Determination of Acrylamide Monomer in Polyacrylamide Degradation Studies by High-Performance Liquid Chromatography

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Abstract

A high-performance liquid chromatography method using C_{18} and ion-exchange columns in series is developed for the determination of acrylamide and acrylic acid monomers in polymeric samples. The C_{18} column acts as a guard column, trapping surfactants and impurities and retaining the nonionic species. The ion-exchange column then separates the monomers according to their respective ionic strengths. This method has been proven in the laboratory to work successfully for all types of acrylamide/acrylic acid polymers and matrices. Detection limits for both monomers can be achieved in the parts-per-billion range. The method is used to study the possible degradation of polyacrylamide to acrylamide monomer in the presence of glyphosate (a herbicide) and sunlight. Polyacrylamide is used as a spray drift reduction aid in combination with glyphosate. In normal applications, the polymer and herbicide are in contact with each other in the presence of sunlight. The results show that the polymer does not degrade to acrylamide in the presence of glyphosate or sunlight or any combination of the two. It is also observed that glyphosate influences the solubility of polyacrylamide, and care must be used when combining the two.

Introduction

Acrylamide monomer is used to produce either homo- or copolymers of polyacrylamide. In the United States, approximately 95% of acrylamide monomer is used in the production of polyacrylamide. Polyacrylamide is applied worldwide in, among others, flocculants in waste and potable water treatments, oil field operations, water retention aids in sandy soil, coal refuse recovery processes, sugar refineries, mineral leach mines, electrophoresis gels, flocculents in paper manufacturing, and adhesives and grouts used as barriers against groundwater seepage (1–5). Another major application is as a spray drift reduction aid used with herbicide applications. The polymer increases the viscosity of the herbicide solution, allowing for more uniform spray applications, and also increases contact time with the plant (6–9).

Acrylamide-based polymers have been under scrutiny for many years because of the highly toxic nature of acrylamide monomer even in low concentrations. Acrylamide monomer is a peripheral neurotoxin that can cause death at high enough concentrations. However, in lower concentrations (which is usually the case in acrylamide exposure), the axonopathy is reversible with time (10–14). Nalco is always concerned with residual monomer concentrations in polyacrylamide and any form of polymer degradation that may occur for any reason.

Degradation of polyacrylamide in the environment has been studied for years. One study showed no degradation in polyacrylamide for an extended period of time in comparison with other polymers tested under sandy desert conditions (15). Another study indicated that polyacrylamide is environmentally acceptable with respect to the German legal standards (16). As long as the residual monomer level in the polymer is low enough, the polymer is safe to handle by a variety of means.

Two studies found in *Ecotoxicology and Environmental Safety* reported that polyacrylamide, in the presence of sunlight and glyphosate, photolytically degrades to acrylamide monomer (17–19). These papers conclude that polyacrylamide degrades to acrylamide monomer via a free-radical process initiated by sunlight. These results are controversial, because polyacrylamide is used in industrial and agricultural applications where the polymer is exposed to direct sunlight. A major objective of the present work was to repeat the photolytic degradation studies to determine if the proposed free-radical process is a reasonable route for polyacrylamide degradation.

To begin the degradation study, a viable method was required for the residual monomer analysis. Over the years, various methods have been reported for determining trace levels of acrylamide monomer in water matrices. However, most of these methods require a time-consuming extraction procedure and are limited by the complexity of the sample matrix (20–24). In 1985, Freshour et al. (25) reported a simple procedure using column switching to determine trace levels of

acrylamide in tissue cultures. This method was slightly modified in 1990 by Tseng (26) at Nalco Chemical Company for determining trace levels of acrylamide in polymeric samples. This newer method required two isocratic pumps and was operator sensitive, especially in regards to switching time calculations.

The residual acrylamide monomer in the present study was analyzed using a tandem column high-performance liquid chromatography (HPLC) method recently developed by Nalco Chemical Company. The method applies a simple dilution followed by separation on C_{18} and ion-exchange columns connected in series and UV detection. The method can be applied to the analysis of residual acrylamide and acrylic acid monomers in solution, dispersion, and emulsion polymers. This paper describes a detailed procedure and validation for determining residual acrylamide and acrylic acid monomer concentrations in polymer matrices. In addition, the method was used to determine the degree of degradation of polyacrylamide to acrylamide monomer in the presence of glyphosate and sunlight.

