ANALYTICAL LETTERS, 26(5), 965-980 (1993)

# DETERMINATION OF POLYACRYLATE SUPER ABSORBENT POLYMERS IN AIR

**KEY WORDS:** Super absorbent polymers, cross-linked sodium polyacrylate, air analysis

Samuel P. Tucker, Mark B. Millson, and Donald D. Dollberg

Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering, Measurements Research Support Branch, 4676 Columbia Parkway, Cincinnati, Ohio 45226

## ABSTRACT

A sampling and analytical method has been developed for measurement of a starch-grafted, cross-linked sodium polyacrylate in air. Also, the method is applicable to measurement of several other polyacrylate super absorbent polymers and involves air sampling with a 37-mm PVC membrane filter, treatment of the sample with 0.07 M cupric acetate solution to form a copper-polymer precipitate, digestion of the precipitate with nitric and perchloric acids, and measurement of the copper content by inductively-coupled plasma-atomic emission spectrophotometry. The interior surface of the front piece of the filter cassette also is analyzed. This analytical method has been compared with a sodium method that currently is used. Detection limits for various super absorbent polymers ranged from 4.4 to 14 micrograms per sample.

## INTRODUCTION

Super absorbent polymers (SAP) make up a class of cross-linked polymers which can absorb many times their weight in water to form gels or hydrogels.[1] Many of these cross-linked polymers are polyacrylates, and many of these polyacrylates are grafted with starch (starch is incorporated into the polymer chains). Examples are Sanwet IM-3500[2] (a sodium polyacrylate grafted with starch), Water Lock A-100[3] (a sodium acrylate-acrylamide copolymer grafted with starch), Water Lock B-204[4] (a potassium acrylate-acrylamide copolymer grafted with starch) and Water Lock G-400[5] (a sodium acrylate-acrylamide copolymer).

Figure 1 shows a simplified structure of a starch-grafted sodium polyacrylate cross-linked with a typical cross-linking agent, N,N'-methylene-2-propenamide. Broken lines separate various parts of the polymer. From left to right, the structural units are starch, acrylic acid, sodium acrylate, and the cross-linking agent. The ratio of acrylic acid to sodium acrylate is approximately 30:70.[1]

---

Mention of company names or products does not constitute endorsement by the Centers for Disease Control and Prevention.

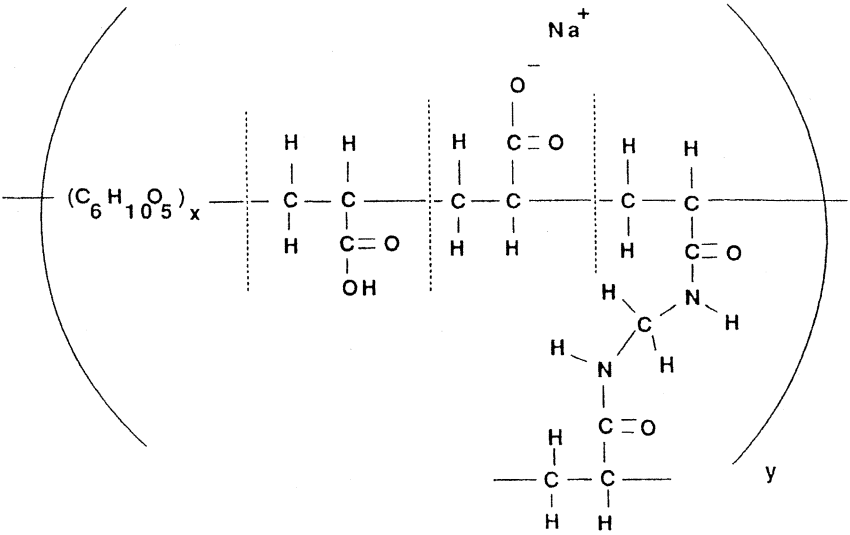

FIG. 1. Simplified structure of a cross-linked, starch-grafted sodium polyacrylate.

