Validation capabilities of a modified internal standard method

Introduction

The quality and safety of alcoholic and alcoholic-containing products is controlled at government level throughout the world. One of the most important indicators that is strictly monitored is the presence of volatile compounds and methyl alcohol, the most toxic compound. Analysis of the current standards for determining their quantitative content in countries and organizations such as the People's Republic of China [1], the Republic of India [2], the European Union [3] and the International Organisation of Vine and Wine (OIV) [4] has shown that their standards are harmonized with the European Commission Regulation EC 2870/2000 [3]. This document was adopted on the basis of the results of interlaboratory tests [5] carried out in 1999 with the financial support of the European Commission, which demonstrated the effectiveness of the method of the internal standard and prescribed its strict observance.

It is important to note that in all governmental and intergovernmental regulations on quality control and safety of alcoholic beverages, including European Commission Regulation 110/2008 [6], the maximum permissible levels of volatile compounds are expressed in mg per litre of anhydrous alcohol (AA). In accordance with the requirements of Regulation (EC) No 2870/2000, the quantification of volatile compounds is carried out using the internal standard method. This method involves a manual procedure of quantitative addition of the internal standard substance to the test sample.

Innovative solution

In order to ensure uniformity, to obtain high reliability of the data obtained and to eliminate the manual procedure of quantitative introduction of the substance of the internal standard into the test sample, it is proposed to use ethyl alcohol, which is always present in all types of alcoholic and alcoholic products, as an internal standard. The scientific novelty of the method and its effectiveness are confirmed by the results of theoretical and experimental studies obtained in numerous laboratory tests on a wide range of alcoholic and alcoholic-containing products. The work was carried out in accordance with the recommendations of the International Union of Pure and Applied Chemistry (IUPAC) [7] and the guidelines of the Association of Official Analytical Chemists (AOAC) [8]. Data from interlaboratory comparisons involving 9 laboratories from Belarus, Russia, Czech Republic and Turkey [9] confirmed the predictions that the main metrological characteristics of the proposed method, its reproducibility and accuracy exceed the similar characteristics of the European Commission Regulation EC 2870/2000.

The simplicity of the method, together with the significant economic efficiency and high reliability of the data obtained, led to interlaboratory tests of the method in 41 EU customs laboratories. On the

basis of the positive results of the tests performed, the method for the determination of the quantitative content of volatile denaturants in ethyl alcohol using ethyl alcohol directly present in the test sample as the internal standard was accepted as an official standard ILIADe 453:2021 | CLEN method [10] for customs laboratories of the European Union.

It is important to note that the proposed method allows direct measurement of the quantitative content of volatile compounds in alcoholic products in the required dimension of mg per litre of anhydrous ethanol. Additional measurements of the density of the test sample and determination of the volumetric content of ethanol (strength) are not required. Consequently, samples with a volume of less than 2 ml can be submitted for testing. The absence of the need to measure the strength of the sample removes the restriction on its minimum volume of 200 ml, which in turn opens up a real opportunity to produce standard samples of volatile compounds that can be used to assess the accuracy of measurements in the quality and safety control of alcoholic beverages.

To evaluate the metrological characteristics of the method, such as repeatability, intermediate precision and expanded uncertainty, experimental studies were carried out on a wide range of the most common alcoholic products with volumetric ethanol contents ranging from 8.5% to 96.0%. During the experiment, the quantitative content of the main volatile compounds (acetaldehyde, methanol, methyl acetate, ethyl acetate, 2-propanol, 1-propanol, isobutanol, 1-butanol and isoamylol) specified in the European Commission Regulation No 110/2008 [6] was determined. The experimental results obtained are summarised in Table 1. The relative difference between the obtained concentration values (Δ, %) measured according to EC Regulation 2870/2000 using the official method of the internal standard and according to the proposed modified method does not exceed 1,5 %.

Table 1. Quantitative contents of acetaldehyde, esters, methanol and higher alcohols (highlighted in green, blue, red and pink respectively) in 27 alcoholic beverages measured by the modified internal standard method and the traditional internal standard method.

