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OIV International Organisation of Vine and Wine
Intergovernmental Organisation

Correct determination of alcoholic strength in alcoholic products

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Determination of alcoholic strength in spirituous beverages: routine laboratory practice

- **OIV-MA-BS-01** Reference method for the determination of alcoholic strength by volume of spirit drinks of viti-vinicultural origin: General remarks
- **OIV-MA-BS-03** Reference method for the determination of real alcoholic strength by volume of spirit drinks of viti-vinicultural origin: measurement by pycnometry
- **OIV-MA-BS-04** Reference method for the determination of real alcoholic strength by volume of spirit drinks of viti-vinicultural origin: measurement by electronic densimetry (based on the resonant frequency oscillation of a sample in an oscillating cell)
- **OIV-MA-BS-05** Reference method for the determination of real alcoholic strength by volume of spirit drinks of viti-vinicultural origin: Measurement by densimetry using hydrostatic balance
- **OIV-MA-AS312-01** Alcoholic strength by volume

- **COMMISSION REGULATION (EC) No 2870/2000 of 19 December 2000** laying down Community reference methods for the analysis of spirit drinks

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European Commission

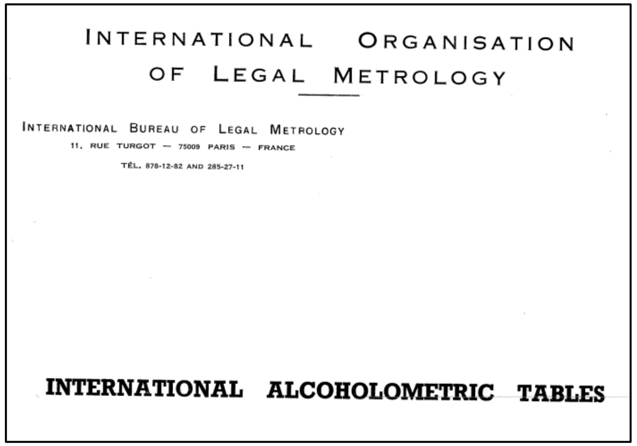
Distillation

↓

Density measurement

↓

Calculations using International Alcoholometric Tables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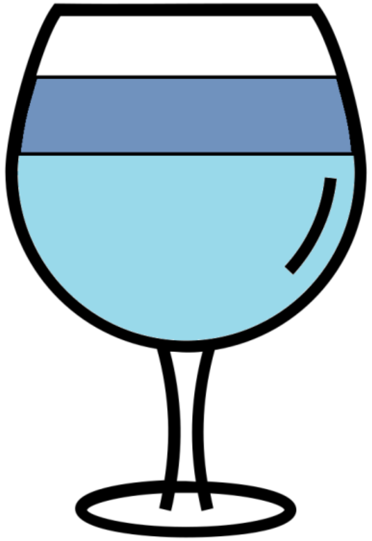
INTERNATIONAL ALCOHOLOMETRIC TABLES

Determination of alcoholic strength in spirituous beverages: routine laboratory practice

Obtained distillate in theory



Obtained distillate on practice

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. !

Correct determination of alcoholic strength in spirituous beverages: solution

1. The density of the solution after mixing **water** with the **anhydrous part** of the sample can be represented by the following formula

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

where ρ_S is the density of the solution, 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 ith **volatile components** , mg/L;

C_i^* is the volume fraction of ith **volatile component** in the **anhydrous part** of the sample;

C_W is the volume fraction of the **water** in the sample.

