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# Application Bulletin

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Of interest to: Wine analysis, food

AG 1, 7

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## Simple wine analysis with the Titrino

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### Summary

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

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### Instruments and accessories

- 702 SET/MET Titrino or 719 SET Titrino
  - 2.728.0040 Magnetic Stirrer
  - Two 6.3014.223 Exchange Units
  - Printer if necessary, e.g. 2.140.002X Citizen iDP562RS dot matrix printer with 6.2125.050 printer cable
  - 6.0258.000 LL Unitrode with Pt 1000 temperature sensor (combined pH glass electrode for the determination of the pH value and the total titratable acid)
  - 6.0309.100 double Pt sheet electrode with 6.2104.020 electrode cable (for the determination of the free and total sulfurous acid)
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### Reagents

#### *For the pH value:*

- Buffer solutions pH = 4.00 (6.2307.100) and pH = 7.00 (6.2307.110)

#### *For the total titratable acid:*

- Titrant: sodium hydroxide solution,  $c(\text{NaOH}) = 0.1 \text{ mol/L}$  (Exchange Unit 1)
- Possibly nitrogen from a compressed gas cylinder (for the removal of  $\text{CO}_2$ )

#### *For the free and total sulfurous acid:*

- Titrant: iodide/iodate solution,  $c(1/6 \text{ KIO}_3) = 1/64 \text{ mol/L}$  (Exchange Unit 2): Dissolve 0.5573 g potassium iodate (dried at a temperature not exceeding  $150 \text{ }^\circ\text{C}$ ) in approx. 700 mL dist. water. Add 3.5 g potassium iodide and dissolve it, then make up to 1 L with dist. water.
- Potassium iodide, puriss. p.a.
- Sulfuric acid,  $w(\text{H}_2\text{SO}_4) = 25\%$
- Sodium hydroxide solution,  $c(\text{NaOH}) = 1 \text{ mol/L}$

## Analysis

### 1. pH value

Calibrate the pH glass electrode using the CAL mode of the Titrino. Afterwards rinse the electrode with dist. water, dab it with a soft paper tissue (e.g. Kleenex) and immerse it in the undiluted wine sample. When the drift criterion has been met, the value is shown in the display or printed out. The measured pH value is stored as constant C40 in the Titrino.

#### Remarks

- The pH value of wines usually lies between 3.3 and 4.0. pH values higher than 3.8 can cause stability problems.
- When not in use, the combined pH glass electrode is stored in  $c(\text{KCl}) = 3 \text{ mol/L}$ . 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 prior to the first series of measurements.

### 2. Total titratable acid

The calibrated pH glass electrode is used for this titration. Carbon dioxide must first be removed from the sample. This is best done by passing nitrogen through the wine sample for 3 ... 5 min. Another possibility is to heat the sample solution to boiling point, then immediately cool it down again.

Pipet 10.0 mL wine and approx. 10 mL dist. water into a glass beaker and remove the  $\text{CO}_2$  from the sample as described above. While stirring, titrate with  $c(\text{NaOH}) = 0.1 \text{ mol/L}$  to  $\text{pH} = 7.0$  using the SET mode (see appendix for parameter settings).

#### Calculation

The result is given in g/L tartaric acid. If a sample volume other than 10.0 mL or if a different titrant concentration is used, the conversion factor has to be modified accordingly.

$$\text{g/L tartaric acid} = \text{EP1} * \text{C01}$$

$$\text{EP1} = \text{titrant consumption in mL}$$

$$\text{C01} = 0.75 \text{ (conversion factor)}$$

#### Remark

After decomposition of the acid, the value for the total titratable acid normally lies between 4.0 and 6.5 g/L.

### 3. Free sulfurous acid

The double Pt sheet electrode is used and connected to the «Pol» input of the Titrino.

Pipet 50 mL wine into a glass beaker. Add approx. 1 g KI and 5 mL  $w(\text{H}_2\text{SO}_4) = 25\%$  and titrate immediately with the iodide/iodate solution using the Ipol mode [ $I(\text{pol}) = 1 \mu\text{A}$ ]. When working with the 702 SET/MET Titrino it is preferable to use the MET Ipol mode. With the 719 SET Titrino, on the other hand, only titrations to a

preset endpoint (SET titrations) can be carried out (see appendix for parameter settings).

