An integrated approach to the rum identification

I M Abramova, M E Medrish*, V B Savelieva, A G Romanova and D A Gavrilova
All-Russian Research Institute of Food Biotechnology, 4b, Samokatnaya str.,
Moscow, 111033, Russia

*E-mail: medrishm@mail.ru

Abstract. In our study, rapid methods were developed for the quantitative determination of cations (sodium, potassium, ammonium, calcium, magnesium) and anions (chlorides, nitrites, nitrates, phosphates, sulfates) using ion chromatography with conductometric detection; phenolic and furan compounds (gallic acid, ellagic acid, vanillin, syringaldehyde, vanillic acid, syringic acid, furfural, 5-HMF, coniferyl aldehyde, sinapaldehyde) by high performance liquid chromatography with spectrophotometric detection; volatile organic impurities (acetaldehyde, ethyl acetate, acetal, methanol, 1-propanol, isobutanol, 2-methylbutanol, 3-methylbutanol) by gas chromatography with flame ionization detection. The developed methods will allow monitoring the technological process of rum production, studying the aging dynamics, and identifying counterfeit products.

1. Introduction
Distilled alcoholic beverages are often subject to counterfeiting due to their high cost. Rum is one of the most popular spirits today. Despite the constant improvement of methods for combating counterfeit alcoholic beverages, it is not possible to solve the problem of a large number of products on the market that do not meet the established requirements, since the methods of counterfeiting are also being modernized.

The authentification of the distilled spirits is based on the analytical determination of a set of impurity components that determine the quality and the origin of the beverage [1].

As a result of the aging of rum distillate in oak barrels, the wood components are extracted with ethanol [2].

Products of wood ethanolysis (gallic acid, ellagic acid, vanillin, syringaldehyde, vanillic acid, syringic acid, sinapic acid, p-coumaric acid, sinapaldehyde, coniferylaldehyde, eugenol, guaiacol and others) accumulate in rum distillate during aging in certain typical proportions The concentration of vanillin and syringaldehyde, formed as a result of the oxidative destruction of lignin, indicates the aging time of the distillate in a wooden barrel and is used as an "age index" [2].

Therefore, the absence of any aging markers in the sample (or a change in their ratios) suggests falsification using the addition of flavors.

Regardless of the country of manufacture, one of the most important properties that determine the quality of rum is its aroma, which is a complex mixture of more than a hundred different compounds that appear during the production and aging of rum.

Rum contains a large amount of esters that impact fruitiness to its aroma. Acetaldehyde, ethyl acetate are one of the main aroma-producing substances formed as a result of the fermentation processes of distilled spirits, their quantity affects the quality of distillates. The moderate quantity of ethyl acetate
has a positive effect on the sensory characteristics of rum. Acetaldehyde adds nut, overripe apple aromas [3].

Trace amounts of microelements in alcoholic drinks are applied as “territorial markers” and are often used to classify alcoholic beverages depending on the geographical origin of the raw materials used [4].

There is very little information in the literature on the identification of rum and sugarcane distillates depending on geographical origin. So, for example, Brazilian scientists have assessed the analytical prospects for determining the geographic origin of cachasa [5]. Sampaio O. M. et al. [6] analyzed 44 samples from different countries in order to study chemical profiles and identify descriptors that would make it possible to distinguish between Cuban rum and rum from other countries. The authors selected the following compounds as descriptors that allow differentiating rum samples with an accuracy of 97.1% (LDA analysis): acetone, ethyl acetate, 2-butanol, 1-propanol, 1-butanol, isoamyl alcohol, barium, strontium, magnesium, zinc, lead, calcium, sodium, vanillin acid, vanillin, syring acid, catechin, epicatechin, acetaldehyde, cyclopentanone, isobutanol, chloraldehyde.

