The quality control system of distilled spirits

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Abstract. Research has been carried out to identify and quantify phenolic and furan compounds (gallic acid, ellagic acid, furfural, 5-methylfurfural, 5-hydroxymethylfurfural, vanillin, syringaldehyde, vanillic acid, syringic acid, synapic aldehyde, coniferyl aldehyde), volatile organic impurities (acetaldehyde, ethyl acetate, methanol, 1-propanol, isobutanol, 2-methylbutanol, 3-methylbutanol), cations (sodium, ammonium, potassium, calcium, magnesium) and anions (chlorides, nitrites, nitrates, sulfates, phosphates, oxalates) in distilled spirits (whiskey, rum, tequila). Some differences were observed in the phenolic profiles of authentic and fake rum samples. The ranges of the cations and anions content in commercial samples of rum, whiskey, tequila have been determined. The data obtained can be used to develop objective criteria for detecting counterfeit products.

1 Introduction

Distilled alcoholic beverages differ from each other by the presence of components that form the "bouquet" characteristic of each drink. These compounds, together with ethyl alcohol, are formed during fermentation, distillation and aging and cause changes in the organoleptic properties of beverages.

The identification of the alcoholic beverages authenticity is based on the analytical determination of a set of impurity components that determine the properties and/or origin of the product [1].

Products of oak wood ethanolysis (gallic acid, ellagic acid, vanillin, syringaldehyde, vanillic acid, syringic acid, sinapic acid, p-coumaric acid, sinapic aldehyde, coniferyl aldehyde, eugenol, guaiacol and others) accumulate in the distillate in contact with oak wood in certain typical proportions. Therefore, the absence of any age markers in the sample (or a change in their ratios) suggests the addition of flavorings. Syringaldehyde and vanillin are formed as a result of oxidative destruction of natural polymeric phenolic substances of oak wood during aging. Thus, their concentration indicates the maturation time of the distillate in an oak barrel and is used as an "age index" [2]. Furan compounds such as furfural or 5-hydroxymethylfurfural (HMF) are formed during distillation or by adding caramel colour [3]. The presence and concentration of these compounds in a

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distilled beverage is highly dependent on the production process, in particular the quality of the raw materials used, the type of fermentation, the type of distillation carried out, the addition of caramel colour, the aging time and the properties of the casks.

The aging of distillates in wooden barrels provides a high degree of extraction of wood components by ethanol, in particular tannins, gallic, ellagic acids. At the same time, reactions of oxidation of higher alcohols and aldehydes occur with the formation of acids, which react with alcohols, forming esters with a specific aroma [3].

Volatile organic impurities play an important role in the formation of the distilled spirits aroma. Their quantity and ratio can be used as criteria for evaluating the spirits quality during their identification. For example, the content of n-propanol, isobutanol is used to differentiate between different brands of whiskey, ethyl acetate is the most common ester, testifying to the quality of the product. Malt and grain whiskeys can be distinguished using 3-methylbutanol/2-methylbutanol ratios [4].

Trace amounts of microelements in alcoholic beverages are used as “territorial markers” and are often applied to classify alcoholic beverages depending on the geographical origin of the raw materials used [5].

The water quality and the methods of water purification used have a significant impact on the physicochemical stability of distilled beverages, in particular on their transparency. The main share of sediments formed in distilled alcoholic beverages is mineral sediments containing cations of calcium, magnesium, sodium and anions such as sulfates, phosphates and chlorides [6,7]. Another potential cause of sedimentation in alcoholic beverages is the formation of insoluble oxalate salts. Oxalic acid is extracted from oak wood during the aging of the distillate and reacts with calcium or magnesium to form insoluble crystals [8].

The aim of the study was to identify universal and specific criteria for the identification of aged distilled alcoholic beverages using highly sensitive techniques in order to introduce them into the quality control system for its improvement.

