Chemical characterization of ethanol and vodka in Russia

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Abstract. The analysis of the regulatory documentation in the Russian industry of ethanol and vodka, overview of the main methods of finished products quality control are presented in this article. The generalized research data of vodka from different manufacturers are presented; the ranges of volatile components mass concentrations, the ionic composition of vodka and special vodka are given.

Russia is one of the traditional manufacturers of vodka.

In the comprehensive analytical control of vodka and ethanol obtained from food raw materials, the paramount task is to establish their quality and safety, namely, identification and determination of the harmful impurities content. The second task is to determine the sort of alcohol, counterfeit alcohol products, low-quality and falsified products.

Technochemical quality control of the finished product is carried out both using the methods of “wet chemistry” and instrumental methods of analysis. The methods of “wet chemistry” in analytical practice traditionally include gravimetric, titrimetric and spectrophotometric methods for monitoring individual indicators [1]. These methods, along with instrumental methods are used in monitoring the quality and safety of alcoholic beverages.

A traditional method for analysing volatiles in alcoholic beverages is gas chromatography with a flame ionisation detector, because this method has many advantages such as high accuracy and high sensitivity. Contemporary production technologies achieve a high degree of alcohol purification resulting in only trace amounts of volatile substances [2]. Thus, effective separation and identification methods should be applied after preconcentration to detect and identify components in the recovered mixtures. Gas chromatography/mass spectrometry is currently the most sensitive technique for this kind of analysis. Sometimes efficient extraction techniques, such as SPME, must be used to isolate volatile substances from the aqueous-alcoholic matrix before they can be analyzed [3].

Gas chromatographic analysis of vodka and ethanol obtained from food raw materials used for the vodka production is carried out in accordance with standardized methods (GOST 32039-2013, GOST 30536-2013) which allow determining up to 23 contaminants:

- alcohols (methanol, 1-propanol, 2-propanol, 1-butanol, isobutanol, 1-pentanol, 1-hexanol, benzyl alcohol, 2-phenylethanol);
- aldehydes (acetaldehyde, crotonic aldehyde, benzaldehyde, furfural);
- ethers and esters (diethyl ether, methyl acetate, ethyl acetate, ethyl propionate, ethyl formate, diethyl phthalate);
- ketones (acetone, 2-butaneone).

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In accordance with regulatory documents (GOST 5962-2013), in Russia, ethanol is produced by the method of alcoholic fermentation of sugar-containing and/or starch-containing raw materials, followed by rectification of the mash. Sugar-containing (sugar beets, molasses, raw sugar) and starch-containing raw materials (potatoes, grain and products of its processing) are used for the production of rectified ethyl alcohol from food raw materials.

Depending on the degree of purification, rectified ethanol is subdivided into: pure spirit of best quality, «Extra», «Lux» and «Alpha». The requirements for physico-chemical indicators for each alcohol grade are shown in table 1.

Table 1. Physico-chemical characteristics of ethanol.

| Indicator name | Norm for ethanol |
|----------------|------------------|
| Volume fractions of ethanol, %, a maximum of | |
| Purity test with sulfuric acid | Stand test |
| Test for oxidizability, min, at 20 °C, a maximum of | |
| Mass concentration of acetic aldehyde in terms of the equivalent amount of absolute alcohol, mg/dm³, a maximum of | |
| Mass concentration of fusel oil (1-propanol, 2-propanol, isobutyl alcohol, 1-butanol and isoamyl alcohol) in terms of the equivalent amount of absolute | |
| Mass concentration of esters (methyl acetate, ethyl acetate) in terms of the equivalent amount of absolute alcohol, mg/dm³, a maximum of | |
| Volume fraction of methanol in terms of the equivalent amount of absolute alcohol, %, a maximum of | |
| Mass concentration of free acids (without CO₂) in terms of the equivalent amount of absolute alcohol, mg/dm³, a maximum of | |
| Mass concentration of solid residue in terms of the equivalent amount of absolute alcohol, mg/dm³, a maximum of | not defined |
| Mass concentration of volatile basic nitrogen, in terms of the equivalent amount of nitrogen, in 1 dm³, absolute alcohol, mg, a maximum of | not defined |
| Furfural | prohibited |

In Russia, vodka is considered to be an alcoholic beverage made on the basis of rectified ethanol and treated water, with a strength of 37.5% vol. up to 56.0% vol., which is a colorless aqueous-alcoholic solution with a soft, inherent vodka taste and characteristic vodka aroma. Also in Russia special vodka is produced - it is vodka with a strength of 37.5% vol. up to 45.0% vol. with a specific aroma and / or taste, obtained by introducing flavor components (GOST 33880-2016, GOST 12712-2013).