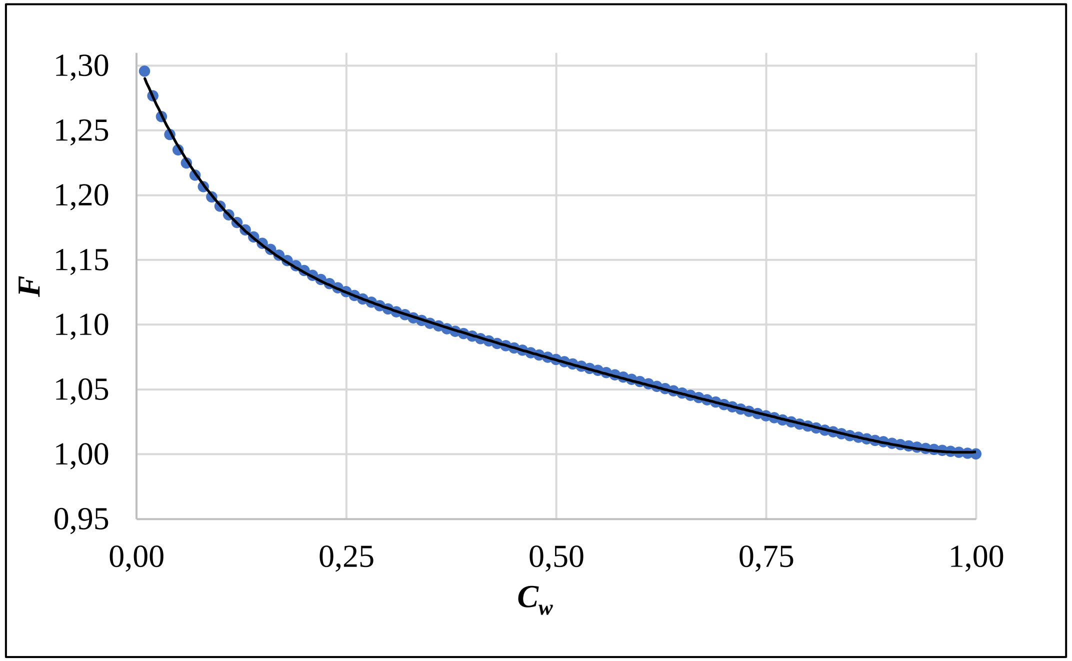
Correct determination of alcoholic strength in spirituous beverages: solution

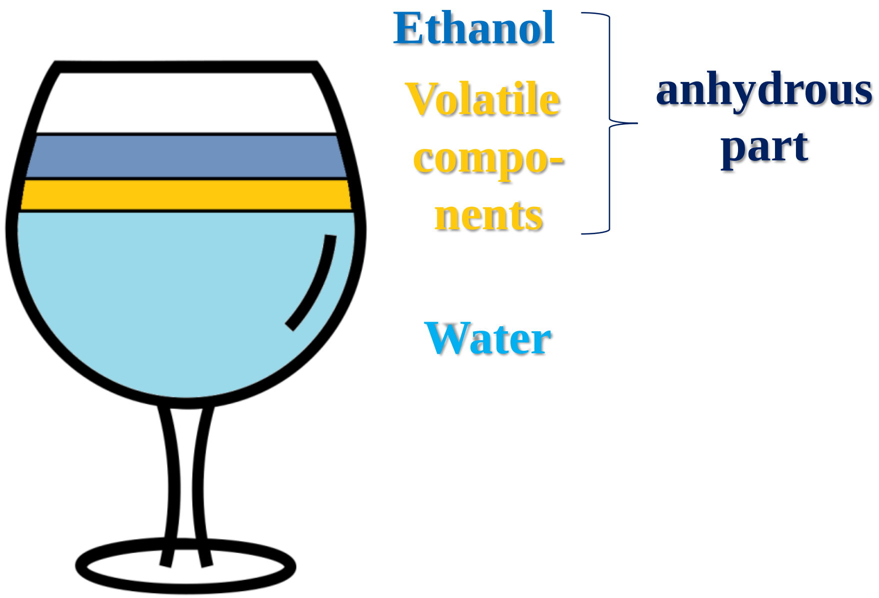
2. The dependence of the factor, $F(C_w)$, on the volume fraction of **water** in the sample, C_w, is a monotonic function without extremum. The analytical dependence of the value in the range of values F of the volume fraction of **water**, C_w, in the test sample from 0.03 to 1.00 can be represented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

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

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.

Function graph





Correct determination of alcoholic strength in spirituous beverages: solution

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

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

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

$$\tilde{C}_i = RRF_i \cdot \frac{A_i}{A_{Eth}} \cdot \rho_{Eth}, \quad \textbf{(4)} \qquad RRF_i = \frac{\tilde{C}_i^{st}}{A_i^{st}} \Bigg/ \frac{\rho_{Eth}}{A_{Eth}^{st}}, \quad \textbf{(5)}$$

where A_i and A_{Eth} are the areas of the chromatographic peaks of the *i*th **volatile component** 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;

A_i^{st} and A^{st}_{Eth} are the areas of chromatographic peaks of the *i*th **volatile component** 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 component** in the standard mixture for chromatograph calibration, mg/L AA.

