute break before sampling allowed discharge of static electricity that may arise as a result of LPG movement, as well as the falling of any water fraction.

There were collected the 30 sample of LPG. This amount accounted for about about 2% of the total consumption of LPG in the tank. For security, each system was grounded and each probe before and after the collection was weighed. Then, each probe was described in detail, and checked for leaks. The samplers were placed in a specialized vehicle to allow safe transportation of LPG containers.

After filling the probes were taken by the organizer to Laboratory of Biofuels Petroleum Products in Automotive Industry Institute.

Homogeneity and stability of LPG samples

During sampling organizer chose from a series of samples, the material to assess the homogeneity and stability of the test material (two samples taken at the beginning, two in the middle and two at the end of the series, including three assigned to the homogeneity and three to stability studies). Determination of homogeneity and stability is to ensure that each participant gets a comparable proficiency testing samples and they will be stable for the duration of the proficiency testing. In order to assess the homogeneity prior to analysis by the organizer the parameters were chosen to evaluate the properties of the test material. From each sample for evaluating the homogeneity of the sample prepared at two parallel samples for the selected parameters of the analysis was performed in the following order:

- hydrocarbon composition [% by mass / mass] according to PN-ISO 7941:1993 / Ap1: 2002
- sulfur content [mg / kg] according to ASTM D 6667–10
- the corrosion test on copper plate according to PN-EN ISO 6251:2001
- evaporation residue [mg / kg] according to PN-EN 15471:2009
- presence of hydrogen sulfide according to PN-EN ISO 8819:2000
- water content according to PN-EN 15469:2009
- odour according to PN-EN 589:2009 Annex A.

Measurements for these samples in terms of repeatability. Standard deviation between the samples was calculated [8]:

$$s_s = \sqrt{s_x^2 - \left(s_w^2 / 2\right)} \tag{1}$$

Where:

$$s_w = \sqrt{\left(\sum_{t=1}^{g} w_t^2\right) / 2g} \tag{2}$$

$$s_x = \sqrt{\left(\sum_{t=1}^{g} \left(\overline{x_t} - \overline{\overline{x}}\right)^2\right) / (g-1)} \tag{3}$$

$$w_t = \left|x_{t1} - x_{t2}\right| \tag{4}$$

$$\overline{x_t} = \left(x_{t1} + x_{t2}\right) / 2 \tag{5}$$

$$\overline{\overline{x}} = \left(\sum_{t=1}^{g} \overline{x_t}\right) / g \tag{6}$$

x_t – the result of the t-th sample (t = 1, ... g) and a portion of the k-th (k = 1,2)

Samples were considered sufficiently homogeneous if the following condition is met:

$s_s \le 0{,}3\ \sigma$

where s_s is the standard deviation between the sample and the standard deviation σ for the assessment of proficiency. In order to assess the stability of samples for proficiency testing samples selected from the series of samples in the laboratory. Stability of the material was studied after 5 weeks (i.e. just before the end of the proficiency testing), the same parameters as for the assessment of uniformity. The average was calculated:

$$\overline{\overline{y}} = \left(\sum_{i=1}^{g} \sum_{k=1}^{2} y_{ik}\right) / 2g \tag{7}$$

Samples were stable if the following condition has been met:

$$\left| \left|\overline{\overline{x}} - \overline{\overline{y}}\right| \le 0{,}3\sigma \right. \tag{8}$$

Where $\overline{\overline{x}}$ is the overall average uniformity achieved in check $\overline{\overline{y}}$ is the average of the overall stability achieved in check, while the standard deviation σ for the assessment of proficiency.

