Application Bulletin 85/2 e

Titrimetric analysis of jams, fruit and vegetable juices and their concentrates

Of interest to:
Food and beverages
A, G 7

Summary

This Bulletin describes analysis methods for determining the following parameters: pH value, total titratable acid, ash alkalinity, formol number, total sulfurous acid, chloride, sulfate, calcium and magnesium. These methods are suitable for the analysis of jams, fruit and vegetable juices and their concentrates.

Instruments and accessories

- Titrino or
  Titrando with Dosino or Dosimat
- Magnetic Stirrer
- Exchange Unit(s) (for NaOH possibly with 6.1608.040 PE reagent bottle)
- 6.0258.000 Unitrode, combined pH glass electrode with fixed ground-joint diaphragm and Pt 1000 temperature sensor
- 6.0309.100 double Pt sheet electrode
- 6.0430.100 Ag Titrode
- 6.0508.110 ion-selective calcium electrode (Ca ISE)
- 6.0750.100 LL ISE Reference, double-junction Ag/AgCl reference electrode with fixed ground-joint diaphragm
- 6.2104.020 and 6.2106.020 electrode cables
- Possibly printer and printer cable

1. pH value

Reagents

- Buffer solutions pH = 4.0 and pH = 7.0 (Metrohm no. 6.2307.100 and 6.2307.110)

Measurement

Calibrate the combined pH glass electrode with the buffer solutions pH = 4.0 and pH = 7.0. Immerse the electrode in the jam and read off the pH value at drift constancy. In the case of fruit and vegetable juices carry out the measurement in the undiluted sample with stirring.

The pH value is given with one decimal place.

2. Total titratable acid

Reagents

- *c*(NaOH) = 0.1 mol/L
- *c*(NaOH) = 1 mol/L

Titration

a) Jams

Add 90 mL dist. water to 10 g sample and heat just to boiling point. After cooling down, titrate with *c*(NaOH) = 0.1 mol/L to pH = 8.5 using the SET mode.

b) Fruit and vegetable juices

Add 40 mL dist. water to 10 mL sample and heat just to boiling point. After cooling down, titrate with *c*(NaOH) = 1 mol/L to pH = 8.5 using the SET mode.

Calculation

The result is expressed in meq./100 g (jams) or in meq./L (juices).

a) meq./100 = EP1 * C01 / C00

b) meq./L = EP1 * C02 / C00

C00 = 10 [sample mass in g (a) or sample volume in mL (b)]

C01 = 10 (conversion factor)

C02 = 1000 (conversion factor)

3. Ash alkalinity

Reagents

- *c*(HCl) = 0.1 mol/L
- *c*(NaOH) = 0.1 mol/L

Sample preparation and titration

Boil down 25 mL juice in a porcelain evaporating dish at 110 °C in a drying cabinet.

After addition of 1 drop paraffin oil, pre-incineration is induced over the flame, then the sample is completely reduced to ash in a muffle furnace at 520 ± 25 °C. (If black carbon particles are still present allow the ash to

cool down, crush with a pestle, moisten with dist. water and repeat the incineration in the muffle furnace. If necessary, repeat this process again until only pure white ash remains.) After cooling down, rinse the ash first with 20 mL *c*(HCl) = 0.1 mol/L, then with a little dist. water into a glass beaker and heat for 15 min in a boiling water bath.

After cooling down again, titrate back to pH = 4.5 with *c*(NaOH) = 0.1 mol/L using the SET mode.

