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# Application Bulletin

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Of interest to: Vinegar production, food

A, G 7

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## Titrimetric analysis of vinegar

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### Summary

The quality of a vinegar depends on various factors. Since the contents of the individual components vary widely even from bottle to bottle, it is impossible to give average values.

This bulletin describes the determination of the following parameters in vinegar: pH value, total titratable acid, volatile and non-volatile acid, free mineral acid as well as free and total sulfurous acid.

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### Instruments and accessories

- Titrino or Titrande with Dosino or Dosimat
  - Magnetic Stirrer
  - Exchange Units (for sodium hydroxide solution possibly with reagent bottle made of polyethylene)
  - 6.0255.100 Profitrode, combined double-junction pH glass electrode with separable ground-joint diaphragm
  - 6.0309.100 double Pt sheet electrode
  - 6.2104.020 electrode cable
  - Apparatus for steam distillation
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### Reagents

- Titrant: sodium hydroxide solution,  $c(\text{NaOH}) = 1 \text{ mol/L}$
- Titrant: sodium hydroxide solution,  $c(\text{NaOH}) = 0.1 \text{ mol/L}$
- Titrant: hydrochloric acid,  $c(\text{HCl}) = 0.1 \text{ mol/L}$
- Titrant: iodide/iodate solution,  $c(1/6 \text{ KIO}_3) = 1/64 \text{ mol/L}$ :  
Dissolve 0.5573 g potassium iodate (dried at a temperature not exceeding 150 °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.
- Sulfuric acid,  $w(\text{H}_2\text{SO}_4) = 25\%$
- Potassium iodide solution,  $w(\text{KI}) = 5\%$
- Buffer solutions pH = 4.00 (6.2307.100) and pH = 7.00 (6.2307.110)

## Analysis

### 1. pH value

Calibrate the pH glass electrode with the buffer solutions pH = 4.00 and pH = 7.00. Afterwards, while stirring, measure the pH value of the undiluted vinegar sample. The result is given with one decimal place.

### 2. Total titratable acid

Dilute 10.0 mL vinegar with 50 mL CO<sub>2</sub>-free dist. water in a glass beaker and titrate with c(NaOH) = 1 mol/L using the combined pH glass electrode.

#### Calculation

1 mL c(NaOH) = 1 mol/L corresponds to 0.06 g acetic acid

g acetic acid / 100 mL sample = EP1 \* C01 \* C02 / C00

EP1 = titrant consumption in mL

C00 = 10.0 (sample volume in mL)

C01 = 0.06

C02 = 100 (conversion factor: the result refers to 100 mL sample)

### 3. Volatile acid

Pour 10.0 mL vinegar and 10 mL dist. water into a round-bottom flask and subject this solution to steam distillation until approx. 400 mL of distillate has been obtained. During distillation the volume of liquid in the distillation flask should be maintained at around 20 mL.

Heat the distillate until it just begins to boil, then cool down and titrate with c(NaOH) = 1 mol/L to pH = 8.5 using the SET mode. The titrant consumption is A mL.

Now add 5 mL w(H<sub>2</sub>SO<sub>4</sub>) = 25% and 10 mL w(KI) = 5% to this distillate and determine any sulfurous acid that may also have been distilled over by titration with the iodide/iodate solution (see point 6.). The resulting titrant consumption is B mL.

#### Calculation

The volatile acid is expressed in g acetic acid / 100 mL sample with one decimal place.

RS1 [consumption of c(NaOH) = 1 mol/L for the sulfurous acid in mL]  
= 1/64 \* B

RS2 = g acetic acid / 100 mL sample = C01 \* (A – RS1)

A = consumption of c(NaOH) = 1 mol/L for the first titration in mL

B = consumption of iodide/iodate solution for the second titration in mL

C01 = 6 (conversion factor)

#### 4. Non-volatile acid

Rinse the distillation residue of 3. (flask contents) with dist. water into a glass beaker and titrate with  $c(\text{NaOH}) = 1 \text{ mol/L}$  to  $\text{pH} = 8.5$  using the SET mode.

