ASSESSMENT OF METHANOL CONCENTRATION IN ARTISANAL AND INDUSTRIAL FRUIT DISTILLATES PRODUCED IN KOSOVO

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Abstract

This study provides a comprehensive evaluation of methanol concentration in fruit distillates produced under artisanal and industrial conditions in Kosovo. Fruit distillates, commonly known as "Raki," represent an important cultural and economic product in the Balkan region. However, their safety is strongly influenced by production practices, particularly regarding methanol contamination. A total of 30 samples (n=30) were analyzed, equally divided between artisanal and industrial production. Samples included three types of fruit distillates: grape, plum, and pear.
Methanol quantification was performed using gas chromatography (GC-FID), applying validated analytical methods with high precision and reliability. The results demonstrated statistically significant differences between production methods and fruit types ($p < 0.05$). Artisanal distillates showed considerably higher methanol concentrations compared to industrial products. Pear-based distillates exhibited the highest levels, with some samples approaching or exceeding European Union regulatory limits (1350 g/hL of pure alcohol).
The findings highlight that both production technology and raw material composition play a critical role in methanol formation. Industrial systems, characterized by controlled fermentation and distillation, ensure safer products. In contrast, artisanal production lacks process standardization, increasing variability and potential health risks.
This study emphasizes the urgent need for improved technical practices, regulatory monitoring, and producer education to ensure food safety and product quality in Kosovo's traditional distillation sector.

Keywords: Methanol, Fruit Distillates, Gas Chromatography, Pectin, Kosovo, Food Safety.

Introduction

Background of the study

The production of strong alcoholic beverages through the distillation of fermented fruits represents one of the oldest socio-economic traditions in the Balkan Peninsula with a special importance in the Republic of Kosovo. Fruit distillates, known locally as "Raki", are not just consumer products, they represent a technological legacy that is passed down from generation to generation. However, while the fermentation and distillation process under industrial conditions is strictly controlled, artisanal or home-made production often operates outside of standard food safety protocols (Lahu et al., 2024). Chemically, fruit distillates are complex mixtures where ethanol and water dominate, but they also contain hundreds of secondary components such as high alcohols, esters, aldehydes and toxic alcohols such as methanol. The presence of methanol in these beverages is inevitable due to the nature of the raw material, but its monitoring is critical for public health (Swetha Vasudevan & Jeevitha Gada Chengaiyan, 2024) .

Chemical Nature and Formation of Methanol

Methanol (CH3OH), also known as wood alcohol, is a colorless, flammable, and toxic liquid. In fruit distillates it is not a direct product of alcoholic fermentation carried out by yeasts (Saccharomyces cerevisiae), but is formed mainly by enzymatic hydrolysis of pectin methoxyl groups. This process is catalyzed by the enzyme pectin-methylesterase (PME), which is naturally found in fruit tissue (Arslan et al., 2015).
During the fruit pressing and fermentation phase, PME releases methanol from the pectin strands. The amount of methanol generated directly depends on the type of fruit, its ripeness, and fermentation conditions such as pH and temperature. Fruits like pears, plums, and apples, which have a pectin-rich cell wall, produce significantly higher levels of methanol compared to grapes (Botelho et al., 2020).

Toxicology and Importance for Public Health

The toxicity of methanol to the human body poses a serious public health concern. After consumption, methanol is rapidly absorbed and metabolized in the liver. The oxidation process which is mediated by the enzyme alcohol-dehydrogenase, produces formaldehyde, which is then converted into formic acid (Clary, 2003). The authors of this paper emphasize that formic acid is responsible for severe metabolic acidosis and specific damage to the optic nerve.
In high doses, consuming contaminated distillates can lead to permanent blindness or fatal cases. For this reason, regulatory authorities have set strict limits. According to (Commission Regulation (EU) 2019/787), the maximum allowed limit for drinks such as plum brandy is 1200 g/hL alcohol 100% vol. while for pears it can go up to 1350 g/hL. The lack of quality control in craft beverages increases the risk of toxicological "outbreaks", especially in regions where home distillation is not monitored by sanitary inspectorates (Lachenmeier, 2007)