Result for	 40 % ABV	 40 % ABV	 43 % ABV	 40 % ABV	 40 % ABV	 40 % ABV	 40 % ABV	 47 % ABV	 45 % ABV
	Rum	**Whiskey**	**Bourbon**	**Grain spirit**	**Brandy**	**Grappa**	**Calvados**	**Gin**	**Slivovice**
IS-Method, mg/L AA	48.1 / 145 / 1043 / 22.2	162 / 589 / 6693 / 132	150 / 645 / 5546 / 88.4	44.0 / 84.7 / 4662 / 110	143 / 396 / 4801 / 297	191 / 289 / 2113 / 414	182 / 583 / 3690 / 910	1.70 / 0 / 1.54 / 4.16	210 / 907 / 6255 / 10546
Eth-RS-Method, mg/L AA	48.4 / 146 / 1051 / 22.3	160 / 584 / 6635 / 130	151 / 649 / 5580 / 88.9	44.4 / 85.4 / 4703 / 111	142 / 396 / 4794 / 297	190 / 288 / 2100 / 412	182 / 585 / 3702 / 913	1.72 / 0 / 1.55 / 4.19	211 / 912 / 6288 / 10603
Δ, %	0.7 / 0.7 / 0.7 / 0.7	-0.9 / -0.9 / -0.9 / -0.9	0.6 / 0.6 / 0.6 / 0.6	0.9 / 0.9 / 0.9 / 0.9	-0.2 / -0.2 / -0.2 / -0.2	-0.6 / -0.6 / -0.6 / -0.6	0.3 / 0.3 / 0.3 / 0.3	0.8 / - / 0.9 / 0.9	0.5 / 0.5 / 0.5/ 0.5
Result for	 38 % ABV	 14.5 % ABV	 38 % ABV	 15 % ABV	 18 % ABV	 8.5 % ABV	 70 % ABV	 27.5 % ABV	 40 % ABV
	Tsikoudia	**Sake**	**Tequila**	**Vermouth**	**Nalewka**	**Mulled wine**	**Rectified spirit**	**Cocktail**	**Vodka**
IS-Method, mg/L AA	356 / 266 / 2297 / 755	37.6 / 47.0 / 1367 / 18.2	34.8 / 126 / 2895 / 1456	30.5 / 0 / 5.94 / 17.5	47.4 / 74.4 / 10.3 / 168	22.7 / 55.9 / 871 / 25.3	4.83 / 25.2 / 0 / 6.05	61.9 / 84.0 / 728 / 77.3	0.504 / 0 / 0 / 21.8
Eth-RS-Method, mg/L AA	359 / 268 / 2316 / 761	37.2 / 46.5 / 1352 / 18.1	34.9 / 127 / 2904 / 1460	30.6 / 0 / 5.98 / 17.6	47.8 / 75.1 / 10.4 / 169	22.5 / 55.6 / 866 / 25.1	4.81 / 25.1 / 0 / 6.03	61.1 / 83.0 / 719 / 76.3	0.50 / 0 / 0 / 21.7
Δ, %	0.9 / 0.8 / 0.9 / 0.9	-1.1 / -1.1 / -1.1 / -1.1	0.4 / 0.3 / 0.3 / 0.3	0.6 / - / 0.6 / 0.6	0.9 / 0.9 / 0.9 / 0.9	-0.6 / -0.5 / -0.6 / -0.6	-0.4 / -0.4 / - / - 0.4	-1.3 / -1.2 / -1.2 / -1.2	-0.7 / - / - / -0.7
Result for	 38 % ABV	 17 % ABV	 35 % ABV	 25 % ABV	 16 % ABV	 16.5 % ABV	 35 % ABV	 40 % ABV	 56 % ABV
	Liqueurs							**Rakia**	**Baijiu**
	Sambuca	**Egg**	**Herbal**	**Limon**	**Cherry**	**Raspberry**	**Sloe gin**		
IS-Method, mg/L AA	4.20 / 0 / 2.44 / 2.32	6.89 / 0 / 125 / 9.75	38.1 / 13.5 / 9.39 / 19.5	25.1 / 0 / 0 / 29.1	18.4 / 266 / 0 / 9.77	36.6 / 31.8 / 0 / 127	1.12 / 0 / 0 / 20.5	92.2 / 1334 / 6165 / 11862	63.9 / 1072 / 2114 / 115
Eth-RS-Method, mg/L AA	4.24 / 0 / 2.46 / 2.34	6.94 / 0 / 125 / 9.81	38.2 / 13.5 / 9.43 / 19.6	25.3 / 0 / 0 / 29.4	18.5 / 267 / 0 / 9.82	36.2 / 31.5 / 0 / 126	1.13 / 0 / 0 / 20.7	91.6 / 1325 / 6217 / 11791	64.3 / 1079 / 2128 / 116
Δ, %	0.8 / - / 0.8 / 0.8	0.8 / - / 0.7 / 0.7	0.4 / 0.4 / 0.4 / 0.4	0.8 / - / - / 0.8	0.5 / 0.6 / - / 0.5	-1.0 / -1.1 / - / - 1.1	0.6 / - / - / 0.6	0.6 / 0.7 / 0.6 / 0.6	0.6 / 0.6 / 0.6 / 0.6

