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Assessment of the Vodka Safety and Detection of Falsification Compared to the Original Ones

تقييم سلامة كحوليات الحبوب وكشف التزوير مقارنة بالأصلية

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Abstract

Vodka is an in-demand alcoholic beverage in Eastern Europe, produced from ethyl alcohol that is prepared through fermentation of raw material rich in carbohydrates. Besides ethanol content, vodka also entails a fixed level of other substances, such as complex esters, aldehydes, fusel alcohols, and methyl alcohol. With the growing number of alcoholic beverage options, it is crucial to identify and verify potentially counterfeit vodkas.

Hence, this investigation aimed to analyze vodka and uncover the falsified products based on their physical and chemical characteristics compared to the original ones, such as alcohol strength, methanol concentration, alkalinity, and mass concentration of complex esters. As the implication of this investigation, the falsified grain vodkas (nearly 97,8 %) have been revealed in the Republic of Armenia. However, none of them has contained hazardous amounts of methanol.

المستخلص

كحولات الحبوب مطلوبة بشدة في أوروبا الشرقية، حيث يتم إنتاجها من الكحول الإيثيلي الناتج عن تخمير المواد الخام الغنية بالكربوهيدرات. بالإضافة إلى محتوى الإيثانول، تحتوي تلك الكحولات أيضًا على مستوى ثابت من المواد الأخرى، مثل الإسترات المعقدة والألدهيدات وكحول الفوزيل والميثانول. مع تزايد عدد خيارات المشروبات الكحولية، من الضروري تحديد والتحقق من الأنواع المزيفة المحتملة.

ومن ثم، تهدف هذه الدراسة إلى جمع الدراسات حول تركيب تلك الكحولات والكشف عن المنتجات المزيفة بناءً على خصائصها الفيزيائية والكيميائية مقارنة بالأصلية، مثل قوة الكحول وتركيز الميثانول والقلوية والتركيز الكتلي للإسترات المعقدة. وكإشارة لهذه الدراسة، تم الكشف عن كحولات الحبوب المزيفة (حوالي 97.8%) في جمهورية أرمينيا. ومع ذلك، لم يحتوِ أي منها على كميات خطرة من الميثانول.

Keywords: Forensic sciences, falsifications, vodkas, volatile compounds, methanol concentration, chromotropic acid method.

الكلمات المفتاحية: علوم الأدلة الجنائية، التزوير، الفودكا، المركبات المتطايرة، تركيز الميثانول، طريقة حمض الكروموتروبيك.

Production and hosting by NAUSS

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1. Introduction

Vodka is mainly considered a specific "Russian" alcoholic beverage, which has always been a currency commodity for Eastern European countries. Therefore, the issue of quality, authenticity, and safety of alcoholic beverages became relevant in the early 1990s. It is a fairly tasteless, distilled alcoholic beverage (with an alcoholic strength of 37.50%–56.00% based on GOST 12712-2013) made from grains or vegetables. The spirit is circulated through charcoal to remove residual scents and endow vodka with its plain nature. It is regarded as one of the purest forms of distilled spirit available [1]. Even though distillation does not allow to the production of 100% ethanol. The resulting fluid with the lowest ethanol content of 96% also contains slight quantities of various components, including esters, aldehydes, fusel alcohols, methyl alcohol, and acetates [2, 3]. Purified alcoholic drinks are marked by the existence of volatile materials which are generated throughout fermentation, distillation, and storage processes, Figure1. Detection of these compounds is a focal point, not only to check the scent characteristics of the beverage, but also to identify the adulterated drinks [4]. Massive production of adulterated drinks have a negative impact on brand reputation. On the other hand, manufacturers must ensure their authenticity by applying specific features, like holograms, which in their turn will increase the prices of production [5]. At first sight, the consumer is unable to differentiate between original and counterfeit samples as the appearance of them looks fairly the same [6]. Another issue tied to the significance of detecting falsified vodkas is regarded as a public health concern. In particular, taking into consideration consumer's earnings some of them cannot afford to gain original brand vodkas by giving a preference to counterfeit alcohol [7].

