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Note

Determination of residual acrylamide monomer in solution and emulsion polymers by column-switching high-performance liquid chromatography

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Acrylamide monomer is used in the manufacture of many polymeric products employed for water treatment applications. Such products may contain residual acrylamide monomers, which because of its toxicity, must be monitored routinely to ensure product safety and to meet government regulations. Currently, most methods used for monitoring manufacturing processes are limited in detection capability to about 0.01% (100 ppm) residual acrylamide [1–9]. As acrylamide levels are likely to come under closer scrutiny in the near future, a lower detection limit will probably be required. New quality control procedures will not only have to be simple and easily automated, but will also have to be capable of determining very low levels of acrylamide without interferences from other components in the sample. Numerous methods for determination of trace levels of acrylamide in water have been reported in literature [10–17]. However, most of these methods require time-consuming sample preparation and are subject to interferences from polymer sample matrices. They are not readily applicable to trace level acrylamide monitoring in polymeric systems. Freshour *et al.* [18] has reported a relatively simple procedure using column switching for determination of trace levels of acrylamide in tissue culture. With modification, this column-switching technique has been adapted for use on polymeric samples. The modified method consists of simple dilution or extraction–precipitation of polymer followed by high-performance liquid chromatographic (HPLC) analysis using UV detection at 210 nm. Detection limits of 5 ppm and 0.5 ppm can be obtained in emulsion polymers and solution polymers, respectively. This paper describes the detailed procedure and validation data for residual acrylamide determinations in both solution and emulsion polymers.

EXPERIMENTAL

Reagents and materials

The following materials and reagents were used: acrylamide (99+%), electrophoresis grade, Gold Label (Aldrich, Milwaukee, WI, U.S.A.), concentrated sulfuric

acid (J. T. Baker, Phillipsburg, NJ, U.S.A.), acetonitrile, methanol and tetrahydrofuran (glass-distilled HPLC grade, Burdick & Jackson, Muskegon, MI, U.S.A.). Water was purified using a Milli-Q water-purification system (Millipore, Bedford, MA, U.S.A.). All solvents for HPLC analysis were filtered through 0.45-μm Durapore filter paper (Millipore) and vacuum degassed before use. All polymer samples analyzed were prepared in-house and are representative of the types of samples used in typical water treatment applications.

Standard solutions

Stock standard solution of acrylamide was prepared by dissolving a known weight of acrylamide in water at a concentration of about 100 ppm. A set of standard solutions were prepared by diluting aliquots of the stock solution with water and 1 ml of acetonitrile in 100-ml volumetric flasks. The concentration range of the working standard solutions was 1.0 ppm to 0.005 ppm.

Sample preparation

Water treatment polymers containing acrylamide can be classified according to their manufacturing process as either solution polymers or emulsion (latex) polymers. The sample preparation for solution polymers was simple dilution of about 1.0 g of polymer product with 1 ml of acetonitrile and water in a 100-ml volumetric flask. These solutions were then mixed well and filtered through 0.45-μm Millipore Millex-HV filter units prior to HPLC analysis.

Emulsion polymers were further classified according to type as either non-ionic, anionic or cationic emulsion polymers. Basic sample preparation for emulsion polymers consisted of initial polymer precipitation with an organic solvent followed by dilution of the supernatant with water. Because the cationic and anionic polymers behaved quite differently in organic solvent matrices, *different* organic solvents were used to precipitate the emulsion polymers to ensure formation of a fine precipitate which would prevent entrapment of the residual monomers. Acetonitrile was used for the precipitation of cationic emulsion polymers, whereas acetonitrile methanol (50:50, v/v) was used for non-ionic and anionic emulsion polymers. In addition, if the emulsions were prepared with polymeric surfactants, acetonitrile–tetrahydrofuran (50:50, v/v) was used for precipitation of both cationic and anionic polymers.

