
Application Bulletin

Of interest to: Food analysis, Viticulture

A G 1, 7

Simple wine analysis with the Titrino

Summary

This Bulletin describes following analysis methods for wines:
pH value, titrable total acid, free sulphurous acid and total sulphurous acid.

Apparatus and accessories

- SM-Titrino 2.702.0010 or SET-Titrino 2.719.0010
 - Magnetic swing-out stirrer 2.728.0040
 - Two exchange units 6.3026.220
 - Ev. printer
 - LL-Unitrode with Pt 1000 Ohm temperature sensor 6.0258.000 (comb. pH glass electrode for pH value and titrable total acid)
 - Double Pt sheet electrode 6.0309.100 with electrode cable 6.2104.020 (for the sulphurous acids)
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Reagents

For the pH value

- Buffer solutions pH = 7.0 (6.2307.110) and pH = 4.0 (6.2307.100)

For the titrable total acid

- Titrant; $c(\text{NaOH}) = 0.1 \text{ mol/L}$ (exchange unit)
- Ev. nitrogen from pressure bottle (degassing of CO_2)

For the sulphurous acids

- Titrant: iodide/iodate solution (exchange unit).
Dissolve 0.5573 g potassium iodate, dried at max. 150 °C in ca. 700 mL dist. H_2O , add and dissolve 3.5 g potassium iodide and fill up to 1 L with dist. H_2O .
- Potassium iodide (KI), puriss p.a.
- Sulphuric acid, $\rho(\text{H}_2\text{SO}_4) = 25 \%$
- Sodium hydroxide, $c(\text{NaOH}) = 1 \text{ mol/L}$

Analyses

1. pH value

Calibrate the pH glass electrode in the „CAL“ mode of the Titrino. Rinse it with dist. H₂O, dab it dry with soft 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, resp. printed out. The measured pH value is stored as constant C40 in the Titrino.

Remarks

- The pH value of wines lies usually between 3.3 and 4.0. Values higher than pH = 3.8 can cause stability problems.
- When not in use, the pH glass electrode is kept in an electrolyte solution c(KCl) = 3 mol/L. If used frequently, the electrode must be calibrated once a week. If the electrode is not used for a longer period of time, calibration must be performed before beginning a new series of analyses.

2. Titrable total acid

The calibrated pH glass electrode is used. The CO₂ must be removed from the sample by degassing with nitrogen during 3 ... 5 min. It can also be heated to boiling point, then immediately cooled down.

Pipette 10.0 mL wine and approx. 10 mL dist. H₂O into a beaker and remove the CO₂ from sample as described above. While stirring titrate with c(NaOH) = 0.1 mol/L to pH = 7.0 using the SET mode of the Titrino. (See annex for instrument parameters).

Calculation

The result is given in g/L tartaric acid. If a sample quantity other than 10 mL or if a different concentration of titrant is used, the conversion factor is changed accordingly.

$$\text{g/L Tartaric acid} = \text{EP1} \times \text{C01}$$

$$\text{EP1} = \text{mL } c(\text{NaOH}) = 0.1 \text{ mol/L up to pH} = 7.0$$

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

Remarks

- After decomposition of the acid, values for the titrable total acid normally lie between 4.0 and 6.5 g/L.

3. Free sulphurous acid

The double Pt sheet electrode is used and connected to the electrode entry „Pol“. Pipette 50 mL wine into a beaker. Add approx. 1 g KI and 5 mL sulphuric acid and titrate immediately with iodide/iodate solution, using the Ipol mode (1 μA) of the Titrino. Using the 702, it is preferable to employ the MET Ipol mode. The 719 can only carry out SET titrations to end-points. (See annex for instrument parameters).

Calculation

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

$$\text{EP1} = \text{mL iodide/iodate solution up to the end-point}$$

$$\text{C01} = 10 \text{ (conversion factor)}$$

Remarks

- The contents of free sulphurous acid can widely vary depending on the country and sort of wine. They usually lie between 20 and 100 mg/L SO₂.
- New double Pt sheet electrodes, or those infrequently used, can respond poorly. If any at all, only small potential jumps are achieved. In this case the electrode is 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, submerge the „electrodes“ in a diluted sulphuric acid solution (also containing some sulphite) and electrolyse during ca. 3 minutes. Gas bubbles will form on the Pt sheets. Afterwards the electrodes are removed from the solution and thoroughly rinsed with dist. water.

4. Total sulphurous acid

The same type of electrode (double Pt sheet electrode) is used for this analysis as for the analysis for free sulphurous acid. The instrument parameters are different, however (see annex). The bound sulphurous acid is first set free by means of hydrolysis with NaOH.

Pipette 50 mL wine into a beaker and add 25 mL $c(\text{NaOH}) = 1 \text{ mol/L}$, stir shortly and allow to stand for 10 min. Finally add approx. 1 g KI and 10 mL H₂SO₄ and titrate **immediately** with iodide/iodate solution, as described under Point 3.