##### Calculation

1 mL  $c(\text{NaOH}) = 1 \text{ mol/L}$  corresponds to

0.07505 g tartaric acid
0.06705 g malic acid
0.06404 g citric acid
0.09008 g lactic acid

$\text{mg non-volatile acid} / 100 \text{ mL sample} = \text{EP1} * \text{C01} * \text{C02} / \text{C00}$

EP1 = titrant consumption in mL

C00 = 10.0 (sample volume in mL)

C01 = conversion factor for the respective carboxylic acid (see above)

C02 = 100 (conversion factor: the result refers to 100 mL sample)

#### 5. Free mineral acid

Pipet 10.0 mL vinegar into a 100 mL volumetric flask, fill to the mark with dist. Water and mix. Pipet 5.0 mL of this dilution (corresponding to 0.5 mL of the original sample) into a glass beaker, dilute to approx. 40 mL with dist. water and titrate with  $c(\text{NaOH}) = 0.1 \text{ mol/L}$  to  $\text{pH} = 8.5$  using the SET mode. The titrant consumption is A mL.

Afterwards, in a second SET titration, titrate back to  $\text{pH} = 3.9$  with  $c(\text{HCl}) = 0.1 \text{ mol/L}$ . The resulting titrant consumption is B mL.

##### Calculation

The result is expressed in mg mineral acid / 100 mL sample without decimals.

1 mL  $c(\text{NaOH}) = 0.1 \text{ mol/L}$  corresponds to

3.65 mg HCl
6.30 mg $\text{HNO}_3$
4.90 mg $\text{H}_2\text{SO}_4$

$\text{mg mineral acid} / 100 \text{ mL sample} = (\text{A} - \text{B}) * \text{C01} * \text{C02} / \text{C00}$

A = consumption of  $c(\text{NaOH}) = 0.1 \text{ mol/L}$  for the first titration in mL

B = consumption of  $c(\text{HCl}) = 0.1 \text{ mol/L}$  for the second titration in mL

C00 = 0.5 (sample volume used in mL original sample)

C01 = conversion factor for the respective mineral acid (see above)

C02 = 100 (conversion factor: the result refers to 100 mL sample)

### **6. Free sulfurous acid**

Pipet 50 mL vinegar into a glass beaker, add 5 mL  $w(\text{H}_2\text{SO}_4) = 25\%$  and 10 mL  $w(\text{KI}) = 5\%$  and titrate with the iodide/iodate solution using the MET  $I_{\text{pol}}$  mode ( $I_{\text{pol}} = 1 \mu\text{A}$ ).

#### **Calculation**

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

EP1 = titrant consumption in mL

C01 = 10 (conversion factor)

### **7. Total sulfurous acid**

The bound sulfurous acid is released by means of sodium hydroxide solution.

Pipet 25 mL  $c(\text{NaOH}) = 1 \text{ mol/L}$  and 50 mL vinegar into a glass beaker and allow to react for 15 min under stirring. Then add 10 mL  $w(\text{H}_2\text{SO}_4) = 25\%$  and 10 mL  $w(\text{KI}) = 5\%$  and titrate with the iodide/iodate solution using the MET  $I_{\text{pol}}$  mode ( $I_{\text{pol}} = 1 \mu\text{A}$ ).

#### **Calculation**

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

EP1 = titrant consumption in mL

C01 = 10 (conversion factor)

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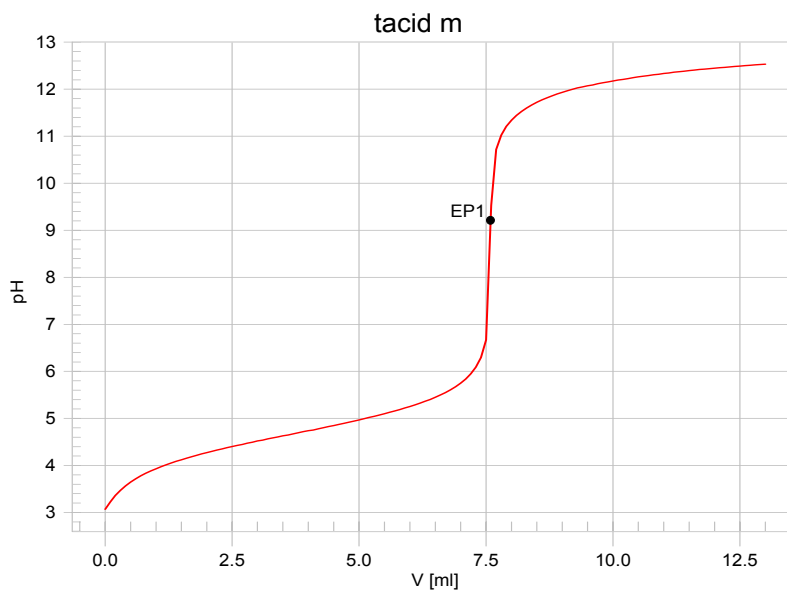
### **Remark**

