Application note AN010

Titratable acidity of red wine by manual titration (potentiometric)

Keywords

Titratable acidity, red wine, manual titration, potentiometric, organic acids, AOAC Method 962.12

Goal

The following application note demonstrates a simple titratable acidity method using a Thermo Scientific™ Orion™ pH Electrode and Meter to signal the endpoint.

Introduction

Titratable acidity (TA) is a measure of acid content in wine, juice, or must. TA is usually reported in units of tartaric acid, malic acid, or citric acid. Since grapes contain significant amounts of organic acids, TA analysis is one of the most basic analyses in a winery lab. The acid content impacts the taste, color, and microbial stability of the juice. This application note demonstrates a simple TA titration method using an Orion pH Electrode and Meter to signal the endpoint.

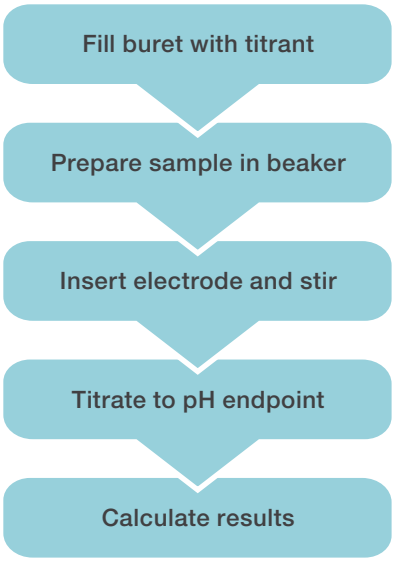
Recommended equipment

- Thermo Scientific™ Orion™ Versa Star™ Pro pH/mV Meter, Thermo Scientific Orion Star A211 pH/mV Meter, or equivalent Orion pH/mV Meter
- Thermo Scientific Orion ROSS™ Sure-Flow™ pH Electrode 8172BNWP or Thermo Scientific Orion GD9156BNWP green pH Electrode, or equivalent
- Orion automatic stirrer probe and paddle (Cat. No. 096019)
- Orion swing arm and electrode holder (Cat. No. 090043)
- 10 mL burette, burette clamp, ring stand

Recommended equipment

- Sodium hydroxide (NaOH) standard solution, 0.10 N or 0.067 N
- Orion pH 7.00 buffer (Cat. No. 910107)
- Orion pH 4.01 buffer (Cat. No. 910104)
- Orion 810007 ROSS filling solution or Orion 910008-WA Double Junction pH fill solution (for GD9156BNWP)
- Orion ROSS pH electrode storage solution (Cat. No. 810001) or Orion pH electrode storage solution (Cat. No. 910001)
- Reagent grade water (RGW) of conductivity <2 uS/cm
- Optional: potassium hydrogen phthalate (KHP); tartaric acid. See appendix for preparation.

Basic titration workflow



Meter setup

Connect the Orion pH electrode, automatic temperature compensation (ATC) probe, and the stirrer probe to the meter. In Setup, select the pH mode, set read type to continuous, and set the stirrer speed to 3. Refer to the Orion meter user guide for more details.

Electrode calibration

Perform a two-point pH calibration using pH 4.01 and 7.00 buffers. Stir the buffer during calibration. The electrode slope should be between 92% and 102%.

Titration setup

Secure the burette on the clamp. Fill the burette with NaOH titrant solution and adjust the level to the zero mark. Eliminate bubbles.

Sample preparation

Make sure the wine sample is at room temperature. To minimize interference from CO_2, degas an amount of the wine sample, e.g. 25 mL. Degas in a flask under vacuum for several minutes with agitation. Alternately, place a sample in an ultrasonic bath for a few minutes, bubble compressed air through to release excess CO_2, or heat a sample to almost boiling, agitate, and let cool.

Sample titration

Pipette 5.0 mL of degassed wine sample into a 150 mL beaker containing 50 mL RGW. Immerse the electrode, ATC, and stirrer in the solution. Turn on the stirrer. Titrate with the NaOH titrant at a faster rate in the beginning and a slower rate when the pH reaches 6.5. It is not necessary to wait for a stabilized reading before pH 6.5. Then, start to add titrant slowly until the pH just reaches 8.2. This is the endpoint of the titration. Record the volume of titrant used (Vs). Calculate the TA in g/L tartaric acid in the wine sample using the equation on page 2. Repeat the titration as desired or required by user's protocol. After each titration, rinse the pH electrode, ATC, and stirrer with RGW and tap gently to remove excess water droplets.

Quality Control (QC)

Recommended QC procedures may include: titrant standardization, blank titration, analysis of tartaric acid standard or QC sample, and/or duplicate sample. For details, refer to the Appendix.

Results

Results obtained using standard solutions prepared in lab and an Orion 8172BNWP electrode.

