Bioliquids – liquid fuels. Validation of methods for denoting quality parameters based on the example of waste glycerine

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1. Introduction

One of the elements of controlling quality in an analytical laboratory is the validation of research methods. The term "validation" comes from the Latin word *validus* and is translated as strong, hard. A validation of a method involves appointing and checking accuracy features and is the process of determining the purpose of the method and precision of measuring tools. Pursuant to norm PN-EN ISO 9000:2005 *"Quality Management Systems. Fundamentals and Vocabulary",* validation is the "confirmation, by presenting objective proof, that specified requirements regarding a specific, intended use or application have been fulfilled. A validation is a declaration of the validity of a research method, the assurance that requirements set before carrying out the process have been fulfilled and that the customer receives a credible and reliable result", i.e. one which places the real value of the inspected feature inside the confidence interval with a determined probability and which, at the same time, has been obtained using good laboratory practice [1].

Biomass is the oldest and most widely applied natural, renewable energy source. The use of renewable energy sources is an important element of the mandatory national action plan regarding the share of energy from renewable sources in the transportation, electric energy, heating and cooling branches by 2020. The bill on renewable energy sources from December, 2011 as well as Directive 2009/28/EC defined biomass as biodegradable product parts, waste or biological remains from agriculture (including plant and animal substances), forestry and related industry branches, including from breeding, fish farming and aquaculture, as well as biodegradable parts of industrial and municipal waste [2]. According to the above documents, bioliquids are liquid fuels produced from biomass used for energy purposes other than in transportation, including in the production of electric energy and heat or coolness. Biofuels are liquid or gaseous fuels for transportation, produced from biomass. According to the act on biofuels and biocomponents, liquid biofuels which fulfil norms contained in separate provisions may not be deemed as biomass whose combustion in the process of producing electric energy constitutes a premise for obtaining certificates of origin of energy from renewable sources. Taking into account the legal regulations pertaining to the notion of biomass as well as liquid biofuels, it should be assumed that pure, non-refined (raw) vegetable oil may be counted among bioliquids for energy purposes. On the other hand, with regard to esters (methyl and ethyl) it should be pointed out that they fulfil the definition of liquid biofuel which constitutes intrinsic fuel; thus, they cannot be qualified for energy purposes. Taking into account these legal criteria it may be indicated that bioliquids used in the production of electric energy and heat may also include fuels produced from biomass in the form of:

- vegetable oils (raw) and their mixtures, produced from oil plants through pressing, extraction (or using comparable methods) or refining, chemically unmodified

- (raw) glycerine which is a by-product of the process of transesterification of rape-seed oil
- used cooking oils ("spent" i.e. used vegetable oils)
- liquefied, utilised animal fats (category 1, 2 and 3) which are the product of management of chemically unmodified slaughter waste.

Pursuant to the Regulation of the Minister of Economy from July 26, 2011 regarding the manner of calculating data submitted in the request for issuing certificates of origin from cogeneration and the detailed scope of the obligation to obtain and present those certificates for remittance, paying a substitution fee and the obligation to confirm data regarding the volume of electric energy produced in high-performance cogeneration, the weight fraction of biomass supplied for the combustion process should equal at least 5% in 2008 and should reach 60% in 2014 [3].

The first installation for the production of FAME (*Fatty Acid Methyl Ester*) in Poland was created at the end of 2004 in the Trzebinia Refinery. Currently in Poland biofuels are produced by a dozen or so companies out of which the largest one, apart from the Trzebinia Refinery, include ADM Malbork S.A., Lotos Biopaliwa (Czechowice-Dziedzice), BIO-TECH LTD Sp. z o.o. and Wratislavia-Bio Sp. z o.o. Approximately 200 kg of so-called glycerine fraction with a complex chemical composition is created per one ton of produced biofuels (fatty acid methyl esters), out of which 80 – 110 kg is raw glycerine [4, 5]. Apart from glycerine, the fraction contains soaps, methanol, esters, non-esterified vegetable oil, catalyst remains, water and solid waste. Colloquially, the following products may be understood as "glycerine":

- glycerine – raw half-product referred to as glycerine fraction (phase), containing over 10% of methanol
- technical glycerine (contains a few percent of water and trace amounts of salts-process catalysts)
- pure (pharmaceutical) glycerine.