Calculation

The ash alkalinity is expressed in meq./L with one decimal place.

meq./L = C01 * (A – B)

A = 20 [added volume of *c*(HCl) = 0.1 mol/L in mL]

B = consumption of *c*(NaOH) = 0.1 mol/L for the back-titration in mL

C01 = 4 (conversion factor)

4. Formol number

Reagents

- *c*(NaOH) = 1 mol/L
- *c*(NaOH) = 0.1 mol/L
- Formaldehyde solution: *w*(HCHO) = 35%, adjusted to pH = 8.5 with NaOH

Titration

Pipet 25 mL juice into a glass beaker and titrate with *c*(NaOH) = 1 mol/L to pH = 8.5 using the SET mode. While stirring, add 15 mL formaldehyde solution and wait for 1 min, then titrate the acid thus liberated in a second SET titration with *c*(NaOH) = 0.1 mol/L again to pH = 8.5 (EP1).

Calculation

The formol number is expressed as mL *c*(NaOH) = 0.1 mol/L per 100 mL juice, without decimals.

Formol number = EP1 * C01

C01 = 4 (conversion factor)

5. Total sulfurous acid

Reagents

- Iodide/iodate solution: Dissolve 0.5573 g KIO_3 (dried at a temperature not exceeding 150 °C) in approx. 700 mL dist. water. Add 3.5 g KI and dissolve it, then make up to 1 L with dist. water.
- *w*(H_2SO_4) = 25%
- KI solution: *w*(KI) = 5%
- *c*(NaOH) = 1 mol/L

Titration

Mix 25 mL juice (a) or 10 g homogenized jam plus 50 mL dist. water (b) in a glass beaker with 25 mL *c*(NaOH) = 1 mol/L and allow to stand for 15 min. Then add 10 mL H_2SO_4 as well as 10 mL KI solution and titrate with the iodide/iodate solution using the MET I_{pol} mode (I_{pol} = 1 µA) and the double Pt sheet electrode.

Calculation

The result is expressed in mg/L SO_2 (juices) or in mg SO_2/100 g (jams).

a) mg/L SO_2 = EP1 * C01

b) mg SO_2/100 g = EP1 * C02

C01 = 20 (conversion factor)

C02 = 5 (conversion factor)

6. Chloride content

Reagents

- *c*($AgNO_3$) = 0.1 mol/L
- *c*(H_2SO_4) = 1 mol/L

Titration

Pipet 10 mL juice, 15 mL dist. water and 2 mL H_2SO_4 into a glass beaker. Then titrate the chloride with *c*($AgNO_3$) = 0.1 mol/L using the Ag Titrode.

Calculation

The result is expressed in mg/L Cl^- without decimals.

1 mL *c*($AgNO_3$) = 0.1 mol/L corresponds to 3.545 mg Cl^-

mg/L Cl^- = EP1 * C01 * C02 / C00

C00 = 10 (sample volume in mL)

C01 = 3.545

C02 = 1000 (conversion factor)

7. Sulfate content

Reagents

- *c*($BaCl_2$) = 0.05 mol/L: Dissolve 12.34 g $BaCl_2$ x 2 H_2O (99%) in *c*(HCl) = 0.1 mol/L and make up to 1 L.
- *c*(EGTA) = 0.05 mol/L: Make a suspension with 19.4 g ethylene glycol-bis-(2-aminoethyl)-tetra-acetic acid and approx. 200 mL dist. water. Add *c*(NaOH) = 10 mol/L with stirring until the substance has completely dissolved. After cooling down, make up to 1 L with dist. water.
- Ca Standard: *c*($CaCl_2$) = 0.1 mol/L (Metrohm no. 6.2301.070)

- Buffer solution pH = 10: Dissolve 9 g NH_4Cl and 60 mL $w(NH_3)$ = 25% in dist. water and make up to 1 L.
- c(HCl) = 2 mol/L

Titration

Add 30 mL dist. water to 20 mL juice and, if necessary, adjust the pH value to 3.5 with HCl. Then add 0.5 mL Ca standard and 5.00 mL $BaCl_2$ solution and allow to react for 3 min with stirring. Add 10 mL buffer solution pH = 10 and titrate with c(EGTA) = 0.05 mol/L using the MET mode and the Ca ISE.

