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Total Carboxylic Acid Group Content

Applicable Products: Carbopol®* Polymers and Pemulen™* Polymeric Emulsifiers

Scope:

This procedure is used for the determination of the total carboxylic acid group content (TCAG) of Carbopol® polymers and Pemulen™ polymeric emulsifiers. Both a manual titration and an auto-titration method are described.

Abstract:

A dispersion of Carbopol® polymer or Pemulen™ polymeric emulsifier is titrated potentiometrically with sodium hydroxide using a glass-calomel electrode. The carboxylic acid content is calculated based on the volume of standard sodium hydroxide solution used.

Safety Precautions:

1. Wear safety goggles and gloves and follow good laboratory practices.
2. Polymer dust is irritating to the respiratory passages and inhalation should be avoided.
3. Sodium hydroxide solutions will cause burns to the skin and eyes. Flush any contact site with large quantities of water.
4. See all Material Safety Data Sheets (MSDS) for additional safety and handling information.

Interferences:

Care should be taken to avoid moisture pick-up during the weighing process. After exposure to moisture, Carbopol® polymers and Pemulen™ polymeric emulsifiers may not completely hydrate when dispersed in water.

Any acidic or alkaline material introduced in the process will cause interferences.

MANUAL TITRATION METHOD:

Instructions for the auto-titration method begin on page 3.

Apparatus:

1. Laboratory balance capable of ± 0.0001 gram accuracy.
2. Laboratory mixer with three-blade marine impeller (see Appendix I).
3. Burette, 25 mL.
4. Beaker, 800 ml.
5. Graduated cylinder, 500 ml.
6. Spatula or rubber policeman.
7. Heat safe glass weighing bottle with top.
8. Magnetic stirring device.
9. Stir bar (3”).
10. pH meter equipped with a calomel-glass electrode.
11. Vacuum oven controlled at 80 ± 2°C (176 ± 4°F) with a vacuum of 29 inches (736 mm) Hg.
12. Vacuum oven controlled at 120 ± 5°C.
13. Weighing dish or plastic boat.
14. Desiccator with silica gel (or other suitable) desiccant.
15. Volumetric flask, 1 L.

Reagents:

1. Distilled or deionized water.
2. Sodium hydroxide solution, 0.25 N. (If not purchased, see Special Instruction 1 for preparation of 0.25 N sodium hydroxide from pellets). Special Instruction 2 describes the standardization of the purchase or prepared 0.25 N solution.
3. Potassium chloride.
4. Potassium hydrogen phthalate (KHP).
5. Phenolphthalein TS (1 g in 100 mL alcohol).

Procedure:

1. Transfer sufficient sample to a heat safe glass weighing bottle and dry in a vacuum oven controlled at 80 ± 2°C (176 ± 4°F) with a vacuum of 29 inches Hg for 1 hour. After drying, place the top on the weighing bottle and move to a desiccator to cool to room temperature.
2. With the mixer in the off position, set the shaft with the 3-blade marine impeller at an angle of 60° and the mixer speed to 1000 rpm.
3. Measure 400 mL distilled or deionized water in a graduated cylinder and transfer to an 800 mL beaker.
4. Set the beaker under the mixer with the impeller to one side and as near the bottom as possible (see Note 1).
5. After the polymer has reached room temperature, weigh 0.4000 g (record the actual weight to four decimals) onto a weighing dish.
6. Turn on the mixer and hold the weighing dish containing the weighed product sample a few inches above the surface of the water. Tilt the weighing dish to the point that sample is ready to spill out. Tap the dish, causing the sample to slowly sift into the water. Total addition time should be 45 to 90 seconds. CAUTION: If addition is too rapid, the polymer will agglomerate on the surface of the water. Inadequate dispersion will result in test error.
7. Continue mixing for 15 minutes at 1000 ± 10 rpm. Scrape any sample from the sides of the beaker and the stirrer shaft with a spatula or rubber policeman.
8. Allow the polymer dispersion to stand for 30 minutes.
9. Transfer the beaker to a magnetic stirring device. Place a 3” stirring bar into the solution and adjust the mixer speed to obtain moderate mixing.
10. Add 1 gram potassium chloride (see Note 2).
11. Insert the pH electrode into the dispersion.
12. Titrate with 0.25 N sodium hydroxide, adding 20 mL of titrant rapidly. Allow the pH value to stabilize. Until a pH 9.0 reading is attained, add the sodium hydroxide in 0.25 mL increments. After pH = 9.0 make additions in 0.1 mL increments. Continue to allow the mucilage pH to stabilize between additions. It may be necessary to increase the stirring speed as the titration progresses.
13. Titrate to a final pH of 9.5.
14. Record the amount of sodium hydroxide consumed in the titration and perform the required calculation.

Calculation:

$$\% \text{ TCAG} = \frac{(V)(N)\ (45.02/1000)\ (100)}{WT}$$

Where V = volume of sodium hydroxide consumed (mL)

N = normality of sodium hydroxide

WT = weight of sample (g)

45.02 = equivalent weight of carboxylic acid group

1000 = conversion factor to obtain correct units

100 = conversion to percent

AUTO-TITRATION METHOD:

Only Carbopol® 980 NF, 981 NF, 5984 EP, 2020 NF polymers and Pemulen™ TR-1 NF polymeric emulsifier have been tested by the auto-titration technique and demonstrated to give equivalent results to the manual titration method.

