21 chapter

Standard Solutions and Titratable Acidity

S.Suzanne Nielsen
Department of Food Science, Purdue University, West Lafayette, IN, USA
e-mail: nielsens@purdue.edu

S.S. Nielsen, *Food Analysis Laboratory Manual*, Food Science Text Series,
DOI 10.1007/978-3-319-44127-6_21, © Springer International Publishing 2017

21.1 INTRODUCTION

21.1.1 Background

Many types of chemical analyses are made using a method in which a constituent is titrated with a solution of known strength to an indicator endpoint. Such a solution is referred to as a standard solution. From the volume and concentration of standard solution used in the titration, and the sample size, the concentration of the constituent in the sample can be calculated.

The assay for titratable acidity is a volumetric method that uses a standard solution and, most commonly, the indicator phenolphthalein. In the titration, a standard solution of sodium hydroxide reacts with the organic acids present in the sample. The normality of the sodium hydroxide solution, the volume used, and the volume of the test sample are used to calculate titratable acidity, expressing it in terms of the predominant acid present in the sample. A standard acid such as potassium acid phthalate can be used to determine the exact normality of the standard sodium hydroxide used in the titration.

The phenolphthalein endpoint in the assay for titratable acidity is pH 8.2, where there is a significant color change from clear to pink. When colored solutions obscure the pink endpoint, a potentiometric method is commonly used. A pH meter is used to titrate such a sample to pH 8.2.

21.1.2 Reading Assignment

Tyl, C., and Sadler, G. D. 2017. pH and titratable acidity. Ch. 22, in *Food Analysis*, 5th ed. S.S. Nielsen (Ed.), Springer, New York.

21.1.3 Notes

1. Carbon dioxide (CO_2) acts as an interfering substance in determining titratable acidity, by the following reactions:

   $H_2O + CO_2 \leftrightarrow H_2CO_3$ (carbonic acid)
   $H_2CO_3 \leftrightarrow H^+ + HCO_3^-$ (bicarbonate)
   $HCO_3^- \leftrightarrow H^+ + CO_3^{-2}$ (carbonate)

   In these reactions, buffering compounds and hydrogen ions are generated. Therefore, CO_2-free water is prepared and used for standardizing acids and base and for determining titratable acidity. An Ascarite® trap is attached to bottles of CO_2-free water, so that as air enters the bottle when water is siphoned out, the CO_2 is removed from the air.
2. Ascarite® is a silica base coated with NaOH, and it removes CO_2 from the air by the following reaction:

   $2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$

21.2 PREPARATION AND STANDARDIZATION OF BASE AND ACID SOLUTIONS

21.2.1 Objective

Prepare and standardize solutions of sodium hydroxide and hydrochloric acid.

21.2.2 Principle of Method

A standard acid can be used to determine the exact normality of a standard base and vice versa.

21.2.3 Chemicals

	CAS No.	*Hazards*
Ascarite	81133-20-2	Corrosive
Ethanol (CH_3CH_2OH)	64-17-5	Highly flammable
Hydrochloric acid (HCl)	7647-01-0	Corrosive
Phenolphthalein	77-09-8	Irritant
Potassium acid phthalate ($HOOCC_6H_4COOK$)	877-24-7	Irritant
Sodium hydroxide (NaOH)	1310-73-2	Corrosive

21.2.4 Reagents

(** It is recommended that these solutions be prepared by the laboratory assistant before class.)

(*Note:* Preparation of NaOH and HCl solutions is described under Procedure.)

- Ascarite trap**
  Put the Ascarite® in a syringe that is attached to the flask of CO_2-free water (see note about CO_2-free water).
- Carbon dioxide-free water**
  Prepare 1.5 L of CO_2-free water (per person or group) by boiling deionized, distilled (dd) water for 15 min in a 2-L Erlenmeyer flask. After boiling, stopper the flask with a rubber stopper through which is inserted in a tube attached to an Ascarite® trap. Allow the water to cool with Ascarite® protection.
- Ethanol, 100 mL
- Hydrochloric acid, concentrated
- Phenolphthalein indicator solution, 1 % **
  Dissolve 1.0 g in 100 mL ethanol. Put in bottle with eyedropper.
- Potassium acid phthalate (KHP)**
  3–4 g, dried in an oven at 120 °C for 2 h cooled and stored in a closed bottle inside a desiccator until use
- Sodium hydroxide, pellets

21.2.5 Hazards, Precautions, and Waste Disposal

Use appropriate precautions in handling concentrated acid and base. Otherwise, adhere to normal laboratory safety procedures. Wear gloves and safety glasses at all times. Waste likely may be put down the drain using a water rinse, but follow good laboratory practices outlined by environmental health and safety protocols at your institution.

