Application Note
No. 785/2021

Determination of volatile acids in wine

Dist Line:
Determination of volatile acids in wine by steam distillation and subsequent titration

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 dry table wine is less than 0.4 g/L. However, levels can range from undetectable up to 3 g/L. High levels of volatile acids are an indicator for a low quality and acetous product. In the European Union and Switzerland, the tolerance level of volatile acids is 18 mEq/L (1.08 g acetic acid/L) for white wine and 20 mEq/L (1.20 g acetic acid/L) for red wine [1, 2]. In the USA, the legal limits of volatile acids, expressed as acetic acid, are 1.20 g/L for white wine and 1.40 g/L for red wine [3].

Steam distillation is the preferred method for volatile acids determination and described in normative procedures [4, 5]. In this Application Note, a method for the measurement of volatile acids using the EasyDist instrument is described. Importantly, the used distillation system can be used for volatile acids and alcohol determination [6, 7, 8, 9].

2. Equipment

- EasyDist with glass splash protector (11K36512040)
- Metrohm Eco Titrator with pH electrode (11072748)
- Sample Tubes 300 mL (037377)

3. Chemicals and Materials

Chemicals:

- Sodium hydroxide 0.1 mol/L, VWR (31770.294)
- DL-Tartaric acid, 99 %, Alfa Aesar (A10683.30)
- Tartaric acid solution 0.1 g/mL: place 25 g of tartaric acid in a bottle and fill it up to 250 mL with deion. water[1]
- Acetic acid 0.1 mol/L, VWR (300652.1000)
- Acetic acid 0.01 mol/L (made from 0.1 mol/L)
- Phenolphthalein solution 1 % in Ethanol
- Sulfuric acid solution (1 aliquot sulfuric acid (96 %): 4 aliquots deion. H2O)
- Iodide-iodate solution Titrisol® 1/64 N (1/128 mol/L), Merck (1.09914.0001)
- 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 a safe handling please pay attention to all corresponding MSDS!

Samples:
In Table 1, the samples used for the measurements are shown. The samples were provided by Coop central laboratory. The declared volatile acidity refers to HPLC measurements.

Table 1: Samples details.

No.	Sample name	Sample details	Declared volatile acidity [g acetic acid/L]
1	Utiel Rouge	Red wine	0.8
2	Swiss Syrah		1.1
3	Sauternes	White wine	1.0
4	La Cote		0.2

[1]Only if a BasicDist or MultiDist instrument is in use.

4. Procedure

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 followed by titration. Sulfur dioxide and sorbic acid are also distilled and lead to increased results. Therefore, it is necessary to determine both and correct the volatile acid results by subtracting the corresponding values.

4.1 Sample preparation

The samples were stored closed at room temperature in dark until the day of analysis. On the day of analysis, the sealed glass bottles were opened. Then, about 100 mL of the wine was transferred into another glass bottle which was shaken for two minutes to release the CO_2.

4.2 Steam distillation

System preparation: Connect an empty sample tube to the EasyDist instrument and place a vessel under the condenser to collect the distillate. Run a preheating before starting the first determination.

Distillation of blanks, references and samples: Add 20 mL of deion. H_2O (blanks), 20 mL of acetic acid stock solution 0.01 mol/L (approx. 12 mg; reference) or 20 mL of the sample to a 300 mL sample tube. Then, add 0.5 g of tartaric acid to each sample tube and connect it to the Distillation Unit[2]. Before distillation, place an 800 mL glass beaker filled with approx. 80 mL of deion. H_2O below the condenser outlet tube. Make sure that the tube outlet is immersed in water to assure the complete collection of volatile acids during distillation. Start the distillation according to the parameters listed in Table 2.

Table 2: Distillation parameters EasyDist.

Method parameters EasyDist		Instrument Settings	
Steam Steps	No	MaxAccuracy mode	On
Steam Power	80 %	Chiller	Chiller F-314
Level Detection	Off	Chiller temperature	15°C
Distillation Time	1200 s		

4.3 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 solution (1:4). Titrate the sulfur dioxide with the 1/64 N iodide-iodate solution according to Reaction 1. To visually determine the SO_2 content, approx. 3 mL of the starch solution are added. Starch and iodine form an intense blue iodine-starch complex, indicating the end of the titration.

$$SO_2 + I_2 + 2\ H_2O \rightarrow 2\ I^- + 4\ H^+ + SO_4^{2-}$$ Reaction 1

[2]If a BasicDist or MultiDist instrument is in use, the acid pump can be used to dose 5 mL of a previously prepared tartaric acid solution (0.1 g/mL) to be more time efficient. It is possible to program the dosing step in the method accordingly.

4.4 Calculation

The calculation of the recovery rate for reference samples is calculated according to equation (1).

$$\text{Recovery rate [\%]} = ((a_{ref}-a_{blank})\cdot c_{NaOH}\cdot t_1)/(v_{AcOH}\cdot c_{AcOH}\cdot t_3)\cdot 100 \quad (1)$$

The content of volatile acids in wine is determined according to equation (2) [5]. As described in the OIV method, 0.3 is used as factor F [4].

$$\text{Volatile acidity} = F\ (a\cdot t_1\text{-}10/64\cdot b\cdot t_2) \quad (2)$$

Volatile acidity	g acetic acid / L
a	titrated volume of NaOH 0.1 M [mL]
b	titrated volume of iodide-iodate solution 1/64 N [mL]
c	concentration of titrant or stock solution [mol/L]
v	volume of stock solution
t_1	titer of NaOH solution 0.1 M
t_2	titer of iodide-iodate solution 1/64 N
t_3	titer of AcOH (acetic acid)
F	factor

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 0.89 mL of NaOH (1 mol/L) or 0.053 g of acetic acid [4].