#### **Calculation**

$$\text{mg/L SO}_2 = \text{EP1} * \text{C01}$$

EP1 = titrant consumption in mL

C01 = 10 (conversion factor)

#### **Remarks**

- The content of free sulfurous acid can widely vary depending on the country and sort of wine. It usually lies between 20 and 100 mg/L SO<sub>2</sub>.
- New double Pt sheet electrodes or electrodes that have been out of use for a longer period of time may respond poorly. If any at all, only small potential jumps are obtained. In this case the electrode can be regenerated as follows:

Connect both Pt sheets to the negative pole of a DC supply (e.g. 4.5 V battery). Connect a Pt wire electrode or an iron nail to the positive pole. While stirring, immerse the electrodes in a diluted sulfuric acid solution (also containing some sulfite) and electrolyze for approx. 3 min. During this procedure gas bubbles should form on the Pt sheets. Afterwards the electrodes are removed from the solution and thoroughly rinsed with dist. water.

### **4. Total sulfurous acid**

The same type of electrode (double Pt sheet electrode) is used for this titration as for the determination of the free sulfurous acid. The parameter settings, however, are different (see appendix). The bound sulfurous acid has first to be released by means of hydrolysis with sodium hydroxide solution.

Pipet 50 mL wine into a glass beaker, add 25 mL c(NaOH) = 1 mol/L, stir briefly and allow to stand for 10 min. Afterwards add approx. 1 g KI and 10 mL w(H<sub>2</sub>SO<sub>4</sub>) = 25% and titrate **immediately** with the iodide/iodate solution as described under 3.

#### **Calculation**

$$\text{mg/L SO}_2 = \text{EP1} * \text{C01}$$

EP1 = titrant consumption in mL

C01 = 10 (conversion factor)

#### **Remarks**

- The allowed maximum value for the total sulfurous acid depends on the country and sort of wine and varies greatly between 160 and 450 mg/L SO<sub>2</sub>. White wines and dessert wines exhibit higher values than red wines.
- Please see 3. for the treatment of the double Pt sheet electrode.
- The determination of the total sulfurous acid can also be carried out directly after the titration of the free sulfurous acid, using the same sample solution. Add enough sodium hydroxide solution to the titrated sample to make it alkaline, then continue with the analysis as described above. The total sulfurous acid is then calculated from the sum of the titrant consumption of the two titrations.

- The method described here is not specific. Other reducing substances (vitamin C, certain reductones) are also determined. This is especially true for wines with a residual sugar content >5 g/L. The most reliable values are obtained by using the distillation method.

## Figures

```
'pa
702 SM Titrino          09139  702.0020
date 2000-03-07      time 15:41      0
MEAS pH              pH
parameters
>measuring parameters
  signal drift          1 mV/min
  equilibr.time        180 s
  meas.input:          1
  temperature          25.0 °C
>statistics
  status:              OFF
>preselections
  req.ident:           OFF
  req.sampl size:     OFF
  activate pulse:     OFF
=====
```

