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Correct determination of alcoholic strength in alcoholic products

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Abstract. The paper describes a method, which combines sample density measurement data and gas chromatographic data to determine the quantitative content of volatile compounds, including ethyl alcohol, in sample. This approach can improve the accuracy of alcohol content measurements. The proposed method takes into account the presence in sample of congeners, such as methanol, fusel oils, esters and etc. The experimental study of 8 brandy samples was carried out. All samples were distilled and measured by GC-FID. The volatile compounds identified in the analyzed distillates were acetaldehyde, isobutanal, ethyl acetate, methanol, butan-2-ol, propan-1-ol, 2-methylpropan-1-ol, isoamyl acetate, butan-1-ol, 3-methylbutan-1-ol, ethyl caproate, ethyl lactate, hexanol, cis-3-hexen-1-ol, ethyl caprylate, furfural, ethyl caprate, ethyl laurate and 2-phenylethanol. The quantitative determination of congeners was carried out using ethanol as a reference substance. The sum of volume content of detected congeners in studied distillates ranged from 0.28 to 0.46%. The absolute difference between results for determination of alcoholic strength using only water-ethanol tables (traditional method) and combination of data from water-ethanol tables and gas chromatography data (proposed method) ranged from 0.22 to 0.40%.

1 Introduction

The correct determination of alcoholic strength by volume in alcoholic products is critical for ensuring product quality, safety, and compliance with legal and regulatory requirements [1]. The traditional method for determination of the alcoholic strength by volume is based on measuring of the density of the sample using a pycnometer, frequency oscillator, hydrostatic balance and the referencing it to the International Alcoholometric Tables [2]. These tables provide the alcoholic strength by volume (ABV) corresponding to the measured density. The water-ethanol tabular method is based on the principle that the density of water-ethanol mixtures has an unambiguous dependence on the strength of the test sample. However, samples of distillates of alcoholic beverages obtained after distillation contain other volatile compounds besides ethanol, which can contribute to the density of the distillate. The presence of other volatile compounds in distilled beverages can affect the accuracy of alcoholic strength values. The use of data from water-ethanol tables for such distillates can lead to incorrect values because these tables are based solely on the properties of water and ethanol. In order to obtain correct value of alcoholic strength for distilled beverage sample, it is necessary to use methods that take into account the presence of other volatile compounds. The developed GC-FID method is based on the use of ethanol as a reference substance, avoids the aforementioned disadvantages of the traditional internal standard method. There is no need to add any internal standard to the analysed sample, since ethyl alcohol is an essential component of any alcoholic beverage. This method was studied and validated for the determination of methanol in spirit drinks [3,4].

The aim of this study was to approbate the developed method on real samples of alcoholic beverages and compare obtained results with the results obtained using official method of analysis (Appendix I of Commission regulation EC) [1] The developed method was tested on 8 brandy samples.

2 Materials and methods

2.1 Reagents and wine samples

All standards at ≥ 99 % purity acetaldehyde (CAS 75-07-0), isobutanal (CAS 78-84-2), ethyl acetate (CAS 141-78-6), methanol (CAS 67-56-1), butan-2-ol (CAS 78-83-1), propan-1-ol (CAS 71-23-8), 2-methylpropan-1-ol (CAS 137-32-6), isoamyl acetate (CAS 123-92-2), butan-1-ol (CAS 71-36-3), 3-methylbutan-1-ol (CAS 123-51-3), ethyl caproate (CAS 123-66-0), ethyl lactate (CAS 97-64-3), hexanol (CAS 111-27-3), cis-3-hexen-1-ol (CAS 928-96-1), ethyl caprylate (CAS 123-68-2), furfural (CAS 98-01-1), ethyl caprate (CAS 110-38-3), ethyl laurate (CAS 106-33-2), 2-phenylethanol (CAS 60-12-8) and ethanol (CAS 64-17-5) were purchased from Sigma-Aldrich (Madrid, Spain). The brandy samples were purchased from local markets.

2.2 Preparation of standard solutions

Four standard solutions with concentration levels of volatile compounds, ranging from 2 to 5000 mg/L of anhydrous alcohol (AA), were prepared by dilution of the stock solution with a hydroalcoholic mixture at 40% (ABV) ethanol. Ethyl alcohol itself is used as a reference substance and all data for the concentration of volatile compounds are calculated in relation to the content of ethanol. There is no need for any further internal standard addition.