These super absorbent polymers have been used in the manufacture of disposable infant diapers, sanitary napkins, adult incontinent pads and surgical dressings because of their ability to absorb large quantities of water.[1,6-9]

Although results of an industry-sponsored study indicate that three cross-linked polyacrylate polymers were not genotoxic with respect to selected genotoxicity assays,[10] some health hazard information is available from material safety data sheets (MSDS's). This information indicates that skin toxicity is extremely low and that the super absorbent polymers may cause eye irritation.[2-5] No evidence of sensitization was found in repeat insult patch testing of animals and humans.[2] Low concentrations of airborne dust of a related product can cause lung irritation and lung inflammation.[2]

Researchers at the National Institute for Occupational Safety and Health (NIOSH) recently conducted environmental and medical surveys to investigate whether exposure to super absorbent polymer (specifically, Sanwet IM-3500) constitutes a health hazard to workers. These surveys were conducted in response to a report that a worker at a diaper manufacturing plant complained of symptoms of asthma.[11]

Literature reviews revealed that methods for super absorbent polymers in air generally involve collection on a filter and measurement of sodium to determine the quantity of super absorbent polymer.[12] A disadvantage of these methods is the potential interference by other sodium compounds collected on the filter. Sodium is the sixth most abundant element in the earth's crust,[13] and cellulose fluff used in diaper manufacturing can contain sodium as an impurity (cellulose can be produced by chemical pulping of wood, which can involve sodium hydroxide).

In the present research, a sampling and analytical method has been developed for measurement of polyacrylate super absorbent polymers in air. This method (NIOSH method 5031[14]) is based on the discovery in this laboratory that polyacrylate super absorbent polymers react with metal ions to form metal-polymer precipitates.

## EXPERIMENTAL SECTION

Amounts of vaporizable matter (presumably water) were determined in super absorbent polymers. A sample of each polymer (5-27 g) was placed into an oven at 130 °C for about 16 h. Weight losses were measured. Also, amounts of water vapor absorbed from the air were determined. Other samples of polymers in 20-mL vials were placed into a room in which the relative humidity (50%) and temperature (21 °C) remained constant. Increases in weight were measured after 7 days.

Calibration curves were prepared with samples of super absorbent polymers which had not been heated to remove water. Standard mixtures of the polymers were prepared with known quantities of sucrose as a diluting agent in order that microgram quantities of polymers could be weighed easily on a five-place balance (standard mixtures were prepared with sucrose because the polymers are insoluble in water and common organic solvents). The standard mixtures were shaken by hand and ground in a Spex 6700 Freezer/Mill (cooled with liquid nitrogen). Quantities of polymer-sucrose mixtures (6-78 mg) were weighed in 20-mL vials. Deionized water (5 mL) and 6 mL of 0.07 M cupric acetate solution [freshly filtered through a 25-mm cellulose ester filter with a pore size of 0.45 $\mu$m (HA filter, Millipore Products Division, Bedford, MA)] were added to each vial, and each mixture was treated in an ultrasonic bath for 10 min. Copper-polymer precipitates were collected on 25-mm cellulose ester filters by vacuum filtration. Each vial was rinsed with two 12-mL quantities of deionized water, and each rinse was added to the filtration apparatus (rinses helped to ensure quantitative transfer of precipitates). Then the filtration apparatus was rinsed with water. Precipitates and filters were digested with 70% nitric acid (10 mL) and 70% perchloric acid (1 mL) at reflux overnight on a hot plate at 150 °C. Copper was measured by inductively coupled plasma-atomic emission spectrophotometry (ICP-AES) with a Jarrell-Ash Model 1140 Plasma AtomComp (incident power, 1.07 kW; reflected power, < 0.005 kW; flow rate of argon, 20 L/min; rate of sample uptake, 1.7 mL/min; view height, 16 mm above coil; wavelength for copper, 324.7 nm; detection limit, 1 $\mu$g per sample). Calibration curves of average quantity of copper found (corrected for average blank) versus average quantity of anhydrous super absorbent polymer were constructed.