Brazilian scientists [7] used the methods of ion chromatography and optical emission spectrometry with inductively coupled plasma, gas chromatography to identify and quantify microelements and volatile organic components in the sugar cane distillate from Brazil and Cabo Verde. The authors chose chloride, copper, ethyl acetate and sulfate as markers for the differentiation of sugar cane distillate from Brazil and Cabo Verde.

Currently, in Russia, the ionic composition, as well as the content of phenolic and furan compounds in rum distillates, rum is not regulated by regulatory documents, however, it is known that cations of calcium, magnesium, phenolic compounds are involved in various physicochemical transformations, including those leading to the formation turbidity and precipitation in alcoholic beverages [8, 9].

Thus, increasing the efficiency of the technological process of rum production requires an integrated approach to assessing its quality and safety.

One of the ways to solve problems aimed at ensuring the quality and safety of alcoholic beverages is the development of express methods for their control, revealing markers for the identification of counterfeit products. It is possible to solve the problem of identifying distillates of various origins using modern instrumental methods.

The aim of the study was to develop new highly sensitive methods for determining not only the quality and safety indicators of rum, but also specific identification parameters with the aim of introducing them into the rum quality control system that meets the needs of modern society.

2. Materials and methods

2.1. Reagents, standards and solvents
All reagents used were of analytical grade. Water (a specific resistance >18.2 MΩ cm) was used in all experiments.

Standard solutions of cations and anions were prepared from state standard reference sample and containing 1 mg/cm³ relative error no more than 1% at = 0.95 of each cation and anion.

Vanillin, vanillic acid, gallic acid, coniferyl aldehyde, sinapaldehyde, syringic acid, syringaldehyde, furfural, 5-HMF, ellagic acid, acetaldehyde, ethyl acetate, 1-propanol, methanol, acetal, isobutanol, 2-methylbutanol, 3-methylbutanol were bought from Merck. Glacial acetic acid according chemically 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.

2.2. Determination individual phenolic and furanic compounds
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 cm³/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.

2.3. Determination of volatile organic compounds
Gas chromatographic analysis was carried out on a gas chromatograph "Khromatek-Kristall 5000.1" with a flame ionization detector. Test conditions: carrier gas - nitrogen, chromatographic capillary column CP-Wax 57 CB 50m × 0.25mm × 0.20 μm, column temperature - 40-90 °C, carrier gas flow rate - 0.048-0.12 dm³/h, sample volume - 0.2-1.00 mm³. Sample preparation conditions for rum samples: 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. Determination of cationic and anionic composition
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/dm³ Na₂CO₃ and 1.0 mmol/dm³ NaHCO₃; eluent flow rate 0.7 cm³/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/dm³ HNO₃ and 0.7 mmol/dm³ dipicolinic acid; eluent flow rate 0.9 cm³/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 rum: before analyzing rum sample were diluted with deionized water. Filters of 0.45 μm pore size were used for sample filtration.

3. Results and discussion
In our study, 4 samples of Cuban rum of the same manufacturer with aging periods of 3, 5, 7, 10 years (№ 1-4) were examined; 3 samples of Dominican rum with aging periods of 2 and 10 years (№ 5-7); a sample of rum from Trinidad and Tobago 5 years old (№ 8), as well as 2 falsified samples (№ 9, 10). The following indicators of the quality and safety of rum were determined: the content of phenolic and furan compounds, volatile organic impurities, ionic composition.

The results of samples examining are presented in tables 1-3.