**Fig. 1:** Parameter settings for the pH measurement.

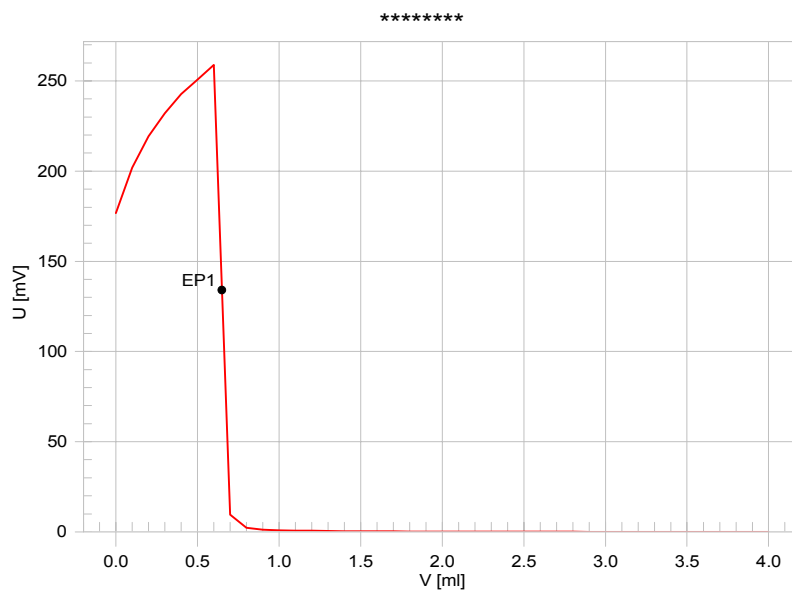
```
'pa
702 SM Titrino          09139  702.0020
date 2000-03-07      time 15:47      0
SET pH              tot acid
parameters
>SET1
  EP at pH             7.00
  dynamics             2
  max.rate            10.0 ml/min
  min.rate            25.0 µl/min
  stop crit:          drift
  stop drift          20 µl/min
>SET2
  EP at pH             OFF
>titration parameters
  titr.direction:     +
  start V:            OFF
  pause              0 s
  meas.input:        1
  temperature        25.0 °C
>stop conditions
  stop V:             abs.
  stop V             20 ml
  filling rate       max. ml/min
>statistics
  status:            OFF
>preselections
  conditioning:      OFF
  req.ident:         OFF
  req.sampl size:   OFF
  activate pulse:   OFF
=====
```

**Fig. 2:** Parameter settings for the determination of the total titratable acid.

```
'pa
702 SM Titrino      09139  702.0020
date 2000-03-08   time 09:34    2
MET Ipol          freeSO2
parameters
>titration parameters
  V step           0.10 ml
  titr.rate        max. ml/min
  signal drift     OFF mV/min
  equilibr.time    10 s
  start V:         OFF
  pause           20 s
  I(pol)          1 µA
  electrode test:  OFF
  temperature     25.0 °C
>stop conditions
  stop V:          abs.
  stop V          4 ml
  stop U          OFF mV
  stop EP         9
  filling rate    max. ml/min
>statistics
  status:         OFF
>evaluation
  EPC             30 mV
  EP recognition: greatest
  fix EP1 at U   OFF mV
>preselections
  req.ident:      OFF
  req.smpl size:  OFF
  activate pulse: ON
=====
```

**Fig. 3:** Parameter settings on the 702 SET/MET Titrino for the determination of the free sulfurous acid (MET Ipol mode).

```
'fr
702 SM Titrino      09139  702.0020
date 2000-03-08   time 09:34    2
U(init)           19 mV MET Ipol freeSO2
EP1               0.650 ml      134 mV
free SO2          6.50 mg/l
stop V reached
=====
```

