

Effect of filter paperboard on metallic elements and phenolic compounds in ice wine pomace brandy

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Abstract Metallic and phenolic compounds significantly impact the stability, flavor, and clarity of brandy, with implications for precipitation formation and human health. This study evaluated the effects of non-mineral pure-fiber paperboard (PF) and paperboard containing mineral filter (MF) on metallic elements and phenolic substances in ice wine pomace brandy aged in oak chips. The contents of 22 metallic elements were determined by inductively coupled plasma–mass spectrometry. Phenolic compounds were profiled by UHPLC–Q Exactive Orbitrap-MS and quantified by UPLC. Results demonstrated that temperature critically influenced metallic precipitation in MF, with Ca, Fe, Mg, Zn, and K increasing significantly at higher temperatures. Filtration markedly reduced polyphenol content, however, PF minimized phenolic loss compared to MF. A comparative analysis revealed that PF was superior to MF in reducing metallic introduction and preserving phenolic content. Thus, PF filtration at low temperatures (e.g., 0 °C) effectively clarifies and stabilizes ice wine pomace brandy while preserving phenolic compounds.

Keywords: ice wine pomace brandy; filter paperboard; metallic elements; phenolic compounds; ICP-MS; UHPLC-MS

1 Introduction

Ice wine pomace brandy was one of the typical spirits produced through distilling, aging and blending the pomace of ice grapes. Resource recyclers used ice grape pomace residue to develop brandy, which met the needs of consumers and produced high economic and social benefits. The production of brandy from ice grape pomace extended the wine industry chain, solving the pollution of waste to the environment, which was of great significance to energy conservation, emission reduction and ecological

environment protection in ice wine production regions.

The content of metallic elements was closely related to the quality of brandy^[1]. Proper amounts of metallic elements can improve the nutritional value of brandy, while some metallic elements exceeding the standard will not only affect the sensory evaluation and stability of brandy, but also bring potential safety hazards to human health^[2]. Metallic elements can affect the production process of brandy or change its taste and quality^[3]. Several metallic elements, including Al, Cu, Fe and Ca, contributed to haze formation and taste effects^[4]. A typical example was iron, which could have a severe influence on the wine evolution during the fermentation process. In brandy, iron ions and phosphate formed an insoluble

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compound iron phosphate, which was a white precipitate. This phenomenon was the most common iron spoilage disease ^[5]. Calcium also had a negative effect on the stability of brandy. There were two types of precipitates, crystalline inorganic precipitates and amorphous organic precipitates ^[6]. The former was mainly an inorganic calcium salt formed by calcium and other inorganic anions, such as calcium carbonate, while the latter was a water-insoluble substance formed by the combination of calcium and macromolecular organic substances in brandy ^[7]. Contrarily, several metals and metalloids, such as Cd, Pb, Sn, Hg, and As, were known to be potentially toxic. Monitoring and determination of other metallic elements, for example As, Cd and Pb, was also of high importance due to their potential toxic effects on human health ^[8-9]. For many reasons, the determination of appropriate metals in different types of biological, environmental and food samples had attracted considerable attention. The most important reason was the nutritional and toxic effects of these elements or their compounds ^[10]. Copper was an essential element, but at the same time, when consumed in excess, it was potentially toxic for humans ^[11].

Phenolic compounds significantly influence the flavor and taste of ice grape pomace brandy. During oak aging, the pomace brandy acquires extractives from the wood, such as phenolic aldehydes, phenolic acids and tannins ^[12]. These phenolic compounds can undergo complex reactions with other compounds in the brandy, imparting unique color and aroma to the spirit. They also possess antioxidant capabilities within the spirit, effectively delaying the oxidation process of the brandy, inhibiting the formation of volatile spoilage compounds, and extending its shelf life ^[13-15]. However, filtration was found to reduce the phenolic content, potentially simplifying the taste and flavor profile due to the interaction and removal of these compounds by the filter medium.

Filtration simultaneously altered the concentrations of metallic element and valuable phenolic compounds, thereby modifying the sensory profile of spirit. Therefore, the selection of appropriate filtration conditions and media was crucial in ice grape

pomace brandy production to improve stability and minimize negative impacts on quality ^[16]. However, current research on the effect of filtration on brandy quality remains limited. In this study, ice grape pomace was used to produce oak-aged brandy and filtration conditions were optimized based on metallic element content ^[17-18]. The investigation aimed to determine the impact of different filter paperboards on the quality of ice wine pomace brandy by evaluating changes in its metallic element and phenolic compound profiles before and after filtration.