Pure glycerine constitutes an important raw material in the cosmetic (40%), food (24%), pharmaceutical (7%), tobacco and leather industry; it is also used in the production of explosives, dyes and coolants. The world demand for glycerine is at the level of 930 – 950 ths t (data for 2006). The problem with managing waste glycerine has determined the development of studies on its use as a "green energy" carrier in power plants and CHP plants in the processes of co-combustion with basic fuels (e.g. with coal, biomass) and as fuel for the partial substitution of ignition fuel. Attempts to use glycerine in the heating sector took place in the USA and Poland, among other countries [6÷11]. The availability of glycerine (glycerine phase) on the market is strictly related to the production of bioesters. Because of the necessity to fulfil the obligation regarding the 10% fraction of biofuel in the balance of fuels used in transportation by 2020, the production of glycerine will systematically increase. Taking into account its varying quality depending on its origin (producer), parameters and way of conducting the transesterification process, together with potential offers from manufacturers, certificates

should be demanded from tests carried out in a laboratory which has necessary competences with regard to performing denotations for liquid fuels.

The result of the co-combustion of additional liquid fuel in the form of glycerine will be the change of the chemical composition and waste gas stream and, in consequence, the change of their radiation properties such as emissivity and absorption. Their velocity and viscosity will also change, which will impact the intensity of the convective heat transfer. At the same time, the change of volume and properties of ash particles convected by waste gas will lead to the change of the intensity of impurities on the boiler's heating surface. The combustion of fuels with different characteristics than those for a given boiler may cause significant changes of the nature and amount of impurities on heating surfaces, which in turn will strongly influence the amount of heat taken over by specific surfaces. The change of the temperature distribution of waste gas and heating factors in the boiler may cause an increase of the required streams of injection water or the failure to maintain the nominal temperature of factors and a change of the temperature of the material in the boiler's elements. The energy use of glycerine is related to the change of combustion conditions which may impact the occurrence of a risk of high-temperature corrosion. Sulphur, potassium and sodium contained in the ash create a risk of the occurrence of a so-called high-temperature sulphur corrosion. The impact of these impurities on the potential corrosion of waterwall pipes may be considerable. Ash from bituminous coal most often creates Fe_2O_3 which, however, may also come from the boiler pipe material. Compounds created as a result of the reaction, such as $K_2S_2O_7$ and $K_3Fe(SO_4)_3$, are aggressive to the metal's surface, while their harmful impact is based on the destruction of oxides (Fe_3O_4, Fe_2O_3) created during normal exploitation of the boiler. Another potential threat created during the co-combustion of glycerine with coal–biomass mixtures may (in the case of biomass with a high share of Cl^-) involve chlorine corrosion related to the creation of KCl [12].

As obvious from these deliberations, the use of glycerine as a bioliquid for energy purposes requires constant monitoring of quality-energy parameters [13÷18]. In order to characterise the market of waste glycerine as a fuel for energy purposes, samples were collected from the largest Polish manufacturers. A method for denoting the combustion heat and methods for denoting the content of water, ash, and basic composition needed for calculating the calorific value were developed and validated. Parameters which characterise energy properties have a significant impact on the decision to use waste glycerine in the process of co-combustion with other fuels and they allow for a proper calculation of energy produced from it [18, 19].

The aim of the work is to present the validation path of the method based on the example of denoting the water content using Karl-Fischer's method.

2. Experimental part

According to Directive 2009/28/EC from April 23, 2009 regarding promoting the use of energy from renewable sources, the final gross consumption of energy from renewable sources in specific Member States is calculated as the sum of: the final gross consumption of electric energy from renewable sources and the final gross consumption of energy from renewable sources in heating and cooling and the final consumption of energy from renewable sources in transportation, while the input of each energy source is calculated based on its energy content. Because of this, the proper determination of the calorific value of fuels plays a key role and translates into the financial result. Taking into account the fact that the analysis result, apart from the employed measuring device, standards, and procedure, is influenced also by the human factor, a validation procedure has been developed based on statistical data analysis for the purpose of determining the variability scopes.