High reliability of the obtained data together with reduction of financial, time and labour costs in comparison with the existing state, interstate and international standards in different countries became the main factors promoting the development on the international markets. In particular, the projects on increasing the efficiency of national standards of the People's Republic of China GB/T 11858 [11], state standard of the Republic of India IS 3752:2005 [12], regulation of the European Commission EC2870/2000 [13] were prepared.

At the 66th meeting of the Sub-Commission "Methods of Analysis" of the General Assembly of the International Intergovernmental Organisation for Viticulture and Wine (IGOV - OIV) on 27 September 2002, it was decided to include the project CII-SCMA 2023-09 06 (Method for the determination of volatile compounds in spirit drinks of viticultural origin using contained ethanol as reference substance) in the IGOV plan for the development of an international standard based on the proposed method.

In accordance with paragraphs 7.2.1.4 and 7.1.2.5 international standard ISO/IEC 17025 [14] “When the customer does not specify the method to be used, the laboratory shall select an appropriate method and inform the customer of the method chosen. Methods published either in international, regional or national standards, or by reputable technical organizations, or in relevant scientific texts or journals, or as specified by the manufacturer of the equipment, are recommended. Laboratory-

developed or modified methods can also be used. The laboratory shall verify that it can properly perform methods before introducing them by ensuring that it can achieve the required performance".

To implement the proposed modified internal standard method in a testing laboratory that determines the quantitative content of volatile components and methanol in alcoholic products on gas chromatographs with a flame ionization detector in accordance with current standards, no additional financial, material and labor costs are required. The calculation of the calibration characteristic of the device, which consists in finding the numerical values of the relative response factors (RRF) of the detector response to the volatile component under study relative to the response to ethanol, can be calculated based on the data of the measured chromatograms of the standard solutions used when determining the calibration characteristic of the device using the external standard method or the traditional internal standard method. Calculation of the quantitative content of volatile compounds in the test sample of alcoholic product is carried out using the method of a modified internal standard, which in this case is ethanol directly present in the sample.

When the modified internal standard method is used for quantitative calculations using ethyl alcohol present in the test sample as reference, the calibration characteristic of the measuring instrument is to determine the value of the relative response coefficient of the detector for the i-th volatile compound of interest in relation to the detector response for ethanol. $RRF_i^{ethanol}$. The value of this coefficient is calculated by the single point calibration method on the basis of the results of the measurements of the standard sample according to the following formula

$$RRF_i^{ethanol} = \frac{\sum_{k=1}^{M} C_i^{Std} \cdot (A_{i\ k}^{Std} / A_{ethanol\ k}^{Std})}{\rho_{ethanol} \cdot \sum_{k=1}^{M} (A_{i\ k}^{Std} / A_{ethanol\ k}^{Sd})^2}, \quad (1)$$

where C_i^{Std} value of the concentration of the i-th investigated volatile compound in the standard sample used to establish the calibration coefficients, expressed in mg/l AA;ρ_{ehanol} – the value of the ethanol concentration in the standard sample, expressed in mg/l AA, is equal to the tabulated density value of anhydrous ethanol, $\rho_{ethanol}$ = 789270 мг/л; $A_{ethanol\ k}^{Std}$ and $A_{i\ k}^{Std}$– is the value of the detector response to ethanol and to the i-th volatile compound of interest, expressed in units of peak area, obtained as a result of the k-th measurement of the standard; M is the number of measurements of the calibration standard. It is important to note that in this case the coefficients $RRF_i^{ethamol}$ are dimensionless values.