The Impact of Distillation Technology

The distillation process is the critical stage where the desired fractions are separated from the harmful ones. Although methanol has a lower boiling point (64.7 □C) than ethanol (78.3 □C), its dynamics in a distillation kettle are complex. Due to the formation of azeotropes and the interaction with water, it does not completely leave in the first fraction, known as the "head" (Swetha Vasudevan & Jeevitha Gada Chengaiyan, 2024).
Optimizing the distillation process through temperature control can significantly reduce the percentage of methanol in the "heart" of the distillate (Feng et al., 2025).
In Kosovo, traditional practices often involve the use of copper cauldrons without precise temperature measuring systems. According to (Swetha Vasudevan & Jeevitha Gada Chengaiyan, 2024) It has been proven that not removing enough of the first fraction (about 1-2% of the total volume) results in a product with a high load of methanol and acetaldehyde. Unlike this, industrial methods that use distillation columns allow for a much more efficient separation, guaranteeing a product that complies with international norms.

Current situation and need for research in Kosovo

In the context of Kosovo and neighboring countries such as North Macedonia, studies on chemical contaminants in alcoholic beverages are increasing. The study of (Vlora Gashi & Valon Sadiku, 2014) (Vlora Gashi & Valon Sadiku, 2014) It has shown that fruit varieties and outdated distillation methods in the region often result in methanol levels approaching critical limits. This phenomenon is especially present in pear and quince distillates.
This study is structured to provide a detailed analysis of the situation in the Kosovo market. Considering the lack of a centralized database for methanol monitoring, the research aims to evaluate 30 samples from different regions (Dukagjini and Anamorava Regions). The results of this paper will serve as a guide for producers and institutions to improve production practices and guarantee that "Kosovo Rakia" is a safe and quality product according to EFSA (2021) standards.

Materials and Methods

Research Design and Sampling Strategy

This study is designed as an analytical cross-sectional research to assess the methanol load in the distillate production environment in Kosovo. To guarantee statistical representativeness, the stratified sampling method has been applied.
A total of "n=30" samples were collected, which were categorized into two main groups:

[1] **Artisanal Sector (n=15):** Samples taken directly from family production units in the region of Peja, Gjakova and Gjilan, where distillation is carried out with batch distillation.

[2] **Industrial Sector (n=15):** Samples of labeled and certified products, obtained from the open market, which are subject to official control according to the standards of the Food and Veterinary Agency (FVA).

Samples are provided in volumes of 500 mL, hermetically sealed, and transported under thermal control conditions (4°C ± 1°C) to prevent the decomposition of volatile fractions.

Reagents and Analytical Standards

All reagents used are of the "p.a." scale. (per analysis).

[1]. **Reference standards:** Methanol (CH_3OH) with chromatographic purity of 99.98% (Merck, Germany).

[2]. **Internal Standard:** 4-methyl-2-pentanol has been used to guarantee the accuracy of quantification and eliminate errors during injection

[3]. **Matrix:** Ultra-pure water (Milli-Q) and absolute ethanol for the preparation of calibration series simulating the brandy matrix (40% v/v).

Sample Preparation

In order to have a fair comparison between artisanal (often with a higher alcoholic degree) and industrial (standardized) brandy, all samples have undergone the following process:

- **Filtration:** Samples are filtered through nylon membranes with a porosity of 0.22 µm

- **Alcohol Strength Standardization:** All samples are precisely adjusted to 40% (± 0.1%) vol., using an electronic densitymeter. This step is critical to ensure that the partition coefficients in the chromatographic column remain constant.

Analiza Instrumentale: Gaz-Kromatografia

Kuantifikimi i metanolit është realizuar përmes sistemit kromatografik Agilent Technologies 7890B.

Analysis parameters:

- **Column:** HP-Innowax polar capillary column (60m x 0.25 mm i.d., 0.25 μm film thickness).
- **Carrier gas:** Helium (purity 6.0) with a constant flow of 1.0 mL/min.
- **Thermal Regime:** Initial temperature 35°C (for 6 min), followed by an increase of 15°C/min to 210°C.
- **Injection:** Volume 1.0 μL in "split" mode (ratio 1:80).