Precipitation was performed by adding about 1.0 g of latex polymer dropwise through a 20 gauge sterile disposable needle into 10 ml of appropriate solvent with continuous stirring. A fine powder of the polymer was formed. The sample was then capped and stirred for an additional 30 min. The precipitated polymer was allowed to settle and 1 ml of the supernatant was further diluted with water to 100 ml in a volumetric flask. The diluted supernatant generally turned cloudy at this point due to the presence of oil and surfactants. An aliquot of this solution was filtered through 0.45-μm Millex-HV filter, and the clear filtrate was used for HPLC analysis.

Instrumentation and chromatography

The HPLC system consisted of two Model M6000A pumps (Waters Assoc., Milford, MA, U.S.A.), two Model SPD-6AV UV–VIS spectrophotometric detectors (Shimadzu, Wood Dale, IL, U.S.A.), one corrosion-resistant six-port switching valve with air actuator (Valco, Houston, TX, U.S.A.; part No. AC6WHC), and two

columns. The first column was an RCM-100 radial compression module with a 10-μm 10 cm × 8 mm Radial-Pak C_{18} column and Guard-Pak Resolve C_{18} (Waters Assoc.). The second column was a Bio-Rad HPLC fast acid analysis column, 10 cm × 7.8 mm (Bio-Rad, Richmond, CA, U.S.A.). A Micromeritics Model 725 Autosampler (Alcott Chromatography, Norcross, GA, U.S.A.) with a 100-μl loop was used for sample injection. Fig. 1 shows the complete instrument set-up. The switching valve was plumbed as described by Freshour *et al.* [18], using heart cut switching technique. Column switching time, chromatographic data collection, and integration were controlled by a P. E. Nelson Analytical Data System Model 4430 (P. E. Nelson Analytical, CA, U.S.A.). The mobile phase for both columns was 0.02 *M* sulphuric acid. A flow-rate of 1.0 ml/min was used for the first column while 0.6 ml/min was used for the second column. The UV detectors were operated at 210 nm with sensitivity of 0.002 a.u.f.s. for monitoring the effluent from the second column. The UV detector at the end of the first column was used solely for the purpose of establishing the column-switching time. After this valve-switching time has been established, only one UV detector is needed for analysis. Quantitation was based on the peak area of the sample and external standard calibration.

RESULTS AND DISCUSSION

Determinations of residual acrylamide in polymeric systems are commonly performed using single-column HPLC techniques. Oligomers, surfactants, additives