Experimental

Materials

The following materials and reagents were used: acrylamide (99%), electrophoresis-grade Gold Label acrylic acid (99%, Aldrich, Milwaukee, WI), concentrated sulfuric acid (J.T. Baker, Phillipsburg, NJ), HPLC-grade methanol (E M Science, Gibbstown, NJ). Round-Up (Monsanto, St. Louis, MO), a 41% solution of glyphosate (GH), was obtained from a local feed store. The polyacrylamide latex polymer (Nalco-Trol II, Nalco, Naperville, IL) was prepared in our plant in Garville, LA. Water was purified using a Milli-Q water purification system (Millipore, Bedford, MA). All solvents for HPLC analysis were filtered through 0.22-mm GS or GV filter paper (Millipore) and vacuum degassed prior to use.

Standard solutions

Standard stock solutions of both monomers were prepared by dissolving a known amount of monomer (~ 0.1 g to the nearest 0.1 mg.) in 100 mL of mobile phase. A set of standard solutions were prepared by diluting aliquots of the stock solution with mobile phase in 100-mL volumetric flasks. The concentration range for the standard solutions was 0.01–5.0 ppm.

Instrumentation and chromatographic conditions

The HPLC system consisted of a Shimadzu LC-600 isocratic pump, a SPD-6A spectrophotometric detector (both from Shimadzu, Kyoto, Japan) and an Alcott model 728 autosampler with a model 732 injection valve (Micromeritics, Norcross, GA). The data was collected and analyzed on a P.E. Nelson data acquisition station using Turbochrom version 3.1 (P.E. Nelson, Cupertino, CA).

Nalco's tandem column method used an ODS-AL-302 column (4.6 × 150 mm, 5-µm particles) from YMC (Wilmington, NC) and an HPLC Fast Acid analysis column (7.8 × 100 mm, 9-µm particles) from Bio-Rad (Hercules, CA) connected in series. The Bio-Rad Fast Acid column uses a sulfonated divinyl benzene–styrene copolymer as the supporting material with a protonated (hydrogen) ionic resin.

The mobile phase used for the separation was 0.01M H_2SO_4 (pH ~ 2.5). The samples first passed through the C_{18} column, then directly into the ion-exchange column, followed by the UV detector (set at 210 nm). The flow rate was 0.6 mL/min. The analysis was conducted at ambient temperature, and a 100-µL injection loop was used to introduce the sample onto the column.

The HPLC system used to test the Ecotoxicology method, noted in references 17–19, consisted of the similar type of instrumentation as used in Nalco's tandem column method except for the column and loop size. For this method, a Hypersil-ODS column (2.1 × 200 mm, 5-µm particles) with a 2.1- × 20-mm guard column from Hewlett-Packard (Wilmington, DE) was used for the separation.

The reversed-phase Hypersil method had a mobile phase of 0.84 g KH_2PO_4 in 960 mL H_2O (pH 4.6)/40 mL methanol. The flow rate was 0.3 mL/min. The UV detector was set at 210 nm, and the samples were analyzed at ambient temperature. A 50-µL injection loop was used to introduce sample onto the column.

The polymer samples were inverted (discussed in the Polymer inversion section) using a Eurostar variable-speed stirrer with a caged blade impeller spinning at 900 rpm (IKA Labortechik, VWR, Geneva, IL). The blending was completed using a Braun high-speed household blending mixer model 4172 (The Gillette Company, Boston, MA) for 30–60 s.