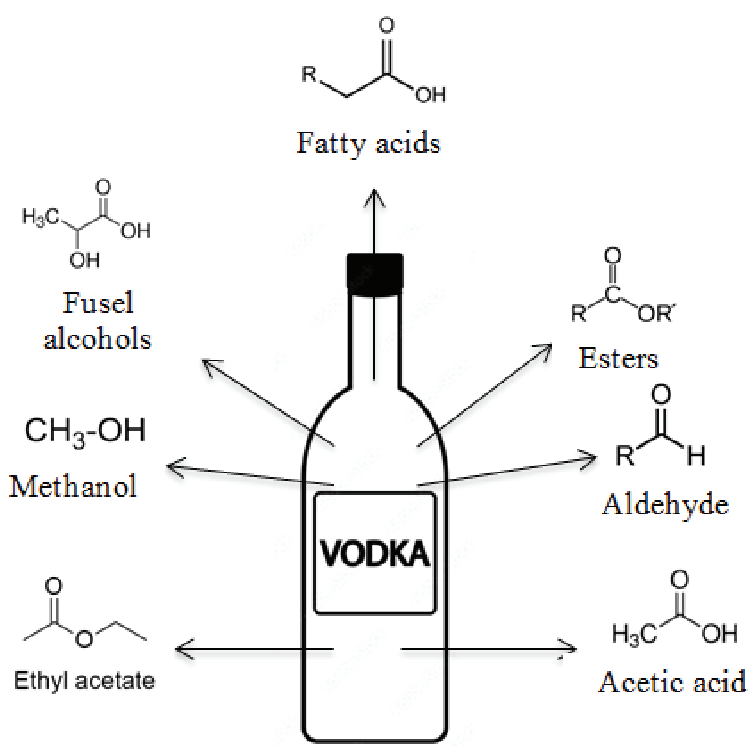

Figure1- *The main chemical compounds in vodkas.*

The most disseminated instance of complex esters is an ethyl acetate which has a crucial effect on the organoleptic properties of refined drinks. The presence of this ester can lead to vinegar-like spoilage notes in the beverage. Elevated levels of ethyl acetate indicate prolonged storage of the base material and possible microbial spoilage [8, 9].

It is crucial to check the vodkas for possible falsifications. Variations in ethanol percentage from what is stated on the vodka label can be an initial sign of falsification. Additionally, the synthetic ethanol may be used instead of ethanol derived from natural processes. Studies using gas chromatography (GC), have detected three components: 2-butanol, acetone, and crotonaldehyde, which are present in synthetic ethanol. It is important to note that 2-butanol is not found in spirit drinks from natural fermentation [3]. Monitoring the quality processes of alcoholic drinks helps prevent the presence of harmful substances, such as methyl alcohol (methanol). The high amount of methanol in alcoholic drinks is a significant public health concern due to harmful effects of its toxic end products. Slight quantity of methanol is not likely to be harmful. Nevertheless, high levels of it in alcohols could be transformed into toxic formaldehyde and formic acid in the human body [10].

Alcoholic drinks contaminated with a noticeable amount of methanol could lead to vomiting, blindness, and eventually fatal result [11].

The highest reported quantity of methanol typically found in alcoholic drinks is 18 g/l ethanol (equivalent to 0.72% [v/v] methanol at 40% alcohol) in specific fruit liqueurs.

Therefore, the overall EU limit of 10 g methanol/l ethanol (0.4% (v/v) methanol at an ethanol concentration of 40% (v/v)) in traditional fruit spirits, is unlikely to result in in a blood methanol concentration, which could lead to toxic effects [12].