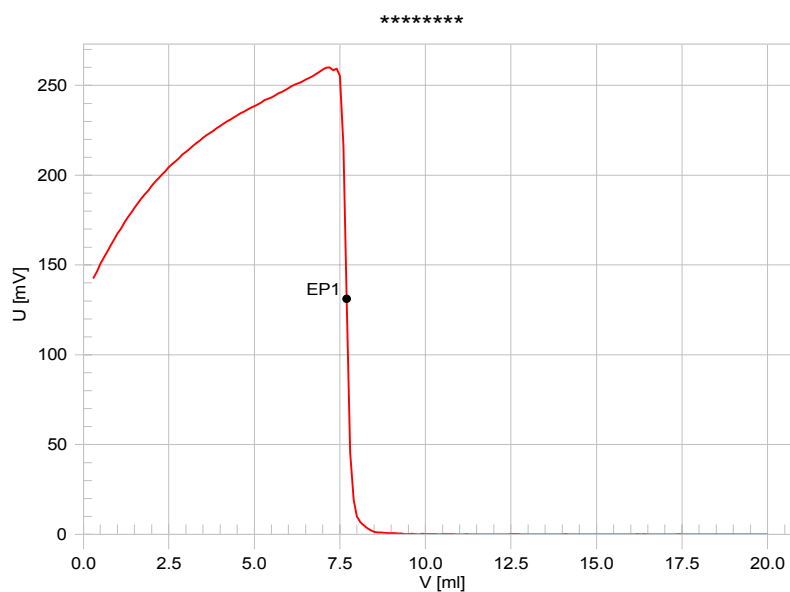


**Fig. 4:** Result block and titration curve for the determination of the free sulfurous acid in wine using the 702 SET/MET Titrino.

```
'pa
702 SM Titrino      09139  702.0020
date 2000-03-08   time 10:13    3
MET Ipol          tot SO2
parameters
>titration parameters
  V step          0.10 ml
  titr.rate       max. ml/min
  signal drift    OFF mV/min
  equilibr.time   0 s
  start V:        abs.
  start V         0.3 ml
  dos.rate        max. ml/min
  pause          20 s
  I(pol)         1 µA
  electrode test: OFF
  temperature     25.0 °C
>stop conditions
  stop V:         abs.
  stop V          20 ml
  stop U          OFF mV
  stop EP         9
  filling rate    max. ml/min
>statistics
  status:         OFF
>evaluation
  EPC            30 mV
  EP recognition: greatest
  fix EP1 at U   OFF mV
>preselections
  req.ident:      OFF
  req.smpl size: OFF
  activate pulse: ON
=====
```

**Fig. 5:** Parameter settings on the 702 SET/MET Titrino for the determination of the total sulfurous acid (MET Ipol mode).

```
'fr
702 SM Titrino      09139  702.0020
date 2000-03-08   time 10:13    3
U(init)           13 mV MET Ipol tot SO2
EP1               7.701 ml      131 mV
tot SO2           77.01 mg/l
stop V reached
=====
```



**Fig. 6:** Result block and titration curve for the determination of the total sulfurous acid in wine using the 702 SET/MET Titrino.

```

'pa
719 S Titrino          06125  719.0020
date 2000-03-07      time 16:15      1
SET Ipol              freeSO2
parameters
>SET1
  EP at U              20 mV
  dynamics             300 mV
  max.rate            5 ml/min
  min.rate            10 µl/min
  stop crit:         time
  stop time          10 s
>SET2
  EP at U              OFF mV
>titration parameters
  titr.direction:     -
  start V:            abs.
  start V             0.3 ml
  dos.rate            30 ml/min
  pause              20 s
  I(pol)             1 µA
  electrode test:     ON
  temperature        25.0 °C
>stop conditions
  stop V:            abs.
  stop V             10 ml
  filling rate       max. ml/min
>statistics
  status:           OFF
>preselections
  conditioning:     OFF
  req.ident:        OFF
  req.smpl size:    OFF
  activate pulse:   OFF
=====
    
```

**Fig. 7:** Parameter settings on the 719 SET Titrino for the determination of the free sulfurous acid (SET Ipol mode).

```

'pa
719 S Titrino          06125  719.0020
date 2000-03-07      time 16:20      2
SET Ipol              tot SO2
parameters
>SET1
  EP at U              20 mV
  dynamics             100 mV
  max.rate            10 ml/min
  min.rate            10 µl/min
  stop crit:         time
  stop time          10 s
>SET2
  EP at U              OFF mV
>titration parameters
  titr.direction:     -
  start V:            abs.
  start V             0.3 ml
  dos.rate            30 ml/min
  pause              20 s
  I(pol)             1 µA
  electrode test:     ON
  temperature        25.0 °C
>stop conditions
  stop V:            abs.
  stop V             50 ml
  filling rate       max. ml/min
>statistics
  status:           OFF
>preselections
  conditioning:     OFF
  req.ident:        OFF
  req.smpl size:    OFF
  activate pulse:   OFF
=====
    
```

**Fig. 8:** Parameter settings on the 719 SET Titrino for the determination of the total sulfurous acid (SET Ipol mode).