| Compound          | №1    | №2    | №3    | №4    | №5    | №6    | №7    | №8    | counterfeit |
|-------------------|------|------|------|------|------|------|------|------|------------|
| Gallic acid       | 0.4±0.0 | 6.0±0.0 | 1.7±0.2 | 2.2±0.2 | 0.3±0.0 | 0.6±0.0 | 5.4±0.5 | 3.6±0.4 | < 0.1       |
| 5-HMF             | 0.2±0.0 | 4.2±0.4 | 6.6±0.7 | 18.9±1.1 | 0.5±0.0 | 3.7±0.4 | 8.2±0.8 | 7.6±0.8 | 8.5±0.9     |
| Furfural          | 0.3±0.0 | 0.4±0.0 | 0.6±0.0 | 1.2±0.2 | 0.1±0.0 | 0.9±0.1 | 2.3±0.3 | 1.7±0.3 | 0.5±0.1     |
| Vanillic acid     | 0.4±0.0 | 0.4±0.0 | 0.7±0.1 | 1.2±0.2 | 0.1±0.0 | 0.3±0.0 | 1.7±0.3 | 2.1±0.3 | 0.1±0.02    |
| Syringic acid     | 0.9±0.1 | 0.9±0.1 | 1.6±0.2 | 2.8±0.4 | 0.2±0.0 | 0.6±0.0 | 3.2±0.5 | 4.8±0.7 | 0.4±0.1     |
| Vanillin          | 0.4±0.0 | 0.5±0.0 | 0.8±0.0 | 1.7±0.2 | 0.1±0.0 | 0.2±0.0 | 2.4±0.2 | 2.5±0.3 | 144±14.6    |
| Syringaldehyd e   | 1.0±0.2 | 1.1±0.2 | 2.5±0.4 | 4.0±0.6 | 0.3±0.0 | 1.0±0.2 | 6.1±0.9 | 6.2±0.9 | 0.8±0.1     |
Ellagic acid | 0.8±0.1 | 1.2±0.2 | 3.9±0.6 | 6.2±0.9 | 0.1±0.0 | 1.3±0.2 | 17.3±2.1 | 17.4±2.6 | 0.4±0.1 | < 0.1
Coniferyl aldehyde | 0.1±0.0 | 0.1±0.0 | 0.2±0.0 | 0.3±0.0 | <0.1 | 0.1±0.0 | 0.7±0.1 | 0.6±0.1 | 0.3±0.03 | < 0.1
Sinapaldehyde | 0.1±0.0 | 0.1±0.0 | 0.5±0.0 | 0.4±0.0 | 0.1±0.0 | 0.3±0.0 | 1.1±0.2 | 0.5±0.1 | 0.6±0.1 | < 0.1

vanillin/syringaldehyde
0.40 | 0.40 | 0.30 | 0.40 | 0.30 | 0.20 | 0.40 | 0.40 | 180.80 | -

syringic acid/syringaldehyde
0.90 | 0.80 | 1.30 | 0.70 | 0.60 | 0.60 | 0.50 | 0.70 | 0.50 | -

vanillin/vanillin
1.00 | 0.80 | 0.90 | 0.70 | 1.00 | 1.50 | 0.70 | 0.80 | - | -

From the data obtained, it can be seen that all samples of rum, except for falsified, have a rich component composition. And the content of aging markers (tanning compounds and compounds formed during the ethanolysis of oak wood lignin) depends on the type of raw material and correlates with the aging time.

It has been found that the ratio vanillin/syringaldehyde is in the range of 0.2-0.4. The increased concentration of vanillin (about 50-60 times the typical), as well as the vanillin/syringaldehyde ratio of 180.8 in the falsified sample № 9, suggests the addition of flavoring. Sample № 10 contained only vanillin and 5-HMF, suggesting that coloring agent and flavor were added.

In the present study, a balance was observed between aging markers (syringic acid/syringaldehyde and vanillin acid/vanillin) formed by two different directions of formation of related compounds associated with aging of rum in contact with oak wood, the guaiacyl series (coniferyl aldehyde, vanillin and vanillin acid) and the syringyl series (syringic acid, syringaldehyde and syringic acid), which indicates the stability and maturity of rums.

