

# Titrateable Acidity of Red Wine by Manual Titration (Potentiometric)

Water Analysis Instruments, Thermo Fisher Scientific

## Key Words

Titrateable acidity, red wine, manual titration, potentiometric, organic acids.

## Goal

The following application note demonstrates a simple titrateable acidity titration method using a Thermo Scientific™ Orion™ pH electrode and meter to signal the endpoint.

## Introduction

Titrateable 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. Because 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

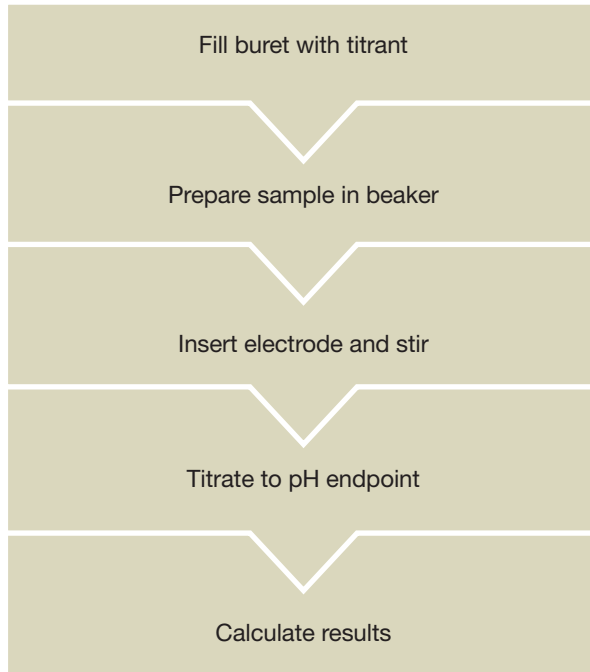
- Thermo Scientific™ Orion Star™ A meter, Thermo Scientific™ Orion™ VERSA STAR™ meter, or equivalent
- Thermo Scientific™ Orion™ ROSS™ Sure-Flow™ pH electrode 8172BNWP or Thermo Scientific™ Orion™ GD9156BNWP green pH electrode, or equivalent
- Orion automatic stirrer probe and paddle (Cat. No. 096019)
- Orion swing arm and electrode holder (Cat. No. 090043)
- 10 mL burette, burette clamp, ring stand



## Required Reagents and Solutions

- 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 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)
- Deionized water (DI) 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 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<sub>2</sub>, 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<sub>2</sub>, 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 DI. Immerse the electrode 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 exceeds 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 and stirrer with DI and tap 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 - Titratable Acids in Red Wine Samples

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

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:

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

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), multiple tartaric acid results by 0.853.
4. For greater accuracy, titrate a blank (50 mL of DI 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:  

$$\text{TA} = (\text{N NaOH}) \times (\text{mLs NaOH}_{(\text{sample titration})} - \text{mLs NaOH}_{(\text{blank titration})}) \times 75 / \text{mLs of sample.}$$

## 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 DI to dissolve the pellets and fill to the mark.  
(Required reagents: NaOH, ACS grade)

0.033 N KHP solution: Dry KHP at 110 degrees C for 2 hours and cool in a desiccator. Weigh ~0.34 g of cool, dried KHP into a 50 mL volumetric flask and record the exact weight (Ws). Fill the flask to the mark with DI and mix well to dissolve the solid.

(Required reagents: KHP, ACS grade)

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

Pipette 10 mL KHP solution to 50 mL DI in a 100 mL beaker. Rinse the electrode and stirrer with DI. Immerse the electrode 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 exceeds 8.2, the titration has reached 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:

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

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
Statistics	Mean	0.0596
	RSD	0.4%

### Optional Analysis of Tartaric Acid Standard – QC Sample

Weigh ~1.00 g tartaric acid into a 200 mL volumetric flask and record the exact weight (Wd). Dissolve and fill to the mark with DI water. The concentration of the tartaric acid standard is  $5 \times Wd$  g/L. (The actual Wd was 1.0081 g 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 DI. 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).



## References

Zoecklein et al. Wine Analysis and Production. Chapman and Hall. 1995.

AOAC International. AOAC Official Method 962.12, Acidity (Titratable) of Wines. Official Methods of Analysis (OMA), 16th edition. 1999. www.aoac.org

To purchase the Orion meters, electrodes and solutions referenced in this application note, please contact your local equipment distributor and reference the part numbers listed below:

Product	Description	Part Number
Electrodes	Thermo Scientific Orion ROSS Sure-Flow pH Electrode	8172BNWP
	Thermo Scientific Orion green pH Electrode	GD9156BNWP
Meters	Thermo Scientific Orion Star A211 pH benchtop meter kit	STARA2115
	Thermo Scientific Orion VERSA STAR pH meter kit	VSTAR12
	Thermo Scientific Orion VERSA STAR 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
Accessories	Thermo Scientific Orion Automatic Stirrer Probe and Paddle	096019
	Thermo Scientific Orion Swing Arm and Electrode Holder	090043

[thermoscientific.com/water](http://thermoscientific.com/water)

© 2014 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific and its subsidiaries.

### Water Analysis Instruments

#### North America

Toll Free: 1-800-225-1480  
Tel: 1-978-232-6000  
info.water@thermo.com

#### Netherlands

Tel: (31) 020-4936270  
info.water.uk@thermo.com

#### China

Tel: (86) 21-68654588  
wai.asia@thermofisher.com

#### India

Tel: (91) 22-4157-8800  
wai.asia@thermofisher.com

#### Singapore

Tel: (65) 6778-6876  
wai.asia@thermofisher.com

#### Japan

Tel: (81) 045-453-9175  
wai.asia@thermofisher.com

#### Australia

Tel: (613) 9757-4300  
in Australia (1300) 735-295  
InfoWaterAU@thermofisher.com

**Thermo**  
SCIENTIFIC

A Thermo Fisher Scientific Brand