The double Pt sheet electrode has to be regenerated from time to time (see corresponding electrode leaflet).

```
'pa
736 GP Titrino          04268  736.0011
date 00-05-22          time 15:00    7
MET pH                  tacid m
parameters
>titration parameters
  V step                0.10 ml
  titr.rate             max. ml/min
  signal drift          50 mV/min
  equilibr.time         26 s
  start V:              OFF
  pause                 0 s
  dos.element:          internal D0
  meas.input:           1
  temperature           22.5 °C
>stop conditions
  stop V:               abs.
  stop V                13 ml
  stop pH               OFF
  stop EP               9
  filling rate          max. ml/min
>statistics
  status:               OFF
>evaluation
  EPC                   0.50
  EP recognition:       all
  fix EP1 at pH        OFF
  pK/HNP:               OFF
>preselections
  req.ident:            OFF
  req.smpl size:        OFF
  activate pulse:       OFF
=====
```

**Fig. 1:** Titrino parameter report for the determination of the total titratable acid.

```
'fr
736 GP Titrino          04268  736.0011
date 00-05-22          time 15:00    7
pHc(init)              3.07    MET pH  tacid m
smpl size               10 ml
EP1                     7.589 ml    9.21
tacid m                 4.56 g/0.1L
temp.                   22.5 C
time                    446 s
stop V reached
=====
```



**Fig. 2:** Result report and titration curve for the determination of the total titratable acid in vinegar.

```

'pa
736 GP Titrino          04268  736.0011
date 00-05-23          time 16:15      1
SET pH                  vol acid
parameters
>SET1
  EP at pH              8.50
  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:      auto
  pause 1              0 s
  start V:             OFF
  pause 2              0 s
  extr.time            0 s
  dos.element:         internal D0
  meas.input:          1
  temperature          26.6 °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:       value
  activate pulse:     OFF
=====
    
```

**Fig. 3:** Parameter report for the determination of the volatile and non-volatile acid.

```

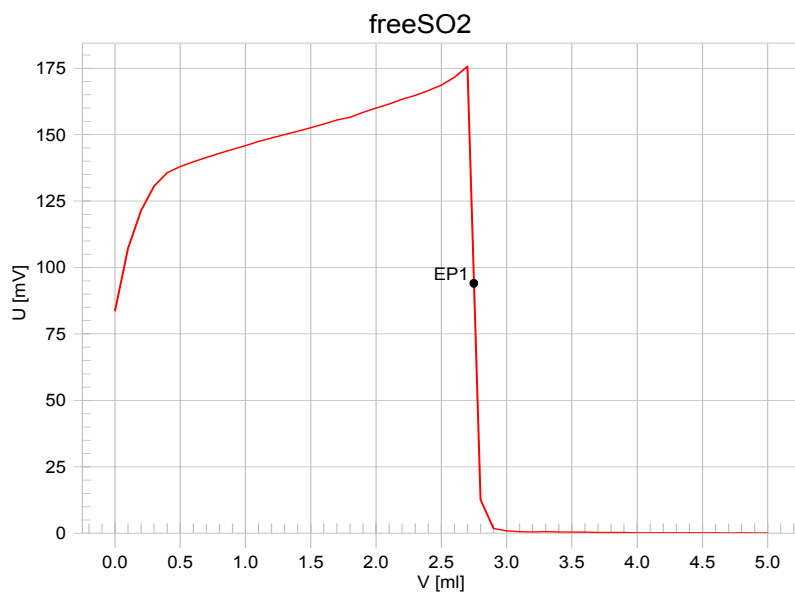
'pa
736 GP Titrino          04268  736.0011
date 00-05-29          time 14:22     13
SET pH                  mineral2
parameters
>SET1
  EP at pH              3.90
  dynamics              2
  max.rate              10.0 ml/min
  min.rate              25.0 µl/min
  stop crit:           drift
  stop drift            20 µl/min
>SET2
  EP at pH              OFF
>titration parameters
  titr.direction:      auto
  pause 1              0 s
  start V:             OFF
  pause 2              0 s
  extr.time            0 s
  dos.element:         internal D0
  meas.input:          1
  temperature          23.6 °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:       value
  activate pulse:     OFF
=====
    
```

