

Residual Acrylic Acid in Polyacrylic Acid Polymers

Applicable Products: Carbopol[®]* Polymers, Pemulen[™]* Polymeric Emulsifiers and Noveon[®]* AA-1 Polycarbophil

Scope:

This procedure is used to determine the level of residual acrylic acid in Carbopol[®] polymers, Pemulen[™] polymeric emulsifiers or Noveon[®] polycarbophil polymers.

Abstract:

A sample of the polymer is dispersed in water and placed on a shaker for 2 hours. The dispersion is centrifuged and an aliquot of the supernatant is injected onto a high performance liquid chromatograph column equipped with a UV detector. The response of acrylic acid in the sample is compared to the responses of prepared standards to determine the concentration in the polymer.

Interferences:

Any component eluting at the same retention time as acrylic acid would interfere. No such interferences have been seen.

Safety Precautions:

1. Wear safety goggles and gloves.
2. Polymer dust is irritating to the respiratory passages and breathing it should be avoided.
3. Handle concentrated phosphoric acid and acrylic acid with extreme caution as they are very corrosive and can cause burns. Wear safety goggles and the appropriate gloves when handling. Perform all work in a hood as prolonged breathing of the vapors should be avoided.
4. See all Material Safety Data Sheets (MSDS) for additional safety and handling information.

Apparatus:

1. Analytical balance capable of 0.0001 gram accuracy.
2. Aluminum weighing dish or plastic boat.
3. Eleven dram vial.
4. Mechanical shaker.
5. Centrifuge.
6. Liquid dropper.
7. Volumetric flask, 100 mL.
8. Volumetric flask, 500 mL.
9. Volumetric flask, 1000 mL.
10. Pipette, disposable, 1 mL.
11. pH meter with glass/calomel electrode.
12. High performance liquid chromatograph with gradient capable pump and UV detector with 200 nm wavelength capability (Agilent 1100 Series or equivalent).
13. Autosampler.
14. Data processing station.
15. Column: μ Bondapak C₁₈, 10 μ m, 8 mm x 100 mm cartridge (or equivalent column).
16. Waters RCM 8 x 10 module.
17. In-line refillable analytical guard column with C₁₈ porous media.
18. Autosampler vial (1.5 dram) with screw cap.
19. 10 μ L syringes.
20. Filter, PTFE membrane, 0.45 μ m.
21. 3 mL syringe.
22. Beaker, 1500 mL.
23. Magnetic stirrer.
24. Stir bar.
25. Thermometer.
26. 11 dram vial with cap.

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Reagents:

1. Water, HPLC grade, submicron filtered.
2. Potassium phosphate monobasic (KH_2PO_4), HPLC grade.
3. Concentrated phosphoric acid.
4. Methanol, HPLC grade.
6. Acrylic acid, anhydrous 99% min, certified analysis (see Note 1).
7. Sodium hydroxide, 50% (w/v) solution.
8. Calcium chloride, 10% (w/v) solution.
9. Methanol, HPLC grade.

Procedure:

Mobile phase preparation.

Potassium Phosphate Monobasic (KH_2PO_4), HPLC Grade. 0.01M KH_2PO_4

1. Add 6.8045 g KH_2PO_4 to a 500 ml volumetric flask and fill to the mark with HPLC water.
2. 0.01M KH_2PO_4 .: Dilute 100 ml of the 0.1M KH_2PO_4 with HPLC water to 1 liter in a volumetric flask.
3. Adjust the 0.01M KH_2PO_4 to a pH=3 by placing 1 liter of 0.01M KH_2PO_4 into a 1500 ml beaker.
4. Place on a magnetic stirrer and immerse the pH electrode.
5. Add concentrated phosphoric acid (H_3PO_4) (85% min.) dropwise until a pH of 3 is obtained.

Use within 2 weeks.

Preparation of Liquid Chromatograph System.

1. Transfer the 0.01 M potassium monobasic phosphate mobile phase to a reagent bottle for supply to the mobile phase pump.
2. Pump mobile phase through the column for 60-90 minutes to insure a stable baseline.
3. Confirm the following settings and conditions:
 - Sample size: 10 μl
 - Mobile phase: 100% 0.01M potassium Phosphate monobasic
 - Flow rate: 1.0 mL/min
 - Column: $\mu\text{Bondapack C}_{18}$, 10 μm , 8 mm X 100 mm cartridge with guard column containing C_{18} porous media in-line before the analytical column
 - Column temperature: 25°C
 - Detector: UV at 200 nm

Standard preparation.

1. Tare a 100 mL volumetric flask and add approximately 0.01 g acrylic acid (9.5 μl from a 10 μl syringe). Record the weight to four decimal places. Dilute to the mark with HPLC water. Label as standard 1. The concentration should be approximately 100 ppm.
2. Prepare two additional standards of approximately 50 ppm and 5 ppm by quantitative dilutions. Identify as standards 2 and 3.
3. Inject each standard
4. Create a calibration curve or calculate the response factor and plot against peak area if the data processor does not handle the calibration internally. The plot should be linear with an R^2 minimum of 0.999

Sample preparation.

1. Accurately weigh 0.1 gram of the polymer into a tared 11 dram vial. Record the weight to four decimal places.
2. Add HPLC grade water to bring the total weight to 10 grams. Record the weight to four decimal places.
3. Cap the vial and shake well to insure sufficient contact of the polymer with the water to attain complete hydration.
4. Place on a mechanical shaker for 2 hours.
5. Add 2 drops of 50% sodium hydroxide solution.
6. Cap the vial and shake vigorously five times by hand (15 seconds)
7. Add 1.0 mL 10% calcium chloride to the sample.
8. Shake until gel collapses.
9. Centrifuge the sample until a clear, non-hazy supernatant is present (typically 15 minutes at 4000 rpm).
10. With a syringe, remove an aliquot of the supernatant from the centrifuge tube.
11. Place a PTFE membrane filter (0.45 μm) on the end of the syringe. Force sample through the filter into a 1.5 dram vial.
12. Prepare control standards (see Note 1) to be analyzed as the first and last samples in a run. If more than 15 samples are to be analyzed, prepare a control standard for each 15 analyses in addition to the first and last.
13. Load samples into the autosampler carousel.
14. Place a vial filled with methanol after the final control standard.

15. Prepare the data processing station by entering sample data. The weight of sample and water divided by weight of sample (approximately 100) is to be entered as a multiplier.

Calculations:

The data processing station will generate a response vs. concentration curve from the standard analyses. Calculations of residual acrylic acid values for samples and control lots are reported using this standard curve (see Note 3).

If a data processing station is not used, the concentration of samples can be manually calculated by comparing responses of samples with the responses of standards.

Residual acrylic acid in sample =

$$\frac{\text{peak area}}{\text{response factor}} \times \frac{\text{weight of water}}{\text{weight of polymer}}$$

Special Instructions:

When analyses are complete, flush the potassium phosphate buffered solution from the system. Leaving this solution in the pump heads can cause damage. Flush with methanol for a minimum of 2 hours.

Notes:

1. Acrylic acid forms a dimer over time. Refrigeration will minimize dimer formation. Therefore, fresh certified acrylic acid (less than 3 months old) should be used in standard preparations to insure accurate results.