Application Note
No. 193/2015

Determination of volatile acids in wine and juice

Distillation Unit K-355:
Volatile acids determination according to Schenk SA
1 Introduction

The main part (>95 %) of the volatile acidity in wine and juice is acetic acid which is formed by oxidative or anaerobic fermentation. The average level of acetic acid in a new dry table wine is less than 400 mg/L, though levels may range from undetectable up to 3 g/L. A too high level of volatile acids is an indicator for a low quality and acetous product. In Switzerland, for example, the tolerance level of volatile acids is 1200 mg/kg [1]. In the USA the legal limits are 1200 mg/kg volatile acids for white wine and 1400 mg/kg for red wine [2].

Here a method for the volatile acid determination, based on steam distillation and performed in the laboratories of Schenk SA in Rolle Switzerland, is presented. Steam distillation is the preferred method for volatile acid determination and described in detail in normative procedures [3, 4]. Importantly, the used distillation equipment can be used for volatile acids and alcohol determination [5].

2 Equipment

- Distillation Unit K-355 (alternatively also the K-360 can be utilized for distillation)
- External titrator
- Sample tubes 500 mL (043982)
- Beaker for sample collection
- Water aspirator vacuum pump
- Vacuum flask

3 Chemicals and Materials

Chemicals:
- Tartaric acid, crystalline
- Sodium hydroxide solution, 0.1 M
- Phenolphthalein solution, 1 %, in neutral alcohol, 70 % (m/v)
- Sulfuric acid (96 %) : water solution (1:4)
- Iodine solution, 1/64 N (1/128 mol/L)
- Starch solution, 25 g/L; Preparation according to SLMB 30A 4.2: A mixture of 500 mL glycerine and 500 mL water are heated to 70 °C. 25 g starch are added in small portions, heated up to 90 °C and then cooled. The solution is stable for at least 6 months.

For safe handling please pay attention to the corresponding MSDS.

Samples:
- Red wine and white wine samples used for an interlaboratory test with 31 participating laboratories as well as eight characteristic Swiss wine samples.
4 Procedure

The procedure was done according to Schenk SA, Rolle Switzerland. The volatile acidity is derived from the acetic acid present in wine in the free state and combined as salts. The official analysis method requires a separation of volatile acids by steam distillation of water and then condensation of the vapors. In case that carbon dioxide is present in wine it has to be eliminated prior to the distillation. Sulfur dioxide and sorbic acid are also distilled and would increase the results. Therefore, it is necessary to determine both and correct the volatile acid results by deducting the sulfur dioxide content.

Preparation of sample
For the elimination of carbon dioxide place about 50 mL of wine in a vacuum flask and apply vacuum to the flask with the water pump for one to two minutes while continuously shaking.

Steam distillation
Preheating of the distillation unit: Distill for 5:30 minutes with 100 % steam power and an empty glass tube.
Pipette 20 mL of wine or juice in the 500 mL sample tube. Add about 0.5 g of tartaric acid. A 500 mL beaker is attached to the outlet tube and filled with a small amount of distilled water in order to immerse the tube outlet in water and assure the complete collection of volatile acids. The sample is then distilled for 10 minutes by applying 100 % steam power. Between each sample distillation a cleaning step is performed including 3 minutes distillation with 100 % steam power.

Depending on the sample volume, the amount of volatile acids, the distillation time and the sodium hydroxide factor (Equation 1) the parameters have been optimized as shown in Table 1. The choice of 20 mL sample volume is in accordance with the OIV method [3], while 10 mL sample are suggested in the SLMB [4].

<table>
<thead>
<tr>
<th>Sample volume [mL]</th>
<th>Distillation time [min]</th>
<th>Factor (F) NaOH 0.1 M</th>
<th>Volume of distillate [mL]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>8</td>
<td>0.6</td>
<td>About 300</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>0.3</td>
<td>About 400</td>
</tr>
<tr>
<td>50</td>
<td>14</td>
<td>0.1</td>
<td>About 500</td>
</tr>
</tbody>
</table>

Titration
To quantify the volatile acids content add 3 drops of phenolphthalein to the distillate. Titrate with 0.1 M NaOH solution until the pink color remains stable for 10 seconds. Since sulfur dioxide is co-distilled with volatile acids during steam distillation the determined volatile acid content has to be corrected for its sulfur dioxide content by a second - iodometric - titration. Therefore, the distillate is acidified with 5 mL sulfuric acid (1:4). Titrate the sulfur dioxide with the 1/64 N iodine solution according to Reaction 1. To visually determine the SO\textsubscript{2} content a few mL of the starch solution are added. Starch and iodide form an intense blue iodine-starch complex, indicating the end of the titration.