2.3 Preparation of brandy samples

The 8 brandy samples were distilled according to the Appendix I of Commission regulation EC [1]. The density and real alcoholic strength by volume of purchased samples was determined according to the Appendix II of Commission regulation EC [1] by Method A (pycnometry). Alcoholic beverage samples were prepared according to the procedure, described in the part III.2 item 8 of Commission regulation EC [1].

2.4 Instrumentation

A gas chromatograph model Crystal-5000.1, coupled with a flame ionization detector (Chromatec, Yoshkar-Ola, Mari El) was used for the chromatographic analyses. The separation was performed with a capillary column Rt-Wax, 50 m × 0.32 mm I.D. × 1.0 µm film thickness (Restek, Bellefonte, USA). The injector and detector temperatures were 200 °C and 280 °C, correspondingly. The GC oven was set as followed: 60 °C (6 min hold), and finally ramped to 190 °C at 12 °C/min (10 min hold). Nitrogen was used as the carrier gas and the injection was a splitless mode. The split ratio was 10:1, the injection volume was 1.0 µL. Data acquisition and processing were controlled by UniChrom software (New Analytical Systems Ltd, Minsk, Belarus).

3 Calculations

To calculate the concentration composition of the alcohol-containing sample being studied, it is assumed that the sample was prepared by mixing two separate solutions – pure water and the anhydrous part of the test sample, which consists of volatile compounds, including ethyl alcohol. The density of the solution after mixing water with the anhydrous part of the sample can be represented by the following formula

$$\rho_S = C_W \cdot \rho_W^{eff} + (1 - C_W) \cdot \sum_{(i)} \rho_i \cdot C_i^*, \qquad (1)$$

where ρ_S is the density of the sample, mg/L; $\rho_W^{eff} = \rho_W \cdot F(C_w)$ is the effective density of water in the mixture, mg/L; ρ_W is the density of pure water at 20 °C, ρ_W = 998230 mg/L; $F(C_w)$ is the factor that takes into account the effect of "increasing the effective density of water"; ρ_i is the density of i*th* volatile compound, mg/L; C_i^* – is the volume fraction of i*th* volatile compound in the anhydrous part of the sample; C_W the volume fraction of the water in the sample.

The dependence of the factor on the volume fraction of water in the sample is a monotonic function without extremum. The analytical dependence of the value in the range of values *F* of the volume fraction of water C_w in the test sample from 0.03 to 1.00 can be represented as an empirical formula

$$F(C_w) = aC_W^6 + bC_W^5 + cC_W^4 + dC_W^3 + eC_W^2 + fC_W + g, \qquad (2)$$

where the numerical values of the coefficients *a, b, c, d, e, f,* and *g* are calculated by approximating the function using water-alcohol tables [2]. The graph of the function is shown in Fig. 1

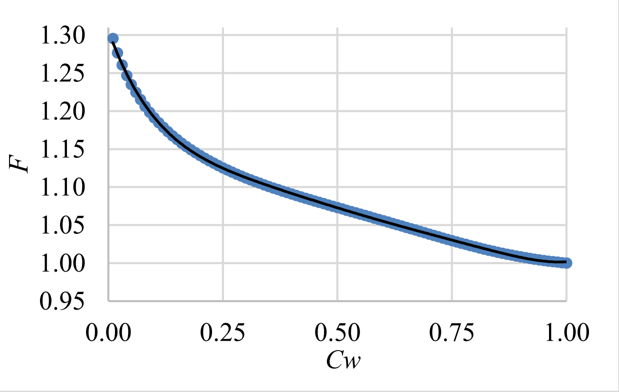

Figure 1. Analytical function of the dependence of the factor *F* on the volume fraction of water in the test sample C_W.