2 Materials and methods

2.1 Reagents, standards and solvents

Vanillin, vanillic acid, gallic acid, coniferyl aldehyde, sinapaldehyde, syringic acid, syringaldehyde, furfural, 5-HMF, 5MF, ellagic acid, acetaldehyde, ethyl acetate, 1-propanol, methanol, acetal, isobutanol, 2-methylbutanol, 3-methylbutanol were purchased from Sigma-Aldrich, Switzerland. Glacial acetic acid according chemically pure grade, ammonium oxalate 1-aqueous pure grade, acetonitrile (HPLC), rectified ethyl alcohol from food raw materials of the highest purity were used. Carrier gas – nitrogen, according to GOST 9293; hydrogen technical grade A in accordance with GOST 3022; compressed air in accordance with GOST 17433. Standard solutions of cations and anions were prepared from state standard reference sample and containing 1 mg/cm^3 relative error no more than 1% at = 0.95 of each cation and anion.

2.2 Samples

During our work, 10 commercial samples of rum, 3 whiskey, 3 tequilas were examined. A description of the samples is presented in table 1.

Table 1. Sample description.

№	Type	Aging time, years	Manufacturer country
R1	rum	3	Cuba

R2	rum	5	Cuba
R3	rum	7	Cuba
R4	rum	10	Cuba
R5	rum	8	Panama
R6	white rum	2	Dominican Republic
R7	rum	2	Dominican Republic
R8	rum	10	Dominican Republic
R9	**adulterated rum**	-	-
R10	**adulterated rum**	-	-
T1	tequila Blanco	2 month	Mexico
T2	tequila Reposado	2-11 month	Mexico
T3	tequila Anejo	1-3	Mexico
W1	blended whiskey	3	Scotland
W2	bourbon	6	USA
W3	malt whiskey	8	Ireland

2.3 Gas chromatography method

Analysis were performed on a gas chromatograph "Khromatek-Kristall 5000.1" equipped with a flame ionization detector using capillary column CP-Wax 57 CB 50m × 0.25mm × 0.20 μm. The carrier gas was nitrogen, chromatographic, carrier gas flow rate – 0.048-0.12 dm^3/h, column temperature – 40-90 °C sample volume – 0.2-1.00 mm^3. Sample preparation conditions: analysis was carried out after preliminary distillation and dilution of the sample with distilled water to obtain a solution with a strength of 40 %.

2.4 HPLC method

The identification and quantification of individual phenolic and furan compounds was performed by high performance liquid chromatography (HPLC). The HPLC system used was a Shimadzu LC – 20 (Japan) equipped with an automatic injector and a variable wavelength UV–vis detector. Stationary phase – SUPELCOSIL LC-18 column (25 cm * 4.6 mm, 5 μm). The mobile phase is 1.0% acetic acid, acetonitrile, the flow rate of the eluent is 0.6 cm^3/min, the temperature of the column is kept at 40 °C, the detection is spectrophotometric at a wavelength of 280 nm. To achieve the maximum separation of the required amount of components, all experiments were carried out in a gradient elution mode. Gradient: 5 min – 85% 1.0% acetic acid, 15 % acetonitrile; 10 minutes – 85% 1.0% acetic acid, 15% acetonitrile; 30 min – 77% 1.0% acetic acid, 23 % acetonitrile; 35 min – 2% 1.0% acetic acid, 98% acetonitrile, 40 min – 2% 1.0% acetic acid, 98% acetonitrile, 50 min – 0% 1.0% acetic acid , 100% acetonitrile; 10 min – column conditioning.

2.5 Ion chromatography method

Ion chromatographic analysis was carried out using the ECO IC System from Metrohm (Switzerland) with a conductometric detector. Anion separations were investigated with the use of chromatographic column, Metrosep A Supp 5 (150/4.0 mm) (eluent – a solution of a mixture of 3.2 mmol/dm^3 Na_2CO_3 and 1.0 mmol/dm^3 $NaHCO_3$; eluent flow rate 0.7 cm^3/min) from Metrohm, Switzerland. Cation separations were investigated with the use of chromatographic column Metrosep C 4 (150/4.0 mm) (eluent: 1.7 mmol / dm^3 HNO_3 and 0.7 mmol / dm^3 dipicolinic acid; eluent flow rate 0.9 cm^3/min) from Metrohm, Switzerland.