2 Experimental

2.1 Materials

Filter paperboards were supplied by Shenyang Great Wall Filtration Cardboard Co., Ltd. (Liaoning, China), including PF (SCC-230, SCC-240, SCC-270) and MF (SCP-311, SCP-312, SCP-334). Multi-element calibration standards were from Agilent Technologies (USA). Ultrapure water (Wahaha Co., Ltd., China) and nitric acid (65%, Merck, Germany) were used. Phenolic standards (gallic acid, chlorogenic acid, vanillin, syringaldehyde, p-hydroxybenzoic acid, vanillic acid, syringic acid) were obtained from Chengdu Manst Biotechnology Co., Ltd. Chromatographic-grade methanol, acetonitrile, and formic acid were purchased from Tianjin Fuyu Fine Chemical Co., Ltd. and Fisher Scientific (USA).

2.2 Ice wine pomace brandy making

The pomace brandy was produced by alcoholic fermentation and subsequent distillation of ice wine pomace. The pomace was provided by Sanhe Ice Wine Company Ltd. (Huanren, Liaoning, China) and derived from ice grapes (*Vitis vinifera*) harvested in winter 2022 under natural freezing conditions in the Huanren region. The pomace was crushed and subjected to alcoholic fermentation in tanks until the density of the fermenting mash decreased to below 1.000 g/mL. After fermentation, the tanks were topped up and stored under airtight conditions prior

to distillation. Double distillation was then performed using the Charentais method. For the first distillation, the head and tail fractions were recycled, while the main fraction was retained for the second distillation. The second distillation was carried out using the main fraction alone or combined with part of the recycled fractions to obtain the ice wine pomace brandy, with an ethanol content of approximately 70% (v/v)^[19]. The ice wine pomace brandy was then aged with different types of oak chips (as shown in Table 1) in 5-L stainless steel tanks for 6 months, respectively, before filtration and analysis.

Table 1 Information of the 5 oak chips for ice grape pomace brandy accelerated aging

No.	Constituent	Abbreviation	Additive amounts (g)
1	Unroasted French oak	UF	10
2	Medium roasted American oak	MA	10
3	Medium toasted French oak	MTF	10
4	Moderately severe roasted French oak	MSF	10
5	Severe toasted French oak	MF	10

2.3 Filtration experiments with filter paperboards

The brandy was filtered using different filter paperboards under controlled parameters. The impact of pH was examined by adjusting the pH of the brandy (60% v/v ethanol) to values ranging from 3.5 to 4.0, with filtration performed at 0 °C. The effect of alcohol concentration was studied by diluting the brandy to 40–60% v/v ethanol at pH 3.6 and 0 °C. The influence of temperature was evaluated by filtering the brandy (60% v/v ethanol, pH 3.6) at temperatures from -5 °C to 20 °C. Additionally, six types of filter paperboards (SCC-230, SCC-240, SCC-270, SCP-311, SCP-312, SCP-334) were compared under optimal conditions (0 °C, pH 3.6, 60% v/v ethanol). The filtered samples were analyzed for metal content and phenolic compounds.

2.4 Preparation of standard and sample solutions

2.4.1 Metallic elements

Mixed standard solutions were diluted with 5% nitric acid to concentrations of 0, 5, 25, 50, 100, and 200 ng/mL. Brandy samples (1.00 mL) were filtered through the paperboard, diluted to 50 mL with 5% nitric acid. Blank solutions were prepared accordingly.

2.4.2 Phenolic compounds

Mixed reference standard stock solution was prepared by accurately weighing gallic acid, p-hydroxybenzoic acid, chlorogenic acid, vanillic acid, syringic acid, vanillin, and syringaldehyde individually, dissolving them in 50% methanol, and mixing to achieve final concentrations of 313.0, 372.0, 169.0, 542.0, 277.0, 319.0, and 604.0 mg/L, respectively. For the test solution, a 10 mL aliquot of the aged ice grape pomace brandy was concentrated by rotary evaporation at 40 °C and 80 rpm. The residue was reconstituted in 50% methanol to a final volume of 10 mL. The resulting solution was then filtered through a 0.22 µm membrane prior to analysis.

2.5 Analysis of metallic elements

2.5.1 Single-factor experiments

Effect of pH on filtration: Brandy samples (60% Vol, 0 °C) were adjusted to pH 3.5, 3.6, 3.7, 3.8, 3.9 and 4.0, and then the filtration was performed by MF.

Effect of alcohol on filtration: The brandy samples at pH 3.6 and 0 °C were diluted alcoholic concentrations from 40% Vol to 60% Vol and filtered with MF.

Effect of temperature on filtration: Brandy samples with 60% Vol and pH 3.6 were filtered at -5 °C, 0 °C, 5 °C, 10 °C, 15 °C and 20 °C with MF.

2.5.2 ICP-MS analysis

The analytical measurements of major and trace

elements (Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Cs, Ba, Ti and Pb) were carried out using ICP-MS instrument (7800 model; Agilent Technologies, Santa Clara, CA, USA). The operating parameters of ICP-MS were shown in Table 2.