The volume fractions of the i*th* volatile compounds, including ethanol, in the anhydrous part of the sample C_i^* can be represented by the following formula

$$C_i^* = \left(\frac{\tilde{C}_i}{\rho_i}\right) \Big/ \left(\sum_{(i)} \frac{\tilde{C}_i}{\rho_i}\right), \qquad (3)$$

where $\tilde{C}_i$ is the concentration of the i*th* volatile compound in the anhydrous part of the sample, including ethanol, mg/L AA, determined from chromatographic data by direct determination of the concentrations of volatile compounds using ethanol as a reference substance [3,4], according to the following formulas

$$\tilde{C}_i = RRF_i \cdot \frac{A_i}{A_{Eth}} \cdot \rho_{Eth}, \tag{4}$$

where

$$RRF_i = \frac{\tilde{C}_i^{st}}{A_i^{st}} \Big/ \frac{\rho_{Eth}}{A_{Eth}^{st}}, \tag{5}$$

where A_i, A_{Eth} are the areas of the chromatographic peaks of the i*th* volatile compound and ethanol in the test sample, correspondingly, arbitrary units (a.u.); ρ_{Eth} is the density of anhydrous ethanol at 20 °C, ρ_{Eth} = 789270 mg/L; *RRFᵢ* is the relative detector response for the i*th* volatile compound relatively to ethanol; A_i^{st} and A_{Eth}^{st} are the areas of chromatographic peaks of the i*th* volatile compound and ethanol, obtained during measuring of the standard mixture, used for calibration, correspondingly, a.u.; $\tilde{C}_i^{st}$ is the concentration of the i*th* volatile compound in the standard mixture for chromatograph calibration, mg/L AA.

After substituting (3) into (1), we find an expression for determining the volume fraction of water in the sample

$$C_W = \frac{\rho_S \cdot \sum\limits_{(i)} \frac{\tilde{C}_i}{\rho_i} - \sum\limits_{(i)} \tilde{C}_i}{\rho_W \cdot F\left(C_W\right) \cdot \sum\limits_{(i)} \frac{\tilde{C}_i}{\rho_i} - \sum\limits_{(i)} \tilde{C}_i}. \tag{6}$$

The volume fraction of the i*th* volatile compound, including ethanol, in the sample can be represented by the following formula

$$C_i = (1 - C_W) \cdot C_i^*. \tag{7}$$

The function $F\left(C_w\right)$ is smooth and the system of equations (1)-(6) can be solved by the method of successive approximations. In the zero approximation, we assume that the value $F^{(0)}(C_w) = 1$.

Then expressions (6) and (7) can be presented in the following formulas

$$C_W^{(0)} = \frac{\rho_S \cdot \sum\limits_{(i)} \frac{\tilde{C}_i}{\rho_i} - \sum\limits_{(i)} \tilde{C}_i}{\rho_W \cdot \sum\limits_{(i)} \frac{\tilde{C}_i}{\rho_i} - \sum\limits_{(i)} \tilde{C}_i}, \tag{8}$$

$$C_i^{(0)} = \left(1 - C_W^{(0)}\right) \cdot C_i^*. \tag{9}$$

In the j*th* approximation, the value of the function $F\left(C_w\right)$ is calculated by formula (2) with the value of the argument $C_W^{(j-1)}$. The corresponding expressions for the concentrations of water and volatile compounds (6) and (7) can be presented in the following formulas

$$C_W^{(j)} = \frac{\rho_S \cdot \sum\limits_{(i)} \frac{\tilde{C}_i}{\rho_i} - \sum\limits_{(i)} \tilde{C}_i}{\rho_W \cdot F\ \left(C_W^{(j-1)}\right) \sum\limits_{(i)} \frac{\tilde{C}_i}{\rho_i} - \sum\limits_{(i)} \tilde{C}_i}, \tag{10}$$

$$C_i^{(j)} = \left(1 - C_W^{(j)}\right) \cdot C_i^*. \tag{11}$$

Solutions to the system of linear algebraic equations (2), (10), (11) can be found numerically by programming the algorithm of successive iterations, for example, in MS Excel. The number of iterations was 16.

4 Results and discussion

The results of the GC-FID analysis of brandy samples are presented in Table 1. The obtained chromatograms of brandy samples in logarithmic scale are shown in Figs. 2, and 3.

Table 1. Results of the GC-FID analysis of brandy samples.