Correct determination of alcoholic strength in spirituous beverages: solution

4. An expression for determining the volume fraction of **water** in the sample

$$C_W = \frac{\rho_S \cdot \sum_{(i)} \frac{\tilde{C}_i}{\rho_i} - \sum_{(i)} \tilde{C}_i}{\rho_W \cdot F(C_W) \cdot \sum_{(i)} \frac{\tilde{C}_i}{\rho_i} - \sum_{(i)} \tilde{C}_i}. \qquad \textbf{(6)}$$

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

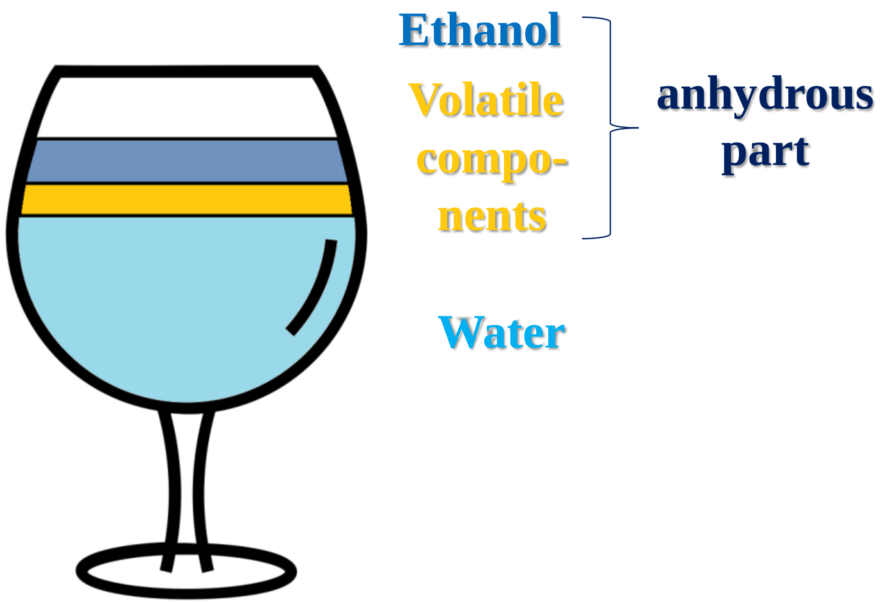
$$C_i = (1 - C_W) \cdot C_i^*. \qquad \textbf{(7)}$$

The function $F(C_w)$ 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

$$C_W^{(0)} = \frac{\rho_S \cdot \sum_{(i)} \frac{\tilde{C}_i}{\rho_i} - \sum_{(i)} \tilde{C}_i}{\rho_W \cdot \sum_{(i)} \frac{\tilde{C}_i}{\rho_i} - \sum_{(i)} \tilde{C}_i}, \qquad \textbf{(8)}$$

