pH and Acidity in Wine and Fruit Juice With a Sample Changer

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Endpoint potentiometric titration
Scope and application: Wines and fruit juices

1. Introduction

This working procedure refers to the titration of total acidity in wines and fruit juices. The main acid in wine is tartaric acid, in juices it is usually citric or malic acid. These beverages also contain several other acids in different proportions: total acidity corresponds to the sum of titratable acidities.

2. Principle

The protocol rests on a weak acid titration by a strong base. Despite the presence of several acids in the sample, the titration curves show only one pH jump.

The equivalent volume is determined from this pH jump in endpoint mode. By default, the endpoint pH value is set to 8.2, according to the AOAC (Association of Analytical Communities) recommendation. It is also possible to set the endpoint to 7.0, as recommended by the OIV (International Organization of Vine and Wine).

Total acidity in eq/L can be directly calculated from the equivalent volume. Total acidity can also be expressed in g/L of a chosen acid, considering its molar weight and the stoichiometry of the acid-base reaction:

Acid	Molar weight (g/mol)	Exchanged electrons
Tartaric	150.1	2
Malic	134.1	2
Citric	192.1	3
Sulfuric	98.1	2
Acetic	60.1	1

3. Electrode and reagents

Electrodes: Intellical combined pH electrode with integrated temperature sensor, PHC725

Titrant: NaOH 0.25 eq/L. Use a commercial solution or dissolve 10.00 g of sodium hydroxide in 1 L of CO_2-free boiled water.

Standard for titrant calibration: Dihydrate oxalic acid, molar weight = 126.07 g/mol

pH standards: Colored 4.01, 7.00, 10.01 (part numbers 2283449, 2283549, 2283649)

Deionized water

4. Ranges and settings

4.1. Default parameters

The working procedure is described using the following parameters:

- V sample = 15 mL
- Syringe volume = 10 mL

4.2. Working range

For most samples, 1 syringe (10 mL) of titrant should be sufficient to reach the equivalent point. It provides the following range:

Veq (mL)	1.0	9.5
Acidity in g/L of tartaric acid	1.3	11.9
Acidity in g/L of citric acid	1.1	10.1

The syringe is allowed to refill once during titration, so the range is widened:

Veq (mL)	1.0	19
Acidity in g/L of tartaric acid	1.3	23.8
Acidity in g/L of citric acid	1.1	20.3

4.3. Settings

4.3.1. pH

Name	Default parameter	Unit
Probe		
Recommended probe	PHC725	
Stirring		
Stirring speed	15	[%]
Time	15	[s]
pH measurement		
Stirring speed	0	[%]
Measured parameter		[pH]
Stability criteria	0.05	[pH/min]
Stability max time	120	[s]

4.3.2. Acidity

Name	Default parameter	Unit
Sample		
Name	Wine or juice	
Amount	15	[mL]
Amount min	0	[mL]
Amount max	20	[mL]
Titrant		
Name	NaOH	
Titrant concentration	0.2500	[eq/L]
Syringe	Syringe 1	
Probe		
Recommended probe	PHC725	
Leveling		
Active	no	
Time	30	[s]
EP titration		
Stirring speed	50	[%]
Measured parameter		[pH]
Predose	0	[mL]
Max volume stop point	20	[mL]
Stop on last EQP	True	
Delay	0	[s]
Min increment size	0.15	[mL]
Max increment size	1.5	[mL]
EP Ordinates	8.2	[pH]
Result 1 name	Acidity (g/L tartaric acid)	
R1 hide	No	
R1 resolution	3 decimals	