Table 2 The working parameters of ICP-MS

Working parameters	Set the result
RF power/W	1550
Sampling depth	7.3
Carrier air velocity/(L/min)	0.96
Auxiliary airflow/(L/min)	0.26
Integration time/s	0.3
Scan mode	Peak jump sweep
Oxide $^{156}\text{CeO}^+ / ^{140}\text{Ce}^+ / \%$	0.36
Atomization chamber temperature/ $^{\circ}\text{C}$	2
Assay mode	He mode
Reaction air velocity/(mL/min)	4.0
Analysis mode	Full quantification
Sample acceleration/(mL/min)	1.0
Number of scans	3
Double charge $^{70}\text{Ce}^{2+} / ^{140}\text{Ce}^+ / \%$	0.93

2.6 Analysis of phenolic compounds

2.6.1 Qualitative analysis by UHPLC-Q-Exactive Orbitrap MS

The UPLC-Q-Exactive Orbitrap-MS analysis was performed using an Acquity UPLC system (Waters Corp., Milford, USA) coupled to a Q-Exactive Orbitrap mass spectrometer (Thermo Scientific, USA). Separation was achieved using an Acquity UPLC BEH C_{18} column (100 mm $\times$ 2.1 mm, 1.7 μm). The mobile phase consisted of (A) 0.2% formic acid in water and (B) acetonitrile, with a gradient elution programmed as follows: 0 min (95% A), 4 min (92% A), 11 min (92% A), 14 min (88% A), 20 min (70% A), 21 min (0% A), 25 min (0% A), 28 min (95% A), and 30 min

(95% A). The flow rate was 0.3 mL/min, the injection volume was 2 μL , and the column temperature was maintained at 30 $^{\circ}\text{C}$.

Mass spectrometric detection was conducted in negative ionization mode using a heated electrospray ionization (H-ESI) source. The instrument parameters were set as follows: capillary voltage, -2.5 kV; sheath gas pressure, 45 psi; auxiliary gas flow rate, 15 arb; capillary temperature, 350 $^{\circ}\text{C}$; and H-ESI heater temperature, 300 $^{\circ}\text{C}$. The mass spectrometer was operated in Full MS/dd-MS² mode, with resolutions set at 70,000 for Full MS and 17,500 for dd-MS², and a mass scan range of m/z 100–1500.

2.6.2 Quantitative analysis by UPLC

The same chromatographic conditions described in section 2.4.1 were applied for quantitative analysis. The seven phenolic compounds were quantified using the external standard method.

2.7 Influence of different filter paperboard on metallic elements and phenolic compounds

The influence of six different filter paperboards (three non-mineral pure fiber boards and three mineral-containing boards) was investigated. Ice grape pomace brandy samples (60% vol, pH 3.6) were filtered at 0 $^{\circ}\text{C}$ using each paperboard. The filtered samples were then analyzed for 22 metallic elements (Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Cs, Ba, Ti, and Pb). Concurrently, the samples were processed into test solutions according to Section 2.4.1, and the contents of phenolic compounds were determined under the chromatographic conditions of Section 2.4.2 using the external standard method.

2.8 Statistical analysis

Statistical analysis was performed using one-way ANOVA in SPSS Version 21.0 (Chicago, USA). Differences between means were compared using Duncan's test at a significance level of $P \leq 0.05$.

3 Results and discussion

3.1 Metallic elements

3.1.1 Method validation of quantitative analysis of 22 metallic elements

Twenty-two metallic elements in ice wine pomace brandy were determined by ICP-MS. The linear parameters and detection limits are summarized in Table 3. Correlation

coefficients (R) for all calibration curves exceeded 0.999. Limits of detection (LOD) and quantification (LOQ) were calculated based on 11 consecutive measurements of the blank solution, yielding LODs of 0.007–0.731 ng/mL and LOQs of 0.008–2.366 ng/mL. The relative standard deviations (RSD) were below 1.25%, confirming the method's accuracy, reliability, and high precision. Six elements (Cu, Cr, Cs, Ba, Ti, Pb) were not detected in the samples. The high content of Fe and Mg may affect brandy clarity.

Table 3 Calibration curve parameters, LOD and LOQ values

Element	m/z	R	LOD/(ng/mL)	LOQ/(ng/mL)	RSD/%
Be	9	0.9999	0.020	0.062	0.15
Na	23	0.9997	0.112	0.358	0.57
Mg	24	0.9999	0.391	1.472	0.45
Al	27	0.9995	0.612	1.886	1.02
K	39	0.9999	0.517	1.562	0.85
Ca	43	0.9991	0.561	1.732	1.23
V	51	0.9999	0.007	0.025	0.45
Cr	52	0.9999	0.081	0.264	1.12
Mn	55	0.9996	0.323	1.041	0.56
Fe	56	0.9998	0.731	2.366	1.41
Co	59	0.9998	0.011	0.039	0.15
Ni	60	0.9998	0.012	0.042	0.48
Cu	63	0.9997	0.334	1.182	0.96
Zn	66	0.9995	0.364	1.265	0.85
As	75	0.9995	0.006	0.019	0.96
Se	78	0.9995	0.012	0.049	0.16
Rb	85	0.9996	0.016	0.059	1.15
Sr	88	0.9999	0.022	0.085	1.25
Cs	133	0.9997	0.021	0.070	0.28
Ba	137	0.9999	0.129	0.454	1.21
Ti	205	0.9999	0.002	0.008	0.45
Pb	208	0.9999	0.189	0.617	0.25