Sample preparation

Three types of water were used for this study: tap, river, and lake. The two outdoor waters were obtained from a forest preserve located in Naperville, IL. The samples were prepared according to Table I. A 100-mL aliquot of each of these samples was placed in a 100-mL glass jar and sealed with two layers of plastic wrap. The glass jars were placed outdoors in a small-rimmed aluminum tray to ensure that the wind would not knock the jars over. The acrylamide and acrylic acid monomer concentrations in each sample were initially taken and then monitored every week for six weeks. The HPLC analyses were completed using both previously discussed methods. The samples monitored by the Nalco method were diluted 1:100 with mobile phase, filtered through a 0.1-µm VV (Millipore) filter

Table I. Sample Preparation

	Amount (mL)			
	Sample A	Sample B	Sample C	Sample D
Water	200	197.5	190	187.5
Polymer*	–	2.5	–	2.5
GH†	–	–	10.0	10.0

* Polymer, polyacrylamide.
† GH, glyphosate.

disk, and injected. In the ecotoxicology method, the samples were filtered through a 0.1-μm VV filter disk and injected without any dilutions.

Weather conditions

The weather conditions during the study are noted in Table II. These conditions include sunrise/sunset, precipitation, and frost dates. The amount of sunlight varied from 12.8 to 10.8 h from the beginning to the end of the study, respectively. Three minor frosts occurred during the study. However, none of these frosts produced any phase changes or stability problems with the solutions.

Polymer inversion

Nalco produces latex polymers as a convenient means to transport and handle high-molecular-weight, water-soluble polymers. A latex polymer is the final product of an emulsion polymerization involving a colloidal dispersion of water-soluble polymers in a continuous oil phase. The polymer is trapped inside the droplet as a dilute homogeneous solution. Before use, the latex polymer needs to be dissolved in a continuous water phase. This process is called an inversion. The inversion process flips the water-in-oil dispersion to an oil-in-water solution dispersion. The polymer in the water droplet then dissolves in the continuous water phase. Basically, the latex polymer is added to a large excess of water in the presence of a small amount of inverting agent, a high hydrophylic lipophylic balance (HLB) surfactant. This allows the water to diffuse through the surfactant layer and swell the polymer, producing a polymer that no longer fits the interior of the particle, causing the particle to rupture. The water continues to swell the particles until an equilibrium is reached.

The inversion process requires a very rapid dispersion of the polymer particles. If the process is too slow, a quick coagulation of the particles occurs, generating beads that are commonly called "fish eyes". In this situation, residual monomer may become trapped inside these beads, which produces a lower residual monomer level when analyzed. Over time, the beads invert, producing an increase in the available residual monomer concentration. This increase may be observed the first few weeks in a poorly inverted polymer (27–31).

Table II. Weather Conditions During the Study*

Day	Sunrise	Sunset	Daylight hours	Rain per week (inches)
0	6:27 a.m.	7:10 p.m.	12:47	0
7	6:34 a.m.	6:57 p.m.	12:23	0
14	6:41 a.m.	6:45 p.m.	12:04	1.59
21	6:44 a.m.	6:33 p.m.	11:44	0
28	6:56 a.m.	6:21 p.m.	11:25	0.1
35	7:04 a.m.	6:10 p.m.	11:06	0.69
42	7:12 a.m.	5:59 p.m.	10:47	0.01

* Frost dates: 10/15 (day 35), 10/17 (day 37), 10/19 (day 39).

Results and Discussion

A main objective of this study was to corroborate or refute the idea that polyacrylamide degradation could occur via a photolytically induced free-radical process as mentioned in references 17–19. This theory could not be found in any other literature than references 17–19 and was not substantiated by polymer chemists in our organization.

Hypersil method

With concern over the free-radical theory, a few of the experiments found in the two *Ecotoxicology and Environmental Safety* papers were repeated in our laboratory. In addition to the free-radical theory, questions arose concerning the chromatographic conditions and the method used to prepare the samples. The samples were analyzed using the method in references 17–19 and by the tandem column method developed by Nalco, both mentioned in the Experimental section. However, a few modifications were made to the published method prior to use.

These modifications were adopted to produce a better scientific experiment that would answer the question concerning the degradation of polyacrylamide. The major difference between the method outlined in references 17–19 and the present modified procedure consists in sample filtering. In the Nalco process, samples were filtered through a 0.1-μm VV filter unit prior to injection, whereas the published method called for a direct injection. Filtering prevents plugging in the injection system and columns by removing the polymer solids, surfactants, and other large-molecular-weight species from the samples. The unfiltered samples could also cause variable sample sizes to be introduced onto the column.