R1 min	1.3	[g/L]
R1 max	23.8	[g/L]
R1 QC min	1.3	[g/L]
R1 QC max	23.8	[g/L]
Result 2 name	Acidity (g/L citric acid)	
R2 hide	No	
R2 resolution	3 decimals	
R2 min	1.1	[g/L]
R2 max	20.3	[g/L]
R2 QC min	1.1	[g/L]
R2 QC max	20.3	[g/L]
Result 3 name	Acidity (g/L malic acid)	
R3 hide	Yes	
R3 resolution	3 decimals	
R3 min	1.1	[g/L]
R3 max	21.2	[g/L]
R3 QC min	1.1	[g/L]
R3 QC max	21.2	[g/L]
Result 4 name	Acidity (g/L acetic acid)	
R4 hide	Yes	
R4 resolution	3 decimals	
R4 min	1.0	[g/L]
R4 max	19.0	[g/L]
R4 QC min	1.0	[g/L]
R4 QC max	19.0	[g/L]
Result 5 name	Acidity (g/L sulfuric acid)	
R5 hide	Yes	
R5 resolution	3 decimals	
R5 min	0.8	[g/L]
R5 max	15.5	[g/L]
R5 QC min	0.8	[g/L]
R5 QC max	15.5	[g/L]

Up to 3 results out of the 5 available can be displayed (select **Hide** > **No**).

4.4. Modification of the settings

The parameters are defined in order to have the best compromise between accuracy and titration time.

For higher concentration with a high titrant volume, titration time can be reduced with an addition of titrant (predose) at the beginning of the titration. Enter the predose volume (in mL) and the stirring time after the addition in the application edit window.

5. Titration procedure

5.1. Leveling

To use this method, an external pump is required. All elements (probes, tubes from the titrator and the tube from the external pump) have to be well installed on the probe holder. The beaker has to contain a level of sample higher than the position of the tube of the external pump. When the beaker is attached to the probe holder, this method allows the system to automatically remove the excess sample by a defined pump working time, and always keep the same sample volume before launching the analysis.

In order to define this volume, autoleveling calibration sequence has to be previously executed (see section **8.3 Autoleveling calibration**).

When this option is active, the working time of the external pump must be set (default 30 s). The minimum working time must allow the pump to be removing air during the last few seconds of the external pump activation.

Note: *Do not forget to re-edit the sample amount with the expected value when deactivating the leveling method.*

5.2. Titration

Rinse the pH probe with deionized water. If leveling is disabled, use a pipette to collect precisely 15 mL of sample.

Pour the sample into the 50 mL polypropylene beaker. Put in a magnetic stir bar, dip the probe and the delivery tip in the solution. Start the application.

At the end of the titration, a first window displays the result. A second window displays the titration curve and the equivalent point coordinates.

After the titration, there are two possibilities:

- Replicate the sample. This is used to study the repeatability by analyzing several samples successively. At the end of each titration, a window displays the average value, the standard deviation (SD) and the relative standard deviation (RSD in %).
- Analyze a new sample. Another titration can be started but no Standard Deviation and RSD value will be made.

6. Results

6.1. Result calculation

The calculation used is:

$$\text{Acidity (g/L)} = \frac{C_{\text{titrant}}\,(\text{eq/L}) \times V_{\text{titrant}}\,(\text{mL})}{n_{\text{e- chosen acid}} \times n_{\text{e- titrant}} \times V_{\text{sample}}\,(\text{mL})} \times M_{\text{chosen acid}}\,(\text{g/mol})$$

$$= \frac{0.25\,(\text{eq/L}) \times V_{\text{titrant}}\,(\text{mL})}{n_{\text{e- chosen acid}} \times 1 \times 15\,(\text{mL})} \times M_{\text{chosen acid}}\,(\text{g/mol})$$

6.2. Experimental results

These results are indicative and have been obtained for a given sample for five successive determinations.

On red wine:

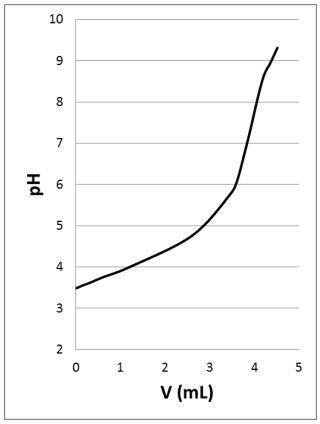
Measurement	Parameter	Unit
Mean concentration	5.135	[g/L of tartaric acid]
Standard deviation	0.039	[g/L of tartaric acid]
Relative standard deviation	0.8	[%]
Mean titration duration	86	[s]

On orange juice:

Measurement	Parameter	Unit
Mean concentration	7.021	[g/L of citric acid]
Standard deviation	0.046	[g/L of citric acid]
Relative standard deviation	0.7	[%]
Mean titration duration	90	[s]

6.3. Example of a titration curve

This curve has been obtained during the analysis of one of the five wine samples.