3.1.2 Effect of filtration conditions on metallic elements in ice wine pomace brandy

The effect of filtration conditions (pH, alcohol and temperature) on metallic elements was

investigated during paperboard filtration by single-factor experiment. As shown as Table 4, pH had significant effect on the concentration of V, As and Sr ($P \leq 0.05$). The content of Sr was the lowest at higher pH (4.0). For other elements, there was no significant

difference through different pH filtration. Compared with different alcohol, the content of Fe, Ni, As and Se increased significantly in brandy with alcohol of 60% Vol ($P \leq 0.05$), as shown in Table 5. Alcohol had no significant effect on other elements.

Temperature was a key factor for paperboard filtration. Using paperboard containing mineral filter, the metallic concentrations of Ca, Fe, Mg, Mn and K presented increase ($P \leq 0.05$) when the temperature was elevated from -5 °C to 20 °C (Table 6).

Table 4 Metallic concentrations (ng/mL) in ice wine pomace brandies with different pH after filtration by containing mineral filter paperboard

pH	Be	Na	Mg	Al	K	Ca	V	Mn
3.5	0.1±0.017a	33.54±1.08a	68.22±0.986a	26.62±1.03a	38.23±0.975a	109±1.709a	0.11±0.017bc	1.21±0.05a
3.6	0.09±0.01a	33.63±0.616a	68.34±0.565a	26.78±1.261a	38.26±0.662a	109.8±0.763a	0.21±0.044a	1.23±0.214a
3.7	0.1±0.026a	33.55±0.178a	68.32±0.13a	26.65±0.046a	38.27±0.149a	109.1±1.054a	0.17±0.044ab	1.29±0.139a
3.8	0.1±0.02a	33.79±0.201a	68.29±0.41a	26.56±0.111a	38.16±1.091a	109.0±1.065a	0.09±0.01c	1.22±0.017a
3.9	0.1±0.02a	33.23±0.383a	68.36±0.147a	26.7±0.125a	38.3±0.935a	109.09±0.197a	0.16±0.046ab	1.26±0.149a
4.0	0.1±0.062a	33.36±0.641a	68.69±0.584a	27.72±0.85a	38.1±1.144a	107.57±0.572a	0.12±0.003bc	1.16±0.017a
pH	Fe	Co	Ni	Zn	As	Se	Rb	Sr
3.5	50.32±1.935a	0.16±0.02a	1.65±0.046a	35.36±0.395a	0.02±0.01c	0.06±0.006b	0.07±0.01a	1.19±0.036a
3.6	50.46±0.217a	0.16±0.05a	1.63±0.026a	35.53±0.951a	0.06±0.018ab	0.09±0.009a	0.06±0.012ab	1.09±0.187ab
3.7	50.56±0.118a	0.19±0.03a	1.56±0.089a	35.56±0.461a	0.03±0.009c	0.05±0.006bc	0.06±0.011ab	1.16±0.089ab
3.8	50.59±1.898a	0.15±0.002a	1.53±0.044a	35.5±0.284a	0.07±0.009a	0.03±0.002c	0.04±0.007c	1.03±0.044ab
3.9	50.51±0.607a	0.19±0.01a	1.56±0.066a	35.6±0.056a	0.04±0.008bc	0.06±0.008b	0.06±0.007ab	0.97±0.141bc
4.0	50.86±0.697a	0.19±0.011a	1.66±0.297a	36.42±0.494a	0.035±0.011c	0.05±0.022bc	0.05±0.002bc	0.88±0.022c

Note: Mean ± 95%-confidence interval, $n = 3$. Other conditions: alcohol, 60% Vol; filtration temperature, 0 °C. For each element, different letters indicate significant differences ($P \leq 0.05$).