The requirements for physical and chemical indicators for vodka and special vodka are presented in table 2.
Table 2. Physico-chemical characteristics of vodka and special vodka.

| Indicator name                                                                 | Norm for vodka (special vodka) from alcohol |
|--------------------------------------------------------------------------------|-------------------------------------------|
|                                                                                 | pure spirit of best quality               |
|                                                                                 | "Extra" "Lux" "Alpha"                     |
| Strength, %                                                                     | 37.5-56 (37.5-45)                        |
| Alkalinity - volume of hydrochloric acid with a concentration of 0.1 mol/dm³ expended on titration of 100 cm³ of vodka, cm³, a maximum of | 3   2.5   2   2                           |
| Mass concentration of acetic aldehyde in 1 dm³ of absolute alcohol, mg, a maximum of | 8   4 (5)   3 (4)   3 (4)                 |
| Mass concentration of fusel oil (1-propanol, 2-propanol, isobutyl alcohol, 1-butanol, isoamyl alcohol) in 1 dm³ of absolute alcohol, mg, a maximum of | 6   5   5   5                             |
| Mass concentration of esters (methyl acetate, ethyl acetate) in 1 dm³ of absolute alcohol, mg, a maximum of | 13  10 (13)  5 (10)  10 (13)             |
| Volume fraction of methyl alcohol in terms of absolute alcohol, %, a maximum of | 0.03 0.02 0.02 0.003                         |

Water for the production of vodka must be soft, slightly mineralized, transparent, colorless and odorless. The optimal values of vodka and special vodka cationic and anionic composition allowing to retain organoleptic characteristics and stability during long-term storage are given in table 3. (PTR 10-12292-99).

Table 3. Minimum and maximum values of cations and anions, mg/dm³.

| Na+K | Ca | Mg | Fe | F | Cl | NO₃ | PO₄ | SO₄ | HCO₃⁻ | Si |
|------|----|----|----|---|----|-----|-----|-----|-------|----|
| 0.1–  | 0.1– | 0.01– | 0.1– | 0.1– | 0.1– | 0.1– | 0.1– | 0.1– | 0.1– | 0.1– |
| 60.0 | 1.6 | 5.0 | 0.1 | 2.5 | 18.0 | 2.5 | 0.8 | 18.0 | 180 | 3.0 |

The quality of the finished product and water used for its production is controlled by methods of ion chromatography and capillary electrophoresis (GOST R 51821-2001, GOST 31867-2012). The ionic composition of vodka is rigidly tied to a specific production and can serve as a marker for its identification. The composition and concentration of sodium, ammonium, potassium, calcium, magnesium, strontium, barium cations and fluoride, chloride, nitrite, nitrate, phosphate, sulfate anions can be used to judge the quality of water treatment and monitor softening and water purification systems [4].

At the All-Russian Research Institute of Food Biotechnology 20 vodka and special vodka samples were tested. The ionic composition is mainly represented by cations of sodium, potassium, calcium and magnesium and anions of chlorides, nitrates, phosphates and sulfates. Table 4 presents the ranges of mass concentrations of cations and anions of the studied samples and, for comparison, shows the ranges of the anionic composition of foreign vodkas (France, Germany, Italy) [5].

Table 4. Mass concentrations of cations and anions, mg/dm³

| Na  | K | Mg | Cl | NO₃ | PO₄ | SO₄ |
|-----|---|----|----|-----|-----|-----|
| Russian vodkas | 0.9– | 0.3–7.8 | < 0.1– | < 0.1– | < 0.1– | < 0.1– | 0.2–25.9 |
| Foreign vodkas | – | – | – | 0.2–47.0 | 0.3–17.0 | – | 6.6–85.8 |
In the alcohol quality control system along with physicochemical methods of analysis, one of the leading positions is organoleptic analysis (OA), which includes determining the appearance (transparency, presence of foreign matter), color, smell, aroma (bouquet) and taste through the human senses. OA is used in determining the organoleptic characteristics of products with the aim of identifying them, i.e. establishing their identity with the requirements stipulated by the recipe, technological instructions and regulatory documents for these products.

Organoleptic evaluation is carried out by specialists-tasters with special knowledge and experience in assessing the organoleptic characteristics of products.

The characteristic of organoleptic indicators is translated into a quantitative assessment, expressed in points. When using a 10-point scale, which provides a characteristic of product quality according to the following main indicators: transparency, color, aroma or smell, taste, the division of maximum points according to individual organoleptic indicators is as follows: appearance (transparency and color) - 2 points; aroma and smell - 4 points; taste - 4 points (GOST 33817-2016).

Impurities, even in trace amounts, can affect the tasting indicators of alcoholic beverages. Almost all aldehydes give ethanol astrignency, viscosity and pungency in taste; the presence of carboxylic acids, unsaturated, nitrogenous, sulfur compounds is accompanied by a deterioration in smell, the appearance of bitterness, astrignency and a long “aftertaste”. Unpleasant suffocating and sharp fusel tones are possessed by samples containing butyl, isobutyl and isoamyl alcohols; samples with a high concentration of propyl alcohol have weak oily-floral tones with a hint of sulfuric ether. Esters add an unusual fruity or floral scent to ethanol [3].

Currently, the consumer market is represented by a huge variety of vodka and special vodka. Types of vodka production also vary, which affects the final composition of the product. The analysis of foreign studies [6-8] and the data obtained at the All-Russian Research Institute of Food Biotechnology made it possible to distinguish between vodka from different countries. The concentration ranges of volatile impurities of Russian and foreign vodkas are presented in table 5.

**Table 5.** The concentration ranges of volatile impurities.

| Indicator name                  | Russian vodkas     | Foreign vodkas   |
|---------------------------------|--------------------|-----------------|
| Acetaldehyde                    | less than 0.5-1.7  | less than 5.0   |
| Higher alcohols (1-propanol, 2-propanol, isobutyl alcohol, 1-butanol, isoamyl alcohol) in 1 dm³ of absolute alcohol, mg | less than 0.5-4.9 | 6.0-45.0 |
| Esters (methyl acetate, ethyl acetate) in 1 dm³ of absolute alcohol, mg | less than 0.5-1.0 | less than 40.0 |
| Methanol in terms of absolute alcohol, % | 0.00014 – 0.00290 | less than 0.04 |

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