Validation of measuring methods is a broad analytical and statistical subject [20, 21]. Carrying it out for all new developed research methods necessary for the proper denotation of the calorific value of the bioliquid – glycerine was based on several key points:
1. Performing tests for different test levels and gathering data.
2. Initial assessment of results, using descriptive and graphical analysis as well as statistical tests.
3. Testing the distribution and verification of basic assumptions.
4. Assessment of accuracy (correctness and precision) and determining the expanded uncertainty.
5. Assessment of the method's stability.
6. Assessment of the method's usefulness in the assumed application.

To start with, it is necessary to perform a suitable number of analyses acc. to the following methodologies:

Denoting water using Karl-Fischer's method is a titration method for the quantitative denotation of the water content.

At the first stage of the process of denoting water content, sulphur dioxide and water react with iodine:
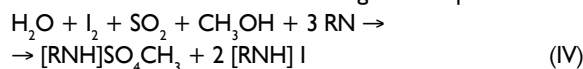$$2\,H_2O + SO_2 + I_2 \rightarrow SO^{2-}_4 + 2I^- + 4H^+ \qquad (I)$$
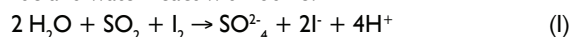
Thanks to the addition of alcohol (e.g. methanol, 2-methoxyethanol, ethanol), the initial reaction may occur in which, together with sulphur dioxide, acid ester is created which then reacts with the added base (e.g. imidazole, further denoted as "RN"):
$$CH_3OH + SO_2 + RN \rightarrow (RNH)\cdot(CH_3OSO_2) \qquad (II)$$

In the presence of water, the yellow-brown iodine oxidises the SO_3^{2-} anion to SO_4^{2-}, at the same time being reduced to colourless iodide:
$$(RNH)\cdot(CH_3OSO_2) + I_2 + H_2O + 2\,RN \rightarrow$$
$$\rightarrow (RNH)\cdot(CH_3OSO_3) + 2(RNH)\cdot I \qquad (III)$$
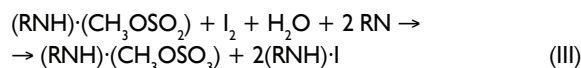
The overall reaction occurs according to the equation:
$$H_2O + I_2 + SO_2 + CH_3OH + 3\,RN \rightarrow$$
$$\rightarrow [RNH]SO_4CH_3 + 2\,[RNH]\,I \qquad (IV)$$

The reaction occurs until the moment of a complete use of water, thanks to which it is possible to detect iodine in the titration solution. Volumetric denotation of the water content using Karl-Fischer's method involves a gradual adding of the titrant containing iodine to the sample containing water until the complete binding of water. This is signalled by the appearance of free iodine in the titration solution. The final titration point is determined using bivoltammetric detection.

Denoting the content of ash in glycerine samples was carried out using the method of slow incineration. The method involves degassing the glycerine sample in a muffle furnace through a gradual increase of the furnace's temperature, its complete combustion, calcination at a temp. of $600 \pm 15°C$, and after cooling the remains – a weight denotation of the remaining mass. The optimised program of temperature increment of the muffle furnace allows for degassing and incineration of the sample.

Denoting the elemental composition of N, C, H, S in a Vario Macro Cube CHNS, O and Cl elemental analyser produced by Elementar Analsensysteme GmbH involved a quantitative combustion of the glycerine sample in an oxygen stream at a temp. of 1150°C. Combustion products (CO, CO_2, NO, N_2, SO, SO_2, PO_2, F, O_2, H_2O) are introduced through a quartz bridge into a reduction pipe where, in contact with copper, sulphur and nitric oxides are reduced to SO_2 and N_2, (the redundant oxygen is also bound) and rid of halogens and other impurities. The analysis of N_2, CO_2, H_2O, SO_2 contained in the combustion product was performed using a thermal conductivity detector. Low concentrations of SO_2 are analysed using an NDIR detector.