Table 5 Metallic concentrations (ng/mL) in ice wine pomace brandies at different alcohol concentration after filtration with containing mineral filter paperboard

Alcohol	Be	Na	Mg	Al	K	Ca	V	Mn
40% Vol	0.08±0.003a	32.2±0.961a	69.32±1.013a	26.32±0.539a	39.41±1.283a	108.86±2.305a	0.16±0.005a	1.56±0.050b
45% Vol	0.09±0.007a	33.96±0.113a	68.51±1.522a	25.91±1.015a	38.26±0.466ab	110.25±0.701a	0.16±0.006a	1.96±0.061a
50% Vol	0.09±0.009a	33.26±1.041a	69.3±1.37a	26.61±0.67a	37.11±1.062b	108.56±0.669a	0.17±0.053a	1.67±0.151b
55% Vol	0.09±0.087a	33.78±33.06a	69.21±0.604a	26.12±26.35a	38.67±1.434ab	108.31±1.519a	0.16±0.12a	1.59±1.6b
60% Vol	0.09±0.01a	33.63±0.616a	68.34±0.565a	26.78±1.261a	38.26±0.662ab	109.8±0.763a	0.21±0.044a	1.23±0.214c
Alcohol	Fe	Co	Ni	Zn	As	Se	Rb	Sr
40% Vol	50.17±0.857b	0.16±0.005a	1.49±0.077ab	35.96±1.286a	0.03±0.006b	0.06±0.006b	0.06±0.002a	1.14±0.037a
45% Vol	50.29±0.714b	0.2±0.026a	1.54±0.046ab	36.3±0.255a	0.03±0.01b	0.05±0.006b	0.05±0.010a	1.1±0.131a
50% Vol	52.45±0.944a	0.19±0.046a	1.37±0.144bc	36.12±0.822a	0.03±0.013b	0.05±0.01b	0.05±0.009a	1.09±0.118a
55% Vol	51.26±1.413b	0.18±0.07a	1.27±1.13c	34.96±1.217a	0.03±0.016b	0.06±0.045b	0.06±0.062a	1.16±1.19a
60% Vol	50.46±0.217b	0.16±0.050a	1.63±0.026a	35.53±0.951a	0.06±0.018a	0.09±0.009a	0.06±0.012a	1.09±0.187a

Note: Mean ± 95%-confidence interval, $n = 3$. Other conditions: pH 3.6; filtration temperature, 0 °C. For each element, different letters indicate significant differences ($P \leq 0.05$).

Table 6 Metallic concentrations (ng/mL) in ice wine pomace brandy with different temperature after filtration with containing mineral filter paperboard

Temperature	Be	Na	Mg	Al	K	Ca	V	Mn
-5 °C	0.08±0.063a	33.49±3.211a	68.03±0.532b	25.42±1.617b	36.34±0.357c	100.01±1.453c	0.27±0.035a	1.04±0.044c
0 °C	0.09±0.01a	33.63±0.616a	68.34±0.565b	26.78±1.26ab	38.26±0.662bc	109.8±0.763b	0.21±0.044bc	1.23±0.214b
5 °C	0.08±0.034a	34.55±2.832a	70.91±0.346ab	25.69±1.568b	41.36±0.643b	109.37±1.109b	0.16±0.046c	1.22±0.056b
10 °C	0.07±0.049a	33.16±2.643a	71.57±0.623a	25.98±1.264b	41.13±0.859b	147.55±1.213a	0.2±0.036bc	1.24±0.036b
15 °C	0.08±0.036a	34.46±2.563a	72.26±0.53a	28.57±1.413a	42.67±0.721ab	146.88±1.231a	0.18±0.032bc	1.85±0.022a
20 °C	0.08±0.009a	34.26±0.63a	72.62±1.524a	28.45±1.341a	43.12±0.711a	148.91±10.044a	0.22±0.044b	1.89±0.092a
Temperature	Fe	Co	Ni	Zn	As	Se	Rb	Sr
-5 °C	48.16±0.315c	0.2±0.016b	1.36±0.049c	34.12±1.423b	0.03±0.008a	0.1±0.005a	0.09±0.006a	1.17±0.045a
0 °C	50.46±0.217b	0.16±0.05c	1.63±0.026ab	35.53±0.951ab	0.06±0.018a	0.09±0.009a	0.06±0.012b	1.09±0.187c
5 °C	50.59±1.723b	0.19±0.017b	1.86±0.042a	34.45±2.339b	0.06±0.008a	0.05±0.005b	0.1±0.007a	1.24±0.039a
10 °C	52.27±2.413a	0.26±0.016a	1.97±0.034a	37.47±2.389a	0.05±0.007a	0.07±0.006ab	0.06±0.006b	1.21±0.036a
15 °C	52.99±1.831a	0.27±0.013a	1.86±0.049a	36.58±1.012a	0.05±0.006a	0.07±0.006ab	0.07±0.007ab	1.24±0.026a
20 °C	52.87±2.62a	0.26±0.026a	1.80±0.148a	36.76±0.261a	0.5±0.007a	0.08±0.013ab	0.09±0.015a	1.43±0.182a

Note: Mean ± 95%-confidence interval, $n = 3$. Other conditions: pH 3.6; alcohol, 60% Vol. For each element, different letters indicate significant differences ($P \leq 0.05$).