Data acquisition and evaluation of chromatograms were carried out with the MagIC Net 2.3 Metrodata (Metrohm) software.Sample preparation conditions for spirits: before analyzing sample were diluted with deionized water. Filters of 0.45 μm pore size were used for sample filtration.

3 Results and discussion

The following indicators of the quality and safety of distilled spirits were determined: the content of phenolic and furan compounds, volatile organic impurities, ionic composition The results of samples examining are presented in tables 2-4.

Table 2. Quantitative analysis data of phenolic and furan compounds in distilled alcoholic beverages.

№		Mass concentration, mg/dm^3												
	Gallic acid a	5-HMF	Furfural	5-MF	Vanillic acid	Syringic acid	Vanillin	Syringaldehyde	Ellagic acid	Coniferyl aldehyde	Sinapaldehyd	vanillin/syringaldehyde	syringic acid/syringaldehyde	vanillic acid/vanillin
R1	0.4	0.2	0.3	< 0.1	0.4	0.9	0.4	1.0	0.8	0.1	0.1	0.40	0.90	1.00
R2	0.6	4.2	0.4	0.1	0.4	0.9	0.5	1.1	1.2	0.1	0.1	0.45	0.91	0.80
R3	1.7	6.6	0.6	0.1	0.7	1.6	0.8	2.5	3.9	0.2	0.5	0.32	0.64	0.88
R4	2.2	18.9	1.2	0.1	1.2	2.8	1.7	4.0	6.2	0.3	0.4	0.43	0.70	0.71
R5	0.3	17.1	1.4	0.3	1.2	4.0	3.1	3.9	2.8	0.4	0.4	0.81	1.03	0.39
R6	0.3	0.5	0.1	< 0.1	0.1	0.2	0.1	0.3	0.1	< 0.1	< 0.1	0.21	0.7	2.0
R7	0.6	2.3	0.5	0.1	0.2	0.4	0.2	0.7	0.7	0.1	0.2	0.22	0.57	1.33
R8	5.1	8.1	2.3	0.3	1.6	3.1	2.4	5.9	14.5	0.7	1.0	0.40	0.53	0.69
R9	**< 0.1**	**8.5**	**0.5**	**< 0.1**	**0.1**	**0.4**	**144.6**	**0.8**	**0.4**	**0.3**	**0.6**	**180**	**0.50**	**-**
R10	**< 0.1**	**68.4**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**14.3**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**-**	**-**	**-**
T1	< 0.1	0.1	5.1	3.5	0.1	0.2	0.1	0.3	< 0.1	< 0.1	< 0.1	0.33	0.67	1.00
T2	< 0.1	0.5	6.1	3.8	0.2	0.5	0.6	0.9	< 0.1	0.1	0.3	0.67	0.55	0.33
T3	0.1	0.4	6.2	3.9	0.3	1.0	0.8	1.9	0.1	0.2	0.5	0.42	0.52	0.37
W1	0.2	15.0	5.3	< 0.1	1.0	1.5	1.7	3.3	1.2	< 0.1	0.3	0.52	0.45	0.59
W2	5.2	2.8	6.0	0.4	2.5	1.6	3.3	10.3	22.8	2.3	2.8	0.32	0.15	0.76
W3	3.0	13.0	6.9	0.1	0.8	1.5	1.6	3.3	7.3	1.6	1.0	0.48	0.45	0.50

From the data obtained, it can be seen that all samples of distilled alcoholic beverages, except for adulterated rums, have a rich component composition. The aging markers content depends on the type of raw material and correlates with the aging time. It was found that the ratio of vanillin/syringaldehyde in rum is on average in the range of 0.2-0.4, in tequila - 0.3-0.7, in whiskey - 0.3-0.5.