Denoting the combustion heat. The method involves a complete combustion of a weighed glycerine sample in a capsule, with a known combustion heat value, in an oxygen atmosphere and in a bomb calorimeter (with a constant volume), using an isothermal or adiabatic system and measuring the increment of water temperature in a calorimetric vessel.

In order to properly determine the calorific value, the obtained result after measurement must be corrected with regard to the heat of sulphuric acid creation and the content of total sulphur, water and hydrogen.

For the purpose of carrying out the validation process, pure glycerine was selected – produced by POCh Gliwice – as well as waste glycerine from the largest Polish biodiesel manufacturers. The scopes of chemical properties of waste glycerine tested acc. to the described methods are listed in Table 1.

Table 1

Chemical properties and scopes of all tested glycerine samples

Denoted parameter/ sample name		Sample 1 pure glycerine	Sample 2 waste glycerine	Sample 3 waste glycerine	Sample 4 waste glycerine	Sample 5 waste glycerine	Parameter scopes denoted for glycerine samples
Denoting water using Karl-Fi-scher's method, W, [%]		0.08	7.62	3.05	10.31	3.11	0.08 – 18.25
Denoting ash, A^d, [%]		0.005	5.66	2.98	4.54	3.26	0.005 – 14.65
Denoting the elemental composition, [%]	N	<0.05	0.15	0.08	0.06	0.10	<0.04 – 0.20
	C	39.12	34.26	36.88	33.37	36.71	32.0 – 39.1
	H^d	8.72	7.70	8.63	7.46	8.23	7.20 – 8.75
	S	<0.03	0.05	1.00	1.46	1.05	<0.03 – 1.46
	O^d	51.99	47.30	50.31	45.97	52.08	43.30 – 52.06
Denoting the combustion heat, Q_s^a, [kJ/kg]		17062	15730	16806	15262	16816	13266 - 21614
Calculated calorific value, Q_s^a, [kJ/kg]		15231	13863	14847	13382	14943	12060 - 19708

When analysing test results obtained at the Laboratory and the most frequently occurring scopes of parameter diversification listed in Table 1, it may be noted that the combustion heat value and the calorific value are significantly influenced by the total content of water in glycerine. It was stated that:

- the combustion heat values of the tested waste glycerines fit within the scope of 13.2 MJ/kg to 21.6 MJ/kg
- based on the tested glycerine samples it is concluded that the combustion heat values which fit within the scope of 13.2 MJ/kg to 16.0 MJ/kg contained water in the amount of 7-18%. On the other hand, when glycerine contained water within the scope of 2-4%, the combustion heat value fit within the scope of 16.2 MJ/kg to 21.6 MJ/kg.

Literature data provide information on the combustion heat value of refined glycerine which reaches even 34.1 MJ/kg, with a water content at a level up to 0.8% [15]. The presence of water is a parameter which determines the amount of obtained heat from the waste glycerine.

2.1. Discussion of validation elements based on the example of denoting water using Karl-Fischer's method

The validation was carried out based on statistical methods provided in norm PN-ISO 5725 [19] and in the collective work edited by P. Konieczka and J. Namieśnik [21]. The statistical analysis used formulas and their interpretation acc. to [20]. Analyses were carried out at various levels of the denoted factor's content. The minimum number of analysis repetitions is always a compromise between manufacturing costs and requirements of statistical analysis. Thus, for the purpose of denoting the content of water using Karl-Fischer's method, five measuring series were performed for denoting water, two repetitions for standard samples with a water concentration of 0.01%, 0.1%, 1%, 5% and 15.6% and for five exemplary glycerine samples with an industrial origin, with a water concentration within the scope of 3.5 – 13.3%. Mean values of measurements and standard deviations were determined.

The next step involved the assessment of divergent values from the population of measurement results. Such values influence the wrong assessment of the standard deviation for repeatability and reproducibility. For the purpose of minimizing the impact of extreme results, graphic methods were employed for checking compliance (Mandel's statistics) as well as numeric methods for detecting divergent values (Grubbs's and Cochran's test), using the calculation procedure described in norm PN-ISO 5725-2. Based on the results of graphical and numerical methods, no divergent values were noted.

