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QUANTITATIVE ANALYSIS OF OAK BARREL AGING EFFECTS ON METHANOL CONTENT AND VOLATILE ACIDITY IN TRADITIONAL QVEVRI AMBER WINES

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ABSTRACT

This research investigated methanol and volatile acid dynamics in Qvevri amber wines produced from four native Georgian grape varieties: Rkatsiteli, Kisi, Mtsvane, and Khikhvi. Laboratory analyses were conducted at four intervals: after fermentation, after opening qvevris, and after six and twelve months of oak barrel aging. Gas chromatography-mass spectrometry identified methanol content, while volatile acids were assessed using the OIV-MA-AS313-01 method. Results showed consistent methanol decreases in all samples during aging, with levels remaining below the OIV safety threshold of 250 mg/L for white wines. Concurrently, volatile acidity increased steadily but remained within regulatory limits, not surpassing 1.00 g/L in most samples. The findings confirm the safety and quality of traditional Qvevri winemaking methods, underscoring the benefits of integrating qvevri fermentation and oak barrel aging in Georgian wine production.

KEYWORDS: Qvevri wine, methanol, volatile acidity, traditional winemaking, amber wine, Georgian wine.

1. INTRODUCTION

Methanol, or methyl alcohol, is a natural constituent of wine primarily arising from the enzymatic degradation of pectins during winemaking. While present in minimal amounts in well-produced wines, methanol raises concern among producers and regulatory authorities due to its potential toxicity at higher concentrations. Understanding the impact of methanol in traditional winemaking is crucial for ensuring consumer safety and preserving cultural practices.

Methanol in wine originates from the demethylation of pectin found in grape cell walls. Pectin methyl esterase (PME) enzymes hydrolyze the methoxyl groups of pectin during fermentation, resulting in methanol formation. Research on PME activity in different grape varieties has shown strong connections between enzyme activity and methanol production.[2] The grape variety is a key factor influencing methanol levels in wine, with multivariate analysis indicating that methanol levels may function as a chemical marker for varietal authentication in specific instances.[3]

Winemaking methods directly influence methanol concentration. Extended maceration (24 hours compared to 3 hours) has been shown to result in a 32-47% increase in methanol content, depending on grape variety. Temperature-controlled maceration notably influences methanol extraction, with 25°C yielding 18% more methanol than 15°C across three white varieties. For red wines, longer post-fermentation maceration leads to 15-20% higher methanol levels in Nebbiolo wines compared to standard protocols.[4]

The International Organization of Vine and Wine (OIV) has established maximum acceptable limits in the International Code of Oenological Practices, with distinct thresholds for white wines (250 mg/L), red wines (400 mg/L), and fortified wines (400 mg/L).[5] The European Commission standardized these regulations among member states through Commission Delegated Regulation (EU) 2019/934.[6]

The qvevri, an extraordinary winemaking vessel, profoundly shapes wine composition and sensory qualities. With origins dating back nearly 8,000 years, Georgian Qvevri winemaking stands as one of the world's oldest uninterrupted viticultural practices, recognized as an intangible cultural heritage of humanity by UNESCO in 2013.

This ancient technique involves fermenting and aging wine in large clay pots known as qvevri, which are buried underground. Prolonged maceration, letting wines ferment and age on pomace (including skins, seeds, and often stems) for extended periods, distinguishes the traditional approach. The distinctive cone shape of the qvevri aids in natural clarification as seeds, yeast lees, and the "cap" collect at the base.[7]

Qvevri amber wines present an ideal subject for methanol research due to their extended skin contact during fermentation and maturation (known to increase methanol production), reliance on native microflora with minimal sulfur dioxide addition, and limited use of commercial yeasts.[8]

Despite extensive research on methanol in wines, there is a lack of scientific investigation on methanol production specifically in traditional Qvevri amber wines from native Georgian grape varieties. This study aims to fill the gap in scientific investigation by examining the dynamics of methanol production in traditional Qvevri amber wines from four Georgian grape varieties and monitoring changes during oak barrel aging.

As Georgia aims to expand wine exports globally, understanding methanol behavior in the nation's flagship Qvevri wines becomes increasingly important for ensuring quality and meeting international standards.

1. MATERIALS AND METHODS

1. Harvest and Vinification

The endemic Rkatsiteli, Kisi, Mtsvane, and Khikhvi grapes were harvested from three Kakheti regions: Telavi, Gurjaani, and Sagarejo in 2023. These municipalities are the primary locations for amber qvevri wine production in Georgia. For experimental validity, only healthy, undamaged grapes with similar maturity levels were selected. Due to different ripening schedules, nine separate harvests were conducted, with grapes processed on different days according to optimal ripeness.