Table 1. Titratable acids in red wine sample

Red wine sample	TA (g/L tartaric acid)
Sample 1	5.82
Sample 2	5.90
Sample 3	5.87
Results statistics	
Mean	5.86
RSD	0.70%
QC sample*	**TA (g/L tartaric acid)**
Tartaric acid standard (5.04 g/L)	5.05
Results statistics	
Recovery	99.8%

* For details on QC sample, see Appendix

Calculation

TA in sample:

$$\text{TA (g tartaric acid/L)} = \frac{\text{(N NaOH) x (mLs NaOH) x 75)}}{\text{mLs of sample}}$$

Notes

1. If sodium hydroxide is 0.067N and 5 mL of sample are used, then the equation simplifies to TA = mLs of NaOH titrant used.
2. To report results as g malic acid/L (e.g. for apple wines), multiply tartaric acid results by 0.893.
3. To report results as g citric acid/L (e.g. for fruit wines), multiply tartaric acid results by 0.853.
4. For greater accuracy, titrate a blank (50 mL of RGW water). If more than 0.10 mL of sodium hydroxide titrant is required to bring pH to 8.2 or higher for the blank, then subtract that volume from the sample titration.
   Calculate TA:
   TA = (N NaOH) × (mLs NaOH $_{\text{(sample titration)}}$ – mLs NaOH $_{\text{(blank titration)}}$) × 75/ mLs of sample.

Appendix

Optional User Prepared NaOH Titrant Solution and KHP Solution for Standardization of Titrant

0.067 N NaOH titrant solution: Weigh 1.34 g NaOH pellets and quickly transfer to a 500 mL volumetric flask. Add RGW to dissolve the pellets and fill to the 500-mL mark. (Required reagents: NaOH, ACS grade)

0.033 N KHP solution: Dry KHP at 110 degrees C for 2 hours and cool in a dessicator. Weigh approximately 0.34 g of cool, dried KHP into a 50 mL volumetric flask and record the exact weight (Ws). Fill the flask to the 50-mL mark with RGW and mix well to dissolve the solid. Calculate N KHP: N KHP = Ws / 10.211 (where 10.211 = 204.22 g/mole KHP x 0.050 L).

(Required reagents: KHP, ACS grade)

Standardization of Titrant — recommended for User Prepared Titrant and for quality control of any titrant solution

Pipette 10.0 mL KHP solution to 50 mL RGW in a 100 mL beaker. Rinse the electrode, ATC, and stirrer with RGW. Immerse the electrode, ATC, and stirrer in the solution. Turn on the stirrer. Tap to release air bubbles trapped on the surface of the electrode. Adding NaOH titrant from the burette, titrate at a moderate rate. It is not necessary to wait for a stabilized reading when the pH is still far from 8.2. Start to add titrant slowly when the pH approaches 8. When the pH reading reaches 8.2, the titration is at the endpoint. Record the volume of titrant used (Vt) at the endpoint. Repeat the standardization procedure if required by user's protocol. Calculate the NaOH titrant concentration (T, mol/L) as follows:

$$\text{Normality of NaOH} = \frac{\text{(N KHP) x (mLs KHP)}}{\text{mLs NaOH}}$$

Results of an example titrant standardization are summarized in the following table.

Titrant standardization	Endpoint volume (mL)	NaOH (M)
Trial 1	5.60	0.0596
Trial 2	5.57	0.0599
Trial 3	5.61	0.0594
Statisitics	Mean	0.0596
	RSD	0.4%

Optional analysis of tartaric acid standard – QC sample

Weigh approximately1.00 g tartaric acid into a 200 mL volumetric flask and record the exact weight (Wd). Dissolve and fill to the 200-mL mark with RGW. The concentration of the tartaric acid standard is 5 × Wd g/L. For example, the Wd was 1.0081 g tartaric acid in the Results section above. The concentration of the standard was calculated to be 5.0405 g/L). Pipette 5 mL of tartaric acid standard into a 100 mL beaker containing 50 mL RGW. Titrate with the NaOH titrant using the titration techniques described in Standardization of Titrant section. Calculate the concentration of tartaric acid using the equation for TA in sample (noted in Results section).

Depending on your sample throughput needs and budget, we have developed application notes for both our electrochemistry meters for manual titrations and potentiometric titrators for automated titrations. Our automated titrators can help improve your titrations by simplifying your process and helping to deliver consistently reliable results. Just program it once and the titrator takes care of the rest — including addition of titrant, endpoint determination, results calculation, and data logging. Please visit **thermofisher.com/titrator** for more information.

Ordering information

Product	Description	Cat. No.
Electrodes	Thermo Scientific Orion ROSS Sure-Flow pH Electrode	8172BNWP
	Orion Green pH Electrode	GD9156BNWP
Meters	Thermo Scientific Orion Star A211 pH Benchtop Meter Kit	STARA2114
	Thermo Scientific Orion Versa Star Pro pH Meter Kit	VSTAR13
	Thermo Scientific Orion Versa Star Pro pH/ISE/Conductivity/RDO/DO Meter Kit	VSTAR92
Solutions	Thermo Scientific Orion ROSS All-in-One pH Buffer Kit	810199
	Thermo Scientific Orion ROSS pH Electrode Filling Solution	810007
	Thermo Scientific Orion Double Junction pH Electrode Fill Solution (For GD9156BNWP)	910008-WA
	Thermo Scientific Orion ROSS pH electrode storage solution	810001
	Thermo Scientific Orion pH electrode storage solution	910001
Accessories	Thermo Scientific Orion Automatic Stirrer Probe and Paddle	096019
	Thermo Scientific Orion Swing Arm and Electrode Holder	090043
Reagent grade water	Thermo Scientific Barnstead Smart2Pure 12 UV Water Purification System	50129890*

*Please contact your local Thermo Scientific representative for support on ordering the best water purification system for your applications, and visit our website at thermofisher.com/labwater

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