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



Correct determination of alcoholic strength in spirituous beverages: solution

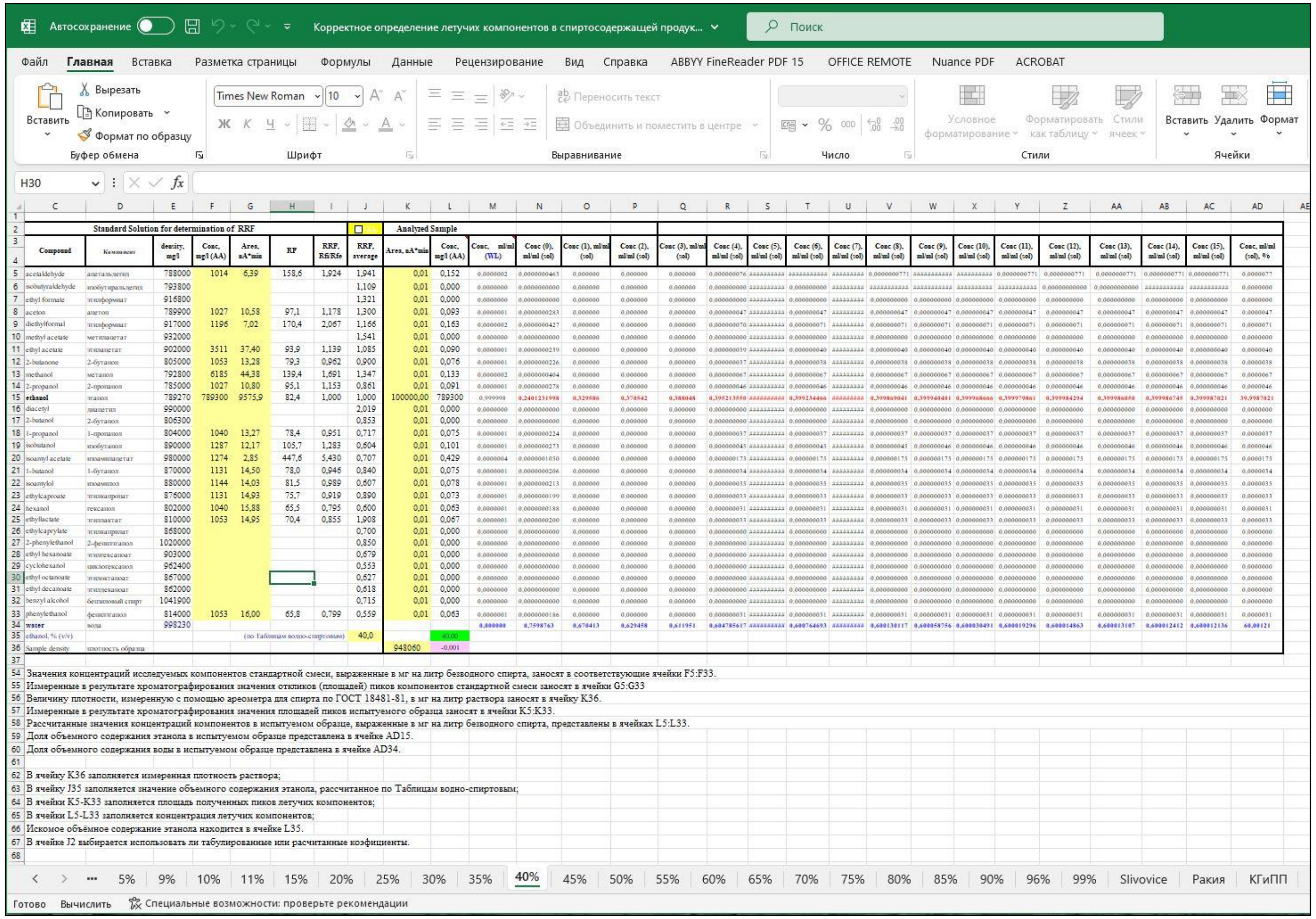
6. In the jth approximation, the value of the function $F\left(C_w\right)$ is calculated by formula **(2)** with the value of the argument $C_W^{(j-1)}$. The corresponding expressions for the concentrations of **water** and **volatile components** **(6)** and **(7)** can be presented in the following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

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

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

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.