**Fig. 4:** Parameter report for the determination of the free mineral acid.

```
'pa
736 GP Titrino          04268  736.0011
date 00-05-31          time 15:27   12
MET Ipol                freeSO2
parameters
>titration parameters
  V step                0.10 ml
  titr.rate             max. ml/min
  signal drift         50 mV/min
  equilibr.time        10 s
  start V:             OFF
  pause                0 s
  dos.element:         internal D0
  I(pol)               1 µA
  electrode test:      OFF
  temperature          25.6 °C
>stop conditions
  stop V:              abs.
  stop V               5 ml
  stop U               OFF mV
  stop EP              9
  filling rate         max. ml/min
>statistics
  status:              OFF
>evaluation
  EPC                  30 mV
  EP recognition:      all
  fix EP1 at U        OFF mV
>preselections
  req.ident:           OFF
  req.smpl size:       value
  activate pulse:      OFF
=====
```

**Fig. 5:** Parameter report for the determination of the free sulfurous acid.

```
'fr
736 GP Titrino          04268  736.0011
date 00-05-31          time 15:27   12
U(init)                29 mV MET Ipol freeSO2
smpl size              50 ml
EP1                    2.750 ml          94 mV
free SO2               27.53 mg/l
time                   189 s
stop V reached
=====
```

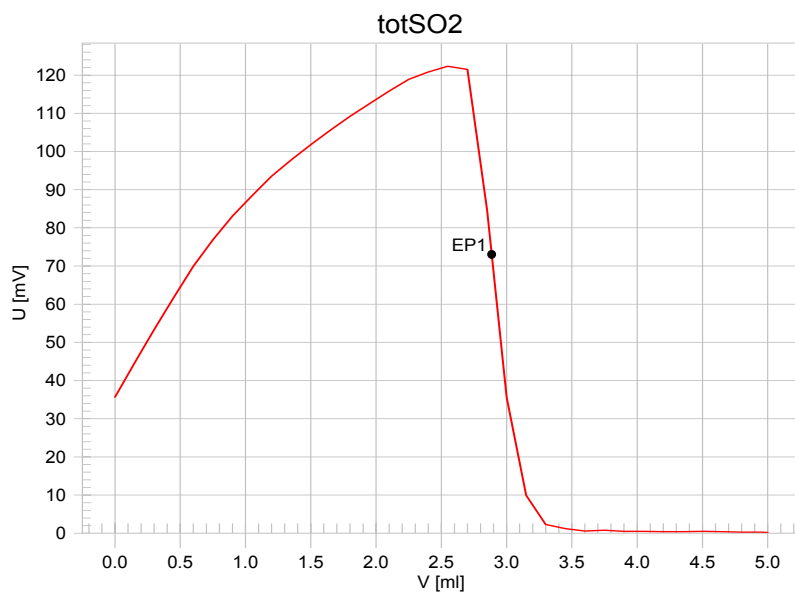


**Fig. 6:** Result report and titration curve for the determination of the free sulfurous acid in vinegar.

```
'pa
736 GP Titrino          04268  736.0011
date 00-05-31          time 15:50    14
MET Ipol                totSO2
parameters
>titration parameters
  V step                0.15 ml
  titr.rate             max. ml/min
  signal drift         50 mV/min
  equilibr.time        1 s
  start V:             OFF
  pause                0 s
  dos.element:         internal D0
  I(pol)               1 µA
  electrode test:      OFF
  temperature          26.1 °C
>stop conditions
  stop V:              abs.
  stop V               5 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:       value
  activate pulse:      ON
=====
```

**Fig. 7:** Parameter report for the determination of the total sulfurous acid.

```
'fr
736 GP Titrino          04268  736.0011
date 00-05-31          time 15:51    14
U(init)                27 mV MET Ipol totSO2
smpl size              50 ml
EP1                    2.886 ml          73 mV
tot SO2                28.90 mg/l
time                   60 s
stop V reached
=====
```



**Fig. 8:** Result report and titration curve for the determination of the total sulfurous acid in vinegar.