

Residual Acrylic Acid in Polyacrylic Acid Polymers

Scope:

This procedure is designed to determine the levels of residual acrylic acid in Carbopol® polymers, Pemulen™ polymers and Noveon® polycarbophil.

Abstract:

A sample of the polymer is extracted in a solution of water for 2.0 hours. The extract is then isolated by centrifugation and filtered prior to analysis. An aliquot of the extract is injected onto a high performance liquid chromatograph column with a variable wavelength detector. The peak area obtained for acrylic acid is then compared to a calibration curve to obtain the actual concentration of the polymer.

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 sites with large quantities of water.
4. Handle concentrated phosphoric acid (H₃PO₄) with extreme care. It is very corrosive and can cause burns when it contacts the skin.
5. When preparing standards of acrylic acid, handle with extreme care. Acrylic acid will burn the skin. Prolonged breathing of the vapors should be avoided.
6. See the MSDS for additional safety and handling information.

Interferences:

Any components which are extractable from the polymer sample which have the same retention time as acrylic acid would theoretically interfere, however, no such interferences have been observed.

Apparatus:

1. Analytical balance capable of 0.0001 g accuracy
2. Weighing dish
3. Metal spatula
4. 50 ml centrifuge tube, flat bottom
5. Wrist action shaker, or equivalent
6. Centrifuge
7. Transfer pipette
8. Volumetric flask, 100 ml
9. Volumetric flask, 500 ml
10. Volumetric flask, 1000 ml
11. Pipette, 1 ml
12. pH meter and electrode
13. Agilent 1100 Series HPLC system with quaternary pump, or equivalent with UV detector capability of 200nm
14. Data system capable of determining peak areas

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15. Column: Phenomenex Luna C18, 4.6 mm x 150 mm or equivalent
16. Syringe Filters PTFE, 0.45 micron
17. HPLC vials, 2 mL and caps

Reagents:

1. pH buffer solutions
2. Water, HPLC grade
3. Potassium Phosphate Monobasic (KH₂PO₄), HPLC Grade 0.1M. Add 6.8045 g KH₂PO₄ to a 500 ml volumetric flask and fill to the mark with HPLC water
4. 0.01M KH₂PO₄. Dilute 100 ml of the 0.1M KH₂PO₄ with HPLC water to 1 liter in a volumetric flask
5. Adjust the 0.01M KH₂PO₄ to pH=3 solution by placing 1 liter of 0.01M KH₂PO₄ into a 1500 ml beaker. Place on a magnetic stirrer and immerse the pH electrode. Add concentrated Phosphoric Acid (H₃PO₄) 85% min) dropwise until a pH of 3 is obtained. An expiration date of two weeks should be observed for the buffer solution
6. Sodium hydroxide (NaOH). 50% (w/v) solution is prepared by adding 50 g NaOH to a 100 ml volumetric flask and diluting to volume with deionized water
7. Calcium chloride (CaCl₂). Prepare a 10% (w/v) solution by adding 10 g to a 100 ml volumetric flask and diluting to volume with deionized water
8. Methanol, HPLC grade.
9. Acrylic acid, anhydrous 99%

Procedure:

ANALYTICAL PARAMETERS:

1. Column temperature: ambient, approximately 25°C.
2. Mobile phase flow rate: 1.0 ml/min.
3. Detector parameters: Wavelength – 200 nm UV
Range – 0.1 AUFS
4. Injection volume: 10 microliter
5. Gradient Timetable:

Event Number	Time	% Methanol	% Buffer	Flow
1	0:00	5	95	1.000
2	8:00	5	95	1.000
3	9:00	10	90	1.500
4	19:00	10	90	1.500
5	20:00	5	95	1.000

6. Run time: 25 minutes. This allows five minutes for flushing the column after each sample run.

STANDARD PREPARATION:

1. A five point calibration is performed. Recommended range is 2ppm to 100ppm. Standards are prepared on a w/w basis with a primary standard of approximately 100ppm.
2. Prepare additional standards by quantitative dilutions on a w/w basis.

CALIBRATION PROCEDURE, EXTERNAL STANDARDS

1. Inject each standard.
2. 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 (recommended minimum r-squared value 0.9990.)

Response Factor = peak area / concentration (ppm)

SAMPLE PREPARATION PROCEDURE:

1. For sample analysis, weigh approximately 0.1 g of polymer into a tared 50 ml flat bottom centrifuge tube. Record the weight to the nearest 0.0001 g. Add HPLC water to make the total weight approximately 10 g. Record the weight of water of the sample to the nearest 0.0001 g. Cap vial and shake well by hand immediately after the water addition to ensure polymer fully hydrates. Place on a shaker for 2 hours. Inspect sample to insure all polymer has been hydrated (swelled and dispersed).
2. After the polymer has been hydrated in the water, add 2 drops of 50% Sodium Hydroxide (NaOH). Cap the vial and shake well for 15 seconds by hand. Add 1.0 ml 10% Calcium Chloride (CaCl₂) to the sample. Record the weight of the additions of the 2 drops of NaOH and 1.0ml of CaCl₂. The weight of these additions is added to the initial weight of water from step 1 in the final calculation. Cap and shake by hand until the gel collapses. Centrifuge the sample for 15 minutes at a 4000 rpm minimum.
3. Remove supernatant from the centrifuge tube by filtering through a 0.45 micron syringe filter and place in the HPLC vial.
4. Equilibrate the HPLC system to the initial method conditions and analyze samples on the HPLC using the methodology cited in the Analytical Parameters.

5. If the data processor does not handle the data internally, find the concentration corresponding to the acrylic acid peak area in the sample:

$$\text{Residual acrylic acid in sample} = \frac{\text{peak area}}{\text{response factor}} \times \frac{\text{weight of solution}^*}{\text{weight of polymer}}$$

***Weight of solution is the total of weight of water from step 1 and the addition of the drops of NaOH and 1.0 ml of CaCl₂ from Step 2.**

SPECIAL INSTRUCTIONS:

1. Never leave buffer solutions standing in HPLC equipment since they are corrosive to metal valves and fittings and crystallization in frits/ equipment may result.
2. Run a gradient from the buffer solution to 100% HPLC water, followed by a gradient to 100% HPLC grade methanol for overnight storage of the system.

Notes:

1. Degassing of the buffer solutions is not necessary for this system but may be needed for other HPLC systems.
2. Acrylic acid forms a dimer upon sitting at a rate of approximately 1% per month. Therefore, fresh acrylic acid should be used in standard preparations to insure accurate results.
3. Standards should be prepared fresh on a weekly basis and stored in a refrigerator to prevent degradation.