



Method of Analysis

No. 3 (rev. 2017)

Titrateable Acidity

Principle

Titrateable acidity is a measure of the content of mineral and organic acids determined by potentiometric titration with standard volumetric sodium hydroxide solution either to a pH value of 7.0, for the determination of the acidity expressed as malic or tartaric acids and / or to a pH of 8.1 for the determination of the acidity expressed as citric acid.

Definition

c = substance concentration.

WORKING INSTRUCTIONS

1. Reagents

Use reagents of recognized analytical grade and degassed water

- 1.1. Sodium hydroxide, standard volumetric solution, $c(\text{NaOH}) = 0.25 \text{ mol/l}$
- 1.2 Buffer solutions of suitable pH for calibration of pH meter

2. Apparatus

Usual laboratory apparatus and, in particular, the following

- 2.1 pH meter accurate to at least 0.01 pH units
- 2.2 pH glass electrode
- 2.3 Reference electrode, e.g. calomel electrode
- 2.4 Combination glass electrode (alternative to 2.2 and 2.3)
- 2.5 Magnetic stirrer
- 2.6 Burette of 25 ml capacity, graduated in 0.05 ml divisions
- 2.7 Low form beaker (typically 50 ml)
- 2.8 One-mark pipette of 25 ml capacity

3. Procedure

3.1 Preparation of the test sample

Normally products shall not be pre-treated and their analysis by this method shall be on a volumetric basis, results being expressed per litre of sample. The analysis of concentrated products may also be carried out on a volumetric basis, after dilution to a known relative density. In this case, the relative density shall be indicated. Based on a weighed sample and taking the dilution factor for analysis into account, the results may also be expressed per kilogram of product. In products with a high viscosity and/or a very high content of cells (for example pulp), a determination on the basis of a weighed test sample is the usual procedure.

If the sample contains appreciable quantities of carbon dioxide, degas it by shaking in a stoppered conical flask and removing the stopper from time to time, or by using vacuum or ultrasound treatment until no more gas is evolved.

3.2 Calibration

Perform two-point calibration of the pH meter at 20°C using the buffer solutions (1.2) with stirring and following the instrument manufacturer's instructions. If the pH meter is equipped with temperature compensation adjustment, the calibration can be carried out at a temperature other than 20°C but in any case, between 10°C and 30°C.

3.3. Determination

Transfer at 20°C, by means of the pipette 25 ml of the test sample (V_0) into the beaker. Start the stirrer and titrate by means of the burette with sodium hydroxide solution (1.1) until a pH of 7.0 and / or 8.1 is obtained. Record the amount of solution (V_1) used.

4. Calculation

4.1 Calculation as titratable acidity

The titratable acidity C_{H^+} expressed in mmoles of H^+ per litre of product, is given by the formula:

$$C_{H^+} = \frac{1000 \cdot V_1 \cdot c}{V_0}$$

where

V_0 is the volume, in millilitres, of the test portion, as a rule 25 ml;

V_1 is the volume, in millilitres, of the sodium hydroxide solution used for the determination to either 7.0 or 8.1

c is the exact concentration, in moles per litre, of the sodium hydroxide solution (for standardisation see 7.1)

If V_0 is 25 ml and c is 0.25 mol/l as specified in this method, the titratable acidity C_{H^+} , expressed in mmoles of H^+ per litre of product, is given by the formula:

$$C_{H^+} = V_1 \cdot 10$$

Report the result without a decimal place.

4.2 Calculation as acid content

It is also possible to calculate the titratable acidity conventionally as content of a particular acid expressed in grams per litre of product, by multiplying the result from the formula above by a factor given in table 1, corresponding to the acid.

Table 1: Factors corresponding to different acids

Acid	Factor	pH
Tartaric acid	0.075	7.0
Malic acid	0.067	7.0
Citric acid, anhydrous	0.064	8.1

Report the result as tartaric, malic, or anhydrous citric acid in accordance with requirements to one decimal place.

Take into account the dilution and the relation of the values to mass or volume. If a concentrated product has been diluted to single strength, report the relative density of the single strength sample.

5. Literature

- [1] Determination of titratable acidity: No 3, 1968
In: The Collection of Analyses of the International Federation of Fruit Juice Producers (IFU).
Loose-leaf edition, as of 1991. - Zug: Swiss Fruit Union.

6. Precision of the method

In an interlaboratory test organized by the Food Chemistry Department of the Max von Pettenkofer Institute of the German Federal Office of Public Health in 1993, the following precision parameters were determined in accordance with the international standard ISO 5725:1986.