Evaluation of interlaboratory studies

The results obtained from participants in proficiency testing were treated statistically. It was assumed that the results obtained are normally distributed, because the participating laboratories use generally accepted and standardized methods. The elimination of the outliers the results was performed using Grubbs test. To determine whether the largest or smallest value is the outlier, who has a collection of data arranged in ascending order xi for i = 1,2 .... p values were calculated by the following formulas [9]:

$$G_p = (x_p - \overline{x}) / s \tag{9}$$

$$G_1 = (\overline{x} - x_1) / s \tag{10}$$

$$\overline{x} = \frac{1}{p} \sum_{i=1}^{p} x_i \tag{11}$$

$$s = \sqrt{\frac{1}{p-1} \sum_{i=1}^{p} (x_i - \overline{x})^2} \tag{12}$$

where:

x_i – the results of the sample

– the expected value (in this case, the average value)

$\overline{x}$ - – standard deviation

p – the number of results

x_1 – the result of the smallest

x_p – the result of the largest.

Means of identification of uncertain results and outliers were as follows:

a) if the value of the test statistic is less than or equal to the critical value corresponding to the level of significance of 5%, the test result is considered to be valid.

b) if the value of the test statistic is larger than the critical value corresponding to the level of significance of 5% and less than or equal to the critical value corresponding to the level of significance of 1%, then the test result is described as the uncertain.
c) if the value of the test statistic is larger than the critical value corresponding to the level of significance of 1%, then the test result is called outliers. Value outlier was discarded and not taken into account in the calculation of mean and standard deviation, unless there was a specific and objective reason to value can not refuse.

As the expected value for the study was taken as the arithmetic mean of the results obtained in a series of studies on the rejection of the results with error thick (outliers). To evaluate the performance of laboratories used the so-called criterion. Deviation of the ratio, calculated according to the formula:

$$z = \frac{x_i - \bar{x}}{s} \quad (13)$$

in which:
x_i – the results of the sample
$\bar{x}$ – the expected value (in this case, the average value)
s – standard deviation

When interpreting the results accepted international criteria for assessment, where:
z – absolute value of the deviation indicator specifies:
z = 0, a very good result
z <1 the result of good
1 < z <2 result satisfactory
2 < z <3 questionable result
z |> 3 unsatisfactory (please take corrective action)

Results of the interlaboratory test

Results obtained by the different participants are shown in Figures 1÷4 and Table 1 contains the results obtained and the value of the parameter z