The chromotropic acid method is the established procedure, also referencing an AOAC-certified protocol for methanol detection [13]. However, this technique requires a significant implementation time (more than 4 hours), involves a laborious process due to the hazardous nature of chromotropic acid, and can be affected by sugars present in the sample [14, 15]. Gas chromatography (GC) is the high-accuracy standard method for detecting vodka composition. Nevertheless, this method is expensive and necessitates both expertise and costly standard solutions. Therefore, it is essential to utilize a simple and cost-effective assay for detecting potential toxic compounds. Ethanol content measurement is typically carried out using the hydrometric or pycnometric method. Given the high toxicity of methanol to humans and its potential presence in alcoholic beverages, it is advisable to employ a straightforward method for its determination [16].

2. Materials and Methods

2. 1. Sample acquisition

Overall, 93 suspected counterfeit vodka samples were sent to the Food and Beverages expertise laboratory of the National Bureau of Expertises of Armenia during 2022-2023. 17 original vodkas from a production facility were used as a control samples.

2. 2. State Standard Specifications (GOST in Russian) applied for the study

The grain vodka brands' samples were analyzed according to the international standard GOST 32035-2013, titled "Vodkas and special vodkas: Acceptance rules ad testing methods." [17]. We have implemented the guidelines outlined in sections 5.3.1, 5.4, 5.7, and 5.8 of the GOST 32035-2013 standard to assess the alcoholic strength by volume (within the range of 37.5-56.0%), alkalinity (not exceeding 3.0 cm^3), ester content (below 13.0 dm^3), and methanol volume (not surpassing 0.03%). The procedure for determining alkalinity involves measuring the volume of a hydrochloric acid solution with a molar concentration of 0.1 mol/dm^3 required to titrate 100 cm^3 of vodka. The measuring range is between 1.5 and 3.5 cm^3 per 100 cm^3. The method of photoelectric colorimetry is utilized for quantifying the mass concentration of esters. This technique involves assessing the color intensity of the reaction products generated from the interaction of iron (III) chloride hexahydrate with hydroxamic acid in an alkaline medium due to the presence of esters in vodka. The measurement range for this method is 3-20 mg/dm^3 of anhydrous alcohol. Additionally, to determine the volume fraction of methyl alcohol, a procedure based on the oxidation of methyl alcohol in a solution containing orthophosphoric acid and potassium permanganate to yield formaldehyde is employed. Formaldehyde then reacts with the disodium salt of chromotropic acid, resulting in a lilac-colored compound whose intensity is assessed using photoelectric colorimetry. The measuring range for this method is 0.01% - 0.05% concerning anhydrous alcohol. The acceptable limits of each character are illustrated in GOST 12712-2013 [18]. The results obtained for each parameter were compared with the specification data after analysis. The product's compliance with the general technical conditions (GOST 12712-2013 and specific technical requirements to be provided by the police), as well as with the original ones, was examined.

2. 3. Data processing

Data analysis was carried out using the appropriate function in Microsoft Excel 2016. Each procedure throughout the analysis has been carried out in duplicate.

Chemical standard solutions used in the research

Methanol, 99.8% anhydrous, chromotropic acid disodium salt dihydrate, orthophosphoric acid, potassium permanganate, sodium sulfite (Sigma-Aldrich), and all other reagents used in the study were of analytical grade.

3. Results and Discussion

93 samples were sent to the Food and Beverages expertise laboratory of the National Bureau of Expertises of Armenia during 2022-2023. Additionally, 17 original vodkas from factory production were used as control samples. The ethanol content by volume ranged from 37.50 to 56.00% according to GOST 12712-2013. Out of the 93 samples, 49 (52.68%) had ethanol content by volume lower than 37.5% as specified in GOST 12712-2013, while 44 (47.31%) samples had content equal to or higher than the mentioned value. Therefore, 52.68% of the samples examined did not meet the specification, while 47.31% conformed to the range of 37.50-56.00%. In addition, 6 out of 44 (13.6%) of them are nearly (±0.2 based on GOST 12712-2013) identical to the original ones. No samples were found to have an ethanol content equal to or higher than 56.00%, Table 1. The median alcohol strength was 36.5%. In all samples, including the originals, methanol was equal to or less than 0.003% and equal to or less than 0.01%, Figure 2. It is worth mentioning that in 21 (22.58%) of the 93 samples, alkalinity levels are higher than 3 cm^3. Apart from this, 20 samples (21.50%) have alkalinity levels nearly (±0.2) identical to the original ones. Meanwhile, only one sample (1.07%) has an alkalinity result that exactly matches the original sample. The median alkalinity level was 0.90 cm^3. Regarding the complex esters content, it is important to highlight that 15 (16.12%) samples