Table 2. Quantitative analysis data of volatile organic impurities in rum.

| Compound            | №1 | №2 | №3 | №4 | №5 | №6 | №7 | №8 | counterfeit |
|---------------------|----|----|----|----|----|----|----|----|-------------|
| Acetaldehyde        | 37.9 | 44.8 | 112.0 | 148.6±2 | 22.5±2.3 | 73.0±11.0 | 169.0±2.0 | 96.2±14.0 | 3.5±0.4 | 47.8±4.8 |
| Ethyl acetate       | 111.0±2 | 54.6±10.0 | 273.7±4 | 429.0±7 | 155.0±2 | 178.0±3 | 552.6±9 | 469.9±7 | 246.8±4 | 964.6±11 |
| Acetol             | 2.2 | 9 | 6.5 | 2.9 | 6.4 | 0.3 | 3.9 | 9.9 | 2.0 | 8.1 |
| Methanol            | 39.1±7.8 | 15.6±3.1 | 54.7±10.9 | 70.4±14.9 | 46.9±9.4 | 46.9±9.4 | 78.2±15 | 62.3±12 | 23.5±4.7 | 13.7±2.7 |
| 1-propanol         | 191.9±1 | 9.2 | 74.7±7.5 | 269.7±3 | 323.2±3 | 233.3±2 | 235.9±2 | 312.4±3 | 173.8±1 | 23.2±2.3 | 3.0±0.3 |
| Isobutanol         | 232.9±2 | 2.4 | 269.7±3 | 321.9±3 | 200.7±2 | 200.4±2 | 151.8±1 | 142.4±1 | 316.4±3 | 8.0 | 4.3±0.4 |
| 2-methylbutanol    | 8.0 | 78.1±7.8 | 2.4 | 26.9±3 | 321.9±3 | 200.7±2 | 200.4±2 | 151.8±1 | 142.4±1 | 316.4±3 | 8.0 | 4.3±0.4 |
| 3-methylbutanol    | 100.2±1 | 0.0 | 40.0±4.0 | 144.8±1 | 160.9±2 | 4.5 | 56.6±5.7 | 60.0±6.0 | 77.3±7.7 | 97.9±9.8 | 114.9±1 | 56.3±5.6 |
| 2-methylbutanol/3-methylbutanol | 0.21 | 2.70 | 3.00 | 2.52 | 0.17 | 0.27 | 0.28 | 0.15 | 0.39 | 0.15 |

It can be seen from the data obtained that acetaldehyde, ethyl acetate, acetol, methanol, 1-propanol, isobutanol, 2-methylbutanol, 3-methylbutanol are present in all the samples studied. In the falsified samples, concentrations of volatile organic impurities were found to be lower than those typical for rums.

It is shown that the mass concentration of the components of volatile organic impurities varies within wide limits. The ratio of 2-methylbutanol/3-methylbutanol for the studied rum samples from the same
manufacturer was similar and was in the range for Cuban rum - 2.21-3.00, Dominican rum - 0.17-0.27, rum from Trinidad and Tobago - 0.15.