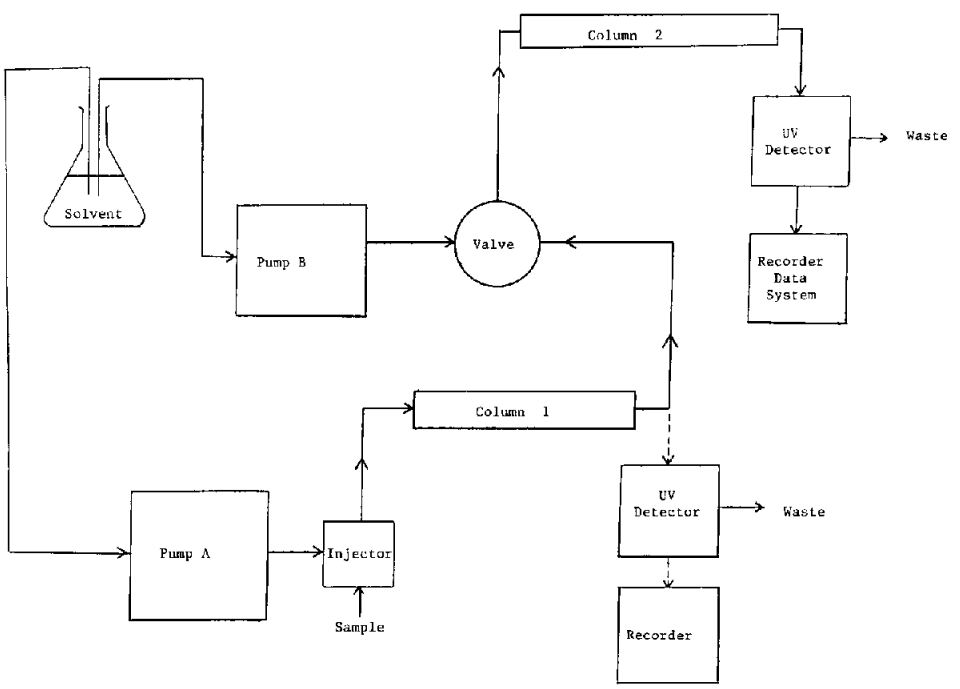

Fig. 1. A block diagram of column-switching system set-up. Pump A: 1.0 ml/min; pump B: 0.6 ml/min; column 1: RCM-100 Radial-Pak C_{18}; column 2: Bio-Rad fast acid analysis column.

and oils frequently interfered with the analysis, particularly when extremely low levels residual acrylamide are being determined. These interferences can be minimized using a two-column separation. This column-switching technique initially separates residual acrylamide on a reversed-phase C_{18} column; the acrylamide peak is then switched onto a second column (fast acid column) for further separation by adsorption chromatography. By combining the two separation techniques (reversed-phase and adsorption) most of the interfering materials in the polymeric sample can be eliminated. Acrylamide can now be determined directly and accurately in both solution and latex polymeric systems at very low levels. Fig. 2 shows a typical chromatogram.

The limit of detection for acrylamide in our current instrumental set up is 0.005 ppm at a 95% confidence level, which corresponds to a detection limit of 5 ppm and 0.5 ppm in emulsion and solution polymer products, respectively. Reproducibility data for residual acrylamide determination are presented in Table I. Percent relative standard deviations range from 0.4 to 5.5% for residual acrylamide levels from 2.5 to 650 ppm.

Spike recovery studies were performed on both solution and latex polymers. An appropriate aliquot of acrylamide standard solution was spiked into the polymer sample directly. The spiked sample was then treated as an unknown and analyzed using the column-switching procedure. Recovery data are shown in Table II. Better than 70% recovery was observed at acrylamide levels ranging from 0.4–200 ppm.