Table 7 Metallic concentrations (ng/mL) in ice wine pomace brandy after filtration with containing mineral filter and non-mineral fiber paperboard

paperboard	Be	Na	Mg	Al	K	Ca	V	Mn
Unfiltered	0.07±0.012c	30.16±1.102c	41.51±0.742b	12.35±1.037b	23.15±0.812b	26.02±2.121b	0.16±0.013b	1.00±0.057ab
SCC-230	0.09±0.009a	31.66±1.244b	42.33±1.347b	13.77±0.813	22.69±0.661b	27.64±1.464b	0.16±0.012b	0.69±0.024b
SCC-240	0.09±0.012a	31.12±0.976b	43.45±0.988b	13.69±0.791	21.13±1.131b	26.99±0.498b	0.16±0.011b	0.55±0.034b
SCC-270	0.08±0.011b	31.48±1.082b	42.7±0.77b	12.47±0.964b	22.87±0.145b	26.27±2.034b	0.11±0.023c	0.44±0.041b
SCP-311	0.09±0.004a	33.21±1.742ab	60.45±2.138a	22.71±1.131a	35.41±0.491a	91.16±1.1674a	0.22±0.064a	1.19±0.131a
SCP-312	0.08±0.024b	34.56±0.783a	65.15±1.221a	29.56±1.461a	39.09±0.464a	88.12±0.491a	0.19±0.019ab	1.39±0.094a
SCP-334	0.08±0.01b	33.63±0.616a	68.34±0.565a	26.78±1.26a	38.26±0.662a	109.8±0.763a	0.21±0.044a	1.23±0.214a
paperboard	Fe	Co	Ni	Zn	As	Se	Rb	Sr
Unfiltered	33.15±1.122b	0.19±0.024a	1.24±0.037c	33.12±1.046b	0.02±0.001b	0.07±0.002b	0.05±0.006c	0.95±0.019a
SCC-230	37.416±2.265b	0.19±0.009a	1.01±0.054cd	33.41±1.214b	0.02±0.001b	0.07±0.002b	0.08±0.006a	1.03±0.012a
SCC-240	37.88±0.466b	0.19±0.011a	1.11±0.016c	33.97±2.111b	0.02±0.001b	0.07±0.003b	0.06±0.002c	0.99±0.019a
SCC-270	35.58±1.365b	0.15±0.013b	0.87±0.026d	34.46±1.624ab	0.03±0.001b	0.05±0.003c	0.08±0.004a	1.02±0.016a
SCP-311	52.71±1.213a	0.17±0.021ab	1.47±0.019b	36.74±0.944a	0.05±0.002a	0.09±0.001a	0.07±0.003b	1.06±0.026a
SCP-312	53.16±1.16a	0.19±0.041a	1.69±0.036a	37.17±0.857a	0.06±0.001a	0.1±0.003a	0.07±0.004b	1.01±0.031a
SCP-334	50.46±1.217a	0.16±0.05ab	1.63±0.026a	35.53±0.951ab	0.06±0.002a	0.09±0.009a	0.06±0.012bc	1.09±0.087a

Note: Mean ± 95%-confidence interval, $n = 3$. Other conditions: pH 3.6; alcohol, 60% Vol; filtration temperature, 0 °C. For each element, different letters indicate significant differences ($P \leq 0.05$).

3.1.3 Effects of different filter paperboards on metallic elements in ice wine pomace brandy

The metallic content after filtration with different paperboards was compared under identical conditions (Table 7). PF demonstrated a superior filtering effect. MF filtration significantly increased the content of Mg, Al, K, Ca, Fe, V, and Mn compared to PF ($P \leq 0.05$). Notably, the increases for Ca, Mg, and Fe were substantial (83.53 ng/mL, 14.88 ng/mL, and 25.64 ng/mL, respectively). These elevated metallic levels can adversely affect brandy quality and organoleptic properties. Elements like Ca, Mg, Fe^{2+} , Al, and Mn can directly react with sulfates and carbonates in brandy to form precipitates. Fe^{3+} acts as a catalyst, promoting the oxidative condensation of proteins and polyphenols into precipitates. Aluminum can form complexes with proteins, causing haze, turbidity, or precipitation, and can also react with organic acids to form aluminum oxide precipitates. Although potassium salts are less prone to precipitation, they can form potassium hydrogen tartrate crystals with tartaric acid.

In conclusion, the effect of two different filter paperboards on metallic elements in ice wine pomace brandy were studied. 22 metallic elements in ice wine pomace brandies before and after filtration under different conditions were analyzed using ICP-MS. It was found that temperature had enormous consequences on filtration. Lower temperature filtration should be used, which was consistent with the temperature used in the production process of the distillery. In comparison to mineral-containing filter paperboard, non-mineral pure fiber paperboard gave less effect on metallic composition and level of ice wine pomace brandy, suggesting its potential application in filtration of this new enological product.