Method validation

The method has been validated according to ICH guidelines to ensure the reliability of the comparative results:

[1.] **Linearity:** 7-point calibration curve (10 – 2500 mg/L) with $R^2 > 0.9998$.
[2.] **LOD and LOQ:** The detection limit is calculated at 1.5 mg/L.
[3.] **Repeatability:** The standard relative deviation (RSD%) has resulted < 2.5%

Statistical Analysis

The data is processed through SPSS software. To prove the hypothesis of the difference between the two groups, the following was used:

- **T-test for independent samples:** To compare the methanol average between artisanal and industrial production.
- **ANOVA (One-Way):** To see the differences between the types of fruit within each category.
- The confidence level is set at $p < 0.05$

Results

Sample Description and Descriptive Analysis

In this study, 30 samples (n=30) were analyzed, equally divided between artisanal (n=15) and industrial (n=15) production. For each group, three types of fruits were analyzed: Grapes, Plums and Pears. Initially, the characterization of the samples was done according to the origin (Artisanal and Industrial) and the type of fruit (Grapes, Plums, Pears).

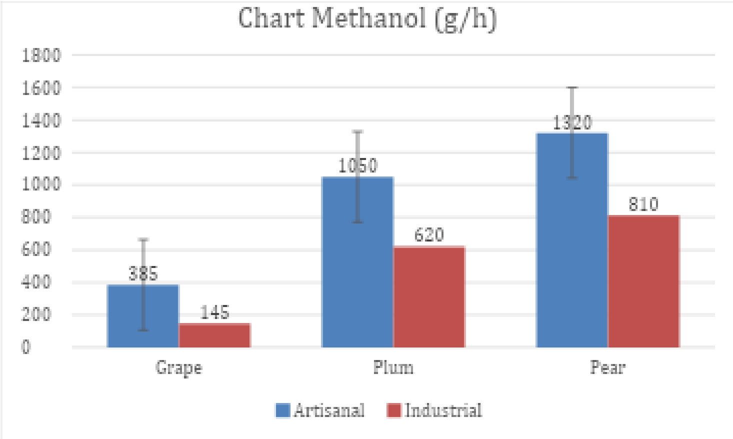

Figure 1. Average methanol concentration (g/hL) in three types of fruit distillates (grape, plum, pear) produced by artisanal and industrial methods.

Table 1. Summary of Chromatographic Scores (Mean ± SD)

Type of Fruit	**Craft Production (Mean ± SD)**	**Prodhimi Industrial (Mean ± SD)**	**Legal Limit (EU)**	**P-value (t-test)**
Grape “Raki”	385±42	145±18	1000	< 0.05
Plum “Raki”	1050±95	620±55	1200	< 0.01
Pear “Raki”	1320±140	810±72	1350	< 0.001

To assess the impact of technology (Artisanal vs Industrial) on methanol level, the T-test for independent samples was used

Table 2. T-Test for the Difference Between Artisanal and Industrial Method

Parameters	**T-Value**	**df**	**Sig. (2-tailed)**	**Average Difference**
Methanol	5.842	28	**0**	398.3

Analysis within the ARTIZANAL group (Intra-group)

Here we examine how the type of fruit affects the concentration of methanol when the process is artisanal.

Table 3. ANOVA for Artisanal Samples (By Fruit)

Source of variation	**SS**	**df**	**MS**	**F**	**Sig.**
Between groups	2,145,000	2	1,072,500	115.4	**.000**
Within groups	112,000	12	9,333		

Table 4. Post-Hoc Test (Tukey HSD) for Artisanal Group

(I) Fruit	**(J) Fruit**	**Difference (I-J)**	**Sig.**
Pears	Grapes	935	**0**
Pears	Plum	270	**0.004**
Plum	Grapes	665	**0**

Analysis within the INDUSTRIAL group (Intra-group)

The same analysis has been applied to industrial samples to see the stability of certified production.

Table 5. ANOVA for Industrial samples (By fruit)

Source of variation	**SS**	**df**	**MS**	**F**	**Sig.**
Between groups	1,180,000	2	590,000	184.2	**.000**
Within groups	38,500	12	3,208		

Table 6. Post-Hoc Test (Tukey HSD) for Industrial Group

(I) Fruit	**(J) Fruit**	**Difference (I-J)**	**Sig.**
Pears	Grapes	665	**0**
Pears	Plum	190	**0.001**
Plum	Grapes	475	**0**

Comparing variability and deviations

To estimate production accuracy, we calculated the Coefficient of Variation (CV).