Grapes were harvested early in the morning and transported in boxes to the cellar. After destemming, the pomace was divided and loaded into four qvevris for each variety. Details of the grape varieties, vineyard locations, and qvevri capacities are presented in Table 1.

Table 1: Vinification of Qvevri Amber Wines.

№ Trial sample	Grape sort/ amount	Vineyard location village	°Brix	Amount/ capacity of Qvevries, L
1.1	Rkatsiteli	Napareuli	24.4	4/1500
1.2		Tsinandali	24.1	4/1350
1.3		Chalauri	23.8	4/750
2.1	Kisi	Chandari	24.0	4/750
2.2		kondoli	24.3	4/780
2.3		kalauri	23.8	4/1000
3.1	Mstavne	Tsinandali	23.9	4/1000
3.2		Kondoli	24.1	4/1000
3.3		Tokhliauri	23.6	4/100
4.1	Khikhvi	Kondoli	23.4	4/750
4.2		Bakurtikhe	23.6	4/750
4.3		Saniore	23.8	6/750

During alcoholic fermentation, adequate headspace was ensured in each qvevri to facilitate mechanical stirring of the pomace for optimal extraction. After fermentation completion, the pomace was evenly redistributed from one qvevri to the remaining three, and the qvevris were filled to capacity. Temperatures were monitored eight times daily during fermentation, with pomace cap punch-downs performed six to nine times daily. Stainless steel cooling spirals connected to a chilling unit maintained fermentation temperatures between 21 and 23°C. Fermentation lasted 9-12 days, depending on the sample. Upon completion (sugar concentration <4 g/L), chemical parameters were evaluated and adjusted. Total acidity was increased to 5.5 g/L using tartaric acid, and potassium metabisulfite was added to raise total sulfur dioxide to 80 mg/L, correcting wine pH and preventing undesirable microbial activity during maturation. Following regional tradition, qvevris were opened six months after grape processing. Free-run fractions were stored in 250-500 L stainless steel tanks, then transferred to new French oak barrels with mild toast after one month. Barrel aging occurred at cellar temperatures of 13-15°C with 82-85% humidity.

2.2 Methods of Laboratory Analyses

Analyses were performed at four critical stages of wine production:

1. Post-fermentation (September 2023)
2. After opening qvevris and separating wine from grape solids (March 2024)
3. After 6 months of oak barrel aging (September 2024)
4. After 12 months of oak barrel aging (March 2025)

Analyses were performed following the Compendium of International Methods of Wine and Must Analysis.[9] The following analyses were conducted:

1. Gas Chromatography (Methanol Content): Method OIV-MA-E-AS312-03-METHAN, using Agilent Technologies GC-MS (Gas Chromatography-Mass Spectrometry) system.
2. Ethanol Content (Volume %): Method OIV-MA-AS312-01A, using Anton Paar Densitometer and Refractometer.
3. Total Sugars: Method OIV-MA-AS313-01, using SHOTT Tirolian Alfa Automatic Titrator.
4. Total Acids: Method OIV-MA-AS311-01A, Loofah Method, converted to tartaric acids.
5. Volatile Acids: Method OIV-MA-AS313-01, using a Titrolina Alfa Automatic Titrator, converted to acetic acid.
6. Free Sulfur Dioxide: Method OIV-MA-AS313-0, Iodometric Titration Method.
7. Total Sulfur Dioxide: Method OIV-MA-AS323-04B, Iodometric Titration, using Automatic Titrators.

1. Statistical Analysis

Results were expressed as mean ± standard deviation (SD) of triplicate measurements and statistically analyzed using IBM SPSS Statistics 21.0 for Windows (SPSS, Chicago, USA). Significant differences between samples were determined using appropriate statistical tests at a significance level of 0.05.

1. RESULTS AND DISCUSSION

The chemical parameters of wine samples from all four varieties at each production stage are presented in Tables 3-6.

Table 3: Chemical parameters of Rkatsiteli Amber Wine.