Although 0.07 M cupric acetate solution can be stored for at least 6 months, it was important to filter the solution immediately (within about 4 h.) before the addition to the super absorbent polymer. Filtration removed undesirable copper-containing particulate matter, which would have caused a positive bias in measurement of copper. Also, the copper-polymer precipitate was collected by filtration within 4 h. after addition of the cupric acetate solution to the sample. The undesirable copper-containing particulate matter was not identified but possibly was solid cupric acetate formed by evaporation of water.

Generally, a mixture of nitric and perchloric acids was used for digestion of copper-polymer precipitate. Use of perchloric acid is optional, however. Digestion procedures with and without perchloric acid were found to be equally effective.

A procedure was employed for determination of approximate recoveries of Sanwet IM-3500 from 37-mm PVC membrane filters with a pore size of 5 $\mu$m. Quantities of mixtures prepared from Sanwet IM-3500 and sucrose (8-54 mg) were weighed in 20-mL vials which contained the PVC filters. Freshly filtered 0.07 $\underline{M}$ cupric acetate solution (6 mL) and 14 mL of deionized water were added to each vial. Each sample was treated in an ultrasonic bath for 15 min. Copper-polymer precipitates were collected by vacuum filtration on 25-mm cellulose ester filters and digested with nitric and perchloric acids (the 37-mm PVC filters remained in the 20-mL vials). Copper was measured by ICP-AES.

The copper-polymer precipitate method (Cu-SAP method) was compared with a reference sodium method in field sampling. Area air samples by each method were collected side-by-side at 2 L/min in a diaper manufacturing plant which used Sanwet IM-3500. In the Cu-SAP method, the 37-mm PVC filters and the interior surfaces of the front pieces of the filter cassettes were analyzed separately. Each PVC filter was transferred to a 20-mL vial, 6 mL of freshly filtered 0.07 $\underline{M}$ cupric acetate solution and 14 mL of deionized water were added, and each vial was placed into an ultrasonic bath for 15 min. The interior surface of the front piece of each filter cassette was treated with 5 mL of cupric acetate solution in a clean ultrasonic bath for 30 s, and copper-polymer precipitate was collected. Precipitates and cellulose ester filters were digested with nitric and perchloric acids, and copper was measured by ICP-AES.

The reference sodium method involved air sampling with 37-mm PVC membrane filters, treatment of the filters with HCl, and measurement of sodium by flame atomic absorption spectrophotometry.[12] Each PVC filter was transferred to a plastic test tube, 6 M HCl (1.0 mL) was added to the tube and the solution was diluted to 10.0 mL. Ionization buffer [lithium solution (0.1 mL, 20,000 ppm) or potassium solution (0.1 mL, 50,000 ppm)] was added. The plastic test tube was placed into a water bath at 95 °C for 30 min. Then the sodium was measured at 589.0 nm. The quantity of sodium found corresponded to the quantity of Sanwet IM-3500 in the sample. All sodium analyses were performed by a laboratory owned by the company which owns the diaper plant.

## RESULTS AND DISCUSSION

Polyacrylate super absorbent polymers reacted rapidly with a wide variety of metal ions in solution at room temperature. These reactions took place after the polymers had absorbed water to form gels. Metal-polymer precipitates formed when Sanwet IM-3500 and the Water Lock polymers reacted with metal ions which included $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Mn^{2+}$, $Pb^{2+}$, $Ag^{+}$, $Mg^{2+}$, $Ca^{2+}$, $Ba^{2+}$, and $La^{3+}$. Many of the precipitates were white. Copper precipitates were blue. Cobalt precipitates were pink or red.