21.2.6 Supplies

(Used by students)

- Beaker, 50 mL (for waste NaOH from buret)
- Beaker, 100 mL
- Buret, 25 or 50 mL
- 5 Erlenmeyer flasks, 250 mL
- Erlenmeyer flask, 1 L
- Funnel, small, to fit top of 25 or 50 mL buret
- Glass stirring rod
- Glass storage bottle, 100 mL
- Graduated cylinder, 50 mL
- Graduated cylinder, 1 L
- Graduated pipette, 1 mL
- Graduated pipette, 10 mL
- Parafilm®
- Pipette bulb or pump
- Plastic bottle, with lid, 50 or 100 mL
- Plastic bottle, with lid, 1 L
- Spatula
- Squirt bottle, with dd water
- Volumetric flask, 50 mL
- Volumetric flask, 100 mL
- Weighing paper/boat
- White piece of paper

21.2.7 Equipment

- Analytical balance
- Forced draft oven (heated to 120 °C)
- Hot plate

21.2.8 Calculations Required Before Lab

1. Calculate how much NaOH to use to prepare 50 mL of 25% NaOH (wt/vol) in water (see Table 2.1, in Chap. 2 for definition of wt%).
2. Calculate how much concentrated HCl to use to prepare 100 mL of ca. 0.1 *N* HCl in water (concentrated HCl = 12.1 *N*).

21.2.9 Procedure

1. Prepare 25% (wt/vol) NaOH solution: Prepare 50 mL of 25% NaOH (wt/vol) in dd water. To do this, weigh out the appropriate amount of NaOH and place it in a 100-mL beaker. While adding about 40 mL of dd water, stir the NaOH pellets with a glass stirring rod. Continue stirring until all pellets are dissolved. Quantitatively transfer the NaOH solution into a 50-mL volumetric flask. Dilute to volume with dd water. The solution must be cooled to room temperature before final preparation. Store this solution in a plastic bottle and label appropriately.
2. Prepare ca. 0.1 *N* HCl solution: Prepare 100 mL of ca. 0.1 *N* HCl using concentrated HCl (12.1 *N*) and dd water. (Note: Do not use a mechanical pipettor to prepare this, since the acid can easily get into the shaft of the pipettor and cause damage.) To prepare this solution, place a small amount of dd water in a 100-mL volumetric flask, pipette in the appropriate amount of concentrated HCl, then dilute to volume with dd water. Mix well, and transfer into a glass bottle, seal bottle, and label appropriately.
3. Prepare ca. 0.1 *N* NaOH solution: Transfer 750 mL CO_2-free water to a 1-L plastic storage bottle. Add ca. 12.0 mL of well-mixed 25% (wt/vol) NaOH solution prepared in Step 1. Mix thoroughly. This will give an approximately 0.1 *N* solution. Fill the buret with this solution using a funnel. Discard the first volume of the buret and then refill the buret with the NaOH solution.
4. Standardize ca. 0.1 *N* NaOH solution: Accurately weigh about 0.8 g of dried potassium acid phthalate (KHP) into each of three 250-mL Erlenmeyer flasks. Record the exact weights. Add ca. 50 mL of cool CO_2-free water to each flask. Seal the flasks with Parafilm® and swirl gently until the sample is dissolved. Add three drops of phenolphthalein indicator and titrate, against a white background, with the NaOH solution being standardized. Record the beginning and ending volume on the buret. Titration should proceed to the faintest tinge of pink that persists for 15 s. after swirling. The color will fade with time. Record the total volume of NaOH used to titrate each sample. Data from this part will be used to calculate the mean normality of the diluted NaOH solution.
5. Standardize ca. 0.1 *N* HCl solution: Devise a scheme to standardize (i.e., determine the exact *N*) the ca. 0.1 *N* HCl solution that you prepared in Step 2. Remember that you have your standardized NaOH to use. Do analyses in at least duplicate. Record the volumes used.

21.2.10 Data and Calculations

Using the weight of KHP and the volume of NaOH titrated in Sect. 21.2.9, Step 4, calculate the normality of the diluted NaOH solution as determined by each

titration and then calculate the mean normality (molecular weight (MW) potassium acid phthalate = 204.228). The range of triplicate determinations for normality should be less than 0.2% with good technique.

