

SUPER ABSORBENT POLYMERS

5035

MW: Varies

CAS: See Table 1

RTECS: None

METHOD: 5035, Issue 1

EVALUATION: PARTIAL

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OSHA : no PEL
NIOSH: no REL
ACGIH: no TLV

PROPERTIES: solids; hygroscopic; form gels with water [1]

SYNONYMS: sodium polyacrylate, Sanwet IM-3500 (sodium polyacrylate grafted with starch), Water Lock A-100 (sodium acrylate-acrylamide copolymer grafted with starch), Water Lock B-204 (potassium acrylate-acrylamide copolymer grafted with starch), Water Lock G-400 (sodium acrylate-acrylamide copolymer).

SAMPLING		MEASUREMENT	
SAMPLER:	MEMBRANE FILTER (PVC, 5- μ m, 37-mm)	TECHNIQUE:	ICP-AES OR AAS
FLOW RATE:	1 to 3 L/min	ANALYTE:	copper
VOL-MIN:	50 L	EXTRACTION:	6 mL of 0.07 M cupric acetate; 14 mL of water; ultrasonic bath, 15 min.
-MAX:	1500 L	ASHING REAGENTS:	70% HNO ₃ , 10 mL; 70% HClO ₄ , 1 mL (optional)
SHIPMENT:	routine	WAVELENGTH:	324.7 nm
SAMPLE STABILITY:	>8 months @ 25 °C [2]	CALIBRATION:	super absorbent polymer in sucrose
BLANKS:	2 to 10 field blanks per set	RANGES:	see Table 1
BULK SAMPLES:	required (20 g)	ESTIMATED LODs:	see Table 1
ACCURACY		PRECISION (\bar{S}_r):	0.086 [2]
RANGE STUDIED:	0.02 to 0.15 mg/m ³ for Sanwet IM-3500		
BIAS:	not significant		
OVERALL PRECISION (\bar{S}_{rT}):	not determined		
ACCURACY:	not determined		

APPLICABILITY: This method has been used to measure Sanwet IM-3500 in air at a diaper manufacturing plant [2].

INTERFERENCES: Aerosols of copper compounds would interfere; however, this problem is uncommon.

OTHER METHODS: Super absorbent polymers in air can be determined by collection on PVC filters, treatment with hot HCl and measurement of sodium by flame AAS [2].

REAGENTS:

1. Super absorbent polymer (the type present in air samples), 99+% pure if water is only impurity. See step 15 to determine the amount of water present.
2. Copper acetate, 0.07 M. Dissolve 27.96 g of cupric acetate monohydrate in water to make 2 L of solution. Solution may be stored at least 6 months. Filter solution through 0.45- μ m cellulose ester filter immediately (<4 h) before use.
3. Water, deionized.
4. Sucrose, 99+% pure.
5. Calibration stock mixture, ca. 4% super absorbent polymer by weight. Mix ca. 380 mg of polymer with 8000 mg of sucrose (do not use polymer which has been heated). Shake mixture 5 min by hand. Grind mixture to fine powder with freezer mill for 12 min (mill cooled with liquid nitrogen).
6. Nitric acid, 70%.
7. Perchloric acid, 70% (optional).*
8. Argon (for ICP-AES).
9. Acetylene (for AAS).
10. Air (for AAS).
11. Dilution acid, 2.8% HNO₃:0.7% HClO₄. Add 40 mL of 70% HNO₃ and 10 mL of 70% HClO₄ to deionized water to make 1 L of solution.
12. Dilution acid, 3.5% HNO₃. Add 50 mL of 70% HNO₃ to deionized water to make 1 L of solution.

* See Special Precautions

EQUIPMENT:

1. Sampler: PVC filter, 37-mm membrane filter, 5- μ m pore size, in two-piece filter cassette.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Instrument for measurement of copper (LOD <2 μ g per sample); e.g., inductively coupled plasma-atomic emission spectrometer or atomic absorption spectrophotometer.
4. Vacuum filtration apparatus, two units (product XX10 025 00, Millipore Corp., Bedford, MA, or equivalent).
5. Filters, cellulose ester, 25-mm diameter, 0.45- μ m pore size.
6. Vials, 20-mL.
7. Pipets, 5- and 6-mL, with pipet bulb.
8. Balance, readable to five decimal places.
9. Ultrasonic bath.
10. Beakers, 50- and 250-mL.
11. Beakers, Phillips, 125-mL, with watch glass covers.**
12. Forceps.
13. Spatulas.
14. Freezer mill, or mortar and pestle.
15. Stirring rod, glass.
16. Hot plate, surface temperature, 150 °C.

** Clean Phillips beakers with 70% nitric acid, and rinse thoroughly with deionized water before use.

SPECIAL PRECAUTIONS: Work with perchloric acid should be performed only in a perchloric acid hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Attach sampler to personal sampling pump with flexible tubing. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 50 to 1500 L. Limit the loading of particulate matter on the filter to a maximum of about 1 mg.
3. Seal the inlet and outlet of the sampler with plugs. Pack securely for shipment. Separately ship a bulk sample (20 g) of the super absorbent polymer.