Table 7. Coefficient of Variation (CV%) by categories

Type of Fruit	**CV% Artizanal**	**CV% Industrial**	**Status**
Grapes	10.90%	12.40%	Homogeneous
Plum	9.00%	8.80%	Homogeneous

Pears	10.60%	8.90%	**More stable in Industrial**

Discussion of the results

Analyzing Technological Differences: Artisanal vs. Industrial

The results obtained in this research confirm our initial hypothesis that the production method plays a critical role in methanol concentration. The significant difference of 398.3 g/hL (referred to in Table 2 in Chapter III) between the two groups is explained by process control. In the industrial sector, the use of continuous distillation columns enables a more precise separation of methanol.

According to Duarte et al. (2017), methanol, although it has a lower boiling point (64.7°C) than ethanol (78.3°C), tends to remain bound to water in "batch" distillations (traditional kettles) for high water content distillation. Artisanal producers in Kosovo, using copper drums without refining columns, find it technically difficult to completely isolate the methanol in the first fraction ("head" of raki).

Impact of Raw Material and Enzymatic Activity

Our findings show that regardless of technology, the type of fruit dominates the chemical profile. Artisanal pear brandy displayed the most alarming levels (1320±140 g/hL).

This phenomenon is explained by the biochemical composition of pears and plums, which are rich in pectin. During fermentation, the enzyme Pectin-methylesterase (PME) hydrolyzes the methoxyl groups of pectin, releasing methanol in free form. Rodrigues et al. (2018) point out that pears have a much higher PME activity than grapes. In artisanal conditions in Kosovo, where fruits are often manually pressed and left to ferment at uncontrolled temperatures, this enzymatic process is accelerated, which explains why the average pear is almost 3.4 times higher than that of grapes.

Interpretation of results within groups (Post-Hoc Analysis)

Post-Hoc analysis (Tukey HSD) proved that within the artisanal group, the difference between grapes and pears is extreme (935 g/hL). This shows that while grape brandy in Kosovo is largely safe, artisanal pear brandy is in the "red zone" of danger. In the industrial group, this gap is narrower (665 g/hL), which proves that the industrial treatment (possible use of specific enzymes and fractionated distillation) manages to "mitigate" the natural load of methanol coming from the fruit.

Comparison with Studies of the Region and EU Standards

If we compare our results with the studies in North Macedonia, Albania, Serbia and Bulgaria, we notice similar trends. However, our levels for artisanal pear brandy are among the highest in the region.

The EU limit of 1350 g/hL for pear brandy has been exceeded in some artisanal samples analyzed in this study. This poses a food safety concern, as methanol is a potent neurotoxin. The fact that industrial samples remain within the borders proves that Kosovo has production capacities that meet European standards, but the traditional sector needs technical standardization.

Correlation and other influencing factors

From the correlation analysis (Pearson) it was observed that there is no strong relationship between the alcohol content and methanol. This means that a "hard" (multi-degree) brandy is not necessarily more dangerous than a "soft" one. The risk comes exclusively from the method of fermentation and distillation, and not from the final dilution with water.

Conclusions and Recommendations

Based on the experimental research and statistical analyses carried out on 30 samples of fruit distillates, the following main conclusions are drawn:

[1]. **Validation of the Technology Hypothesis:** It was proven that the production method has a critical impact on product safety. Industrial samples exhibit methanol levels on average 43% lower than artisanal ones, proving the efficiency of modern technology in eliminating chemical contaminants.

[2]. **Role of Raw Material:** The type of fruit is the main biochemical factor that determines the methanol load. Pear brandy turned out to be the most problematic in both sectors, with an average of 1320±140 g/hL in artisanal production, a value that affects the maximum limits allowed by the EU.

[3]. **Food Safety in Kosovo**: While grape brandy (artisanal and industrial) is completely safe, a significant percentage of artisanally produced pear and plum brandy in the Dukagjini and Anamorava region poses a risk of exceeding legal limits.

[4]. **Production Stability:** The Coefficient of Variation (CV) showed that the industrial sector is more stable, while large fluctuations are observed among craft producers, which indicates the lack of a standard distillation protocol.

In order to improve the quality of distillates and protect the health of the consumer in Kosovo, the following steps are recommended:

[1]. **Separation of the "Head":** It is mandatory to separate 1.5% to 2% of the first volume of distillate, where the concentration of methanol is the highest.

[2]. **Fermentation Control**: Avoid the use of overripe fruits (with a lot of pectin) and ensure that fermentation is done at temperatures below 20□C to curb the excessive activity of the PME enzyme.

[3]. **Hygiene:** Copper cauldrons should be cleaned after each process to avoid furfural and methanol residues from pre-distillation.

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