

44th World Congress of Vine and Wine



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





OIV



International Organisation

Intergovernmental Organisation

of Vine and Wine

Determination of alcoholic strength in spirituous beverages: routine laboratory 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.

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

$$\rho_{S} = C_{W} \cdot \rho_{W}^{eff} + (1 - C_{W}) \cdot \sum_{(i)} \rho_{i} \cdot C_{i}^{*},$$

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, $\rho_W = 998230$ 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 components**, mg/L;

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

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



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

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

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.





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

where \tilde{C}_i is

reference su

$$C_{i}^{*} = \left(\frac{\tilde{C}_{i}}{\rho_{i}}\right) / \left(\sum_{(i)} \frac{\tilde{C}_{i}}{\rho_{i}}\right),$$
(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
 $\tilde{C}_{i} = RRF_{i} \cdot \frac{A_{i}}{A_{Eth}} \cdot \rho_{Eth},$ (4)

$$RRF_{i} = \frac{\tilde{C}_{i}^{st}}{A_{i}^{st}} / \frac{\rho_{Eth}}{A_{Eth}^{st}},$$
 (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, $\rho_{Eth} = 789270$ mg/L;

 A_i^{st} and A_{th}^{st} 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.

(6)

(7)

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

$$C_{W} = \frac{\rho_{S} \cdot \sum_{(i)} \frac{\tilde{C}_{i}}{\rho_{i}} - \sum_{(i)} \tilde{C}_{i}}{\rho_{W} \cdot F(C_{W}) \cdot \sum_{(i)} \frac{\tilde{C}_{i}}{\rho_{i}} - \sum_{(i)} \tilde{C}_{i}}.$$

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

$$C_i = (1 - C_W) \cdot C_i^*.$$

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

$$C_{W}^{(0)} = \frac{\rho_{S} \cdot \sum_{(i)} \frac{\tilde{C}_{i}}{\rho_{i}} - \sum_{(i)} \tilde{C}_{i}}{\rho_{W} \cdot \sum_{(i)} \frac{\tilde{C}_{i}}{\rho_{i}} - \sum_{(i)} \tilde{C}_{i}}, \quad (8)$$

$$C_{i}^{(0)} = \left(1 - C_{W}^{(0)}\right) \cdot C_{i}^{*}. \quad (9)$$



6. In the jth approximation, the value of the function $F(C_w)$ 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



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.

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vlacetate	Incompany Tart	980000	1274	2.85	447,6	5,430	0,707	0,01	0,429	0.0000004	0.0000001010	0,000000	0.000000	0.000000	0.0000001	3	0.000000173	444344444	0.000000175	0.000000175	0.000000175	0.000000173	0.000000175	0.0000000175	0.000000173	0.000000175	0.0000175
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ryikal	ariog saginou	880000	1144	14,03	81,5	0,989	0,607	0,01	0,078	0.0000001	0,000000213	0,000000	0,000000	0,000000	0,0000000	2 22222222	0,00000033	******	0,000000035	0.00000035	0,000000035	0,000000035	0,000000035	0.00000035	0,00000035	0.00000035	0,0000035
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clancate	TERMONTANOAT	\$67000		1	1	1	0,627	0,01	0,000	0,0000000	0.0000000000	0,000000	0,000000	0,000000	6,00000000	0 2222222222	0.000000000	333333333	0.000000000	0,000000000	0,0000000000	0.000000000.0	0.000000000	0,0000000000	0.000000000	0,0000000000	0.0000000
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- 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

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

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

10

	Compound	Concentration, mg/L AA										
JNō	Compound	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			
				Sum	of the volatile co	mnonents concen	trations					
Dimer	Dimension of the concentration		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			
					Alaah	ol 9/ vol						
Method	Method for strength determination		Sample 2	Sample 3	Alcon Sample A	<u>01, 70 VUI.</u> Sample 5	Sample 6	Sample 7	Sample 8			
Interneti	onal Alcoholometric Tables			62 34	<u> </u>	<u> </u>		<u> </u>	<u> </u>			
mundu	New method	30 00	30 8/	61 04	40.10	30 01	30 78	40.52	30 87			
	Difference	-0 24	-0.22		-0.24	_0 22	-0.26	-0.24	_0 24			
	DIIITITIC	-0.44	-0.44	-0.40	-0.44	-0.44	-0.40	-0.44	-0.44			

Measured concentrations of volatile components in brandies

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