Calculation

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

EP1 = mL iodide/iodate solution up to the end point

C01 = 10 (conversion factor)

Remarks

- The allowed maximum value for the total sulphurous acid depends on the country and sort of wine, and varies greatly between 160 ... 450 mg/L SO₂. White wines and natural sweet wines exhibit higher values than red wines.
- Please see Point 3. for the treatment of the double Pt sheet electrode.
- The analysis of the total sulphurous acid content can be carried out subsequent to that of the free sulphurous acid, using the same wine sample.
Add enough NaOH to the titrated sample to make it alkaline, then continue with the analysis as described above. Both results are added together to get the final result.
- The method described here is not specific. Other reducing substances (vitamin C, sometimes reductones) are also recorded. This is especially true in wines with residual sugar contents > 5 g/L. The most reliable values are achieved by employment of the distillation method.

Figures

```

'pa
702 SM Titrino          09139  702.0020
date 2000-03-07      time 15:42      0
MEAS 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.smpl size:       OFF
  activate pulse:      OFF
=====
    
```

Fig. 1 Parameters Titrino for the pH measurement

```

'pa
702 SM Titrino          09139  702.0020
date 2000-03-07      time 15:48      0
SET pH              *****
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.smpl size:       OFF
  activate pulse:      OFF
=====
    
```

Fig. 2 Instrument parameters (702/719) for the total acid determination

```
'pa
702 SM Titrino      09139  702.0020  >statistics
date 2000-03-08    time 09:36    2    status:                OFF
MET Ipol           ***** >evaluation
parameters          EPC                    30 mV
>titration parameters EP recognition:    greatest
  V step            0.10 ml          fix EP1 at U            OFF mV
  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
```

Fig. 3 Instrument parameters 702 for the determination of free sulphurous acid (MET Ipol)

```
'fr
702 SM Titrino      09139  702.0020
date 2000-03-08    time 09:36    2
U(init)            19 mV MET Ipol*****
EP1                0.650 ml          134 mV
RS1                6.50 mg/l
stop V reached
=====
*****
```

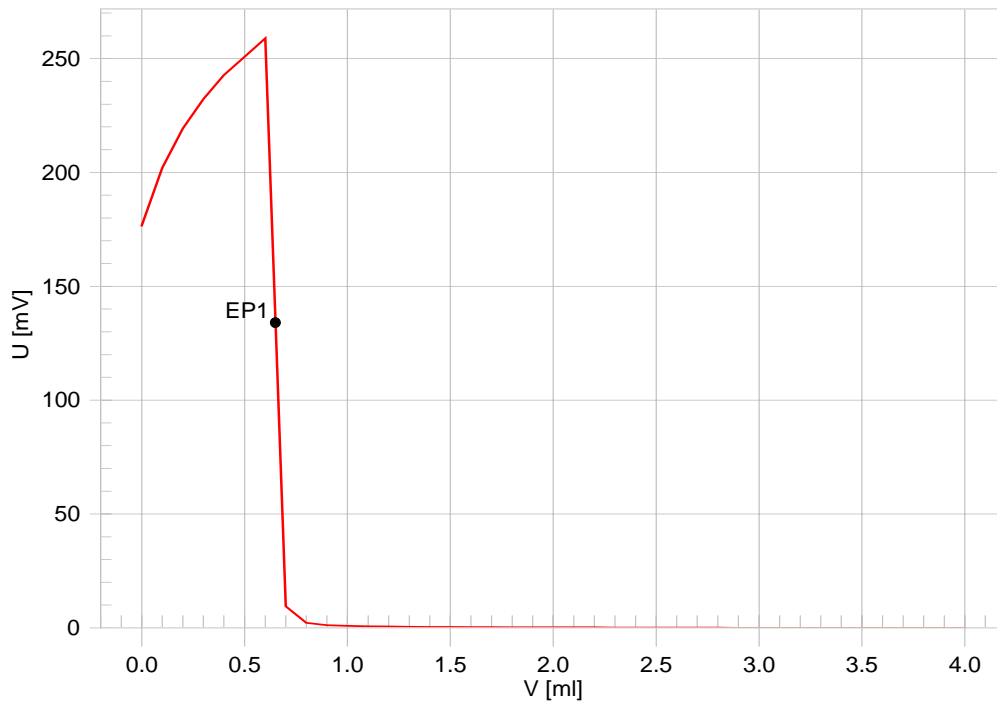


Fig. 4 Titration curve and results 702 for free SO₂

```
'pa
702 SM Titrino      09139  702.0020  >stop conditions
date 2000-03-08    time 10:14    3    stop V:          abs.
MET Ipol           *****    stop V          20 ml
parameters        stop U          OFF mV
>titration parameters  stop EP         9
  V step           0.10 ml      filling rate     max. ml/min
  titr.rate        max. ml/min  >statistics
  signal drift     OFF mV/min    status:         OFF
  equilibr.time    0 s          >evaluation
  start V:         abs.         EPC             30 mV
  start V          0.3 ml      EP recognition: greatest
  dos.rate         max. ml/min  fix EP1 at U   OFF mV
  pause           20 s          >preselections
  I(pol)           1 µA        req.ident:      OFF
  electrode test:  OFF         req.smpl size:  OFF
  temperature     25.0 °C      activate pulse: ON
                                     =====
```