Another difference in the present study is that our laboratory used local water samples and exposed 100 mL of the sample to the sunlight. The water used in references 17–19 was obtained by their laboratory in Kansas, and only 50 mL were exposed to the sunlight.

Additionally, water and glyphosate blanks were analyzed throughout the study to ensure that these components did not produce any interfering peaks. There is no mention in the referenced papers of blanks being analyzed throughout the study. By not analyzing blanks, questions are raised concerning any degradation or microbial growth that could occur in the glyphosate or water, causing possible interferences.

Problems

A problem noted when employing the method from references 17–19 is the interference of acrylic acid with the acrylamide monomer determination. Figure 1 shows the chromatogram of a 1-ppm mixture of acrylamide and acrylic acid on the Hypersil-ODS column. Notice the overlap between the two monomers. After numerous injections, peak resolution between acrylamide and acrylic acid continuously decreased, and reasonable separation on this column was only accomplished for one set of samples (12 injections) before either the resolution or selectivity collapsed.

This loss of selectivity is further shown by analyzing a calibration standard over time. Figure 2 shows a chromatogram of

a 0.1-ppm acrylamide standard at the beginning and end of a day's analyses. Notice the dramatic change in the peak shape, affording coelution of the compound at 3 min with the peak of acrylamide.

In the original papers (17–19), the amount of glyphosate used in the high-level studies was less than 10 times the normal amount used in "real life" applications. This was to minimize interferences associated with the glyphosate. Figure 3 shows the chromatograms for glyphosate (2%) and a mixture of glyphosate and acrylamide monomer. Notice the substantial peak overlap of both components at the trailing end of the glyphosate signal, giving rise to more or less marked uncertainty in peak integration.

The results from the polymer–glyphosate interaction studies would be more reliable if a more robust and accurate method, such as the newly developed tandem column technique, was used. The next portion of this paper will detail the newly developed tandem column chromatography technique that was also used to analyze the samples. This method is robust enough for polymer samples and precise enough to ensure the results of the study.

Nalco method

The tandem column technique combines the ruggedness of a C_{18} column with the selectivity of an ion-exclusion column.

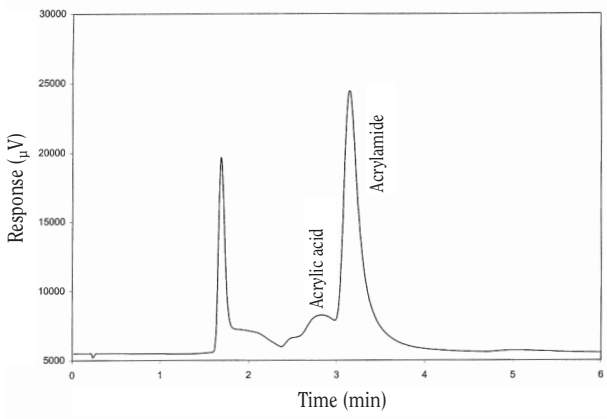

Figure 1. Chromatogram of a mixture of acrylamide and acrylic acid using the Hypersil method.

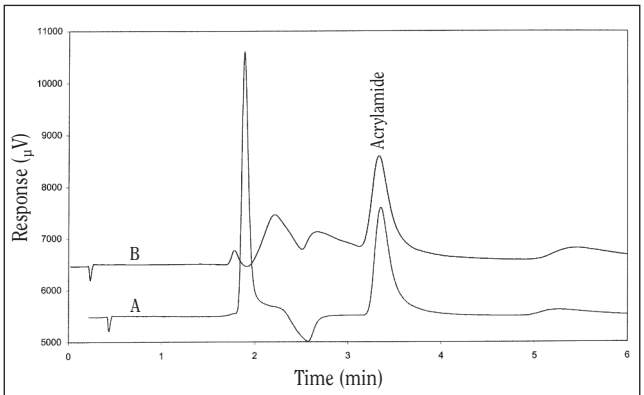

Figure 2. Chromatograms of a 0.1-ppm acrylamide standard using the Hypersil method: initial (A) and final injections (B).