Repeatability, $r = 1.03 \text{ mmol H}^+/\text{l}$

Reproducibility, $R = 2.28 \text{ mmol H}^+/\text{l}$

No. of Laboratories participating: 14

No. of samples 5

Fruit juices tested: Apple, grape, orange, grapefruit, apricot nectar

Range of mean values 72 - 222 mmol H⁺/l

7. Addendum:

7.1 Standardisation

The sodium hydroxide solution should be standardised at very regular intervals. This can be performed conveniently as follows:

Transfer to a titration vessel approximately 300 mg of pure potassium hydrogen phthalate (CAS No 877-24-7) which is previously dried for 2 hours at 120°C. Note the exact weight in grams to minimum 4 decimal places, W.

Dissolve the solid in distilled water or similar quality, then titrate the resulting solution with the sodium hydroxide using phenolphthalein as the indicator. Note the volume V in milliliters.

The concentration, c, is given by the general expression:

$$c \text{ (mol/l)} = W \text{ (g)} \times 4.897 \text{ (mmol/g)} / V \text{ (ml)}$$

To standardize lower concentrations of sodium hydroxide the weight W should be adjusted to come to reasonable titration volumes. E.g. for 0.01 mol/l NaOH, approximately 20 mg may be advisable.

7.2 Units

The units of mmol H⁺/l are identical with the units sometimes mentioned in juice specifications, i.e. mEq/l or mval/l. The milliequivalent (earlier known as mval) expresses the chemical activity, or combining power, of a substance relative to the activity of 1 mg of hydrogen. In this case, 1 mEq is represented by 1 mg of hydrogen ions.

7.3 Calculation of titratable non-volatile acids

Titrateable non-volatile acids are defined as the non-volatile free mineral and organic acids present in the beverage. Their determination is effected by subtraction of the volatile acids (IFU Method No. 5) from the titrateable acid as measured above.

Calculation of results expressed in grams per litre:

Titrateable non-volatile acids per litre,
calculated as tartaric acid: $a - (1.25 \cdot b)$

where a = grams titrateable acid per litre, calculated as tartaric acid
 b = grams volatile acid per litre, calculated as acetic acid

Calculation of results in milliequivalents per litre:

Milliequivalents of non-volatile
acids in one litre: $c - d$

where c = milliequivalents titrateable acid per litre
 d = milliequivalents volatile acid per litre

Results are stated as grams per litre (g/l) with one decimal place or as milliequivalents per litre (mEq/l) without a decimal place.

7.4 Calculation of GPL

In lemon and lime juice concentrates the total acid is often expressed in gram citric acid per litre (GPL). GPL calculation is based on the total acidity at pH 8,1 expressed as citric acid as stated in this method. The determination of the absolute density of the concentrate (20°C) follows this calculation:

First: Use the equation IFU No. 8 (rev. 2017); 3.1.1. for the acid correction of refractometric brix (Brix ref.) of the concentrate. The result is the Brix corr. value.

Second: The Brix corr. value is used for the calculation of the absolute density (20°C) with the equation IFU No.8 (rev. 2017); 3.2.

Finally, GPL is calculated by the following equation:

$$\text{GPL [g/l]} = \text{total acidity pH 8.1 [g/kg]} \times \text{absolute density [kg/l]}$$

For a better understanding an example for the calculation in a lemon juice concentrate is given below. The Brix is measured with 48.12°Brix_{ref} and the titratable acidity (pH 8.1) is 325.04 g/kg:

First perform the correction of the measured Brix with the acid via the equation IFU No. 8 (rev. 2017); 3.1.1.:

Caution: You must divide the acid value by 10 to convert it from g/kg into %:
 $325.04 \text{ g/kg} / 10 = 32.504 \%$

$$48.12 \text{ }^\circ \text{Brix}_{\text{ref}} + 0.012 + (0.193 * 32.504 \%) - (0.0004 * 32.504 \%^2)$$

⇒ Brix corr. = 53.98 °Brix

Second use the Brix corr. value to calculate the absolute density via the equation from IFU No. 8 (rev. 2017); 3.2.:

$$(998.203 + 385.1761 * (53.98 \text{ }^\circ \text{Brix corr.} / 100) + 135.3705 * (53.98 \text{ }^\circ \text{Brix corr.} / 100)^2 + 40.9299 * (53.98 \text{ }^\circ \text{Brix corr.} / 100)^3 - 3.9643 * (53.98 \text{ }^\circ \text{Brix corr.} / 100)^4 + 13.4853 * (53.98 \text{ }^\circ \text{Brix corr.} / 100)^5 - 17.289 * (53.98 \text{ }^\circ \text{Brix corr.} / 100)^6) / 1000$$

⇒ absolute density = 1.25187 kg/l

Finally, the GPL is calculated as follows:

$$\text{GPL [g/l]} = 325.04 \text{ g/kg} * 1.25187 \text{ kg/l} = \underline{\underline{407 \text{ g/l}}}$$