The value of the quantitative content of the i-th investigated volatile compound expressed in mg/l AA in the test sample is calculated according to the following formula,

$$C_i\ [\text{мг/ л AA}] = RRF_i^{ethanol} \cdot \rho_{ethanol} \cdot \frac{A_i}{A_{ethanol}}, \quad (2)$$

where A_i and $A_{ethanol}$ – is the value of the detector response to the i-th volatile compound and to ethanol, respectively, expressed in units of peak area.

Calculation of determination coefficients R_i^2 is performed according to the following formula

$$R_i^2 = 1 - \frac{\sum_{l}^{S} (C_{i,l}^{Std} - RRF_i^{ethanol} \cdot \rho_{ethamol} \cdot A_{i,l}^{Std} / A_{ethanol\ 1}^{Std})^2}{\sum_{l}^{S} (C_{i,l}^{ethanol} - \frac{1}{S} \sum_{k}^{S} C_{i,k}^{Std})^2}, \quad (3)$$

where S is the total of all measured chromatograms of standard solutions.

The relative standard deviation of the measured value of the concentration of the i-th volatile compound under investigation, expressed in per cent, is calculated by the following formula

$$OCKO(C_i)[\%] = \left(\sqrt{\frac{1}{n-1} \sum (C_i - \bar{C}_i)^2}\right) / \bar{C}_i \cdot 100\%, \quad (4)$$

where $\bar{C}_i$ is the mean value of the measured concentration of the i-th volatile compound tested in the standard solution tested, n is the number of measurements.

The value of the precision of the measurement of the concentration of the volatile compound, expressed as a relative offset, is calculated by the following formula

$$Bias(C_i)[\%] = (C_i^{Std} - \bar{C}_i)/C_i^{Std}) \cdot 100\%. \quad (5)$$

The limit of quantification is calculated using the following formula

$$LOQ_i = k * \frac{RSD(C_i)}{\sqrt{n}}, \quad (6)$$

where k=10.

Let consider an example of validation of the proposed method in a testing laboratory performing quantitative determinations of volatile compounds in alcoholic beverages according to EC 2870/2000 using the traditional internal standard method. The experimental test data obtained in the laboratory during the validation of the method according to EC 2870/2000 can be used to determine the values of the calibration coefficients, the linearity of the calibration characteristic, the limit of quantification and the accuracy of the measurements. Aqueous ethanol standard solutions with a volume content of 40 % ethyl alcohol were prepared by adding the volatile substances of interest and the internal standard 3-pentanol by weight to each standard solution.

The values of the concentrations of the volatile compounds tested in the aqueous standard solutions prepared, obtained during the validation of the EC 2870/2000 method, expressed in the required unit "mg/l AA", and the values of the detector response to the volatile compounds tested, expressed as arbitrary values of the peak area on the measured chromatograms of the standard solutions, are given in Table 2.

Values of the relative response coefficient of the detector for the i-th tested volatile compound in relation to the detector response for ethanol $RRF_i^{ethanol}$ is determined according to the recommendation EC 2870/2000 on the basis of test data of the standard solution "1.0".

Calculated values of the coefficients $RRF_i^{ethanol}$; values of the coefficient of determination characterizing the linearity of the constructed calibration characteristics; average values of measured concentrations of volatile components in standard solutions; correctness values expressed in relative displacement values; The standard deviation of the determination of the concentration of the volatile component under study, expressed in the required dimension “mg/l AA” is given in Table 3.

Chromatograms obtained during method validation according to EC 2870/2000 regulation are shown in Figures 1-3.

Table 2. Concentration values of the studied volatile components in the prepared standard solutions, expressed in the dimension “mg/l AA” and the magnitude of the detector response to the studied volatile components, expressed in arbitrary peak areas on the measured chromatograms.