Rep	*Weight of KHP (g)*	*Buret start (mL)*	*Buret end (mL)*	*Vol. NaOH titrated (mL)*	*N NaOH*
1					
2					
3					
					$\bar{X}$ =
					SD=

Sample calculation:

Weight of KHP = 0.8115 g
MW of KHP = 204.228 g/mol
Vol. of ca. 0.10 *N* NaOH used in titration = 39 mL
Mol KHP = 0.8115 g/204.228 g/mol
= 0.003974 mol
Mol KHP = mol NaOH
= 0.003974 mol = *N* NaOH × L NaOH
0.003978 mol NaOH/0.039 L NaOH = 0.1019 *N*

With the volumes of HCl and NaOH used in Sect. 21.2.9, Step 5, calculate the exact normality of the HCl solution as determined by each titration and then calculate the mean normality.

Rep	*Vol. HCl (mL)*	*Vol. NaOH (mL)*	*N HCl*
1			
2			
			$\bar{X}$ =

21.2.11 Questions

1. What does 25% NaOH (wt/vol) mean? How would you prepare 500 mL of a 25% NaOH (wt/vol) solution?
2. Describe how you prepared the 100 mL of ca. 0.1 *N* HCl. Show your calculations.
3. If you had not been told to use 12 mL of 25% NaOH (wt/vol) to make 0.75 L of ca. 0.1 *N* NaOH, how could you have determined this was the appropriate amount? Show all calculations.
4. Describe in detail how you standardized your ca. 0.1 *N* HCl solution.

21.3 TITRATABLE ACIDITY AND pH

21.3.1 Objective

Determine the titratable acidity and pH of food samples.

21.3.2 Principle of Method

The volume of a standard base used to titrate the organic acids in foods to a phenolphthalein endpoint can be used to determine the titratable acidity.

21.3.3 Chemicals

	CAS No.	*Hazards*
Ascarite	81133-20-2	Corrosive
Ethanol (CH_3CH_2OH)	64-17-5	Highly flammable
Phenolphthalein	77-09-8	Irritant
Sodium hydroxide (NaOH)	1310-73-2	Corrosive

21.3.4 Reagents

(** It is recommended that these items/solutions be prepared by the laboratory assistant before class:)

- Ascarite trap**
  Put the Ascarite® in a syringe that is attached to the flask of CO_2-free water:
- Carbon dioxide-free water**
  Prepared and stored as described in Method A
- Phenolphthalein indicator solution, 1%**
  Prepared as described in Method A
- Sodium hydroxide, ca. 0.1 *N*
  From Sect. 21.2.9, Step 4; exact *N* calculated
- Standard buffers, pH 4.0 and 7.0

21.3.5 Hazards, Precautions, and Waste Disposal

Adhere to normal laboratory safety procedures. Wear safety glasses at all times. Waste likely may be put down the drain using a water rinse, but follow good laboratory practices outlined by environmental health and safety protocols at your institution.

21.3.6 Supplies

- Apple juice, 60 mL
- 3 Beakers, 250 mL
- 2 Burets, 25 or 50 mL
- 4 Erlenmeyer flasks, 250 mL
- Funnel, small, to fit top of 25 or 50 mL buret
- Graduated cylinder, 50 mL
- Soda, clear, 80 mL
- 2 Volumetric pipettes, 10 or 20 mL

21.3.7 Equipment

- Hot plate
- pH meter

21.3.8 Procedure

21.3.8.1 *Soda*

Do at least duplicate determinations for unboiled soda and for boiled soda sample; open soda well before use to allow escape of carbon dioxide, so that the sample can be pipetted.

1. Unboiled soda: Pipette 20 mL of soda into a 250-mL Erlenmeyer flask. Add ca. 50 mL CO_2-free dd water. Add three drops of a 1% phenolphthalein solution and titrate with standardized NaOH (ca. 0.1 *N*) to a faint pink color (NaOH in buret, from Method A). Record the beginning and ending volumes on the buret to determine the total volume of NaOH solution used in each titration. Observe the endpoint. Note whether the color fades.
2. Boiled soda: Pipette 20 mL of soda into a 250-mL Erlenmeyer flask. Bring the sample to boiling on a hot plate, swirling the flask often. Boil the sample only 30–60 s. Cool to room temperature. Add ca. 50 mL CO_2-free dd water. Add three drops of the phenolphthalein solution and titrate as described above. Record the beginning and ending volumes on the buret to determine the total volume of NaOH solution used in each titration. Observe the endpoint. Note whether the color fades.