The first column, a C_{18} column, is used to separate the polymer from the analytes of interest. The second column, a resin-based column, uses ion-exchange and ion-exclusion mechanisms to separate the ionic species. In a polymer sample, the acrylic acid is separated from ionic oligomeric species while the acrylamide is separated from the oils and surfactants used in polymer formulations. The combination of these two column chemistries in tandem provides separation and quantitation of the two monomers (contained in one polymer) without complicated column switching or time-consuming extractions.

Linearity

The concentration of acrylamide and acrylic acid in the samples was calculated with a new calibration curve each week on the tandem column method. This system has been proven to be stable over time. Figure 4 shows the chromatogram for a ~ 0.1-ppm standard of both monomers in the same solution. The analytes are baseline resolved with an α value of 1.4. Throughout the use of this tandem column system, the calibration curves ranged from 0.01 to ~ 5–10 ppm, depending on the range required for the analysis. For acrylamide, this produced a correlation coefficient of 0.999, a slope of 192,844 mV.s/ppm, and a y-intercept of 103 mV.s. The acrylic acid calibration curve produced a correlation coefficient of 0.999, slope of 881,779 mV.s/ppm, and a y-intercept of –2805 mV.s.

Precision

For the stability study, the samples were analyzed in duplicate on the 21st day to determine the method precision for acrylamide monomer for this particular study. The results are noted in Table III. The pooled standard deviation (calculated using the σ values for each sample) was calculated to be 0.031 ppm. The precision of the method, therefore, is 3σ or 0.093 ppm.

System integrity

Figure 5 shows the chromatograms for the D series (water–GH–polymer) from Table I of the three water types used at the beginning of the study. Figure 6 represents the same samples analyzed six weeks later. The shift in retention times for the two monomers is related to a new column set

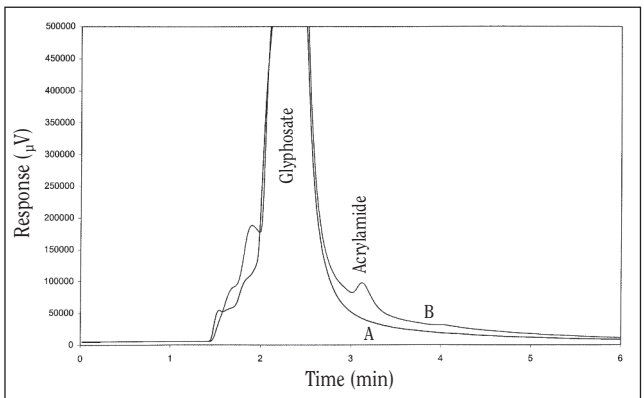

Figure 3. Chromatograms of glyphosate and acrylamide using the Hypersil method: 2% glyphosate (A) and 2% glyphosate–2 ppm acrylamide (B).

Table III. Acrylamide Precision Study

		Acrylamide (ppm)*				
	Label	Run 1	Run 2	Average	Range	Sigma
Naperville Water						
water–polymer (stirred)	B	1.46	1.47	1.46	0.01	0.00707
water–polymer (blended)	B2	1.54	1.47	1.50	0.07	0.0495
water–polymer–GH (stirred)	D	1.34	1.34	1.34	0	0
water–polymer–GH (blended)	D2	1.53	1.57	1.55	0.04	0.0283
DuPage River Water						
water–polymer (stirred)	B	nd†	nd†	nd†	nd†	nd†
water–polymer (blended)	B2	nd†	nd†	nd†	nd†	nd†
water–polymer–GH (stirred)	D	1.77	1.72	1.74	0.05	0.0354
water–polymer–GH (blended)	D2	1.85	1.84	1.84	0.01	0.00707
Mud Lake Water						
water–polymer (stirred)	B	0.95	0.96	0.96	0.01	0.00707
water–polymer (blended)	B2	0.79	0.75	0.77	0.04	0.0283
water–polymer–GH (stirred)	D	1.54	1.48	1.51	0.06	0.0424
water–polymer–GH (blended)	D2	1.80	1.85	1.82	0.05	0.0354

* Using Nalco HPLC method, day 21; pooled standard deviation = 0.031 ppm.
† nd, nondetectable.