Compound	Standard solution “0.1”				Standard solution “0.5”				Standard solution “1.0”				Standard solution “1.5”				Standard solution “2.0”			
	Conc mg/l AA	Area-1, a. e.	Area-2, a. e.	Area-3, a. e.	Conc mg/l AA	Area-1, a. e.	Area-2, a. e.	Area-3, a. e.	Conc mg/l AA	Area-1, a. e.	Area-2, a. e.	Area-3, a. e.	Conc mg/l AA	Area-1, a. e.	Area-2, a. e.	Area-3, a. e.	Conc mg/l AA	Area-1, a. e.	Area-2, a. e.	Area-3, a. e.
Acetaldehyde	45.61	0.0780	0.0798	0.0811	226.74	0.3977	0.4058	0.4015	428.25	0.7568	0.7690	0.7611	658.4	1.177	1.195	1.196	881.1	1.591	1.593	1.556
Methyl acetate	72.70	0.1002	0.0999	0.1014	361.35	0.5073	0.5077	0.5020	682.51	0.9839	0.9915	0.9713	1049.4	1.515	1.525	1.521	1404.2	2.047	2.043	1.985
Ethyl acetate	65.67	0.1247	0.1286	0.1259	326.41	0.6435	0.6441	0.6390	616.51	1.2443	1.2454	1.2275	947.9	1.912	1.923	1.915	1268.4	2.579	2.573	2.495
acetal	58.90	0.1521	0.1558	0.1560	292.77	0.7832	0.7744	0.7767	552.98	1.4915	1.5026	1.4733	850.2	2.291	2.331	2.295	1137.7	3.097	3.082	3.001
methanol	51.28	0.1054	0.1059	0.1048	254.88	0.4824	0.4807	0.4839	481.41	0.9052	0.9102	0.8994	740.2	1.396	1.412	1.406	990.5	1.876	1.884	1.831
ethanol	789300	1740.1	1737.5	1735.9	789300	1736.7	1734.3	1722.8	789300	1728.2	1741.0	1716.1	789300	1738	1753	1748	789300	1750	1754	1703
2-buthanol	53.03	0.1836	0.1797	0.1834	263.61	0.9169	0.9162	0.9003	497.89	1.7181	1.7394	1.7122	765.5	2.673	2.704	2.688	1024.4	3.599	3.614	3.504
1-propanol	51.56	0.1737	0.1732	0.1792	256.29	0.8688	0.8643	0.8607	484.06	1.6397	1.6487	1.6196	744.2	2.531	2.553	2.553	995.9	3.420	3.421	3.322
2-methyl-1-propanol	50.53	0.2014	0.1983	0.1984	251.15	1.0010	1.0049	0.9974	474.36	1.8939	1.9215	1.8839	729.3	2.943	2.970	2.969	976.0	3.970	3.975	3.852
3-penthanol	542.12	2.0776	2.0785	2.0763	539.56	2.0793	2.0766	2.0534	536.02	2.0405	2.0621	2.0242	539.9	2.069	2.082	2.081	535.1	2.079	2.085	2.020
n-buthanol	52.91	0.1976	0.1950	0.1937	263.02	0.9881	0.9811	0.9712	496.77	1.8451	1.8596	1.8334	763.8	2.871	2.904	2.897	1022.1	3.864	3.879	3.770
2-methyl-1-buthanol	54.75	0.2168	0.2208	0.2237	272.14	1.1072	1.0945	1.0905	514.01	2.0689	2.0810	2.0601	790.3	3.247	3.255	3.252	1057.5	4.329	4.357	4.237
3-methyl-1-buthanol	52.48	0.2028	0.2149	0.2114	260.86	1.0571	1.0330	1.0388	492.71	1.9608	1.9650	1.9456	757.5	3.062	3.088	3.084	1013.7	4.101	4.142	4.024

Table 3. Calculated coefficient values $RRF_i^{этанол}$, average values of measured concentrations of volatile components in standard solutions, expressed in the required dimension “mg/l AA”, accuracy values expressed in relative bias values, relative standard deviations in determining the concentration of the volatile component under study and calculated limits of quantification.