Apparatus:

1. Vacuum oven controlled at 80 ± 2°C (176 ± 4°F) with a vacuum of 29 inches (736 mm) Hg.
2. Balance, capable of 0.0001 g resolution.
3. Beaker, 150 mL.
4. Weighing dish or plastic boat.
5. Auto-titrator, 808 Titrando Metrohm (or equivalent).
6. Metrohm dosimat 805 (or equivalent)
7. Volumetric flask, 100 mL.
8. Desiccator with silica gel or other suitable desiccant.
9. Heat safe weighing bottle with top.
10. Graduated cylinder, 100 mL.
11. Oven controlled at 120 ± 5°C.
12. Volumetric flask, 1L.

Reagents:

1. Distilled or deionized water.
2. Sodium hydroxide solution, 0.25 N. (If not purchased, see Special Instruction 1 for preparation of 0.25 N sodium hydroxide from pellets). Special Instruction 2 describes the standardization of the purchase or prepared 0.25 N solution.
3. KCl solution (12.5%). See Special Instruction 3.
4. Potassium hydrogen phthalate (KHP).
5. Phenolphthalein TS (1 g in 100 mL alcohol).

Procedure:

1. Transfer sufficient sample to a heat safe glass weighing bottle and dry in a vacuum oven controlled at 80 ± 2°C (176 ± 4°F) with a vacuum of 29 inches Hg for 1 hour. Place the top on the weighing bottle and move to a desiccator to cool to room temperature.
2. After the polymer reaches room temperature, weigh out 0.1000 (record the actual weight to four decimals) into a 150 mL beaker.
3. Add 100 mL deionized water.
4. Check the lines delivering the 0.25 NaOH and KCl solution for the presence of air bubbles. Degas, if necessary, by dosing 5 mL quantities of the solutions.
5. Recall the program stored in the auto-titrator that performs the TCAG determination.
6. Place the beaker in the holding device of the auto-titrator. Insert the pH-electrode and the dosing tubes into the liquid.
7. Input sample identification and sample weight.
8. When the “START” button is pressed the method sequentially performs the following steps:
   - Mix for 15 minutes
   - Add 5 mL of KCL solution (see Note 2)
   - Perform a pH=9.5 end-point titration
9. A report with the results of the %TCAG is printed.

Special Instructions:

1. Sodium Hydroxide solution, 0.25 N. This solution can be purchased commercially or prepared in the laboratory. In either case it must be standardized (Special Instruction 2).

   Laboratory preparation of 0.25 N sodium hydroxide:
   a. Weigh 10.0 g of sodium hydroxide pellets and transfer to a clean 1000 mL volumetric flask.
   b. Add approximately 500 mL deionized water and invert several times to mix thoroughly.
   c. After the solution has cooled to room temperature, fill the volumetric flask to the mark with deionized water and mix.
   d. Transfer the solution to a reagent bottle or burette reservoir and label appropriately.
   e. Standardize the solution as outlined below.
2. Standardization of 0.25 N Sodium Hydroxide:
   a. Dry at least one gram of potassium hydrogen phthalate primary standard material in an oven at 120 ± 5°C for a minimum of two hours to remove any absorbed moisture.
   b. Remove to a desiccator and allow to cool to room temperature.
   c. To an 800 mL beaker, add 400 mL of distilled or demineralized water.
   d. Place the 3” magnetic stir bar into the beaker.
   e. Weigh 1 ± 0.10 gram of the standard material onto a weighing dish. Record the

weight to four decimals.

f. Dump the weighed standard material into the beaker of water.
g. Place the beaker on the magnetic stirring device and begin mixing at a speed to attain a vortex.
h. Add 2 drops of 1% phenolphthalein solution.
i. Using the automatic burette, titrate the acid with the sodium hydroxide to be standardized.
j. Slowly add sodium hydroxide until a faint pink color remains with continuous stirring. Record the number of mL of NaOH required to neutralize the acid.
k. The calculation of the exact normality of the sodium hydroxide is as follows:

$$N = \frac{\text{grams of KHP} \times 1000}{(204.23\ \text{g/g-eq}) \times (\text{mL NaOH})}$$

3. KCl solution. To a 100 mL volumetric half-filled with deionized water, add 12.5 g KCl. Invert several times. Fill to the mark with water and again invert.

Notes:

1. The 60° angle setting and placement of the stirring shaft to one side of the beaker creates vigorous stirring with a minimum of vortexing.

2. Potassium chloride prevents a build of viscosity as NaOH is added, permitting effective stirring and contact of the base with the acid groups on the Carbopol® polymers and Pemulen™ polymeric emulsifiers.

References:

- *Current edition of the United States Pharmacopeia/National Formulary (USP/NF)*

Appendix I
(Actual Size)

Three-Blade Marine Impeller