Compound	**Concentration, mg/L AA**							
	sample 1	***sample 2***	***sample 3***	***sample 4***	***sample 5***	***sample 6***	***sample 7***	***sample 8***
Acetaldehyde	182	85	150	206	156	250	193	248
Isobutanal	11.8	20.0	10.6	9.9	12.1	4.7	4.4	7.9
Ethyl acetate	417	411	457	334	404	388	237	546
Methanol	332	371	415	334	307	347	343	363
Butan-2-ol	1.2	0.6	70.5	2.0	0.8	3.4	3.1	1.2
Propan-1-ol	294	297	334	284	279	317	290	278
Isobutanol	1341	1111	1242	1281	1096	1317	1255	1249
Isoamyl acetate	3.7	4.9	4.8	3.5	3.0	3.9	2.8	3.4
Butan-1-ol	4.4	3.5	7.5	4.4	4.1	5.4	4.2	4.2
3-methylbutan-1-ol	3445	3168	3044	3407	3137	3613	3410	3331
Ethyl caproate	5.3	6.1	6.2	4.1	4.1	3.4	3.4	5.7
Ethyl lactate	193	105	136	112	91	111	104	82
Hexanol	22.3	11.3	15.9	15.5	12.2	19.1	16.5	13.7
Cis-3-hexen-1-ol	2.9	2.8	3.2	3.0	2.9	3.6	3.2	2.8
Ethyl caprylate	23.9	38.5	36.4	20.2	25.2	16.0	22.3	35.5
Furfural	26.4	23.3	14.9	22.6	27.7	25.9	27.9	35.9
Ethyl caprate	15.2	77.4	54.1	12.3	38.0	9.6	18.3	49.4
Ethyl laurate	2.7	18.8	23.1	1.7	8.6	1.5	2.9	13.8
2-phenylethanol	21.5	14.2	21.7	25.2	20.3	32.6	25.5	26.4