		Standard solution “0.1”				Standard solution “0.5”			Standard solution “1.0”			Standard solution “1.5”			Standard solution “2.0”			
Compound	RRF_i^{ethano}	Conc mg/l AA	Bias., %	RSD, %	LOQ, mg/l AA	Conc mg/l AA	Bias., %	RSD, %	Conc mg/l AA	Bias., %	RSD, %	Conc mg/l AA	Bias., %	RSD, %	Conc mg/l AA	Bias., %	RSD, %	R^2
ацетальдегид	1.230	44.49	-2.5	1.5	5.2	225.3	-0.6	1.2	428.2	-0.0028	0.6	661.2	0.4	0.5	883.8	0.3	0.4	0.9998
Acetaldehyde	1.522	69.45	-4.5	0.7	3.4	350.8	-2.9	0.2	682.5	-0.0008	0.3	1045.7	-0.4	0.1	1401	-0.2	0.2	0.9995
Methyl acetate	1.090	62.55	-4.7	2.4	5.8	319.0	-2.3	0.1	616.5	-0.0010	0.4	943.9	-0.4	0.2	1263	-0.4	0.3	0.9999
Ethyl acetate	0.813	57.11	-3.0	1.5	5.0	288.5	-1.5	0.6	553.0	-0.0006	0.3	847.4	-0.3	0.6	1131	-0.6	0.4	0.9998
acetal	1.165	55.75	8.7	0.7	1.6	256.2	0.5	0.7	481.4	-0.0001	0.1	739.7	-0.1	0.1	987.3	-0.3	0.2	0.9998
methanol	1.000	789300			0.0	789300	0.0	0.0	789300		0.0	789300	0.0	0.0	789300	0.0	0.0	
ethanol	0.633	52.36	-1.3	1.7	3.6	262.8	-0.3	0.6	497.9	-0.0004	0.3	768.8	0.4	0.2	1028	0.3	0.1	0.9997
2-buthanol	0.648	51.60	0.1	1.7	5.9	255.4	-0.4	0.2	484.1	-0.0005	0.3	745.5	0.2	0.2	998	0.2	0.1	0.9998
1-propanol	0.547	49.51	-2.0	0.9	2.2	249.6	-0.6	0.3	474.4	-0.0009	0.4	731.7	0.3	0.2	977.7	0.2	0.1	0.9996
2-methyl-1-propanol	0.575	542.31	0.0	0.1	3.4	542.3	0.5	0.3	536.0	-0.0003	0.2	539.6	-0.1	0.1	538.7	0.7	0.1	
3-penthanol	0.589	52.31	-1.1	0.7	2.7	263.3	0.1	0.5	496.8	0.0000	0.0	769.9	0.8	0.2	1028	0.6	0.2	0.9996
n-buthanol	0.544	54.44	-0.6	1.3	5.4	272.0	0.0	0.5	514.0	-0.0003	0.2	799.0	1.1	0.3	1065	0.7	0.3	0.9994
2-methyl-1-buthanol	0.551	52.81	0.6	2.9	8.7	262.1	0.5	1.1	492.7	-0.0005	0.3	262.1	0.5	1.1	1025	1.1	0.5	0.9993

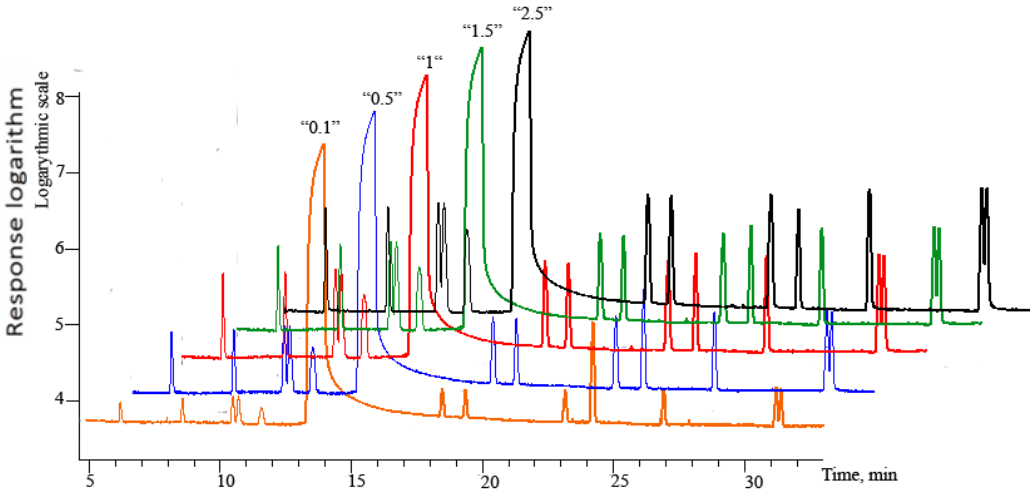

Figure 1. Chromatograms of prepared standard solutions "0.1", "0.5", "1.0", "1.5" and "2.0": 1 – acetaldehyde, 2 – methyl acetate, 3 – ethyl acetate, 4 – acetal, 5 – methanol, 6 – ethanol, 7 – 2-butanol, 8 – 1-propanol, 9 – 2-methyl-1-propanol, 10 – 3-pentanol, 11 – n-butanol, 12 – 2-methyl-1-butanol, 13 – 3-methyl-1-Butanol