5. Result

Table 3 shows the results of all measurements. The recovery rates of the reference samples are within 101.3 % and 104.7 %. Therefore, the system delivers reproducible results for acetic acid at the level of around 0.7 g/L. The volatile acidity determined for sample No. 1 is 1.09±0.01 g/L (declared: 0.8 g/L). For sample No. 2, a volatile acidity of 1.12±0.00 g/L was measured (declared: 1.1 g/L). The measured volatile acidity for sample No. 3 and 4 is 1.13±0.01 g/L (declared: 1.0 g/L) and 0.30±0.01 g/L (declared: 0.2 g/L).

Table 3: Results of all performed measurements.

Type	Titrated volume NaOH [mL]	ØBlank volume NaOH [mL]	Titrated volume iodide-iodate [mL]	Recovery rate [%]	Volatile acidity [g acetic acid/L]	ØVolatile acidity [g acetic acid/L]	RSD [%]
Blank	0.2020	0.2057	n/a	-	-	-	2.0
	0.2100						
	0.2050						
Acetic acid (reference)	2.2420			**101.3**	0.61	**0.66±0.05**	1.7
	2.3110			**104.7**	0.69		
	2.2810			**103.2**	0.69		
Red wine (No. 1)	4.4310	n/a	5.2690	-	1.08	**1.09±0.01**	1.1
	4.4420		5.1810		1.09		
	4.5610		5.6190		1.11		
Red wine (No. 2)	4.5890		5.4940		1.12	**1.12±0.00**	0.1
	4.6120		5.5750		1.12		
	4.6020		5.5250		1.12		
White wine (No. 3)	4.9760		7.4440		1.15	**1.13±0.01**	1.0
	5.0440		8.2260		1.13		
	5.0270		8.2290		1.12		
White wine (No. 4)	1.7580		4.6000		0.31	**0.30±0.01**	4.5
	1.7240		4.8880		0.29		
	1.7030		4.7330		0.29		

6. Comparison to Standard Methods

Table 4 shows a comparison between the method of this Application Note, the OIV method [4] and the method described in the SLMB [5].

Table 4: Comparison between the method of this Application Note (785), the OIV method [4] and the SLMB method [5].

Parameter	Application Note 785	OIV-MA-AS313-02:R2009	SLMB 30A
Addition of tartaric acid	yes	yes	no
Sample volume [mL]	20 mL	20 mL	10 mL
Factor F	0.3	0.3	0.6
Distillate volume [mL]	620 mL	≥250 mL	100 mL
Distillation Time [s]	20 min	not given	30 min
Subtraction of SO_2	yes	yes	yes
Subtraction of sorbic acid	yes (if present)	yes (if present)	yes (if present)

7. Conclusion

The determined recovery rates for the reference samples at the level of around 0.7 g acetic acid/L are close to 100 %. Moreover, the measured volatile acidity of the wine samples is reproducible and close to the values declared from Coop central lab. Nevertheless, in comparison to the declared values, the presented method gives slightly higher values in some cases (e.g. sample No. 1). The method of this Application Note is slightly more sensitive to non-volatile acids (e.g. lactic acid; see Appendix) which may be a reason for this.

8. References

[1] 817.022.12: Verordnung des EDI über Getränke (Stand am 1. Juli 2020)
[2] Delegierte Verordnung (EU) 2019/934 der Kommission vom 12. März 2019
[3] 27 CFR 4.21 – The standards of identity, (a) Class 1; grape wine (iv).
[4] Compedium of the international methods of analysis – OIV, Method OIV-MA-AS313-02:R2009.
[5] Bestimmung der flüchtigen Säuren durch Wasserdampfdestillation, Schweizer Lebensmittelbuch, SLMB, 30 A Wein aus Trauben, Untersuchungsmethode 5.2, 1993.
[6] Application Note No. 756/2021 Alcohol determination in ethanol/water mixtures
[7] Application Note No. 757/2021 Alcohol determination in wines
[8] Application Note No. 758/2021 Alcohol determination in beer
[9] Application Note No. 759/2021 Alcohol determination in spirits

9. Appendix

Table 5 shows the results of measurements performed using acetic acid and lactic acid. For distillation, the parameters shown in Table 2 were used. The distillations were carried out in order to check, if the instrument meets the requirements regarding the recovery rates mentioned in OIV-MA-AS313-02:R2009 (acetic acid: ≥99.5 %; lactic acid: ≤0.5 %). The recovery rates for acetic acid and lactic acid are outside this range. Therefore, the EasyDist or higher models of the Dis Line do not meet the requirements of the norm.

Table 5: Measurements performed using acetic acid (0.1 mol/L) and lactic acid (1.0 mol/L).

Type	Titrated volume NaOH [mL]	ØBlank volume NaOH [mL]	Recovery rate [%]	ØRecovery rate [%]	RSD [%]
Blank	0.1620	0.1580	-	-	2.2
	0.1560				
	0.1560				
Acetic acid (20 mL; 0.1 mol/L)	19.9100		**98.9**	**99.1±0.2**	0.2
	19.9910		**99.3**		
	19.9730		**99.2**		
Lactic acid (20 mL; 1.0 mol/L)	6.7590		**3.3**	**3.3±0.1**	3.0
	6.9390		**3.4**		
	6.5480		**3.2**		