7. Recommendations

Always rinse the pH probe and the delivery tip between measurements.

Refill the electrode regularly with KCl saturated solution to maintain the level of internal solution around 1 cm (0.4 inches) below the refill hole.

8. Appendices

8.1. Electrode calibration

For the precision of the titration, it is recommended to calibrate the probe with pH standards at the same temperature as the samples. For calibration, the pH is compensated at 25 °C.

Pour a sufficient amount of the first buffer into a 50 mL beaker and add a magnetic stir bar. Place it on the titrator under the probe holder and dip the probe into the beaker. Start the electrode calibration sequence. Rinse the probe between two buffers. Repeat this operation for each buffer (at least two buffers are recommended).

At the end of the calibration, the results of the slope and offset are displayed and the user can accept or reject this result.

Default settings for electrode calibration

Name	Setting	Unit
Stirring speed	25	[%]
Stability criteria	0.05	[pH/min]
Stability max time	300	[s]
Slope limit min	97	[%]
Slope limit max	102	[%]
Offset limit min	29	[mV]
Offset limit max	89	[mV]

8.2. Titrant calibration

The sodium hydroxide solution can be calibrated. The exact concentration can be determined from an acid-base titration using oxalic acid.

Weigh 75 mg of dihydrate oxalic acid in a 50 mL beaker and use a graduated cylinder to add 15 mL of deionized water. Put in a stir bar, dip the probe and the delivery tip into the solution and launch the titrant calibration sequence. When prompted, type in the exact weighed amount (three digits). At the end of the titrant calibration, titer (eq/L) is displayed and the user can reject, replicate, or save the result.

Default settings for titrant calibration

Name	Default parameter	Unit
Titrant		
Name	NaOH	
Titrant concentration	0.2500	[eq/L]
Syringe	Syringe 1	
Standard		
Name	Oxalic acid	
Amount	75	[mg]
Amount min	60	[mg]
Amount max	100	[mg]
Molar weight	126.07	[g/mol]
EP titration		
Stirring speed	50	[%]
Measured parameter		[pH]
Predose	2	[mL]
Max volume stop point	8	[mL]
Stop on last EQP	True	
Delay	0	[s]
Min increment size	0.08	[mL]
Max increment size	0.8	[mL]
EP Ordinates	8.55	[pH]
Result name	Titer	
Result resolution	4 decimals	
Result min	0.2250	[eq/L]
Result max	0.2750	[eq/L]

8.3. Autoleveling calibration

The aim of this method is to calibrate the volume of sample by leveling. The result of this calibration will be used as sample volume for the following titrations.

This option is **ONLY** available from the calibration menu if **Method Leveling** is set to Active (**Yes**). Refer to the documentation delivered with the external pump for a correct installation, paying particular attention to the suction tube from the pump.

Prepare a 0.04 mol/L oxalic acid solution: dissolve 5.043 g of dihydrate oxalic acid in 1 L of deionized water. Pour a sufficient amount of the solution into a beaker allowing the external pump tube to be immersed in the liquid. In the calibration menu select **Autoleveling calibration** and then **pH acidity wine/juice**.

The result in mL is compared to minimum and maximum amounts defined for the sample volume. The calculation used is:

$$V_{sample} = \frac{V_{titrant}(mL) \times C_{titrant}\ (eq/L)}{n_{e-\ oxalic\ acid} \times C_{oxalic\ acid\ solution}\ (mol/L)}$$

$$= \frac{V_{titrant}(mL) \times 0.25\ (eq/L)}{2 \times 0.04\ (mol/L)}$$

Autoleveling calibration uses the same settings as for a titrant calibration (see section **8.2 Titrant calibration**).

Default settings for autoleveling calibration

Name	Default parameter	Unit
Sample		
Amount min	0	[mL]
Amount max	20	[mL]
Autoleveling calibration		
Solution name	Oxalic Acid	
Concentration	0.04	[mol/L]
Resolution	3 decimals	

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