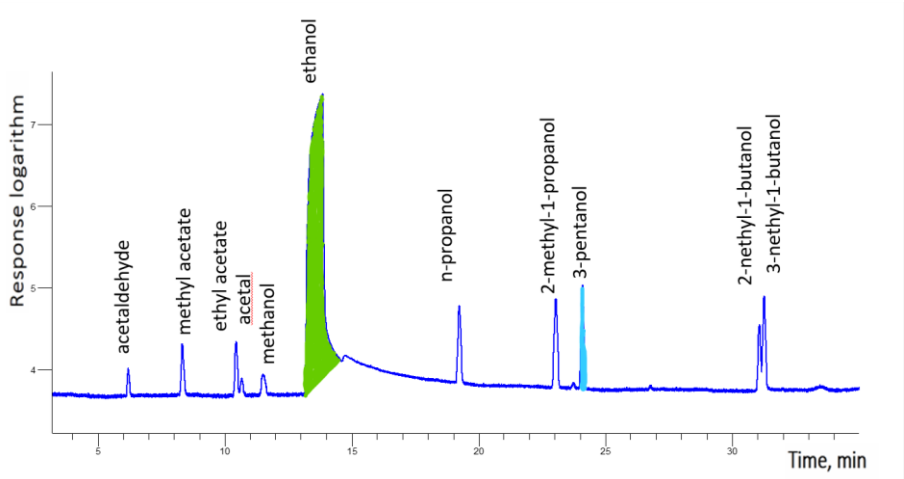

Figure 2. Chromatogram of a sample of the alcoholic beverage Brandy.

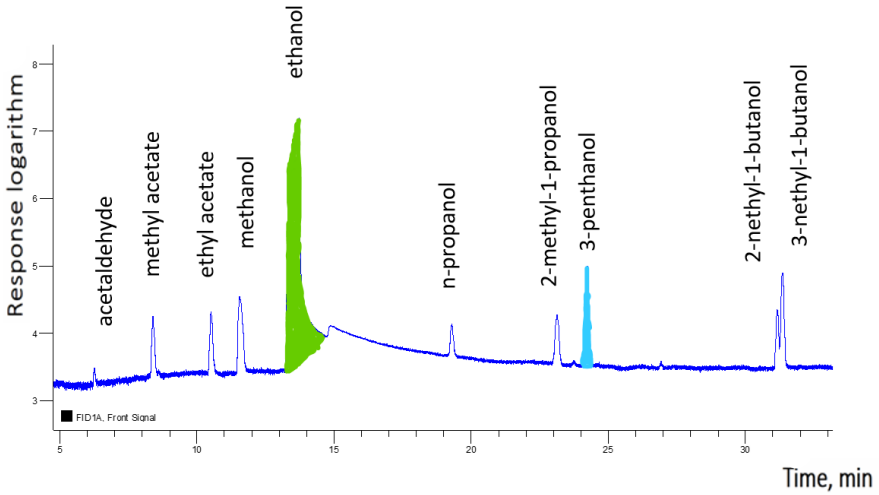

Figure 3. Chromatogram of a sample of the alcoholic drink Wine.

Conclusion

The innovation of the proposed method naturally revealed a number of effective solutions for determining the quantitative content of volatile compounds and methyl alcohol in alcoholic and alcoholic products.

1. No need to purchase an internal standard.

2. There is no need for a procedure to quantitatively introduce an internal standard substance into both the prepared standard solutions and the test samples.

3. The uncertainty of the concentration of the internal standard, ethyl alcohol, expressed in mg per litre of anhydrous ethanol, is zero.

4. The values of the relative response coefficients of the RRF detector to the volatile component of interest versus the detector response to ethyl alcohol for modern gas chromatographs with a flame ionisation detector are highly reproducible and can be tabulated. As a result, the interval between periodic calibrations of the instrument can be significantly increased.

It can be said that the determination of the quantitative content of volatile components in alcoholic products is becoming more reliable, less expensive, faster and more accurate. The undeniable advantages of the proposed method indicate good prospects for its application in production and testing laboratories all over the world.

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