Two equivalence points are obtained: EP1 corresponds to Ca, the difference between EP1 and EP2 to the Ba excess.

First, the EGTA consumption for the $BaCl_2$ has to be determined. This is done by means of a blank sample (without sulfate), which is prepared and titrated in the same way as the actual sample. This blank consumption is stored as common variable C31 in the titrator.

Calculation

The result is expressed in g/L K_2SO_4 with one decimal place.

1 mL c(EGTA) = 0.05 mol/L corresponds to 8.713 mg K_2SO_4

RS1 = EP2 – EP1; mL

RS2 = g/L K_2SO_4 = (C31 – RS1) * C01 / C00

C00 = 20 (sample volume in mL)

C01 = 8.713

C31 = blank consumption in mL [use the same quantity of $c(BaCl_2)$ = 0.05 mol/L as for the sample (5.00 mL)!]

8. Calcium and magnesium

Ca and Mg are present only partially as free ions in these foodstuffs. The rest is bound in a complex manner to organic components. In order to determine the total contents, it is therefore necessary to incinerate the samples.

Reagents

- Titrant: $c(Na_2EDTA)$ = 0.05 mol/L in c(KOH) = 0.1 mol/L
- Auxiliary complexing solution: c(acetylacetone) = 0.1 mol/L in c(TRIS) = 0.2 mol/L [TRIS = tris(hydroxymethyl)-aminomethane]
- w(HCl) = 20% and w(NaOH) = 20%

Sample preparation and titration

Pipet 25 mL juice into a porcelain evaporating dish and boil down at 120 °C in a drying cabinet. Afterwards, heat to redness in a muffle furnace at 600 °C until only pure white ash remains. After cooling down, add 2 mL HCl, heat in order to dissolve the ash and rinse into a glass beaker with dist. water. Adjust the pH value of this solution to 8.5 with NaOH. Add 20 mL auxiliary complexing solution and titrate with $c(Na_2EDTA)$ = 0.05 mol/L using the Ca ISE.

Two equivalence points are obtained: EP1 corresponds to Ca, the difference between EP1 and EP2 to Mg.

Calculation

The results are expressed in mg/L without decimals.

1 mL $c(Na_2EDTA)$ = 0.05 mol/L corresponds to
2.004 mg Ca^{2+} or
1.261 mg Mg^{2+}

mg/L Ca^{2+} = EP1 * C01 * C03 / C00

mg/L Mg^{2+} = (EP2 – EP1) * C02 * C03 / C00

C00 = 25 (sample volume in mL)

C01 = 2.004

C02 = 1.261

C03 = 1000 (conversion factor)

Remark

In jams the calcium and magnesium contents are given in mg/100 g. In these cases 25 g homogenized sample is reduced to ash. For the calculation the following applies:

C00 = 25 (sample mass in g)

C03 = 100 (conversion factor)

Figures

```
'pa
736 GP Titrino           04268   736.0011
date  10-01-01       time  13:40        12
SET  pH                   SET
parameters
>SET1
  EP at pH                 8.50
  dynamics                  7.8
  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              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. 1: *Titrino parameter report for the determination of the total titratable acid and the formol number (SET titration to pH = 8.5).*

```
'pa
736 GP Titrino           04268   736.0011
date  15-01-02       time  15:13        10
SET  pH                   SET
parameters
>SET1
  EP at pH                 4.50
  dynamics                  3.8
  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              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. 2: *Parameter report for the determination of the ash alkalinity (SET titration to pH = 4.5).*

```
'pa
736 GP Titrino           04268   736.0011
date  15-01-05      time  14:16          0
MET  Ipol                SO2
parameters
>titration parameters
  V step                   0.1 ml
  titr.rate               max. ml/min
  signal drift             OFF mV/min
  equilibr.time              1 s
  start V:                 OFF
  pause                      0 s
  dos.element:    internal D0
  I(pol)                     1 µA
  electrode test:          OFF
  temperature             25.0 °C
>stop conditions
  stop V:                  abs.
  stop V                    10 ml
  stop U                   OFF mV
  stop EP                    9
  filling rate            max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                       20 mV
  EP recognition:    greatest
  fix EP1 at U             OFF mV
>preselections
  req.ident:               OFF
  req.smpl size:           OFF
  activate pulse:          OFF
          ============
```