3.2 Phenolic compounds

3.2.1 Identification of phenolic compounds

Fourteen phenolic compounds were identified, including 12 oligomeric polyphenols (e.g., gallic acid, syringaldehyde, coniferaldehyde, sinapaldehyde,

p-hydroxybenzoic acid, chlorogenic acid, vanillin, syringic acid, caffeic acid, vanillic acid, gentisic acid, ferulic acid) and two hydrolysable tannins (vescalagin, ellagic acid) as shown in Table 8.

3.2.2 Effect of oak chip type and roasting degree on phenolic content in ice wine pomace brandy

Analysis of ice grape pomace brandies aged with five types of oak chips revealed distinct phenolic profiles influenced by oak origin and roasting degree, with the results shown in Table 9. While seven target phenolic compounds were detected in brandies aged with roasted oak chips (medium/heavy-roasted American/French oak), four of these compounds were absent in brandy aged with unroasted French oak. Significant origin-related differences were observed, with medium-roasted American oak imparting significantly higher levels of syringic acid, vanillin, and syringaldehyde than medium-roasted French oak, suggesting an origin-dependent phenolic profile. Furthermore, phenolic content showed a positive correlation with roasting intensity, as heavy-roasted French oak yielded the highest concentrations of p-hydroxybenzoic acid, syringic acid, syringaldehyde, and vanillin among all French oak samples.

3.2.3 Effects of different filter paperboards on phenolic compounds in ice wine pomace brandy

Filtration led to a significant reduction in phenolic compounds, as summarized in Table 10. The six paperboards exhibited a range of reduction rates for each analyte compared to the unfiltered brandy, with chlorogenic acid showing the greatest loss (up to 41.6%) and vanillic acid the least (as low as 7.7%). The non-mineral (PF) paperboards, such as SCP-311 and SCP-334, consistently demonstrated a superior capacity to preserve phenolic content relative to the mineral-containing (MF) types, suggesting a differential affinity and binding capacity of the filter media for these compounds.

In summary, this study demonstrates that the phenolic compounds in ice grape pomace brandy

originate primarily from oak aging and consist mainly of phenolic acids and phenolic aldehydes. Using LC–MS and UPLC, a total of 14 phenolic compounds, including 12 oligomeric polyphenols and 2 hydrolyzable tannins—were identified, and seven major phenolics were quantitatively analyzed. The results revealed a positive correlation between the

roasting degree of oak chips and phenolic content, along with notable compositional differences linked to oak origin. Furthermore, all six filter paperboards tested significantly reduced phenolic levels, with mineral-containing boards exhibiting greater removal efficacy likely due to enhanced adsorption interactions.

Table 8 List of compounds identified in ice grape pomace brandy

No.	Compounds	t_R (min)	Formula	Theoretical m/z (Da)	Measured m/z	MS ²	Error (ppm)
1	Gallic acid	1.561	C ₇ H ₆ O ₅	169.0146	169.0135	125.0243	2.072
2	Vescalagin	3.316	C ₄₁ H ₂₆ O ₂₆	933.0634	933.0632	300.9978	2.104
3	2,5-dihydroxybenzoic acid	4.456	C ₇ H ₆ O ₄	153.0190	153.0193	109.0794	4.998
4	Caffeic acid	5.679	C ₉ H ₈ O ₄	179.0352	179.0343	135.0447	2.317
5	Vanillic acid	5.933	C ₈ H ₈ O ₄	167.0337	167.0343	152.0108	2.483
6	P-hydroxybenzoic acid	6.087	C ₇ H ₆ O ₃	137.0229	137.0238	137.0238	3.499
7	Chlorogenic acid	6.368	C ₁₆ H ₁₈ O ₉	353.0844	353.1002	191.0558/135.0454	-4.998
8	Vanillin	10.035	C ₈ H ₈ O ₃	151.1473	151.0394	151.0394	2.843
9	Syringic acid	16.2418	C ₉ H ₁₀ O ₅	197.0450	197.0445	197.0445	0.254
10	Syringaldehyde	13.851	C ₉ H ₁₀ O ₄	181.0500	181.0499	181.0499	2.015
11	Ellagic acid	16.168	C ₁₄ H ₆ O ₈	300.9984	300.9979	300.9979	0.012
12	Sinapaldehyde	17.573	C ₁₀ H ₁₀ O ₃	177.0551	177.0550	177.0550	2.142
13	4-Hydroxy-3-methoxycinnamaldehyde	17.969	C ₁₁ H ₁₂ O ₄	207.0657	207.0652	192.0420	0.071
14	Ferulic acid	18.279	C ₁₀ H ₁₀ O ₄	193.0500	193.0496	178.0624	0.335

Table 9 Contents (μg/mL) of 7 compounds in ice grape pomace brandies aged with different oak