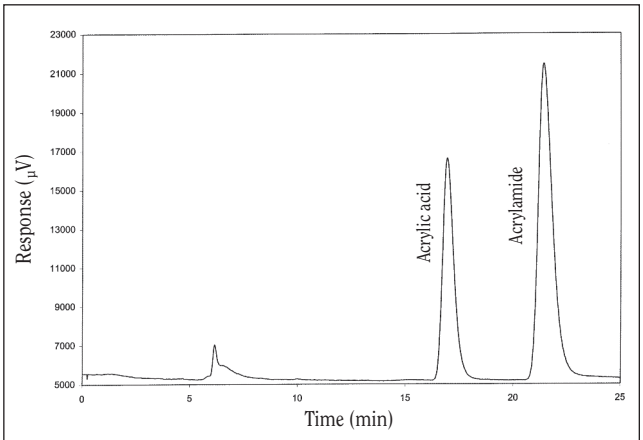

Figure 4. Chromatogram of 0.1 ppm acrylamide and acrylic acid standards at the beginning of the study using the Nalco method.

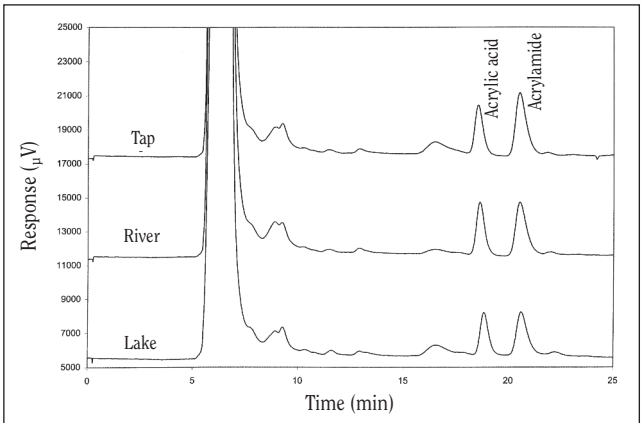

Figure 6. Chromatograms of three types of water with glyphosate and polymer at the conclusion of the study using the Nalco method.

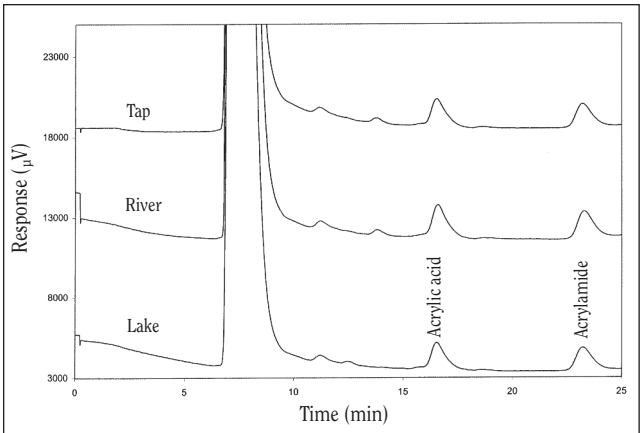

Figure 5. Chromatograms of three types of water with glyphosate and polymer at the beginning of the study using the Nalco method.

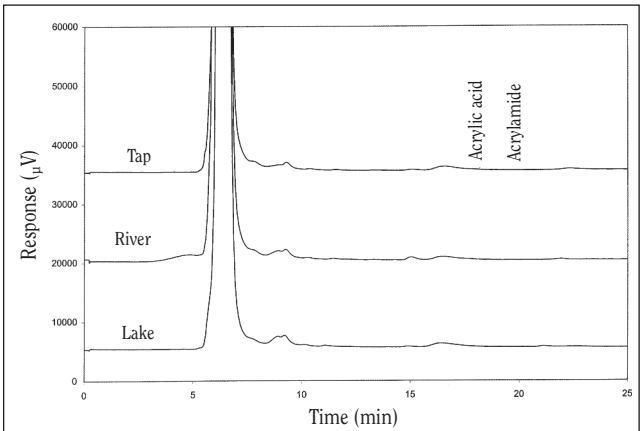

Figure 7. Chromatograms of three types of water and glyphosate using the Nalco method.

being used for the analysis after the 5th week. This HPLC system was not only used for this study but for other ongoing Nalco studies. This column set replacement did not have any effect on the results for this or any of the other ongoing studies. The monomers were still baseline resolved without the presence of any interferences.