\[
\text{SO}_2 + \text{I}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{I}^- + 4 \text{H}^+ + \text{SO}_4^{2-} \\
\text{Reaction 1}
\]

5 Calculation

The content of volatile acids in wine and juice is determined according to Equation 1 [4]. The factor F in Equation 1 is dependent on the sample volume as listed in Table 1.

\[
\text{Volatile acidity} = F \left( a \cdot t_1 - 10/64 \cdot b \cdot t_2 \right) \\
\text{Equation 1}
\]
Volatile acidity  \( g \) acetic acid / L

\[ \begin{align*}
\text{a} & \quad \text{titrated volume of NaOH 0.1 M [mL]} \\
\text{b} & \quad \text{titrated volume of iodine solution 1/64 N [mL]} \\
\text{t}_1 & \quad \text{titer of NaOH solution 0.1 M} \\
\text{t}_2 & \quad \text{titer of iodine solution 1/64 N} \\
F & \quad \text{factor NaOH}
\end{align*} \]

Example:
Sample volume: 20 mL
Titrated volume of NaOH 0.1 M: 2.7 mL
Titrated volume of iodine solution 1/64 N: 0.92 mL

Volatile acidity \( = 0.3 \left( 2.7 \cdot 1 - 10/64 \cdot 0.92 \cdot 1 \right) = 0.77 \text{ g/L} \)

The precision of the method according to [4]:
Repeatability \( r \) (all wines) = 0.04 g/L acetic acid
Reproducibility \( R \) (all wines) = 0.08 g/L acetic acid

NOTE:
Some wines include sorbic acid as a preservative. Since 96 % of sorbic acid is steam distilled with a distillate volume of 250 mL, its acidity must be subtracted from the volatile acidity. 100 mg of sorbic acid corresponds to an acidity of 0.89 mL NaOH 1 M or 0.053 g of acetic acid [3].

6 Results and Discussion

For this study Schenk SA tested two unknown wine samples, a red and a white wine, within a proficiency testing campaign with 31 participating laboratories as well as eight characteristic Swiss wine samples. The volatile acid content was determined in a single measurement for each sample. The volatile acid content is given in g acetic acid per liter wine. Measured volatile acid contents were in line with the average content determined by the 31 laboratories that performed the proficiency testing. The allowed accuracy limit was 0.05. From the tested samples one sample (Dunkel (Red)) was above the tolerance level [1] while the others were well below.

<table>
<thead>
<tr>
<th>Table 2: Results of the volatile acidity determination in red wine.</th>
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<tbody>
<tr>
<td><strong>Volatile acidity [g acetic acid/L]</strong></td>
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<tr>
<td>Average labs (31 labs)</td>
</tr>
<tr>
<td>Result determined with K-355</td>
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<table>
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<tr>
<th>Table 3: Results of volatile acidity determination in white wine.</th>
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<tr>
<td><strong>Volatile acidity [g acetic acid/L]</strong></td>
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<td>Average labs (31 labs)</td>
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<td>Result determined with K-355</td>
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<th>Table 4: Results of volatile acidity determination in red and white wine samples.</th>
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<tr>
<td><strong>Samples</strong></td>
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<tr>
<td>Garanoir (Red wine)</td>
</tr>
<tr>
<td>Dunkel (Red)</td>
</tr>
<tr>
<td>Garanoir (white)</td>
</tr>
<tr>
<td>Gewurtz (Red)</td>
</tr>
<tr>
<td>Chasselas (Red)</td>
</tr>
<tr>
<td>Gamay (Red)</td>
</tr>
<tr>
<td>Gewurtz (White)</td>
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<tr>
<td>Chasselas (White)</td>
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</table>
7 Conclusion

The determination of volatile acids in wine using the Distillation Unit K-355 provides reliable and well comparable results. With the method described, Schenk SA reported volatile acid concentrations in test samples that exactly represent the average value of the 31 testing labs. In addition, the K-355 used for steam distillation of volatile acids is also employed for the determination of the alcohol content in the mentioned samples. Hence, the K-355 has a broad application range in the wine and juice analysis.

8 Acknowledgement

Büchi Labortechnik AG would like to thank Schenk SA in Rolle, Switzerland, for sharing experience and providing the data shown in chapter 6.

9 References

[2] 27 CFR 4.21 - The standards of identity, (a) Class 1; grape wine (iv)

*The K-360 can also be used for alcohol and volatile acid determinations as this distillation unit fulfills the same requirements.