SAMPLE PREPARATION:

4. Transfer the 37-mm PVC filter to a 20-mL vial, and allow the exposed side of the filter to face inward.
5. Add 6 mL of 0.07 M copper acetate solution (filtered through a 0.45- μ m cellulose ester filter

- within about 4 h before use).
6. Add 14 mL of deionized water. Cap the vial.
 7. Place the vial into an ultrasonic bath for 15 min.
 8. Collect the copper-polymer precipitate on a 25-mm cellulose ester filter (0.45- μ m pore size) by vacuum filtration.
NOTE: The copper-polymer precipitate should be collected within about 4 h after the addition of copper acetate solution to samples and blanks. Particles containing copper may appear in copper acetate solution if the solution stands for a few days. These particles would cause a positive interference.
 9. Rinse the vial with two 12-mL portions of deionized water, and add the rinses to the filtration apparatus. If blue particles of copper-polymer precipitate are observed in the vial after the two rinses, rinse the vial with additional water until blue particles are not observed in the vial. Add the additional rinses to the filtration apparatus.
 10. Recover super absorbent polymer from the interior surface of the front piece of the cassette filter holder.
 - a. Seal inlet of front piece of the cassette filter holder with a plug.
 - b. Add 5 mL of 0.07 M copper acetate to this cassette piece.
 - c. Place this cassette piece into a clean ultrasonic bath for about 30 sec.
NOTE: If a visible coating of copper-polymer precipitate does not become dislodged during ultrasonic treatment, the coating may be dislodged with a glass stirring rod.
 - d. Pour solution from cassette piece to the vacuum filtration apparatus.
 - e. Rinse cassette piece with 5 mL of deionized water.
 11. Transfer the 25-mm cellulose ester filter with collected precipitate to a 125-mL Phillips beaker. Cover with a watch glass.
 12. Rinse the bottom part of the top piece of the filtration apparatus with deionized water in a 50-mL beaker.
 13. Assemble the vacuum filtration apparatus with a clean 25-mm cellulose ester filter. Add the rinse from the 50-mL beaker to the filtration apparatus. Transfer the 25-mm filter to the same Phillips beaker (step 10).
NOTE: Steps 12 and 13 are applicable if the vacuum filtration apparatus is the type that sandwiches the filter between the top piece (vertical column) and the bottom piece. When the vertical column is separated from the filter, water with copper-polymer precipitate may travel by capillary action to the underside of the vertical column. Also, precipitate may cling to the inside wall of the vertical column.
 14. Add 10 mL of 70% nitric acid and 1 mL of 70% perchloric acid to filters in the Phillips beaker.
NOTE: Use of perchloric acid is optional.
 - a. Cover the beaker with the watch glass.
 - b. Place the beaker onto a hot plate at 150 °C, and reflux overnight.
 - c. Remove the watch glass, and heat the mixture just to dryness at 150 °C.
 - d. Remove the beaker from the hot plate. Add 0.5 mL of 4:1 70% nitric acid:70% perchloric acid (v/v) or 0.5 mL of 70% nitric acid (choice depends on whether the standard solutions contain perchloric acid).
 - e. Dilute the mixture to 10 mL with deionized water.

CALIBRATION AND QUALITY CONTROL:

15. Determine the amount of water present in a bulk sample of the super absorbent polymer. Place an accurately weighed 20-g sample of the super absorbent polymer into an oven at 130 °C for about 16 hours. Determine the weight loss, and calculate the amount of water in the original sample (percent by weight).
16. Calibrate with at least six working standards.
 - a. Prepare a series of working standards of super absorbent polymer in sucrose by dilution of portions of the calibration stock mixture with sucrose. Calculate the quantities of calibration stock mixture which will be diluted with about 8 g of sucrose in order that 50 to 300 mg of each working standard contains a desirable quantity of anhydrous super absorbent polymer

in the calibration range (8 to 1000 µg is an approximate calibration range). Shake each dilution in a 20-mL vial by hand for about 5 min, and then grind each mixture in a freezer mill (cooled with liquid nitrogen) for 12 min or with a mortar and pestle.

NOTE: Although the super absorbent polymer in the calibration stock mixture and working standards may contain water, it is convenient to express a quantity of super absorbent polymer on the basis of anhydrous super absorbent polymer.

- b. Prepare six samples at each level and six blanks. For each sample, accurately weigh 50 to 300 mg of a working standard (polymer-sucrose mixture) in a 20-mL vial with a five-place balance.
 - c. Add 5 mL of deionized water to each vial. Agitate each vial to dissolve the sucrose.
 - d. Add 6 mL of 0.07 M copper acetate solution [filtered (see step 5)].
 - e. Place each vial into an ultrasonic bath for 10 min.
 - f. Collect the copper-polymer precipitates (steps 8 and 9), prepare samples (step 14), and analyze samples (steps 18 and 19).
 - g. Prepare a calibration graph of instrument response for copper versus µg of anhydrous super absorbent polymer.
17. Estimate recovery (R) of super absorbent polymer from 37-mm PVC membrane filters.
- a. Prepare six samples at each level. For each sample, accurately weigh 50 to 300 mg of a working standard polymer-sucrose mixture) in a 20-mL vial on a five-place balance. Place a 37-mm PVC filter into each vial.
 - b. Follow steps 9, 11 through 14, and 18 and 19.
 - c. Determine each quantity of super absorbent polymer found from the calibration graph (step 16. g).
 - d. Calculate the recovery for each sample by dividing the quantity of super absorbent polymer found by the original quantity of polymer.

