Metrohm

Application Bulletin 225/3 e

Simple wine analysis

Branch

General analytical chemistry; food, stimulants, beverages, flavours;

Keywords

Wine, pH value, ascorbic acid; titration; free sulfurous acid; total acid; total sulfurous acid; branch 1; branch 7; 6.0309.100; 6.0258.600

Summary

This bulletin describes the determination of the following parameters in wine: pH value, total titratable acid, free sulfurous acid, total sulfurous acid as well as ascorbic acid and other reductones.

Instruments

- Titrator with MET and SET mode
- 20 mL burette
- Stirrer

Electrode

Double Pt-sheet electrode	6.0309.100
LL Unitrode with Pt 1000	6.0258.600

Reagents

- Sodium hydroxide solution, c(NaOH) = 0.1 mol/L
- Potassium iodate solution c(1/6 KIO_3) = 1/64 mol/L
- Potassium iodide, puriss p.a.
- Sodium hydroxide solution, c(NaOH) = 1 mol/L
- Sulfuric acid, w(H_2SO_4) = 25%
- Glyoxal, w($C_2H_2O_2$) = 40%
- Buffer solutions pH 4 and 7

Solutions

Titrant NaOH	c(NaOH) = 0.1 mol/L
Titrant KIO_3	c(1/6 KIO_3) = 1/64 mol/L = 0.00260 mol/L
	If possible this solution should be bought from a supplier
Glyoxal solution	w($C_2H_2O_2$) = 40% 200 mL w($C_2H_2O_2$) = 40% is adjusted with c(NaOH) = 1 mol/L to pH = 7.0. The solution has to be stored in a dark bottle in a refrigerator. It may precipitate and get yellow after lengthy storage.

Sample preparation

No sample preparation is required

1 pH value

Analysis

The Unitrode is calibrated with buffer solutions pH 4 and 7. Afterwards the electrode is rinsed with dist. water and then immersed in the undiluted wine sample. Wait until the drift criterion is met.

Parameters

Mode	MEAS pH
Signal drift	1 mV/min
Min. waiting time	180 s

Comments

- The pH value of wines usually lies between 3.3 and 4.0. pH values higher than 3.8 can cause quality problems.
- When not in use, the combined pH glass electrode is stored in storage solution.
- If used frequently, the electrode has to be calibrated once a week. If the electrode has not been used for a longer period of time, calibration is carried out before the first series of measurements.
- Don’t clean or dry the electrode with paper tissue. Never let the membrane of the electrode get dry.

2 Total titratable acid

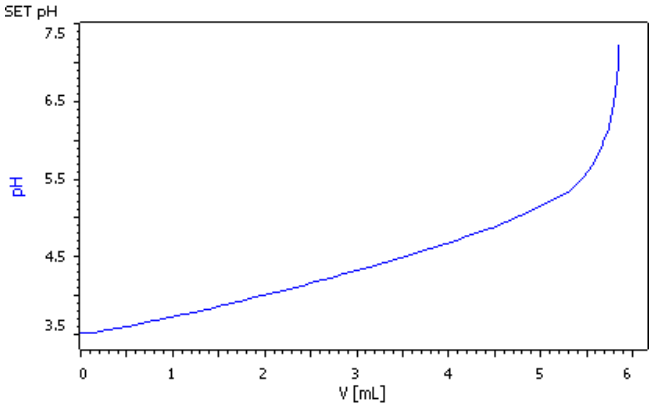

Figure 1 : Set titration of white wine to pH 7

Analysis

The calibrated pH glass electrode can be used for this titration. First, carbon dioxide must be removed from the sample. This is best done by passing nitrogen through the sample for 3 to 5 min.

Exact 10.0 mL wine and approx. 10 mL dist. water are pipetted into a titration beaker. The CO_2 is removed as described above. While stirring, the solution is then titrated with c(NaOH) = 0.1 mol/L to pH = 7 using the SET mode.

Parameters

Mode	SET pH
EP1 at pH	7.00
Dynamics	2
Max. rate	10 mL/min
Min. rate	25 µL/min
Stop criteria	Drift
Stop drift	20 µL/min
Stop vol.	20 mL
Stirring rate	6

Calculation

The result is given in g/L tartaric acid.

$$\text{g/L tartaric acid} = \frac{V_{EP1} \times c_{NaOH} \times M_A}{V_S \times 2} = V_{EP1} \times C_F$$

V_{EP1}: Titrant consumption in mL until pH 7 is reached

C_{NaOH}: Concentration of titrant in mol/L, here 0.1 mol/L

M_A: Molar mass of analyte, here 150.087 g/mol

V_S: Sample volume in mL, here 10 mL

2: Stoichiometric factor

C_F: 0.75 (conversion factor for the given parameters)

Comments

- After decomposition of the acid, the value for the total titratable acid normally is between 4.0 and 6.5 g/L.
- If sample volume other than 10.0 mL or if a different titrant concentration is used the conversion factor (C_F) must be modified accordingly.