It is necessary to determine amounts of vaporizable matter (presumably water) which are present in bulk quantities of the polymers in order to produce meaningful calibration curves. Expression of a quantity of polymer on the basis of "anhydrous" polymer is appropriate because the actual quantity of water present can vary from sample to sample. A super absorbent polymer was considered to be anhydrous after it has been stored overnight at 130 °C. Amounts of water present in samples of four polymers (Sanwet IM-3500, Water Lock A-100, Water Lock B-204, and Water Lock G-400) which were analyzed as received ranged from 6 to 14%.

Although super absorbent polymers rapidly absorb many times their weight when water is added, the rate of absorption of water vapor from the air during a seven-day period is slow (final amounts of water present ranged from 11 to 24%). Thus, brief exposures of super absorbent polymers to moisture in the air will not affect the preparation of standards and construction of calibration curves significantly.

Calibration curves for super absorbent polymers were linear or nearly linear for quantities less than 160 μg (see Figure 2). Each correlation coefficient was greater than 0.999. Deviation from linearity became readily apparent at a higher level of Sanwet IM-3500; i.e., at about the 1400-μg level. With the exception of the lowest data point for Water Lock G-400, which was based on five samples, all data points in Figure 2 are based on six samples.

Detection limits of anhydrous Sanwet IM-3500, Water Lock A-100, Water Lock B-204, and Water Lock G-400 are 4.4, 14, 13, and 8.3 μg per sample, respectively. The detection limit is defined as three times the standard deviation of blank values.[15] A small quantity of copper (about 3 μg) will be found in a blank 25-mm cellulose ester filter used for collection of the copper-polymer precipitate because a residual amount of copper will remain in the filter after cupric acetate solution has passed through the

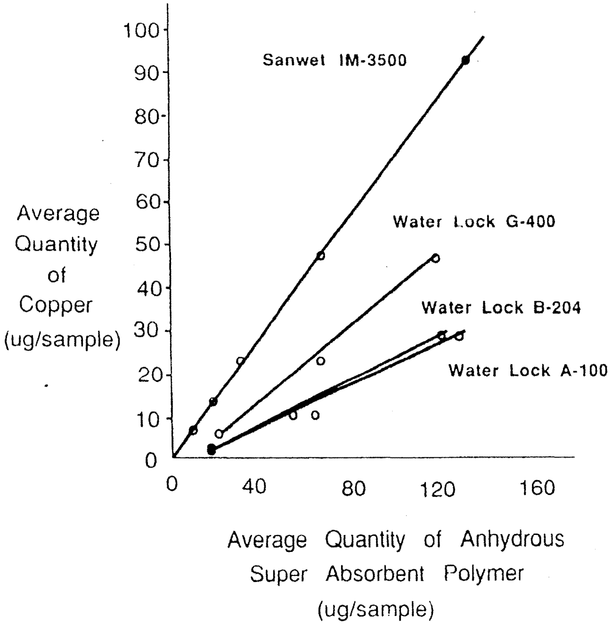

FIG. 2. Calibration curves for super absorbent polymers.

filter and after the filter has been washed with deionized water. Generally, the standard deviation for blank filters was about 1 $\mu$g of copper.

Values of recovery of Sanwet IM-3500 from 37-mm PVC membrane filters in Table 1 are approximations because the method for determination of recovery involved placement of polymer-sucrose mixtures into vials which contained PVC filters (see Experimental Section). Accurate values of recovery could not be determined because the insolubility of Sanwet IM-3500 in common solvents prevented the use of the ordinary method of fortification of filters (application of a solution of the analyte and evaporation of solvent is the ordinary method).

TABLE 1

Recoveries of Sanwet IM-3500 from PVC Filters

| Average Quantity of Anhydrous Sanwet IM-3500 (μg) | Average Recovery* | Relative Standard Deviation |
|---|---|---|
| 8.3 | 127% | 43% |
| 16.9 | 84% | 16% |
| 63.3 | 83% | 5% |
| 526 | 100% | 8% |

*There were six samples at each level.