Figures 7 and 8 are the chromatograms for the water–GH and water–polymer samples at the conclusion of the study, respectively. Figure 9 is the chromatogram for the 0.1-ppm standard analyzed at the end of the study. Comparing Figures 7–9 reveals that acrylamide and acrylic acid monomer elute within the peaks at 16.5 and 23 min and are baseline resolved for the final analysis.

As in any HPLC system, the retention time for the monomers will decrease over time. This is evident in the retention time changes from the beginning to the end of this study. Even though the retention times decreased over time, the monomers were still baseline resolved. The acrylamide and acrylic acid peaks were identified by standards throughout the use of this column set. The degradation of the columns does not occur rapidly but rather slowly over time, thereby allowing the chromatographer the opportunity to monitor the decrease in reten-

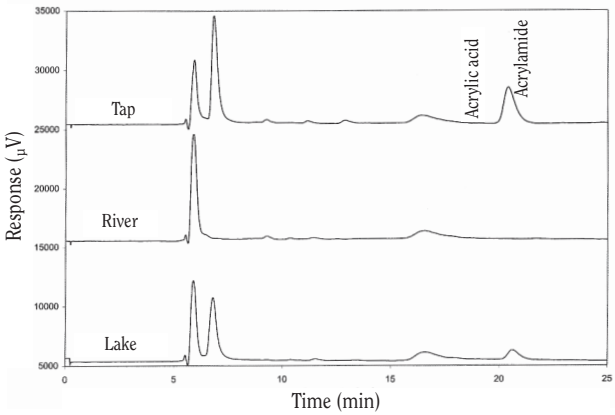

Figure 8. Chromatograms of three types of water and polymer using the Nalco method.

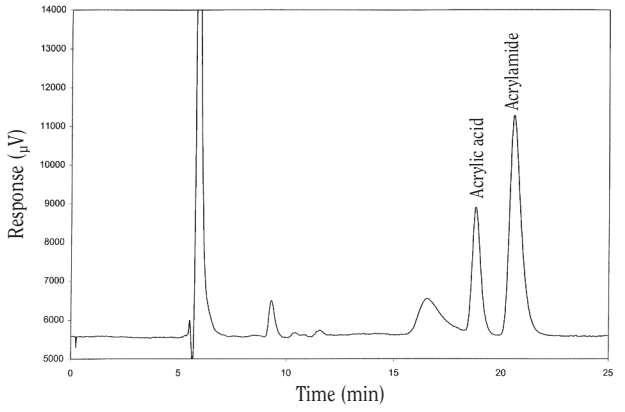

Figure 9. Chromatogram of 0.1 ppm acrylamide and acrylic acid standards at the conclusion of the study using the Nalco method.

Table IV. Acrylamide Levels During the Study

	Acrylamide (ppm)*						
Sample	**Day 0**	**Day 7**	**Day 14**	**Day 21**	**Day 28**	**Day 35**	**Day 42**
Naperville A	nd†	nd†	nd†	nd†	na‡	nd†	nd†
Naperville B	1.65	1.77	1.62	1.46	1.42	1.50	1.38
Naperville B2	2.37	2.20	1.75	1.50	1.63	1.53	1.34
Naperville C	nd†	nd†	nd†	na‡	na‡	na‡	nd†
Naperville D	0.42	1.66	1.34	1.34	1.36	1.52	1.78
Naperville D2	0.97	2.00	1.92	1.55	1.96	2.09	1.85
DuPage River A	nd†	nd†	nd†	na‡	na‡	na‡	nd†
DuPage River B	2.07	1.64	0.47	nd†	nd†	nd†	nd†
DuPage River B2	1.76	0.80	0.23	nd†	nd†	nd†	nd†
DuPage River C	nd†	nd†	nd†	na‡	na‡	na‡	nd†
DuPage River D	0.88	1.84	1.78	1.74	1.80	2.03	1.71
DuPage River D2	1.14	2.10	1.80	1.84	1.97	2.00	2.00
Mud Lake A	nd†	nd†	nd†	na‡	na‡	na‡	nd†
Mud Lake B	1.59	1.50	1.18	0.96	0.64	0.48	0.41
Mud Lake B2	1.96	1.50	0.99	0.77	0.66	0.38	0.28
Mud Lake C	nd†	nd†	nd†	na‡	na‡	na‡	nd†
Mud Lake D	0.83	3.50	1.46	1.51	1.79	1.61	1.45
Mud Lake- D2	0.93	2.20	1.76	1.82	2.10	2.00	1.95