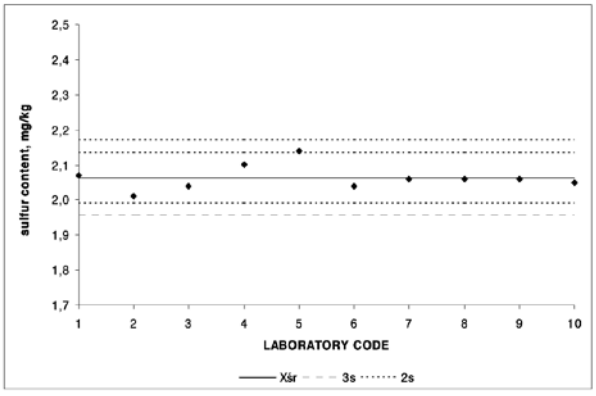

Fig. 1 Sulfur content in LPG samples

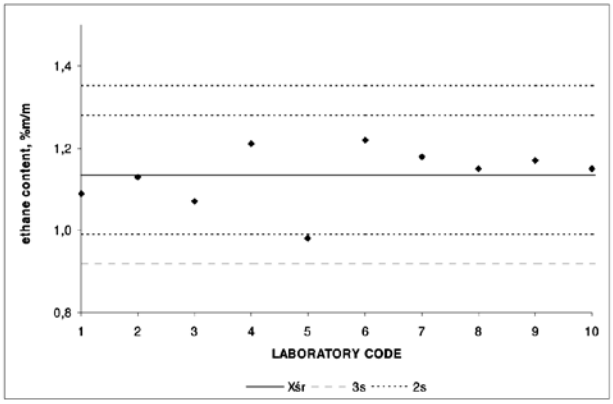

Fig. 2 Ethane content in LPG samples

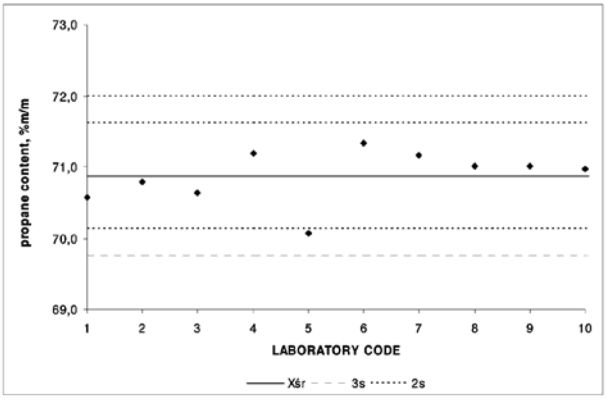

Fig. 3 Propane content in LPG samples

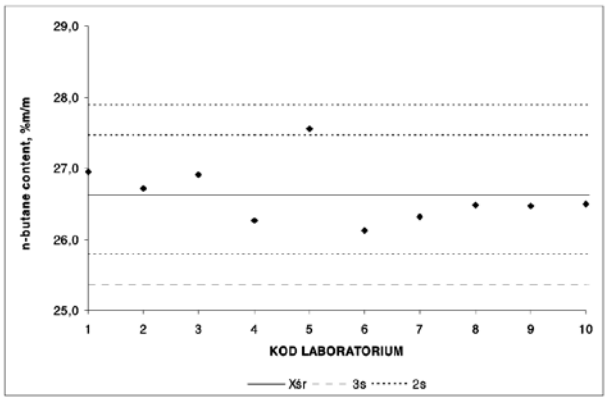

Fig. 4. n-butane content in LPG samples

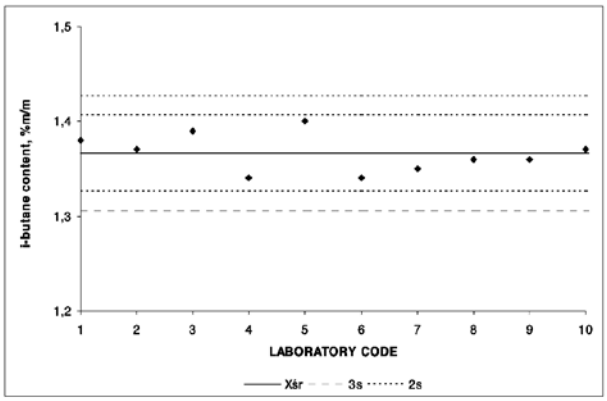

Fig. 5 i-butane content in LPG samples

Table 1

Ratio of the hydrocarbon composition of the test results and the sulfur content of LPG samples

item	Code lab	z				
		ethane	propane	n-butane	i-butane	sulfur content
1	LAB 1	-0.62	-0.80	0.77	0.70	0.20
2	LAB 2	-0.07	-0.23	0.20	0.20	-1.49
3	LAB 3	-0.90	-0.64	0.67	1.19	-0.65
4	LAB 4	1.04	0.84	-0.87	-1.29	1.04
5	LAB 5	-2.15	-2.18	2.19	1.69	2.16
6	LAB 6	1.18	1.22	-1.20	-1.29	-0.65
7	LAB 7	0.62	0.79	-0.75	-0.80	-0.08
8	LAB 8	0.21	0.36	-0.33	-0.30	-0.08
9	LAB 9	0.49	0.36	-0.37	-0.30	-0.08
10	LAB 10	0.21	0.28	-0.30	0.20	-0.37
The mean value		**1.135**	**70.877**	**26.627**	**1.366**	**2.063**
The standard deviation		**0.072**	**0.371**	**0.421**	**0.020**	**0.036**
The calculated reproducibility		**0.20**	**1.04**	**1.18**	**0.06**	**0.10**

In the case of LPG downloading of test results from the hydrocarbon composition and the total sulfur content, given the rate of, 4 results were considered questionable. Other results were correct and satisfactory

Summary and conclusions

The team of authors as the first in Poland organized a proficiency testing of liquefied petroleum gas (LPG) sampling. The study was performed according to the PN-EN ISO / IEC 17043:2011 "Conformity assessment – General requirements for proficiency testing." This standard applies competent proficiency testing organizer. The aim of the study was LPG sampling by the participants and analyze them in the organizer laboratory. This way allowed us to assess the competence of a laboratory only in sampling. The homogeneity and stability of the test material was analyzed. This material was sufficiently homogeneous and stable. In the proficiency testing took part 10 research laboratories. These were the key laboratories in the area of both Polish and European. Proficiency testing helped assess the competence of all laboratories and confirmed the essence of the process of sampling from a material set. The proficiency testing of LPG sampling should be organized because of not all results were satisfied and the sampling is a key influence on the final result.