Sanwet IM-3500 was found to be stable in a standard mixture with sucrose (4.48% Sanwet IM-3500 by weight) in a vial for more than eight months of storage at room temperature. Thus, one can conclude that this polymer is stable on PVC filters after air sampling.

Results of a comparison of the Cu-SAP method with the sodium method in the diaper manufacturing plant suggest that the sodium method has a positive bias (see Table 2). Average concentrations of anhydrous Sanwet IM-3500 by the sodium method were 60% and 66% higher than the corresponding average concentrations by the Cu-SAP method in sets 1 and 2, respectively; these comparisons of the two methods were based on PVC filters only. PVC filters and interior surfaces of front pieces of filter cassettes were analyzed in the Cu-SAP method; however, interior surfaces

TABLE 2

Comparison of the Cu-SAP Method with the Sodium Method

| Set | Analytical Method | Volume of Air (liters) | Average Concentration of Anhydrous Sanwet IM-3500 | | | |
|---|---|---|---|---|---|---|
| | | | Filters Only ($mg/m^3$) | RSD | Filters and Cassettes ($mg/m^3$) | RSD |
| 1a | Cu-SAP | 840 | 0.0673 | 19% | 0.0891 | 9.9% |
| 1b | sodium | 908 | 0.108 | 2.3% | ------ | ----- |
| 2a | Cu-SAP | 425 | 0.0978 | 35% | 0.133 | 19% |
| 2b | sodium | 420 | 0.162 | 5.2% | ------ | ----- |

were not analyzed in the sodium method because the laboratory performing the sodium analyses was not in practice of analyzing the interior surfaces. Average concentrations by the sodium method would have been higher if interior surfaces had been analyzed. Quantities of Sanwet IM-3500 found on the interior surfaces of the front pieces of filter cassettes ranged from 12 to 39% of the total quantities found.

According to a t-test, the average concentration of 0.108 $mg/m^3$ by the sodium method in set 1b of Table 2 was significantly different from the concentration of 0.0673 $mg/m^3$ by the Cu-SAP method in set 1a at the 95%

confidence level (n = 3 in sets 1a and 1b). A similar difference in sets 2a and 2b was not statistically significant because the numbers of samples were too small (n=2 in sets 2a and 2b).

Discrepancies of 60% and 66% between the Cu-SAP method and the sodium method are serious, and one would question which method is biased. A positive bias in the sodium method is highly probable because interference by sodium from other sources is possible. A negative bias in the Cu-SAP method is possible when one is not careful to ensure quantitative transfer of copper-polymer precipitate. However, a true negative bias to the extent of 60 or 66% in the Cu-SAP method in Table 2 is doubtful because effort was made to transfer copper-polymer precipitate quantitatively. Also, the high specificity of the Cu-SAP method for polyacrylate super absorbent polymers helps to prevent a positive bias in the Cu-SAP method.

Large relative standard deviations (19% and 35%) for the Cu-SAP method in Table 2 do not necessarily reflect poor precision of measurement in the method because (a) large concentration gradients are possible in field situations and (b) distributions of polymer between the PVC filter and the interior surface of the filter cassette help to account for large RSD's. Note that the values of RSD for the total concentrations are considerably smaller (9.9% and 19% for filters and cassette pieces).

The reaction of polyacrylate super absorbent polymers with metal ions involves virtually quantitative replacement of sodium or potassium ions with cupric ions. In one experiment, six samples of Sanwet IM-3500 (1436-1525 $\mu$g/sample) in water were treated with an excess of cupric acetate solution.

Although the lot of anhydrous Sanwet IM-3500 contained 16.4% sodium by weight, the quantity of sodium found in each copper-polymer sample was less than 1.5 μg.