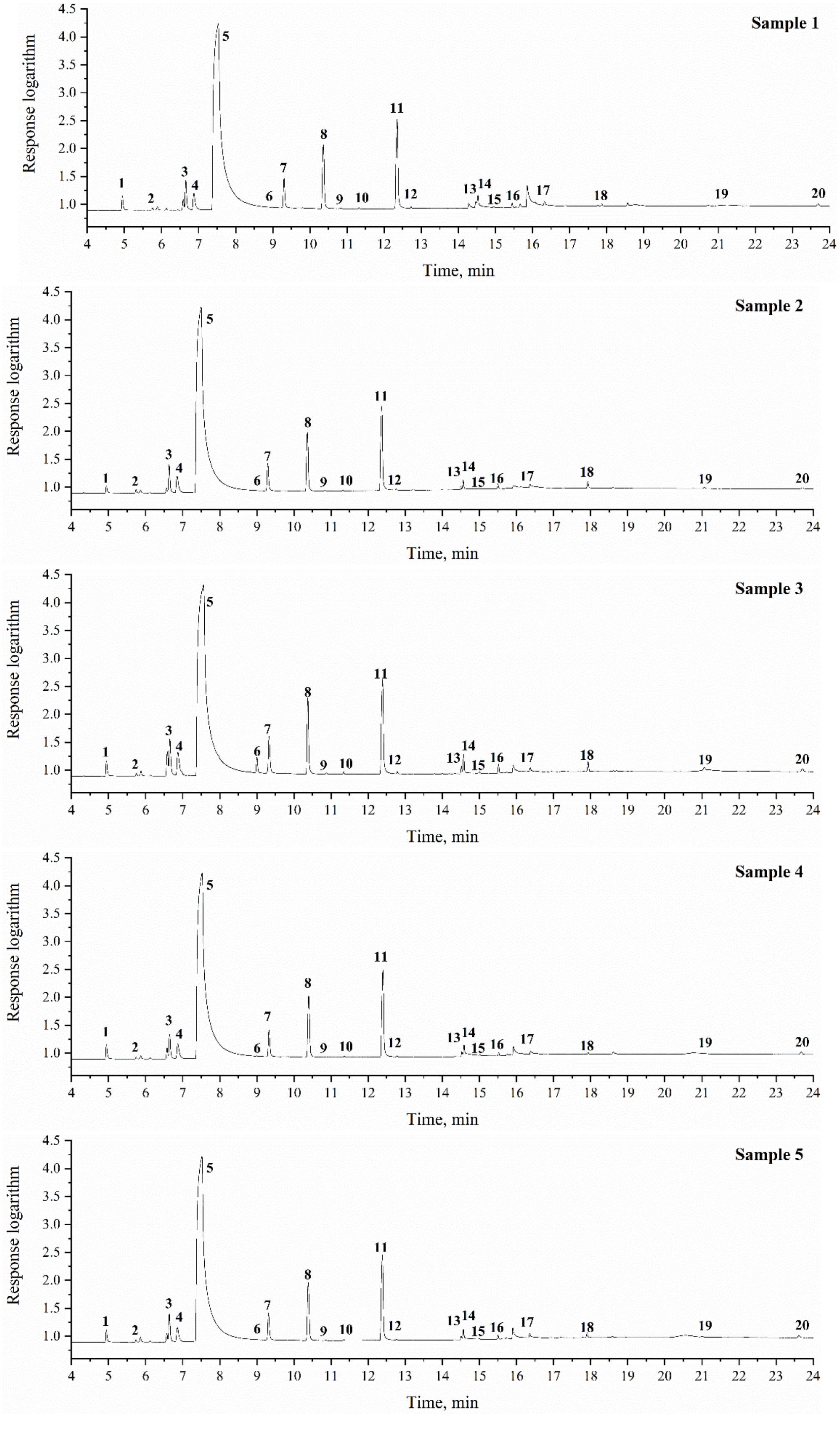

Figure 2. Chromatograms of samples 1-5 in the logarithmic scale. 1 – acetaldehyde, 2 – isobutanal, 3 – ethyl acetate, 4 – methanol, 5 – ethanol, 6 – butan-2-ol, 7 – propan-1-ol, 8 – 2-methylpropan-1-ol, 9 – isoamyl acetate, 10 – butan-1-ol, 11 – 3-methylbutan-1-ol, 12 – ethyl caproate, 13 – ethyl lactate, 14 – hexanol, 15 – cis-3-hexen-1-ol, 16 – ethyl caprylate, 17 – furfural, 18 – ethyl caprate, 19 – ethyl laurate, 20 – 2-phenylethanol.