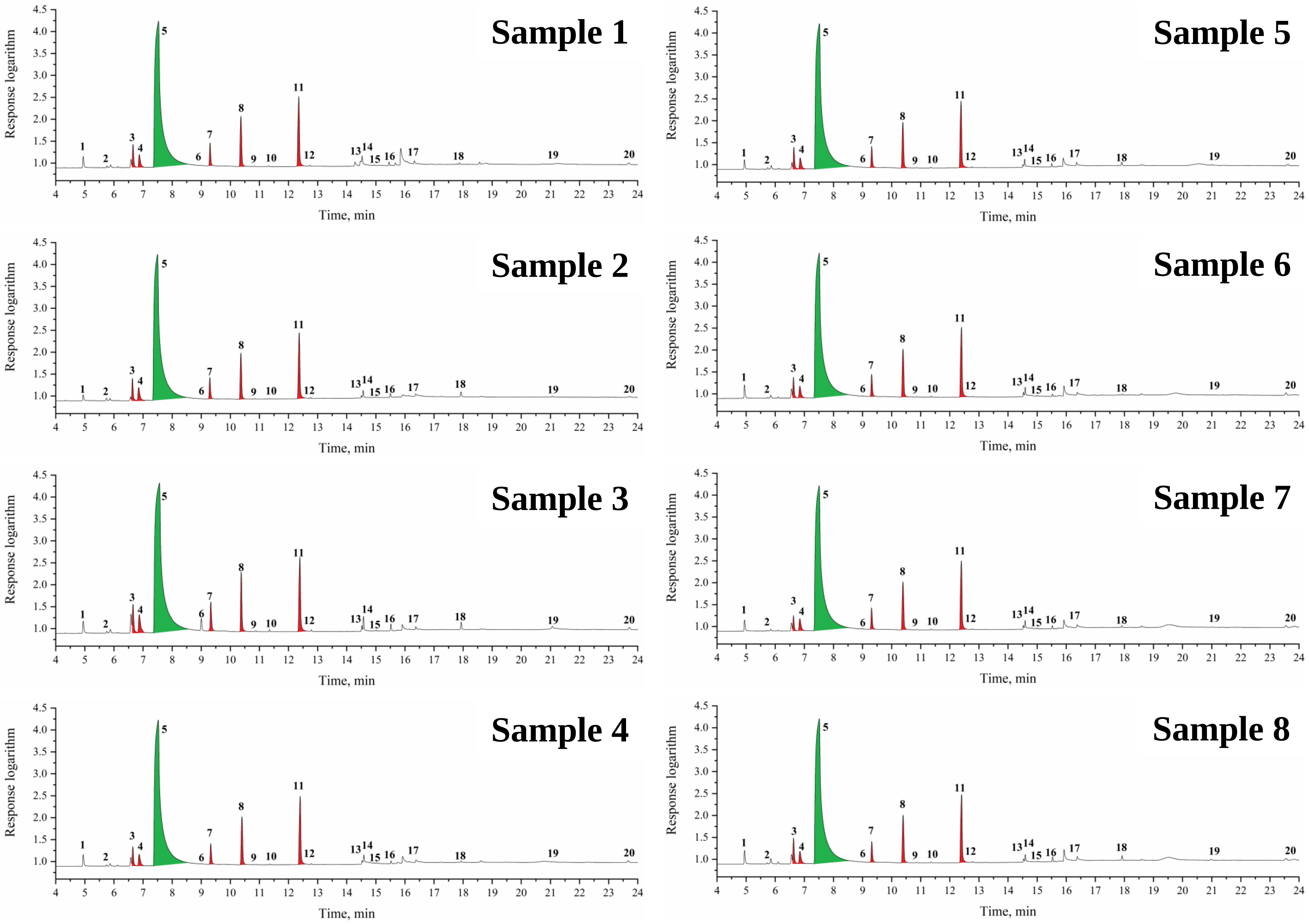
Correct determination of alcoholic strength in spirituous beverages: solution



MS Excel program for online and offline calculation of the corrected alcoholic strength: https://elab.bsu.by/article/747

- **Computer calculation program can help to automate and streamline the analysis of spirituous beverages**
- **The implementation of new approach can help to improve the accuracy and reliability of measurements**
- **Since during the analysis of alcoholic products it is necessary to analyze the density sample and measure the chromatogram of the sample, there is no need to carry out any additional measurements, financial or labor costs to implement the proposed method**

Determination of alcoholic strength in spirituous beverages: GC measurements in brandies



1	Acetaldehyde
2	Isobutanal
3	**Ethyl acetate**
4	**Methanol**
5	**Ethanol**
6	Butan-2-ol
7	**Propan-1-ol**
8	**Isobutanol**
9	Isoamyl acetate
10	Butan-1-ol
11	**Isoamylol**
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