The increased vanillin concentration (about 50-60 times the typical) and the 180 vanillin/syringaldehyde ratio in falsified rum № 9 suggest the addition of flavor. Rum Sample № 10 contained only vanillin and 5-HMF, indicating the addition of caramel colour and flavor. In the present study, a balance was observed between aging markers (syringic acid/syringaldehyde and vanillic acid/vanillin) formed in two different directions associated with the aging of rum in contact with oak wood, guaiacyl series (coniferyl aldehyde, vanillin and vanillic acid) and syringyl series (synapic aldehyde, syringaldehyde and syringic acid), indicating the stability and maturity of rums.

In tequila samples, an increased content of 5-methylfurfural was found, which is associated with the peculiarities of the carbohydrate composition of blue agave and the process of making tequila [9].

Table 3. Quantitative analysis data of volatile organic impurities in distilled alcoholic beverages.

№	Mass concentration, mg/dm^3 in terms of absolute alcohol								
	Acetaldehyde	**Ethyl acetate**	**Acetal**	**Methanol** *	**1-propanol**	**Isobutanol**	**2-methylbutanol**	**3-methylbutanol**	**2-methylbutanol//3-methylbutanol**
R1	37.9	111.0	40.7	0.004649	191.9	232.9	100.2	414.7	0.24
R2	44.8	54.6	30.8	0.002005	74.7	78.1	40.0	171.2	0.23
R3	112.0	273.7	152.1	0.007166	269.7	267.7	144.8	664.7	0.22
R4	148.6	429.0	242.1	0.0094	323.2	321.9	160.9	649.0	0.25
R5	94.0	197.8	48.1	0.004932	149.4	117.6	75.8	461.7	0.16
R6	22,5	155,0	16,2	0,006	233,3	200,7	56,6	325,7	0,17
R7	73.1	173.3	26.9	0.005	220.0	194.6	59.0	321.2	0.18
R8	160.9	544.3	56.3	0,009	319.2	155.0	78.4	293.8	0.27
R9	**3.5**	**246.8**	**<10.0**	**0.002938**	**23.2**	**316.4**	**114.9**	**297.5**	**0.39**
R10	**47.8**	**694.6**	**65.6**	**0.001755**	**3.0**	**4.3**	**56.3**	**364.7**	**0.15**
T1	62.2	154.6	31.1	0.255652	284.5	654.4	374.2	1556.5	0.24
T2	80.0	198.0	39.6	0.184049	248.5	358.3	246.4	1261.1	0.20
T3	112.0	415.8	52.6	0.280841	264.2	661.7	350.2	1718.7	0.20

W1	8.8	11.4	5.0	0.011134	423.3	643.2	261.5	689.3	0.37
W2	54.2	579.5	118.8	0.001424	129.8	615.9	540.5	1702.4	0.32
W3	99.4	318.6	54.4	0.008842	462.5	435.9	342.8	1232.7	0.28

*methanol, %

It can be seen from the data obtained that all the samples contain congeners characteristic of all distilled spirits: acetaldehyde, ethyl acetate, acetal, methanol, 1-propanol, isobutanol, 2-methylbutanol, 3-methylbutanol. Fake samples were found to have lower volatile organic impurities concentrations than genuine samples. It is shown that the mass concentration of volatile organic impurities varies within wide limits. The ratio of 2-methylbutanol/3-methylbutanol for the studied samples of rum from one manufacturer was within the limits for Cuban rum - 0.22-0.25, Dominican rum - 0.17-0.27, Panamanian rum - 0.16, tequila – 0.20-0.24, whiskey of various manufacturers 0.28-0.37.