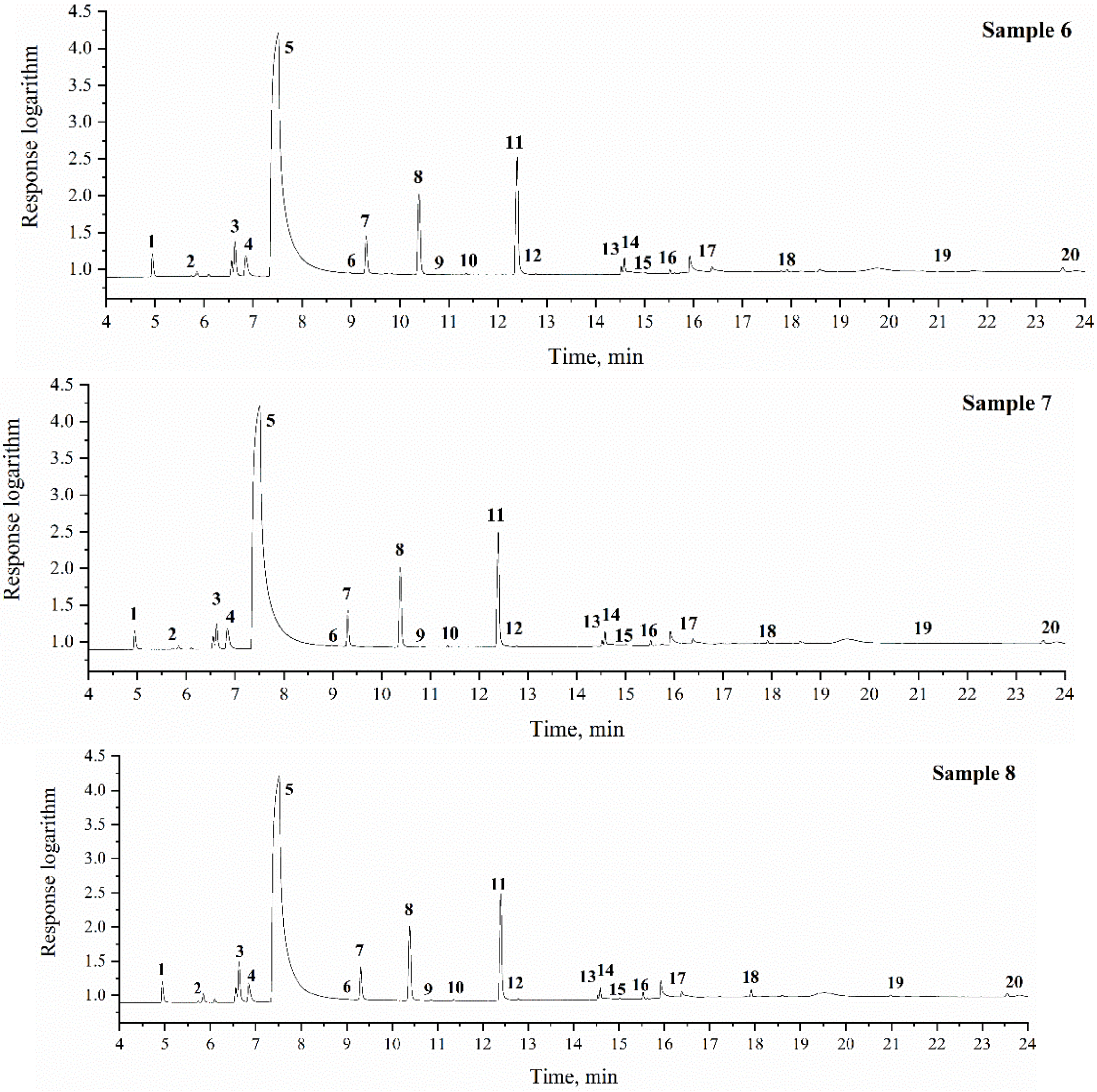

Figure 3. Chromatograms of samples 6-8 in the logarithmic scale. 1 – acetaldehyde, 2 – isobutanal, 3 – ethyl acetate, 4 – methanol, 5 – ethanol, 6 – butan-2-ol, 7 – propan-1-ol, 8 – 2-methylpropan-1-ol, 9 – isoamyl acetate, 10 – butan-1-ol, 11 – 3-methylbutan-1-ol, 12 – ethyl caproate, 13 – ethyl lactate, 14 – hexanol, 15 – cis-3-hexen-1-ol, 16 – ethyl caprylate, 17 – furfural, 18 – ethyl caprate, 19 – ethyl laurate, 20 – 2-phenylethanol.

The results of determining the strength of the samples according to the official [1] and developed methods are presented in the Table 2.

Sample #	**Alcoholic strength by volume, %**		**Absolute difference, %**
	official method	***developed method***	
Sample 1	40.14	39.90	-0.24
Sample 2	40.06	39.84	-0.22
Sample 3	62.34	61.94	-0.40
Sample 4	40.34	40.10	-0.24
Sample 5	40.13	39.91	-0.22
Sample 6	40.04	39.78	-0.26
Sample 7	40.76	40.52	-0.24
Sample 8	40.11	39.87	-0.24

The sum of volume content of detected congeners in studied distillates ranged from 0.28 to 0.46%. The absolute difference between results for determination of alcoholic strength using only water-ethanol tables (traditional method) and combination of data from water-ethanol tables and gas chromatography data (developed method) ranged from 0.22 to 0.40%.

5 Conclusions

The use of a computer calculation program that implements this method can help to automate and streamline the analysis of alcohol-containing products, and can help to reduce measurement uncertainty and improve the accuracy of results. The implementation of these proposals can help to improve the accuracy and reliability of measurements, promoting consistency and transparency in the alcoholic beverages industry. An example of performing calculations using the proposed method in MS Excel can be found at the link https://elab.bsu.by/article/747. Since during the analysis of alcoholic products it is necessary to establish the density of the sample and measure the chromatogram, there is no need to carry out any additional measurements, financial or labor costs to implement the proposed method.

High efficiency and wide international testing of the method using ethanol as a reference substance can serve as the basis for initiating, in the established manner, interlaboratory study under patronage of the International Organization of Vine and Wine (OIV) for the purpose of its subsequent approval as a standardized reference method on the international level.

Conflicts of interest

The authors declare no conflict of interest.

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