Measured concentrations of volatile components in brandies

№	Compound	Concentration, mg/L AA							
		Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8
1	Acetaldehyde	182	85	150	206	156	250	193	248
2	Isobutanal	11.8	20.0	10.6	9.9	12.1	4.7	4.4	7.9
3	**Ethyl acetate**	**417**	**411**	**457**	**334**	**404**	**388**	**237**	**546**
4	**Methanol**	**332**	**371**	**415**	**334**	**307**	**347**	**343**	**363**
5	**Ethanol**	**789270**	**789270**	**789270**	**789270**	**789270**	**789270**	**789270**	**789270**
6	Butan-2-ol	1.2	0.6	70.5	2.0	0.8	3.4	3.1	1.2
7	**Propan-1-ol**	**294**	**297**	**334**	**284**	**279**	**317**	**290**	**278**
8	**Isobutanol**	**1341**	**1111**	**1242**	**1281**	**1096**	**1317**	**1255**	**1249**
9	Isoamyl acetate	3.7	4.9	4.8	3.5	3.0	3.9	2.8	3.4
10	Butan-1-ol	4.4	3.5	7.5	4.4	4.1	5.4	4.2	4.2
11	**Isoamylol**	**3445**	**3168**	**3044**	**3407**	**3137**	**3613**	**3410**	**3331**
12	Ethyl caproate	5.3	6.1	6.2	4.1	4.1	3.4	3.4	5.7
13	Ethyl lactate	193	105	136	112	91	111	104	82
14	Hexanol	22.3	11.3	15.9	15.5	12.2	19.1	16.5	13.7
15	Cis-3-hexen-1-ol	2.9	2.8	3.2	3.0	2.9	3.6	3.2	2.8
16	Ethyl caprylate	23.9	38.5	36.4	20.2	25.2	16.0	22.3	35.5
17	Furfural	26.4	23.3	14.9	22.6	27.7	25.9	27.9	35.9
18	Ethyl caprate	15.2	77.4	54.1	12.3	38.0	9.6	18.3	49.4
19	Ethyl laurate	2.7	18.8	23.1	1.7	8.6	1.5	2.9	13.8
20	2-Phenylethanol	21.5	14.2	21.7	25.2	20.3	32.6	25.5	26.4

Dimension of the concentration	Sum of the volatile components concentrations							
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8
mg/L AA	6345	5769	6047	6082	5629	6472	5967	6297
mg/L	2532	2299	3745	2439	2247	2575	2418	2511

Method for strength determination	Alcohol, % vol.							
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8
International Alcoholometric Tables	**40.14**	**40.06**	**62.34**	**40.34**	**40.13**	**40.04**	**40.76**	**40.11**
New method	**39.90**	**39.84**	**61.94**	**40.10**	**39.91**	**39.78**	**40.52**	**39.87**
Difference	**-0.24**	**-0.22**	**-0.40**	**-0.24**	**-0.22**	**-0.26**	**-0.24**	**-0.24**

Conclusions

- The pycnometric method for determining strength, based on the use of water-ethanol tables, leads to incorrect strength values for distillates of most spirituous beverages since these tables are intended exclusively for binary water-ethanol solutions.

- In practice, many types of spirituous beverages of grape (e.g. cognac, brandy, rakia etc.) as well as non-grape origin (e.g. slivovice, tequila etc.) contain a significant proportion of other volatile compounds, such as ethyl acetate, methanol, fusel oils, and more.

- A method is proposed, based on measuring the density of the test sample and utilizing chromatographic data on the concentrations of volatile compounds. This method enables reliable determination of the volume fraction of ethyl alcohol (i.e., the strength of spirituous beverages).

- An analysis of the results from experimental studies reveals that considering the concentrations of volatile compounds in various spirituous beverages of grape origin (e.g. cognacs, brandies) leads to significant deviations in the calculated strength values (ranging from -0.22 to -0.40%) when compared to the strength values derived directly from water-alcohol tables.

- Importantly, no additional measurements are required. The concentrations of ethanol, water, and all volatile compounds in the investigated sample can be calculated based on the initial data obtained from chromatographic analysis and density measurement of the sample.

- The high efficiency and broad international testing of the method, using ethanol as a reference substance, can provide a solid foundation for initiating an interlaboratory study under the patronage of the International Organization of Vine and Wine (OIV). The objective of this study would be to seek subsequent approval of the method as a reference method on an international level.

Thank you for your attention