Table 1- The physical and chemical parameters studied for Vodka samples during this study

The name of parameters	Results	Specification to GOST 12712-2013
%,.Max. Ethanol vol	45,34	37,5-56,00
%,.Min.Ethanol vol	33	37,5-56,00
%,.Avg. Ethanol vol	37,63	37,5-56,00
% ,.Med.Ethanol vol	36,5	37,5-56,00
Max. Alkalinty, cm^3	3,9	3≥
Min. Alkalinity, cm^3	0,05	3≥
Avg. Alkalinity, cm^3	1,52	3≥
Med. Alkalinity, cm^3	0,9	15≥
Max. Complex Esters, mg/dm^3	60,25	15≥
Min. Complex Esters, mg/dm^3	0,425	15≥
Avg. Complex Esters, mg/dm^3	9,23	15≥
Med. Complex Esters, mg/dm^3	1,1	15≥

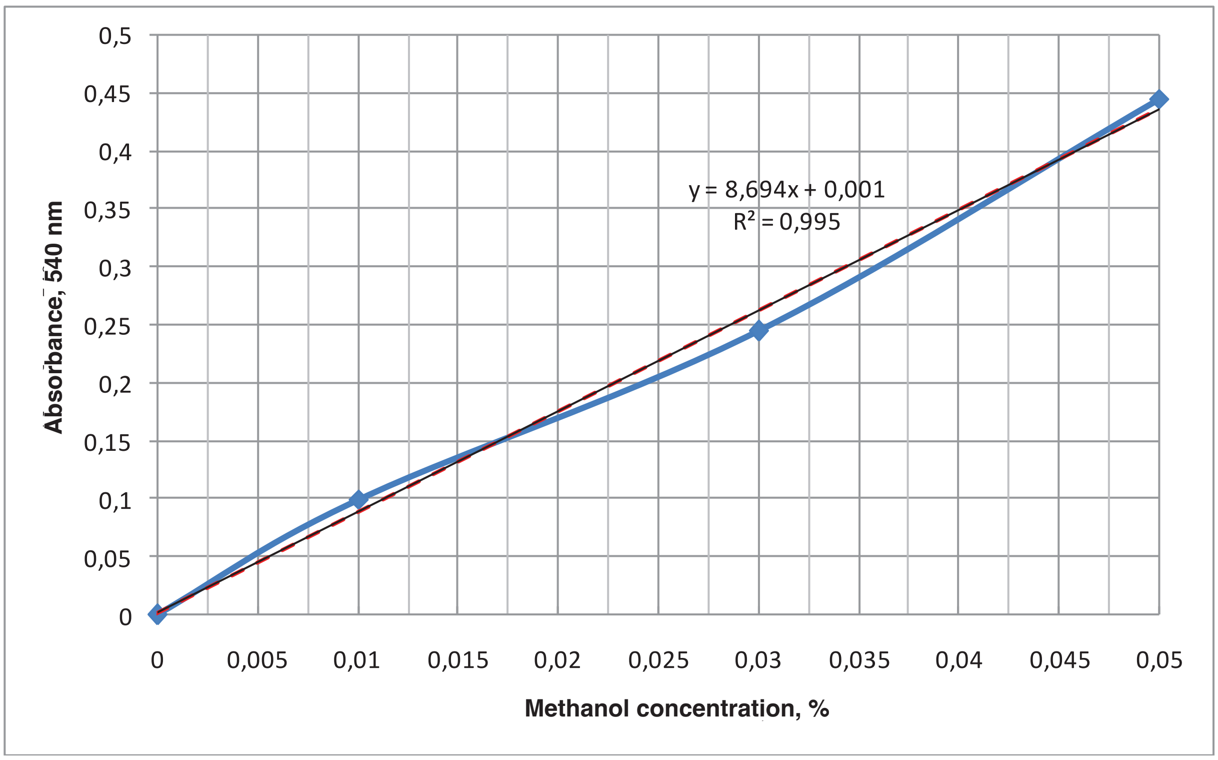

Figure 2- *Methanol calibration curve.*

have a complex esters concentration higher than 15 dm^3. Additionally, 5 (5.37%) samples have complex ester levels nearly (±0.1) identical to the original ones. The obtained results comply with the specification (≤10 dm^3) stated in the relevant normative document provided by the authorities,

Table 2 - The percentage of studied samples conformed to the technical conditions of GOST 12712-2013 in terms of physical-chemical characteristics

Total Samples	Parameter	The quantity of the samples that meets the technical conditions of GOST 12712-2013	m±%	95%CI
93	Alcoholic strength by volume, %	44	47,3±5,2	37,2-57,49
93	Alkalinity, cm^3	71	76,34±4,4	67,7-84,96
93	Mass concentration of complex esters per dm^3 of anhydrous alcohol, mg	78	83,87±3,8	76,42-91,31
93	Methanol content by volume, %	93	100	

Table 2. Non-compliance with GOST standards highlights the production of handmade beverages. Conversely, our results, along with other findings [19, 20], have revealed that a significant amount of counterfeit vodkas meet the standard parameters for alkalinity, complex esters, and methanol contents. This is more likely to occur due to the various ranges of values within the GOST parameters. It is important to note that the ethanol content by volume is consistently accurate (40±0.1%) in all original samples compared to counterfeits, in which the ethanol volume is more likely to be higher. As mentioned by Jenny et al., 2011 [20] the higher ethanol concentration in unregulated alcoholic drinks itself could be a crucial concern from a public health point of view.