21.3.8.2 *Apple Juice*

1. Standardize the pH meter with pH 7.0 and 4.0 buffers, using instructions for the pH meter available.
2. Prepare as described below three apple juice samples that will be compared:

   A – Apple juice (set aside, to recall original color)
   B – Apple juice; titrate with std. NaOH
   C – Apple juice; add phenolphthalein; titrate with std. NaOH; follow pH during titration

   Procedure: Into each of three (A, B, C) 250-mL beakers, pipette 20 mL of apple juice. Add ca. 50 mL CO_2-free water to each. To sample C, add three drops of a 1% phenolphthalein solution. Using two burets filled with the standardized NaOH solution (ca. 0.1 *N*), titrate Samples B and C simultaneously. Follow the pH during titration of Sample C containing phenolphthalein. (*Note:* If only one buret is available, titrate Samples B and C sequentially, i.e., add 1 mL to B and then 1 mL to C.) Record the initial pH and the pH at ca. 1.0 mL intervals until a pH of 9.0 is reached. Also, observe any color changes that occur during the titration to determine when the phenolphthalein endpoint is reached. Sample A is intended to help you remember the original color of the apple juice. Sample B (without phenolphthalein) does not need to be followed with the pH meter but is to be titrated along with the other beakers to aid in observing color changes.

21.3.9 Data and Calculations

21.3.9.1 *Soda*

Using the volume of NaOH used, calculate the titratable acidity (TA) of each soda sample as percentage citric acid, and then calculate the mean TA of each type of sample (MW citric acid = 192.14; equivalent weight = 64.04) (Note: See Eq. 22.20 in Tyl and Sadler, 2017).

Rep	*Buret start*	*Buret end*	*Vol. NaOH titrant*	*Color fades?*	*TA*
Unboiled soda:					
1					
2					
					$\bar{X}$ =
Boiled soda:					
1					
2					
					$\bar{X}$ =

Sample calculation:

$$\%\,\text{Acid} = \frac{(\text{mL base titrant}) \times (N \text{ of base in mol/liter}) \times (\text{Eq. Wt. of acid})}{(\text{sample volume in mL}) \times 10}$$

N NaOH = 0.1019 N
mL base = 7 mL
Eq. wt. citric acid = 64.04
Vol. sample = 20 mL

$$\%\ \text{Acid} = (7\,\text{ml} \times 0.1019 \times 64.04)/(20\,\text{ml} \times 10)$$
$$= 0.276\%\ \text{citric acid}$$

21.3.9.2 *Apple Juice*

Sample B
Color change during titration:
Color at end of titration:

Sample C (titrate to >pH 9.0)

mL NaOH	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
pH										

mL NaOH	*11*	*12*	*13*	*14*	*15*	*16*	*17*	*18*	*19*	*20*
pH										

Plot pH versus mL of 0.1*N* NaOH (but use the normality of your own NaOH solution) (pH on the *y*-axis) for the sample that contained phenolphthalein (Sample C). Interpolate to find the volume of titrant at pH 8.2 (the phenolphthalein endpoint).

Calculate the titratable acidity of the apple juice as percentage malic acid (MW malic acid = 134.09; equivalent weight = 67.04).

21.3.10 Questions

1. Soda samples. (a) Did any color changes occur in either the boiled or the unboiled sample within several minutes of the phenolphthalein endpoint being reached? (b) How did boiling the sample affect the determination of titratable acidity? (c) Explain the differences in color changes and titratable acidity between the two samples.
2. What caused the color changes in the apple juice titrated without any phenolphthalein present? (Hint: Consider the pigments in apples.) How would you recommend determining the endpoint in the titration of tomato juice?
3. You are determining the titratable acidity of a large number of samples. You ran out of freshly boiled dd H_2O with an Ascarite trap on the water container, so you switch to using tap distilled H_2O. Would this likely affect your results? Explain.
4. The electrode of your pH meter has a slow response time and seems to need cleaning, since it is heavily used for a variety of solutions high in proteins, lipids, and minerals. You would ideally check the electrode instructions for specific recommendations on cleaning, but the instructions were thrown away. (As the new lab supervisor, you have since started a policy of filing all instrument/equipment instructions.) What solutions would you use to try to clean the electrode?

RESOURCE MATERIALS

AOAC International (2016) Official methods of analysis, 20th edn. (On-line). AOAC International, Rockville, MD

Tyl C, Sadler GD (2017) pH and titratable acidity. Ch. 22. In: Nielsen SS (ed) Food analysis, 5th edn. Springer, New York