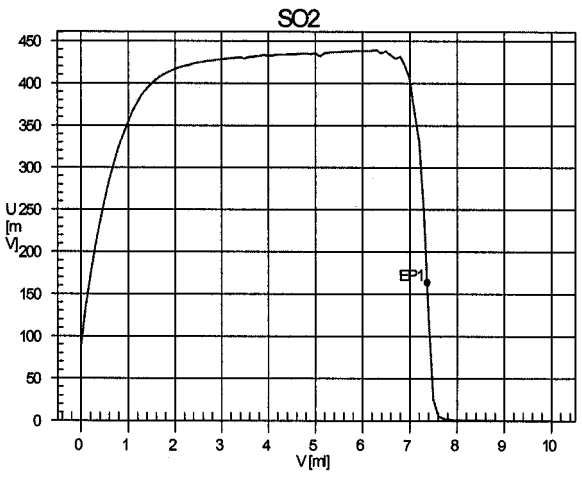

Fig. 3: *Parameter report and titration curve for the determination of the total sulfurous acid.*

```
'pa
736 GP Titrino          04268   736.0011
date  10-01-01      time  15:50       19
DET  U              CHLORID
parameters
>titration parameters
  meas.pt.density          4
  min.incr.             10.0 µl
  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           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                      5
  EP recognition:    greatest
  fix EP1 at U           OFF mV
  pK/HNP:                OFF
>preselections
  req.ident:             OFF
  req.smpl size:         OFF
  activate pulse:        OFF
          ============
```

```
'fr
736 GP Titrino          04268   736.0011
date  10-01-01      time  15:50       19
U(init)          157 mV  DET U    CHLORID
smpl size         10 ml
EP1           15.456 ml              11 mV
CHLORID         5479 mg/L
stop V reached
          ============
```

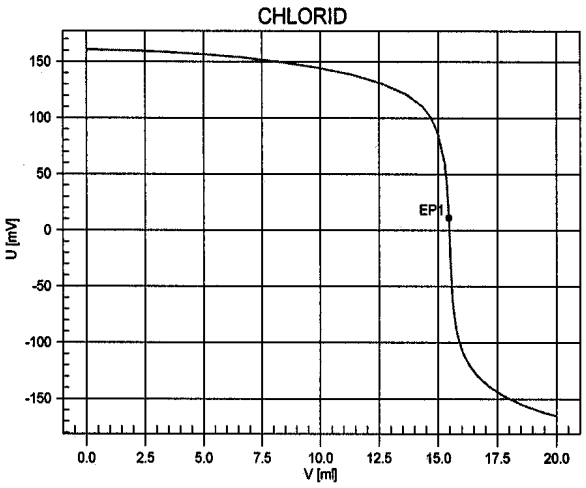

Fig. 4: *Parameter report, result report and titration curve for the determination of chloride in tomato juice.*

```
'pa
736 GP Titrino          04268   736.0011
date  15-01-03      time  10:59       13
MET  U               Sulfat
parameters
>titration parameters
  V step                0.10 ml
  titr.rate             max. ml/min
  signal drift            50 mV/min
  equilibr.time           20 s
  start V:               OFF
  pause                    0 s
  dos.element:    internal D0
  meas.input:              1
  temperature           25.0 °C
>stop conditions
  stop V:               abs.
  stop V                  10 ml
  stop U                 OFF mV
  stop EP                  9
  filling rate          max. ml/min
>statistics
  status:                OFF
>evaluation
  EPC                    5.2 mV
  EP recognition:        all
  fix EP1 at U           OFF mV
  pK/HNP:                OFF
>preselections
  req.ident:             OFF
  req.smpl size:         OFF
  activate pulse:        OFF
         ============
```

```
'fr
736 GP Titrino          04268   736.0011
date  15-01-03      time  10:57       13
U(init)          -21 mV  MET U      K2SO4
smpl size         20 ml
EP1            1.318 ml             -51 mV
EP2            3.269 ml             -86 mV
RS1             1.95 ml
K2SO4           18.5 g/l
stop V reached
          ============
```