**Table 3.** Quantitative analysis data of cations and anions in rum.

| Detected ion | Mass concentration, mg/dm³ | Counterfeit |
|--------------|-----------------------------|-------------|
|              | No1                         | No2         | No3         | No4         | No5         | No6         | No7         | No8         | |
| Sodium       | 1.4±0.2                     | 22.7±3.4    | 21.2±3.2    | 19.1±2.9    | 9.9±1.7     | 10.8±1.6    | 8.5±1.4     | 5.0±0.8     | 76.2±11.4  |
| Ammonium     | < 0.1                       | 0.3±0.1     | 0.4±0.1     | 1.0±0.2     | 0.1±0.02    | < 0.1       | < 0.1       | 0.5±0.1     | 0.4±0.08   |
| Potassium    | 0.3±0.1                     | 3.4±0.6     | 9.9±1.7     | 7.4±1.3     | 1.0±0.2     | 3.8±0.6     | 6.3±1.1     | 3.9±0.7     | 5.1±0.9    |
| Calcium      | 0.5±0.1                     | 0.8±0.1     | 1.6±0.2     | 1.7±0.2     | 0.8±0.1     | 1.0±0.1     | 2.4±0.2     | 1.9±0.2     | 2.9±0.3    |
| Magnesium    | < 0.1                       | < 0.1       | 0.1±0.02    | 0.6±0.1     | 0.2±0.04    | 0.3±0.06    | 0.6±0.1     | 0.1±0.02    | 1.6±0.3    |
| Chloride     | 0.5±0.1                     | 0.4±0.1     | 1.0±0.2     | 1.3±0.3     | 0.5±0.1     | 0.7±0.1     | 1.1±0.2     | 1.0±0.2     | 4.6±0.9    |
| Nitrite      | < 0.1                       | 0.1±0.02    | 0.1±0.02    | 0.1±0.02    | < 0.1       | < 0.1       | < 0.1       | 0.1±0.02    | < 0.1      |
| Nitrate      | < 0.1                       | < 0.1       | < 0.1       | < 0.1       | < 0.1       | < 0.1       | < 0.1       | < 0.1       | 3.8±0.7    |
| Phosphate    | 0.1±0.1                     | 0.2±0.03    | 0.1±0.02    | 0.2±0.03    | 0.1±0.02    | 0.2±0.03    | 0.5±0.1     | 2.1±0.3     | 3.0±0.4    |
| Sulfate      | 0.8±0.2                     | 1.9±0.4     | 3.1±0.6     | 2.8±0.6     | 1.4±0.3     | 0.8±0.2     | 2.5±0.5     | 2.5±0.5     | 6.8±1.4    |

Based on the analysis of experimental data, it was shown that all samples of rums have an identical qualitative composition of cations and anions, but the quantitative composition differs significantly, which is probably due to the peculiarities of water treatment in different countries. It has been established that the mass concentration of cations in the investigated rum samples is in the range: ammonium 0.1-1.0 mg/dm³; potassium 0.3-9.9 mg/dm³; calcium 0.5-2.4 mg/dm³; sodium 1.4-22.7 mg/dm³; magnesium 0.1-0.6 mg/dm³; anions - chlorides 0.5-1.3 mg/dm³, nitrates - 0.1 mg/dm³, nitrates - in concentrations below the detection limit, phosphates 0.1-0.5 mg/dm³, sulfates 0.8-3.1 mg/dm³.

4. Conclusions

This article describes the means to identify rum using the content and the correlation of their characteristic compounds. The described procedure can be useful for the verification of rum quality and their brand identification. The use of the developed methods makes it possible to increase the efficiency of technological control of distilled alcoholic beverages, to comprehensively investigate the dynamics of aging and blending processes.

Reference

[1] Savchuk S A 2014 *Medicine* **3** 16-46
[2] Vlassov V N and Maruzhenkov D S 1999 *Analisis* **27** 663-7
[3] Coldea T E, Mudura E and Socaciu C 2017 *Ideas and Applications Toward Sample Preparation for Food and Beverage Analysis* ed M Stauffer (Croatia: InTech) Chapter 6 pp 109-31
[4] Yadav P K and Sharma R M 2019 *Arab Journal of Forensic Sciences & Forensic Medicine* **1(9)** 1232-47
[5] Serafim F A T and Lanças F M 2019 *Production and Management of Beverages* **11** 335-59
[6] Sampaio O M 2006 *Diferenciacao entre rums cubanos e nao cubanos* (Sao Carlos: Instituto de Quimica de Sao Carlos) pp 1-153
[7] Pereira R F R, Melo D Q, Barros A L, Lima A C A and Nascimento R F 2012 *African Journal of Food Science* **6(17)** 427-40
[8] Abramova I M et al. 2021 *IOP Conf. Ser.: Earth Environ. Sci.* **640** 1-5
[9] Berezhnaya A V 2004 *Improvement of technological methods for improving the quality of cognac spirits and cognacs* (Krasnodar) pp 1-24