After an initial analysis of the results of denoting the water content using Karl-Fischer's method in glycerine samples, parameters were analysed which characterise the accuracy of the method, i.e. precision (repeatability, reproducibility), correctness (bias, recovery), linearity, limits of quantification and detection as well as the measurement uncertainty.

2.2. Testing the distribution and verification of basic assumptions

An analysis was carried out of the normality of the population distribution of obtained results from waste glycerine and standard samples tested for the validation process. For this purpose, histograms were created which represent the empirical distribution of properties. The histogram scopes have a standard deviation width. Theoretical normal distribution curves, whose maxima determine mean values from the population, were matched to the histograms.

An exemplary histogram for a 0.1% water standard is presented in Figure 1.
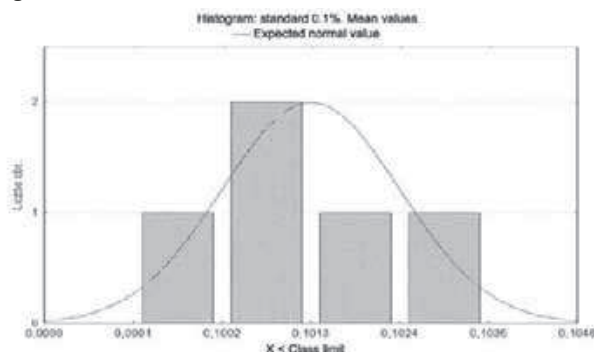

Fig. 1. Histogram of mean values for a 0.1% water standard

Normal distribution was obtained for all the tested waste glycerine and standard samples.

2.3. Assessment of accuracy (correctness and precision) and determining the expanded uncertainty

Precision determines the degree of compliance between independent results obtained in specified conditions. Precision elements include repeatability and intermediate precision (intralaboratory reproducibility). Table 2 contains calculation results.

Table 2

Standard deviation of repeatability (s_r), limit of repeatability (r) and coefficient of variance (%s_r)

	Standard 0.01%	Standard 0.1%	Standard 1%	Sample 1	Sample 2
s_r	0.0003	0.0017	0.0034	0.0319	0.0635
r	0.0009	0.0048	0.0096	0.0903	0.1796
%s_r	3.1234	1.6811	0.3384	0.8931	1.5772
	Standard 5%	Sample 3	Sample 4	Sample 5	Standard 15.6%
s_r	0.0764	0.0499	0.0564	0.0816	0.0617
r	0.2160	0.1411	0.1595	0.2308	0.1746
%s_r	1.4732	0.5105	0.4900	0.6119	0.3937

Intermediate precision treats about the degree of compliance of measurement results from the same measured value, performed under changed measurement conditions. Table 3 contains calculation results.

Table 3

Standard deviation of intermediate precision (s_I), limit of intermediate precision (I) and coefficient of variance (%s_I)

	Standard 0.01%	Standard 0.1%	Standard 1%	Sample 1	Sample 2
s_I	0.0005	0.0017	0.0035	0.0374	0.0635
I	0.0014	0.0048	0.0099	0.1059	0.1796
%s_I	5.0655	1.6811	0.3482	1.0473	1.5772
	Standard 5%	Sample 3	Sample 4	Sample 5	Standard 15.6%
s_I	0.0776	0.0499	0.0676	0.0821	0.0792
I	0.2195	0.1411	0.1913	0.2323	0.2241
%s_I	1.4973	0.5105	0.5876	0.6160	0.5053

Correctness is the degree of compliance between the mean value obtained from measurements and the reference value. The first parameter which characterises correctness is bias, i.e. the difference between the mean value from measurements and the reference value. Recovery is a part of the analyte contained in the sample of the tested material or added to it; it may be denoted using a given method.

The difference between the concentration value in standards and the mean value obtained from measurements is acceptable if: $\Delta m \leq U\Delta$. Calculation results are presented in Table 4.

Table 4

Calculation results for the method's bias

	Standard 0.01%	Standard 0.1%	Standard 1.0%	Standard 5.0%	Standard 15.6%
Δm	0.0003	0.0014	0.0058	0.0244	0.0022
$U\Delta$	0.001	0.0020	0.0100	0.0470	0.0680
Commentary	+	+	+	+	+

+ – the method is not biased

Values Δm obtained for all standards are lower than values $U\Delta$, which proves that the method is not biased. Table 5 contains calculation results for recovery.