Grape Variety	Rketsiteli											
Trial Sample	1.1				1.2				1.3			
Technology Stage	1	2	3	4	1	2	3	4	1	2	3	4
Chemical Parameters												
Alcohol by vol. %	13.7	13.6	13.1	12.6	13.5	13.1	12.8	12.4	13.3	13.1	12.8	12.4
Total Sugars	3.4	3.34	3.1	3.05	2.7	2.56	2.52	1.97	2.1	1.82	1.82	1.83
Total acids, g/l	4.1	5.3	5.21	5.1	4.8	5.3	5.2	4.8	5.6	5.4	5.3	5.1
Volatile acids, g/l	0.48	0.51	0.56	0.79	0.46	0.5	0.58	0.63	0.22	0.41	0.51	0.7
Free SO_2	6	18	21	21	8	21	23	21	7	21	18	21
Total SO_2	12	83	121	140	10	84	101	144	14	81	101	130
Methanol mg/l	95.1	94.3	84.1	76	94	92.4	83.1	79	93.7	91	83.1	71.9

Table 4: Chemical parameters of Kisi Amber Wine.

Grape Variety	kisi											
Trial Sample	1.1				1.2				1.3			
Technology Stage	1	2	3	4	1	2	3	4	1	2	3	4
Chemical Parameter												
Alcohol by vol. %	13,4	13,0	12.8	12	13.6	13.4	12.8	12.2	13.1	12.9	12	11.8
Total Sugars	2.25	2.21	2.2	2.2	3.2	2.9	2.78	2.7	3.14	3.11	3	3
Total acids, g/l	5.8	5.6	5.3	5.1	5.4	5.2	5.2	5.12	6.3	5.8	5.6	5.48
Volatile acids, g/l	0.41	0.51	0.61	0.71	0.51	0.58	0.64	0.84	0.35	0.42	0.5	0.6
Free SO_2	6	18	21	16	4	18	20	21	8	18	21	24
Total SO_2	12	84	98	107	11	82	94	114	14	82	89	145
Methanol mg/l	99.7	95.9	82.2	74.1	111.3	105.2	88.2	76	109.4	98.4	81,2	72.8

Table 5: Chemical parameters of Mtsvane Amber Wine.

Grape Variety	Mtsvane											
Trial Sample	1.1				1.2				1.3			
Technology Stage	1	2	3	4	1	2	3	4	1	3	3	4
Chemical Parameter												
Alcohol by vol. %	13.3	12.9	12.3	11.7	13.7	13.5	12.4	11.6	12.9	12.7	12.2	11.5
Total Sugars	2.1	1.9	1.8	1.8	3.63	3.6	3.58	3.58	2.45	2.1	2.1	2.1
Total acids, g/l	6.4	6.1	5.8	5.61	5.4	5.11	5.0	4.8	6.6	6.3	5.9	5.4
Volatile acids, g/l	0.48	0.51	0.64	0.71	0.33	0.49	0.68	0.84	0.3	0.41	0.6	0.74
Free SO_2	5	15	21	18	12	21	22	18	11	22	16	25
Total SO_2	11	84	87	118	18	88	125	130	18	84	130	150
Methanol mg/l	88.4	87.1	80	72.4	87.3	85.3	74.1	68.7	85.9	84.1	70.1	67.5

Table 6: Chemical parameters of Khikhvi Amber Wine.

Grape Variety	khikhvi											
Trial Sample	1.1				1.2				1.3			
Technology Stage	1	2	3	4	1	2	3	4	1	3	3	4
Chemical Parameter												
Alcohol by vol. %	13.2	12.8	12.1	11.5	13.4	13.1	12	11.4	13.2	13	12.5	11.4
Total Sugars	2.7	2.2	2	2	2,5	1.9	1.78	1.78	3.2	3.2	3.14	3.14
Total acids, g/l	4.3	5.5	5.3	5	6	5.4	5	5.1	4.4	5.6	4.8	4.6
Volatile acids, g/l	0.54	0.58	0.61	0.8	0.55	0.6	0.72	0.94	0.51	0.55	0.7	1.1
Free SO_2	4	18	21	14	8	22	18	14	4	24	14	12
Total SO_2	6	81	110	148	15	84	110	138	14	82	144	148
Methanol mg/l	93.4	91	80.2	70.1	90.3	87.2	84.4	72.7	88.4	86.3	74.5	70.6

The analysis of methanol concentrations across all four grape varieties revealed a consistent and gradual decline throughout the production and aging process.[5] Initially, the highest methanol levels were recorded post-fermentation (stage 1), ranging from 85.9 to 111.3 mg/L. Kisi samples had slightly higher starting methanol levels (99.7-111.3 mg/L) than Mtsvane samples (85.9-88.4 mg/L), but there wasn't a statistically significant difference between varieties in methanol content when examined over the entire aging period ($p > 0.05$). This suggests that varietal characteristics have minimal impact on methanol changes during aging, despite potential differences in pectin structure.