NOTE: Each recovery is an estimate because the PVC filters have not been fortified with super absorbent polymer.

MEASUREMENT:

18. Set instrument for measurement of copper according to conditions specified by the manufacturer.
19. Analyze samples and standards.

NOTE: If the concentrations of the samples are above the range of the standards, dilute the samples with dilution acid, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

20. Determine the quantity (corrected for recovery) of anhydrous super absorbent polymer in µg, W, in the air sample from the calibration graph (step 16. g).
21. Calculate the concentration, C, of the super absorbent polymer in the air volume sampled, V (L):

$$C = \frac{W}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated with Sanwet IM-3500, Water Lock A-100, Water Lock B-204, and Water Lock G-400. Average ratios of quantity of copper found to quantity of anhydrous Sanwet IM-3500 were 0.66, 0.78, 0.69, 0.72, 0.63 and 0.57 for 8-, 16-, 32-, 63-, 515-, and 1466-µg quantities of anhydrous polymer (values of S_r for the average ratios were 0.34, 0.12, 0.13, 0.05, 0.05, and 0.03, respectively;

pooled \bar{S}_r was 0.086). A second method for calculation of precision involved division of the standard error of the calibration curve by the average y value (average value of copper); precision for the analytical method (\bar{S}_r) = $16.7/247 = 0.068$.

This sampling and analytical method (Method 5035, Cu-SAP method) was compared with the sodium method [2] for determination of Sanwet IM-3500 in area air samples at a diaper manufacturing plant.

Comparison of Cu-SAP Method (Filters Only) with Sodium Method

<u>Set</u>	<u>Analytical Method</u>	<u>Volume of Air (liters)</u>	<u>Average Concentration of Sanwet IM-3500 (mg/m³)</u>	<u>Relative Standard Deviation</u>
1a	Cu-SAP	840	0.0673	0.19
1b	sodium	908	0.108	0.023
2a	Cu-SAP	425	0.0978	0.35
2b	sodium	420	0.162	0.052

Air samples for each method were collected at 2 liters/min. Sets 1a and 1b had three samples each; sets 2a and 2b had two samples each. Although PVC filters and interior surfaces of front pieces of cassette filter holders were analyzed in the Cu-SAP method, interior surfaces were not analyzed in the sodium method; thus, the comparisons above are for PVC filters only. Quantities of Sanwet IM-3500 found on interior surfaces of front pieces of cassettes ranged from 12 to 39% of the total quantities found. A bulk sample of Sanwet IM-3500 from the diaper plant contained 7.20% water. See additional information in reference [2].

The average of six blanks was 2.95 μg of copper, and the standard deviation of these blanks was 1.04 μg of copper (cellulose ester filters will retain small quantities of copper during filtration of copper acetate solutions and rinses with deionized water). Average recoveries of 8-, 17-, 63-, and 526- μg quantities of Sanwet IM-3500 from 37-mm PVC filters were 1.27, 0.84, 0.83 and 1.01, respectively. A standard mixture of Sanwet IM-3500 in sucrose (4.48% Sanwet IM-3500 by weight) was stable during storage in a vial for a period of more than eight months at room temperature. Digestion procedures involving (a) nitric and perchloric acids and (b) nitric acid only were evaluated for digestion of copper-polymer precipitate prepared from 500- μg quantities of Sanwet IM-3500. The two procedures were found to be equally effective.

REFERENCES:

- [1] Masuda, F., "Super Absorbent Polymers--Characteristics and Trends in Development of Applications," Chemical Economy & Engineering Review, 15(11):19-22 (1983).
 [2] Tucker, S.P., M.B. Millson, and D.D. Dollberg, "Determination of Polyacrylate Super Absorbent Polymers in Air," Analytical Letters, 26(5):965-980 (1993).

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Table 1

CAS Numbers, Detection Limits, and Analytical Ranges for Super Absorbent Polymers

<u>Super Absorbent Polymer</u>	<u>CAS Number</u>	<u>Detection Limit* ($\mu\text{g}/\text{sample}$)</u>	<u>Analytical Range ($\mu\text{g}/\text{sample}$)</u>
Sanwet IM-3500	60323-79-7	4	15 to 1000
Water Lock A-100	65930-07-6	14	45 to 1000
Water Lock B-204	72162-30-2	13	42 to 1000
Water Lock G-400	61788-39-4	8	28 to 1000

* The detection limit is defined as three times the standard deviation of blanks. The standard deviation of six blanks was 1.04 μg of copper per sample. The average blank value was 2.95 μg of copper. Detection limits in Table 1 are quantities of anhydrous super absorbent polymer per sample.