Oak	UF	MA	MTF	MSF	SF
Gallic acid	43.5 ± 0.13c	63.45 ± 0.61bc	97.22 ± 0.13a	73.75 ± 0.13b	89.6 ± 0.15ab
P-hydroxybenzoic acid	5.16 ± 0.21c	85.87 ± 0.15c	125.11 ± 0.21b	115.43 ± 0.33b	159.33 ± 1.12a
Chlorogenic acid	-	16.22 ± 0.95b	14.23 ± 0.12c	16.91 ± 0.56b	21.13 ± 0.45a
Vanillic acid	-	174.17 ± 0.21c	219.24 ± 0.13b	263.55 ± 0.22a	202 ± 0.21b
Syringic acid	-	56.67 ± 1.1b	29.47 ± 0.44c	64.88 ± 0.66b	104.7 ± 0.22a
Vanillin	4.45 ± 0.78d	66.01 ± 0.54b	35.56 ± 0.65c	74.94 ± 1.21b	110.12 ± 0.64a
Syringaldehyde	-	124.87 ± 0.66b	62.71 ± 0.2c	139.02 ± 1.1b	274.1 ± 0.23a
Total	53.11	529.53	503.76	691.08	982.98

Note: Each analysis was performed in triplicate. All data was expressed as the mean value ± the standard deviation. Values with the different letters (a to d) in the same line indicate significant statistical differences ($P < 0.05$).

Table 10 Contents ($\mu\text{g/mL}$) of 7 compounds in ice grape pomace brandies after filtration with different filter paperboards

	Unfiltered	SCC-230	SCC-240	SCC-270	SCP-311	SCP-312	SCP-334
Gallic acid	89.60 $\pm$ 0.15a	81.51 $\pm$ 0.16b	80.66 $\pm$ 0.68b	80.53 $\pm$ 0.96b	80.16 $\pm$ 0.46b	83.11 $\pm$ 0.23b	77.52 $\pm$ 0.74c
P-hydroxybenzoic acid	159.33 $\pm$ 1.12a	128.65 $\pm$ 0.67c	136.36 $\pm$ 0.59b	133.16 $\pm$ 1.16b	129.66 $\pm$ 0.67c	133.64 $\pm$ 0.46b	129.61 $\pm$ 1.32c
Chlorogenic acid	21.13 $\pm$ 0.45a	14.66 $\pm$ 0.79bc	15.64 $\pm$ 0.44bc	12.61 $\pm$ 0.15c	16.64 $\pm$ 0.53b	13.34 $\pm$ 0.32c	12.34 $\pm$ 0.69c
Vanillic acid	202.0 $\pm$ 0.21a	181.56 $\pm$ 0.46bc	179.61 $\pm$ 0.66c	176.11 $\pm$ 0.64c	181.09 $\pm$ 0.51bc	183.55 $\pm$ 0.33bc	186.42 $\pm$ 0.31b
Syringic acid	104.7 $\pm$ 0.22a	94.65 $\pm$ 0.79b	93.66 $\pm$ 0.49b	88.12 $\pm$ 0.18c	87.26 $\pm$ 0.66c	91.55 $\pm$ 0.62bc	91.73 $\pm$ 0.46bc
Vanillin	110.12 $\pm$ 0.64a	101.13 $\pm$ 0.46b	99.6 $\pm$ 0.31b	100.21 $\pm$ 0.46b	97.56 $\pm$ 0.43c	96.64 $\pm$ 0.34c	91.2 $\pm$ 0.64d
Syringaldehyde	274.1 $\pm$ 0.23a	253.36 $\pm$ 0.41b	248.64 $\pm$ 0.43b	251.33 $\pm$ 0.33bc	242.54 $\pm$ 0.47c	249.65 $\pm$ 0.66b	241.1 $\pm$ 0.64c
Total	1083.64	951.94	945.38	941.28	926.13	943.84	933.23

Note: Each analysis was performed in triplicate. All data was expressed as the mean value $\pm$ the standard deviation. Values with the different letters (a to d) in the same line indicate significant statistical differences ($P < 0.05$).

4 Conclusion

Filtration is a crucial step in the production of ice grape pomace brandy, significantly impacting its quality. This study evaluated its effects using metallic content and phenolic compounds as indicators. Key findings reveal that filtration temperature significantly influenced the levels of seven metallic elements (Ca, Fe, Mg, Mn, K, Al, Zn), with 0 °C identified as the optimal temperature. Furthermore, compared to mineral-containing filter boards, pure fiber non-mineral filter boards markedly reduced the leaching of eight elements (Na, Mg, Al, K, Ca, V, Fe, Mn). Analysis of phenolic compounds identified 14 types, including 12 oligopolyphenols and 2 hydrolyzable tannins. While their content positively correlated with oak chip roasting degree, filtration caused a significant reduction. Importantly, the pure fiber non-mineral filter board also minimized this phenolic loss. These results collectively confirm the superior application value of pure fiber non-mineral filter boards, as they effectively mitigate undesirable metallic changes and better preserve valuable phenolic compounds during filtration.

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