A significant observation was the continual reduction in methanol levels during oak barrel aging. After 12 months of aging (stage 4), methanol levels decreased to 67.5-79.0 mg/L across all varieties, representing an average reduction of approximately 25-30% from initial values. This reduction was most pronounced between stages 2 and 4, corresponding to the oak barrel aging period. This decrease aligns with previous research, showing that aging in oak barrels helps reduce methanol through interactions with oak compounds, such as tannins, and changes in the micro-oxidative environment.

The chromatographic analysis of methanol in Kisi amber wine after 6 and 12 months of oak barrel aging (Figures 1 and 2) visually confirms this reduction pattern. The chromatograms show clear peaks for methanol with decreasing intensity over the aging period. Obtained data presented in Figure 3 shows that with the length of barrel aging, the ethanol and methanol content in amber qvevri wine decreases.

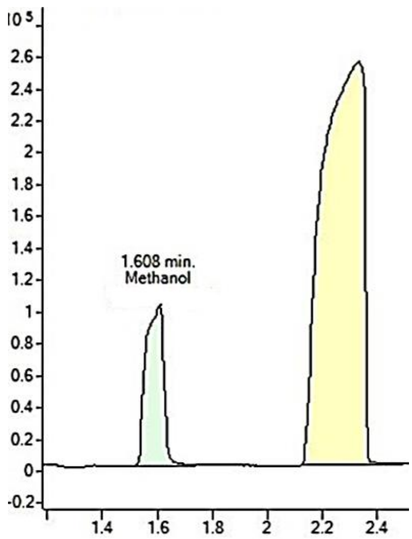

Figure 1: Kisi Amber Wine Chromatogram, GC-MS - Methanol, After 6 Months of Oak Barrel Aging.

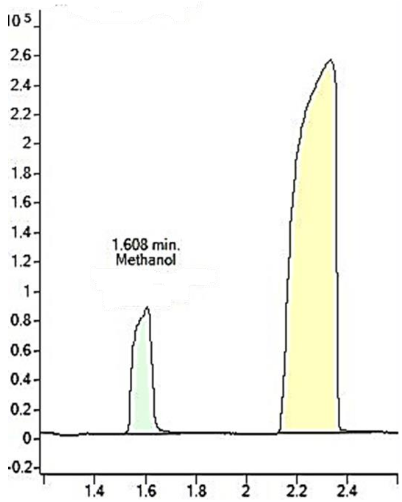

Figure 2: Kisi Amber Wine Chromatogram, GC-MS - Methanol, After 12 Months of Oak Barrel Aging.

Importantly, all samples maintained methanol concentrations well below the 250 mg/L limit established by the International Organization of Vine and Wine (OIV) for white wines, confirming the safety of traditional Qvevri winemaking when combined with oak barrel aging, even with the extended maceration periods characteristic of amber wine production.

Traditionally, qvevri wines are characterized by high alcohol content; however, given the results of the study, the winemaker should estimate how long the wine can be aged in a qvevri based on laboratory analyses. This study showed that the amount of methanol can be reduced by aging in the kari, but constant monitoring of chemical parameters during aging is necessary. The results presented in Table 3-6 and Figure 4 demonstrate that as aging time increases, the content of volatile acids rises, posing a risk to the quality of the wine.

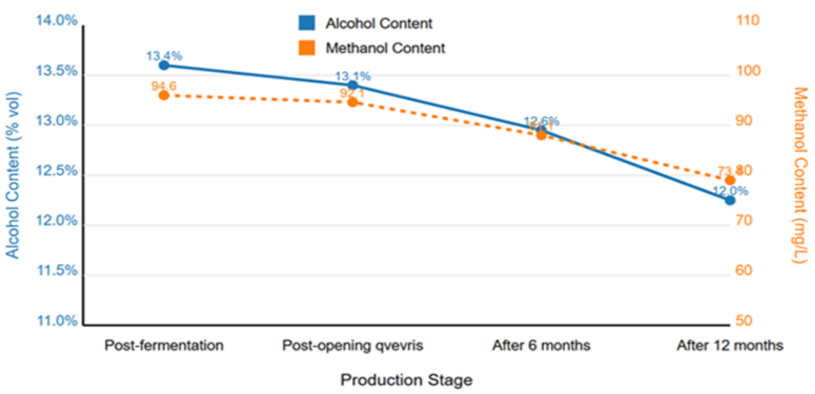

Figure 3: Methanol and Ethanol Content Dynamics in Qvevri Amber Wines, Average Values of All Trial Samples.