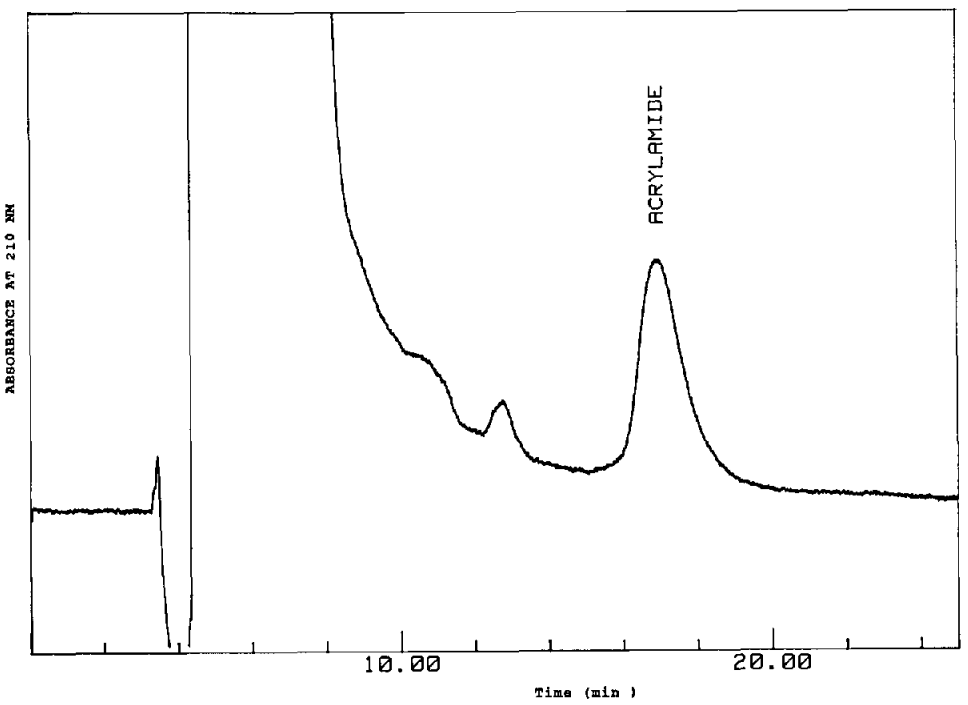

Fig. 2. Typical chromatogram of acrylamide analysis. 0.02 ppm acrylamide in a diluted sample solution. HPLC conditions as described under Experimental.

TABLE I

REPRODUCIBILITY STUDIES OF THE PRECIPITATION–COLUMN-SWITCHING PROCEDURE IN A POLYMERIC SYSTEM

Analysis	Acrylamide in polymers (ppm)					
	Solution polymers		Emulsion polymers			
	Sample A	Sample B	Anionic		Cationic	
			Sample C	Sample D	Sample E	Sample F
1	8.8	2.5	5.6	641	15.3	125
2	8.8	2.5	5.7	642	15.6	120
3	8.8	2.5	5.8	643	15.1	126
4	8.7	2.5	5.1	638	14.8	124
5	8.8	2.7	5.9	645	15.6	113
Mean	8.76	2.54	5.62	642	15.28	121.7
S.D.	0.055	0.089	0.31	2.59	0.34	5.37
Relative S.D. (%)	0.62	3.5	5.5	0.40	2.2	4.4

TABLE II

DATA OF THE SPIKE RECOVERY STUDIES

Sample type	Acrylamide spiked (ppm)	Acrylamide found (ppm)	Recovery (%)
Anionic latex	(A) 4.7	4.2	89.4
	(B) 5.0	4.7	94.0
	(C) 8.6	7.0	81.4
	(D) 12.2	10.0	82.0
	(E) 16.5	14.3	86.7
Cationic latex[a]	(A) 9.3	7.0	75.3
	(B) 16.6	12.0	72.3
	(C) 21.3	16.8	78.9
	(D) 49.6	35.3	71.2
	(E) 93.4	75.2	80.5
Cationic latex[b]	(A) 69.8	69.0	98.8
	(B) 144.0	126.3	87.7
Cationic latex[b]	(A) 100.0	100.0	100.0
	(B) 200.0	198.4	99.2
Non-ionic latex	(A) 220.0	202.0	91.8
	(B) 129.0	114.0	88.4
Solution polymer	(A) 19.5	19.5	100.0
	(B) 7.6	7.8	102.6
	(C) 3.4	3.5	102.9
	(D) 0.8	0.8	100.0
	(E) 0.4	0.5	125.0

[a] This sample contained polymeric surfactants.
[b] These emulsions contained common non-polymeric surfactants.

This method has been used in our laboratory for more than two years. With heavy usage, slowly eluting substances such as surfactants, oligomers and additives will build up on the guard column and the C_{18} column. Consequently, the guard column must be changed and the C_{18} column cleaned periodically. Our experience indicated that with a daily load analysis of about 30 samples, the C_{18} guard column has to be changed once a month. However, the fast acid guard column can last as long as six months without change. After each guard column or analytical column change, the valve switching time must be re-established by running standard solutions.

CONCLUSION

The column-switching HPLC method described has been shown to provide good separation of residual acrylamide from matrix interferences in both solution and emulsion polymeric systems. This allows very low residual acrylamide determination in such samples. The procedure for sample preparation and analysis is relatively simple, precise, and accurate and can be easily automated for routine analysis of residual acrylamide in polymer products.

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