Table 4. Quantitative analysis data of cations and anions in distilled alcoholic beverages

№	Mass concentration, mg/dm^3										
	Sodium	**Ammonium**	**Potassium**	**Calcium**	**Magnesium**	**Chloride**	**Nitrite**	**Nitrate**	**Phosphate**	**Sulfate**	**Oxalate**
R1	1.4	<0.1	0.3	0.5	< 0.1	0.5	< 0.1	< 0.1	< 0.1	0.8	0.5
R2	22.7	0.3	3.4	0.8	< 0.1	0.4	0.1	< 0.1	0.2	1.9	4.3
R3	21.2	0.4	9.9	1.6	0.1	1.0	0.1	< 0.1	0.1	3.1	4.4
R4	19.1	1.0	7.4	1.7	0.6	1.3	0.1	< 0.1	0.2	2.8	4.2
R5	7.5	1.3	4.7	3.3	1.4	<0.1	1.4	0.1	7.4	6.9	4.4
R6	7,8	0,7	12,4	<0,1	0,1	7,9	1,3	0,1	9,7	14,4	2,2
R7	19.1	1.5	13.9	0.8	0.1	< 0.1	1.4	0.1	4.2	15.7	6.6
R8	46.9	2.8	22.3	1.7	0.3	6.3	1.7	0.9	13.5	54.0	12.2
R9	**76.2**	**0.4**	**5.2**	**2.2**	**1.5**	**4.6**	**<0.1**	**3.9**	**2.0**	**6.8**	**1.3**
R10	**2.6**	**0.1**	**0.2**	**1.5**	**0.3**	**4.3**	**<0.1**	**< 0.1**	**3.0**	**3.2**	**2.2**
T1	5.0	0.1	0.1	0.6	0.2	<0.1	1.3	0.1	1.6	1.6	2.1
T2	5.3	0.8	1.6	3.1	0.5	<0.1	1.4	0.1	1.5	2.8	2.3
T3	9.7	1.4	2.7	4.8	1.4	<0.1	1.4	0.1	1.7	3.4	3.1
W1	21.1	0.7	6.9	1.2	0.5	5.7	1.4	0.1	13.5	54.0	12.2

W2	1.0	0.5	14.2	0.8	0.3	<0.1	1.8	0.1	1.9	4.0	5.0
W3	6.5	0.4	10.1	1.0	0.5	<0.1	1.5	0.1	2.9	8.1	4.3

Based on the analysis of experimental data, it was shown that all samples of distilled spirits have the same qualitative composition of cations and anions, but the quantitative composition differs significantly due to the peculiarities of water treatment from different manufacturers. However, the dependence of the increase in the mass concentrations of cations and some anions with the exposure time (R1-R4, R6-R8, T1-T3) has been established. This can serve as an additional identification criterion for distilled alcoholic beverages from one manufacturer.

4 Conclusions

The article defines the quality criteria characteristic of aged distilled beverages and describes methods of identification by their content and ratio. The described methods are universal and can be useful for checking the quality of distilled alcoholic beverages and identifying their brand. The use of the developed methods will improve the efficiency of the quality control system for distilled alcoholic beverages, comprehensively study the dynamics of the aging process and promptly identify counterfeit products.

References

1. S.A. Savchuk, Medicine **3,** 16-46 (2014)
2. V.N. Vlassov, D.S. Maruzhenkov, Analusis **27,** 663-667 (1999)
3. T.E. Coldea, E. Mudura, C. Socaciu, Ideas and Applications Toward Sample Preparation for Food and Beverage Analysis (Croatia: InTech, 2017)
4. P.K. Yadav, R.M. Sharma, Arab Journal of Forensic Sciences & Forensic Medicine, **1 (9)**, 1232-1247 (2019)
5. P. Wiśniewska, T. Dymerski, W. Wardencki, J. Namieśnik, Journal of the Science of Food and Agriculture **95(11)** (2004)
6. I.M. Abramova et al, IOP Conf. Ser.: Earth Environ. Sci. **640,** 1-5 (2021)
7. A.V. Berezhnaya, Improvement of technological methods for improving the quality of cognac spirits and cognacs (Krasnodar, 2004)
8. M. Bordiga, Post-Fermentation and -Distillation Technology: Stabilization, Aging, and Spoilage (CRC Press, 2017)
9. N. Prado-Jaramillo, M. Estarrón-Espinosa, H. Escalona-Buendía, R.Cosío-Ramírez, S. T. Martín-del-Campo, LWT - Food Science and Technology, **61(2),** 471-483 (2015)