Data presented in Figure 4 shows that, in contrast to the declining methanol trend, volatile acidity demonstrated a consistent increase throughout the production process across all varieties. Initial volatile acid concentrations ranged from 0.22 to 0.55 g/L post-fermentation, increasing to 0.60 to 1.10 g/L after 12 months of aging. This increase can be attributed to controlled oxidation and microbial activity during oak aging.

The Khikhvi variety exhibited higher volatile acidity levels compared to other varieties, indicating a potential sensitivity to oxidative processes. Most wines, except for one Khikhvi sample (which reached 1.10 g/L), maintained volatile acidity levels below 1.00 g/L, meeting quality production standards. This indicates that despite the extended maceration characteristic of traditional Qvevri amber wines, the combination with oak aging provides sufficient structural stability while allowing beneficial oxidative development.

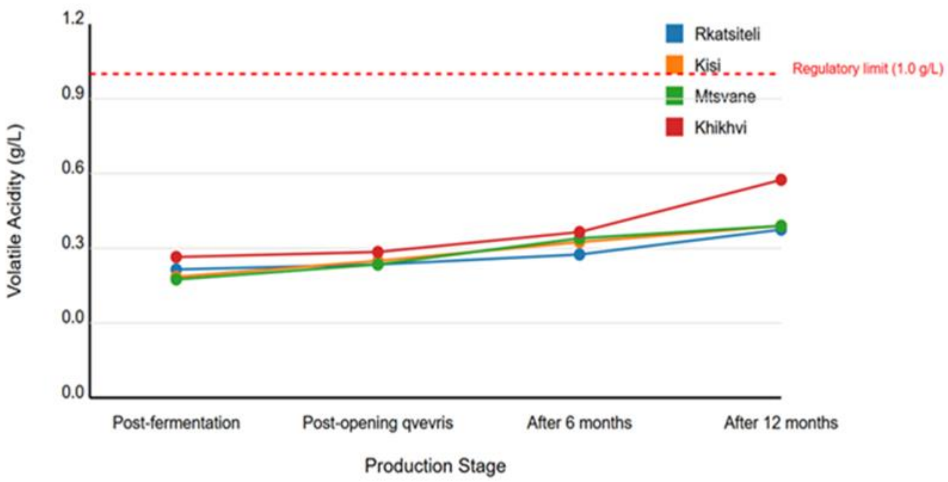

Figure 4: Volatile Acidity of Qvevri Amber Wines, Average Values of All Trial Samples.

The rise in volatile acidity during oak aging exhibited an inverse correlation with the decrease in methanol, underscoring the significant interplay between these two parameters throughout the wine aging process. Oak aging appears to facilitate reduced methanol levels while enhancing aromatic complexity through interactions with oak compounds.

CONCLUSION

This study provides crucial insights into the impact of oak barrel aging on methanol levels and volatile acidity in traditional Georgian Qvevri amber wines:

1. During oak barrel aging, methanol decreases and volatile acidity increases within acceptable limits in Georgian amber wines.

2. The decrease in methanol levels during oak aging across all varieties confirms the safety of traditional Qvevri winemaking techniques, even with extended skin contact.

3. Oak barrel aging has a greater impact on methanol dynamics than grape varieties, indicating that standardized oak aging protocols can consistently reduce methanol regardless of the grape variety.

4. Oak barrel aging for at least 6 months is recommended in Qvevri amber wines to reduce methanol levels effectively and maintain appropriate volatile acidity levels within acceptable limits. At the 6-month mark, methanol concentrations decreased by 10-25% from initial levels, and volatile acidity levels stayed below sensory thresholds for all varieties.

5. Beyond 6 months, further aging led to more methanol reduction, but with diminishing returns and an increased risk of excessive volatile acidity development, particularly for sensitive varieties like Khikhvi.

Combining traditional Qvevri fermentation with oak barrel aging improves the safety and quality of Georgian amber wines. This method safeguards the cultural heritage of Qvevri winemaking, producing commercially viable wines that meet international safety standards and quality expectations.

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Conflict of Interest

The authors confirm that they do not have any financial or any other forms of conflicts of interest or personal relationships that could have biased the study.

Author Contribution

Mariam Khomasuridze: Research planning, research design, writing original draft.

Maia Kiladze: Implementation of chemical and statistical analysis, data curation, and writing the original draft.

Shurman Tatulashvili: Conceptualization, project administration, supervision, and funding acquisition.

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