The study showed the importance of the method of sampling, trained personnel and proper equipment selection and prior preparation.

Demonstration of competence in sampling is required to obtain or maintain accreditation by the Polish Centre for Accreditation. PCA requirements in this area are clearly defined in the documents and compliance with these requirements allows laboratories to monitor the LPG sampling process implemented in these laboratories. Improper supervision of LPG sampling can lead to obtaining inaccurate test results, and thus the transmission of incorrect information to the client. This may lead to wrong decisions taken by the client based on the test results. Introduction by the client the product does not meet the requirements not introduce a product that meets the requirements can result in huge financial losses. Therefore, as an essential element is giving by laboratory reliable results which takes its beginning from the appropriate sampling of the fuel.

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Translation into English by the Author

Pawel BUKREJEWSKI – M.Sc., is a graduate of the Faculty of Chemistry, Gdansk University of Technology (2004). He also completed post-graduate studies „Innovation Manager" (Warsaw School of Economics) and „Innovative management of R&D in scientific" (School of Information Technology under the auspices of the Polish Academy of Sciences). Since 2004 he has been employed at the Central Laboratory of Petroleum in Warsaw. Since 2010 is a senior technical research at the Institute for Fuels and Renewable Energy, currently serves as the Head of the Laboratory of Analytical Laboratory of Analytical Laboratory in Automotive Industry Institute. He was honored in 2007 for „Mobile Laboratory – to improve efficiency and reduce the cost of quality control LPG", bronze medal at the Exhibition of Innovation „Concours Lepine" in Paris, and a gold medal with distinction for

56 World Exhibition of Innovation, Research and New Technology „Brussels Eureka „and the award of the Ministry of Industry of the Republic of Macedonia. In 2008 he graduated at 15 Exchange Inventions Distinction at the International Exhibitions of Inventions awarded by the Ministry of Science and Higher Education Research interests: Instrumental Analysis of liquid and gaseous fuels, unconventional energy sources, sustainable development. He is the author of articles in scientific and technical press, and papers at national and international conferences.

e-mail: p.bukrejewski@pimot.eu; phone: +48 22 777 72 61

Marta SKOLNIAK – M.Sc., is a graduate of the Faculty of Chemistry, Warsaw University of Technology (2007), She has also completed post-graduate studies "Innovation Manager" (Warsaw School of Economics) and "Innovative management of R&D in research units" (School of Information Technology under the auspices of the Polish Academy of Sciences) . In 2007 he began working at the Institute for Fuels and Renewable Energy, currently the Automotive Industry Institute. She is deputy head of Laboratory of Petroleum Products and Biofuel and technical research specialist. Research interests: analytical chemistry, metrology, research of fuels. She is the author of articles in scientific and technica lpress and papers at national conferences.

e-mail:m.skolniak@pimot.eu; phone:+ 48 22 777 72 48

Jarosław FRYDRYCH – MA, is a graduate of the Faculty of Chemistry of the University of Warsaw. He completed post-graduate studies in the field of Chemical Metrology at the University of Warsaw. In 1995, he started working at Central Laboratory of Petroleum, Institute for Fuels and Renewable Energy, is currently head of Laboratory of Petroleum Products and Biofuels in Automotive Industry Institute. He received gold medals at the International Fair in Paris and Brussels (2006). In 2007 he received the award of the Minister of Economy invention fair for developing lubricants for use in the food industry. Research interests: lubricants, LPG, tribology. He is the author of many research papers, patent applications, publications, papers and lectures at national and international conferences in the field of lubricants.

e-mail: j.frydrych@pimot.eu; phone: +48 22 777 72 46