Fig. 5 Instrument parameters 702 for the determination of total sulphurous acid (MET Ipol)

```
'fr
702 SM Titrino      09139  702.0020
date 2000-03-08    time 10:14    3
U(init)            13 mV MET Ipol*****
EP1                7.701 ml      131 mV
RS1                77.01 mg/l
stop V reached
=====
```

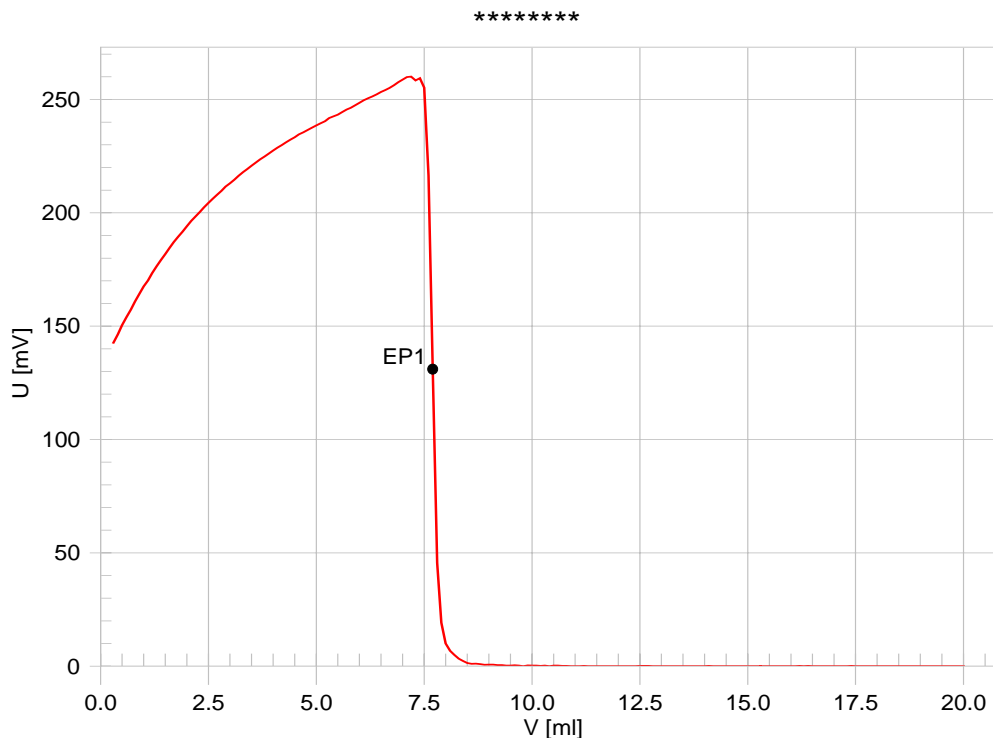


Fig. 6 Titration curve and results 702 for total SO₂

```

'pa
702 SM Titrino      09139  702.0020  >stop conditions
date 2000-03-07    time 15:57    0      stop V:          abs.
SET Ipol           *****      stop V          10 ml
parameters         filling rate     max. ml/min
>SET1              >statistics
  EP at U           20 mV          status:         OFF
  dynamics          300 mV        >preselections
  max.rate          5 ml/min       conditioning:   OFF
  min.rate          10 µl/min      req.ident:     OFF
  stop crit:        time           req.smpl size: OFF
  t(delay)          10 s          activate pulse: OFF
>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
    
```

Fig. 7 Instrument parameters 719 for the determination of free sulphurous acid (SET Ipol)

```

'pa
702 SM Titrino      09139  702.0020  >stop conditions
date 2000-03-07    time 16:00    0      stop V:          abs.
SET Ipol           *****      stop V          50 ml
parameters         filling rate     max. ml/min
>SET1              >statistics
  EP at U           20 mV          status:         OFF
  dynamics          100 mV        >preselections
  max.rate          10 ml/min      conditioning:   OFF
  min.rate          10 µl/min      req.ident:     OFF
  stop crit:        time           req.smpl size: OFF
  t(delay)          10 s          activate pulse: OFF
>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
    
```

Fig. 8 Instrument parameters 719 for the determination of total sulphurous acid (SET Ipol)