Cupric ion is a good choice of a metal ion for use in the analytical method because (a) detection limits are low (1 μg/sample), (b) other metals do not interfere with the measurement of copper by ICP-AES, and (c) copper-polymer precipitates in sufficient quantity are visible on white cellulose ester filters (copper-polymer precipitates are blue). The appearance of blue precipitate on the filter will give the analyst an indication that super absorbent polymer was present in the air sample. The smallest quantity of blue precipitate visible to the unaided eye depends on the super absorbent polymer; this limit corresponds to about 1 μg of Sanwet IM-3500.

Cellulose and starch are not interferences in the Cu-SAP method. Cellulose is a major contaminant in the air at the diaper manufacturing plant, and starch is a component of various super absorbent polymers. In order to be an interference, a substance would need to react with copper ions to produce a copper-containing solid, which would be collected on the filter with the copper-polymer precipitate.

The sampling and analytical method developed for polyacrylate super absorbent polymers involves (a) air sampling with a 37-mm PVC membrane filter at 1-2 liters/min., (b) treatment of the sample with 0.07 M cupric acetate solution in an ultrasonic bath for 15 min., (c) collection of the copper-polymer precipitate, (d) acid digestion of the precipitate, (e) measurement of copper by ICP-AES, and (f) determination of the quantity of polymer from a calibration curve of quantity of copper versus quantity of polymer.

## ACKNOWLEDGMENT

A helpful discussion with Barry R. Belinky and grinding of polymer-sucrose mixtures in a freezer/mill by Ceola H. Moore are acknowledged.

## REFERENCES

1. F. Masuda, Chem. Econ. Eng. Rev. 154 (11), 19 (1983).
2. Material Safety Data Sheet for Sanwet$^R$ IM-3500, Hoechst Celanese, Portsmouth, VA (Feb., 1989).
3. Material Safety Data Sheet for Water Lock$^R$ A-100, Grain Processing Corp., Muscatine, IA (Mar., 1986).
4. Material Safety Data Sheet for Water Lock$^R$ B-204, Grain Processing Corp., Muscatine, IA (June, 1986).
5. Material Safety Data Sheet for Water Lock$^R$ G-400, Grain Processing Corp., Muscatine, IA (Apr., 1986).
6. E. Richman, M. Thorn, W. Schlauch. In: Nonwovens: Innovative Fabr. Future, Proceedings of the 8th Technical Symposium, Bridgewater, NJ, INDA (1980), Assoc. Nonwoven Fabr. Ind., NY (1980), pp. 77-87; Chem. Abstr. 93, 120374s (1980).
7. Chemical & Engineering News (March 23, 1987), p. 13.
8. R. Korpman, C. Gandy, European Patent 157,960 (1985); Chem. Abstr. 104, 136114p (1986).
9. Japan Chemical Week, (July 4, 1985), p. 6.
10. E.D. Thompson, J.L. Seymour, M.J. Aardema, R.A. LeBoeuf, B.L.B. Evans, D.B. Cody, Environmental and Molecular Mutagenesis 18, 184 (1991).
11. Hazard evaluation and technical assistance report (to be published), Cincinnati, OH. U.S. department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health. NIOSH Report No. HETA 89-189.

12. T.S. Turan, Round Robin Study of Analytical Methods for Polyacrylate Absorbent (PA) Dust. Unpublished report, Institute for Polyacrylate Absorbents, Washington, D.C. (March 15, 1989).

13. M.J. Sienko, R.A. Plane, Chemistry, McGraw-Hill Book Company, Inc., New York (1961), p. 373.

14. National Institute for Occupational Safety and Health, NIOSH Manual of Analytical Methods, 4th ed., method 5031 (to be published, 1993).

15. ACS Committee on Environmental Improvement and Subcommittee on Environmental Analytical Chemistry, Anal. Chem. 52, 2242 (1980).

Received November 30, 1992
Accepted January 22, 1993