3 Free sulfurous acid

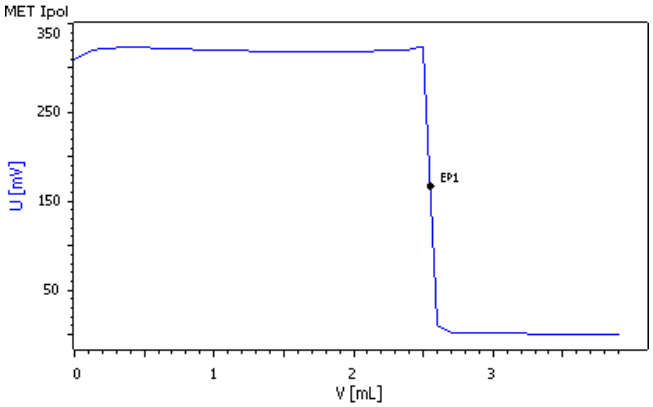

Figure 2: Determination of free SO_2 content in red wine

Analysis

To determine the free sulfurous acids, the double Pt sheet electrode is used and connected to the «Pol.» input of the instrument.

50 mL sample is pipetted into a titration beaker, 1 g KI is added and the mixture is stirred briefly. After the addition of 5 mL sulfuric acid w(H_2SO_4) = 25%, it is titrated with c(1/6 KIO_3)= 1/64 mol/L using the MET Ipol mode.

Parameters

Mode	MET Ipol
Pause	20 s
Min waiting time	10 s
Signal drift	off
I(pol)	1 µA
Stop volume	5 mL
EP criterion	30 mV
EP recognition	greatest

Calculation

$$\text{mg/L free } SO_2 = \frac{V_{EP1} \times c_{1/6\ KIO3} \times M_A \times 3 \times 1000}{V_S} = V_{EP1} \times C_F$$

V_{EP1}: Titrant consumption in mL

$C_{1/6\ KIO3}$: Concentration of titrant in mol/L, here 0.0026 mol/L

M_A: Molar mass of analyte, here 64.066 g/mol

V_S: Sample volume in mL, here 50 mL

3: Stoichiometric factor

C_F: 10 (conversion factor for the given parameters)

Comments

- The content of free sulfurous acid can widely vary depending on the country of origin and type of wine. It usually lies between 20 and 100 mg/L SO_2.
- New double Pt-sheet electrodes or electrodes that have been out of use for a longer period of time may respond poorly. If only small potential jumps are obtained, the electrode can be regenerated as follows: Dissolve a spatula tip of sodium sulfite in 50 mL of deionized water and immerse the electrode in this solution for an hour.
- If the determination of the free sulfurous acid shows a result exceeding the maximum permitted value, check for the presence of ascorbic acid according to the method described under point 5 of this AB. Then the real content of free sulfurous acid is calculated as follows:
  $\text{mg/L free } SO_2 = (V_{EP1\_free\ acid} - V_{EP1\_ascorbic\ acid}) \times C_F$

4 Total sulfurous acid

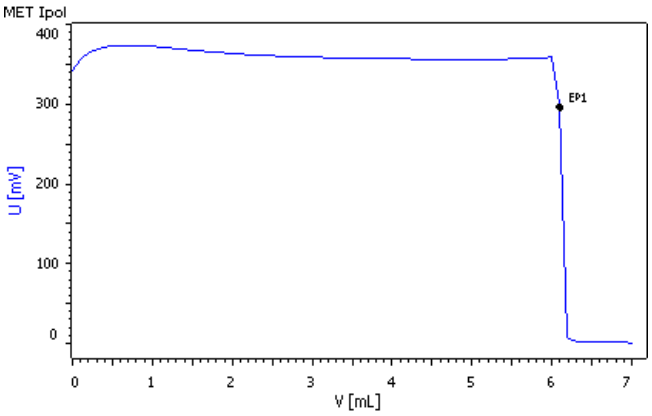

Figure 3: Determination of total SO_2 content in red wine

Analysis

To determine the total sulfurous acid, the bound sulfuric acid has to be released first. This is done by means of hydrolysis with the sodium hydroxide solution. For that, a Pt electrode is used.