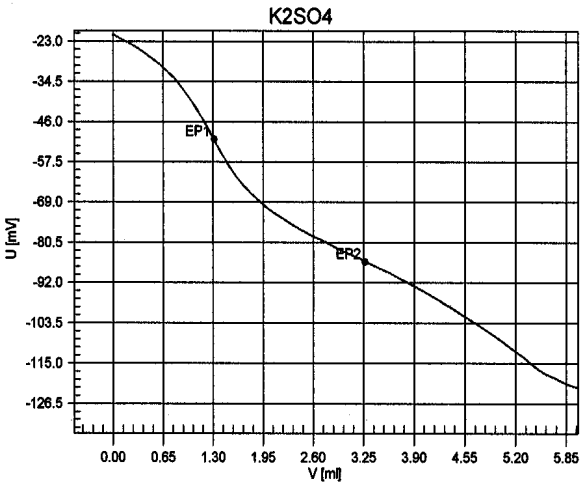

Fig. 5: *Parameter report, result report and titration curve for the determination of sulfate in grape juice.*

```
'pa
736 GP Titrino          04268   736.0011
date  15-01-03      time  15:01        17
MET  U                  CaMg
parameters
>titration parameters
  V step                0.10 ml
  titr.rate             max. ml/min
  signal drift            50 mV/min
  equilibr.time           20 s
  start V:               OFF
  pause                    0 s
  dos.element:    internal D0
  meas.input:              1
  temperature           25.0 °C
>stop conditions
  stop V:               abs.
  stop V                  10 ml
  stop U                 OFF mV
  stop EP                  9
  filling rate          max. ml/min
>statistics
  status:                OFF
>evaluation
  EPC                    7.1 mV
  EP recognition:        all
  fix EP1 at U           OFF mV
  pK/HNP:                OFF
>preselections
  req.ident:             OFF
  req.smpl size:         OFF
  activate pulse:        OFF
         ============
```

```
'fr
736 GP Titrino          04268   736.0011
date  15-01-03      time  15:00        17
U(init)            -9 mV  MET U       CaMg
smpl size          25 ml
EP1             2.232 ml             -36 mV
EP2             4.960 ml            -102 mV
Ca                179 mg/l
Mg                138 mg/l
stop V reached
           ============
```

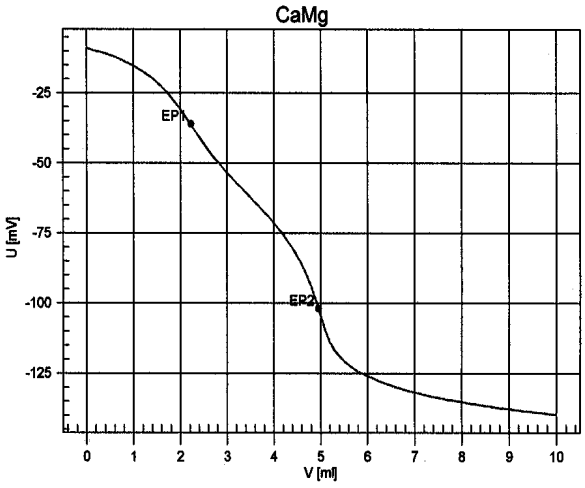

Fig. 6: *Parameter report, result report and titration curve for the determination of calcium and magnesium in grapefruit juice.*