One part of our samples (52.68%) corresponds to the reports, which mentioned the actual alcoholic strength by volume of the counterfeit alcoholic drink samples was lower than that appearing on the label [21-23]. Meanwhile, the alcoholic strength of the remaining (47.31%) samples was found to be close to the ethanol content by volume higher than 37.5% of unrecorded drinks from other investigations [24].

The hazardous effects of ethanol on humans and experimental organisms have been well investigated and broadly depicted [25-28]. The causes of those outcomes are probably its noxious derivatives: acetaldehyde and acetic acid [25]. Hence, counterfeit samples with higher amounts of ethanol would probably cause adverse impacts on the human body.

4. Conclusion

This investigation revealed the falsified grain vodkas consumed in the Republic of Armenia. As illustrated, the majority (nearly 97,8 %) of the examined samples were found to be falsified based on comprehensive set of physical and chemical characteristics (ethanol volume, alkalinity, and mass concentration of complex esters per dm^3 of anhydrous alcohol). Only two samples (2,2%) of the studied items exactly conformed to all characteristics of the original ones. Indicating that these samples are more likely to be authentic. In addition, the constant accurate (40±0.1%) volume of ethanol in all original samples could act as an initial indicator in the process of uncovering. This can serve as a reliable and easy-to-use indicator, which could be readily applied even by consumers to detect potential falsifications.

Notably, the methanol content in all investigated samples is low enough (≤0,003% and ≤0,01%) to be safe for consumers. Hence, it is fairly consolatory that even counterfeit samples will be harmless to consumers.

It is worth emphasizing that the method applied (the chromotropic acid colorimetric method) is cheaper and easier than gas chromatography (GC). While GC is a more accurate and faster method, in some cases, even meticulous gas chromatographic assays may not provide conclusive results regarding the authenticity of an alcoholic drink. Therefore, using a combination of methods is necessary to ensure the precise information about in various alcoholic beverage analysis. These studies highlight the importance of strict control not only in alcohol production facilities but also in retail outlets.

Conflict of interest

The authors declare no conflicts of interest.

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