50 mL sample is pipetted into a titration beaker, 25 mL of c(NaOH) = 1 mol/L is added and the mixture is stirred briefly for 10 min. Then, 1 g KI is added. Finally, 25 mL w(H_2SO_4) = 25% is added and titrated immediately until after the first equivalence point with c(1/6 KIO_3)= 1/64 mol/L using the MET Ipol mode.

Parameters

Mode	MET Ipol
Pause	20 s
Start volume	0.3 mL
Min waiting time	10 s
Signal drift	Off
I(pol)	1 µA
Stop volume	20 mL
EP criterion	30 mV
EP recognition	greatest

Calculation

$$\text{mg/L total } SO_2 = \frac{V_{EP1} \times c_{1/6\ KIO3} \times M_A \times 3 \times 1000}{V_S} = V_{EP1} \times C_F$$

V_{EP1}: Titrant consumption in mL

$C_{1/6\ KIO3}$: Concentration of titrant in mol/L, here 0.0026 mol/L

M_A: Molar mass of analyte, here 64.066 g/mol

V_S: Sample volume in mL, here 50 mL

3: Stoichiometric factor

C_F: 10 (conversion factor for the given parameters)

Comments

- The allowed maximum value for the total sulfurous acid depends on the producing country and sort of wine and varies widely between 160 and 450 mg/L SO_2. White wines and dessert wines exhibit higher values than red wines.
- For treatment of the double Pt sheet electrode, see remarks in chapter 3, «free sulfurous acid».
- The determination of the total sulfurous acid can also be carried out directly after the titration of the free sulfurous acid, using the same beaker. Add sodium

hydroxide solution to the titrated sample to make it alkaline, and then continue with the analysis as described in this chapter. The total sulfurous acid is then calculated from the sum of the EPs of the two titrations.

- The method described here is not specific for total acid. Other reducing substances (vitamin C and other reductones) are also determined.

5 Ascorbic acid and other reductones

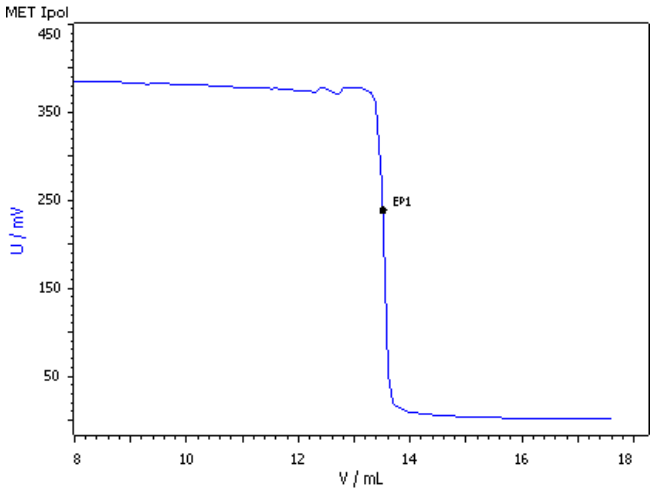

Figure 4: Titration curve of the bi-voltametric ascorbic acid determination with iodine

Analysis

50 mL sample is pipetted into a titration beaker, 2 mL of the glyoxal solution is added and then the mixture is stirred briefly for 5 min. Then, 25 mL w(H_2SO_4) = 25% is added (no KI) and titrated immediately with c(1/6 KIO_3)= 1/64 mol/L using the MET Ipol mode.

Parameters

Mode	MET Ipol
Pause	20 s
Min waiting time	10 s
Signal drift	Off
I(pol)	1 µA
Stop volume	5 mL
EP criterion	30 mV
EP recognition	greatest

Calculation

$$\beta_{Aa} = \frac{V_{EP1} \times c_{1/6\ KIO3} \times M_A \times 3 \times 1000}{V_S} = V_{EP1} \times C_F$$

β_{Aa}: Concentration of ascorbic acid in mg/L

V_{EP1_C}: Titrant consumption in mL

$C_{1/6\ KIO3}$: Concentration of titrant in mol/L, here 0.0026 mol/L

M_A: Molar mass of analyte, here 176.13 g/mol

V_S: Sample volume in mL, here 50 mL

3: Stoichiometric factor

C_F: 27.5 (conversion factor for the given parameters)

Comments

- The addition of the glyoxal solution ensures that no SO_2 is determined together with the ascorbic acid.
- This method does not determine ascorbic acid alone. Under the given conditions other oxidizable compounds will also be determined. For a more selective titration, the method with 2,6-dichlorophenol indophenol (DPIP) as titrant should be used.

References

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