Table 5

Calculation results for the method's recovery

	Standard 0.01%	Standard 0.1%	Standard 1.0%	Standard 5.0%	Standard 15.6%
%R	102.63	101.43	100.58	100.48	99.99

It is stated that the recovery value should be included within the range of 80 – 120%; therefore, it may be stated that the recovery values for denoting water using Karl-Fischer's method are correct.

Linearity is the capability of a measurement method to provide results which are proportional to the measured value. The linearity assessment is a tool for planning calibration performed during the use of the method. Linearity is determined using linear regression which has the form of: $\hat{y}_i = ax_i + b$

Figure 2 presents measurement points for water standard samples with a different concentration, as well as regressions lines. The tested level of water concentration in samples was divided into two scopes: the first one from 0.01 to 1.0% and the second one from 1.0 to 15.6%.
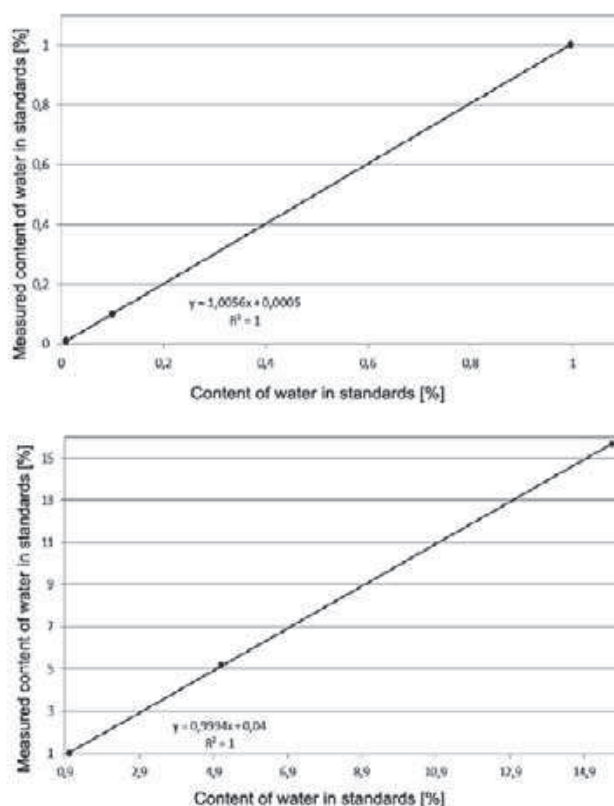

Fig. 2. Linear dependence of measurement points of standards with a different water concentration in glycerine

The regression line encompassing the concentration scope from 0.01 to 1.0% has a $\hat{y}_i = 1.0056x_i + 0.0005$ equation, with a correlation coefficient of $R^2 = 1$; on the other hand, the regression line encompassing the concentration scope from 1.0 to 15.6% has a $\hat{y}_i = 0.9994x_i + 0.04$ equation, with a correlation coefficient of $R^2 = 1$.

Based on calibration curves the limit of detection (LOD) was determined, i.e. the smallest amount of denoted substance which may be detected in a tested sample using a given measuring method (technique). The limit of detection equals 0.002% for a calibration line within the scope of 0.01 – 1.0% and 0.19% for a line within the scope of 1.0 – 15.6%. In order to check the correctness of the calculated limit of detection, the following conditions were inspected: 10LOD > c and LOD < c, and c is the smallest water concentration in standard samples. In both cases (for both scopes) these conditions are fulfilled; thus, the value of the limit of quantification was calculated correctly.

The limit of quantification (LOQ) is the lowest value of the analyte concentration which may be determined with suitable precision and accuracy. In the analysed test results it equals 0.006% for a calibration line within the scope of 0.01 – 1.0% and 0.579% for a line within the scope of 1.0 - 15.6%. Both limits are lower than the smallest water concentration in standards; thus, they have been properly determined.

Another important parameter is the expanded uncertainty of the measurement; it is related to the measurement result and characterises the spread of values which may justifiably be ascribed to the measured size. The basic source of measurement uncertainty for denoting water using Karl-Fischer's method is the standard uncertainty of the weight equal to $u_w = 0.00015$ g. Table 6 contains a list of measurement data values and expanded uncertainties. The measurement uncertainty of denoting water content using Karl-Fischer's method takes into account the standard uncertainty of the weight ($u_w = 0.00015$ g) and the intralaboratory deviation s_l.

Table 6

List of mean values and expanded uncertainties of the measurement

	Standard 0.01%	Standard 0.1%	Standard 1%	Sample 1	Sample 2
Value	0.0099	0.100	1.001	3.58	4.02
U_x	0.0010	0.003	0.007	0.075	0.127
	Standard 5%	Sample 3	Sample 4	Sample 5	Standard 15.6%
Value	5.18	9.77	11.51	13.34	15.68
U_x	0.155	0.100	0.135	0.164	0.158

Table 6 contains expanded uncertainties which take into account the expansion coefficient k=2, at a 95% level of significance.

Limits of repeatability and reproducibility were specified for the test results and they are presented in Table 7.

Table 7

Limits of intralaboratory repeatability and reproducibility for specific scopes of water concentration in glycerine samples

Water content, %	Repeatability (r)	Reproducibility (l)
0.01 – 1.0	0.0096	0.0099
1.0 – 15.6	0.2308	0.2323

Assessment of the method's stability

For the purpose of monitoring the stability of the method for denoting water over time, control charts are used referred to as Shewhart's charts (examples of charts in Fig. 4 and 3). They have been created based on results of 5 double measurements. All measurement points in the entire scope of water concentrations in glycerine samples, i.e. from 0.01% to 15.6% fit within control limits which proves the stability of the measurement method.
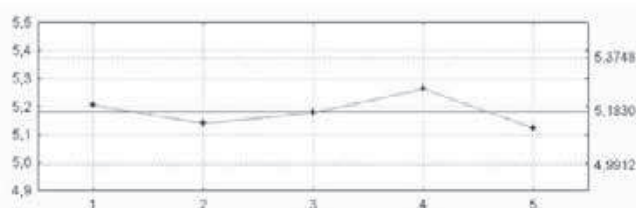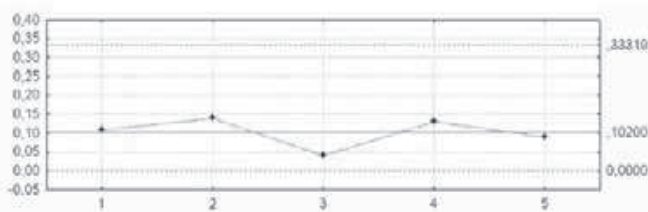

Fig. 3. Control chart for mean values

Fig. 4. Control chart for ranges

3. Testing the co-combustion of waste glycerine

Tests of the co-combustion of glycerine with bituminous coal and biomass were carried out using an OP-650k steam boiler. Based on the determined shares of specific types of biomass in the mixture with coal, characteristic mixture parameters were selected (additively). Glycerine was supplied for combustion using a special constructed installation for industrial glycerine combustion. The energy efficiencies of the boiler obtained during co-combustion tests were created at a very similar level compared to the combustion of coal.

Generally, it may be stated that the combustion of additional fuel, i.e. technical waste glycerine has no negative impact on the efficiency of the OP-650k boiler. The remaining data (pertaining to the calorific value, load of blocks, deviations from nominal values for live and secondary steam, the amount of dosed liquid fuel, emissivity, analysis of coefficients c_m and $R_{(B/A)}$, as well as characteristic melting points of ashes) from co-combustion tests of waste glycerine will be the subject of another article.

Summary and conclusions

The validation process for a selected method – denoting the content of water – was presented. One of the reasons behind selecting Karl-Fischer's method is the impact of the total content of water in glycerine on the combustion heat value which is the most important parameter characterising the usefulness of glycerine for energy purposes.

Due to the properties of glycerine, its use as a bioliquid for energy purposes requires constant monitoring of quality and energy parameters. Thanks to developed and validated procedures as well as the presented validation path based on denoting the content of water, it is possible to accurately characterise the properties of the bioliquid.

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