* Using the Nalco HPLC method. A, water; B, water–polymer (stirred); B2, water–polymer (blended); C, water–glyphosate; D, water–polymer–glyphosate (stirred); D2, water–polymer–glyphosate (blended).
† nd, nondetectable.
‡ na, not analyzed.

tion time, peak shape, and resolution. The daily use of this system allows us the capability to compare chromatograms from the start and finish of a project, noting the differences in the monomer retention times. Over 500 samples were injected on this column set during the course of this study without any interferences from sample matrices.

The extra peaks noted in Figures 6 and 7 may also explain the problems that occurred with the previously published method (17–19). The chromatograms show that the Nalco method and study did not produce any additional peaks that would interfere with the analysis of acrylamide monomer. This may not be true with the chromatograms obtained using the Hypersil-ODS column.

After six weeks

The samples were analyzed for six weeks using the Nalco tandem column method. The results for the six-week time study of acrylamide and acrylic acid are depicted in Tables IV and V, respectively. The series labeled B2 and D2 were started a day after the base study. When the original dilutions were prepared, "fish eyes" were noted in the jars. These globules represent polymer that had not been inverted, as described in the Experimental section. Therefore, on the following day, two new series were prepared (B2 and D2). The new series were prepared in the same manner as the previous day; however, after the components were added together, the samples were blended in a high-speed blender for 30 s prior to being placed outside. Unfortunately, this inversion technique still left some globules, but to a lesser amount than the previous day when the samples were only stirred for an hour on a stir plate.

The acrylic acid monomer was analyzed throughout this study to ensure that the acrylamide monomer had not hydrolyzed. This hydrolysis would decrease the acrylamide concentration while increasing the acrylic acid concentration. Over time, the acrylic acid concentration did not increase but rather decreased. This is a good indication that the acrylamide monomer did not hydrolyze into acrylic acid.

Figures 10 and 11 show the results for acrylamide monomer in sample series B/B2 and D/D2, respectively, in a graphic form. In Figure 10, the curves for each type of water have relatively consistent slopes. However, the curve's shapes are different for the three types of water. This indicates that some species in the water may be interacting with the acrylamide monomer, either accelerating or hindering monomer degradation. In contrast, the curves in Figure 11 all have comparable curve shapes. This shows the protective effect of GH on acrylamide monomer degradation.

Tables IV and V show that sample series A and C (the water and water–GH blanks) were not analyzed on days 21, 28, and 35. This was done to save time in the analysis over the time period indicated. However, these samples were analyzed on the final day to ensure that the water and glyphosate did not produce any interferences (Figure 7).

Poor inversion

When the D series samples were prepared, "fish eyes" were noted in the jars. This poor inversion process was also noted in references 18 and 19. An initial poor inversion of the latex polymer causes low residual levels of acrylamide at the start of a study. Upon further aging and thus complete polymer dissolution, the acrylamide monomer concentrations will increase to the appropriate monomer level and then remain constant. This is noted in Table IV, where the initial values for the D series were low, then increased by the second week, and either remained constant or slightly decreased during the remainder of the study.

Another cause for the poor inversion was the presence of glyphosate. This was confirmed by the data in Figures 10 and 11. Notice that the acrylamide levels in the B series (Figure 10) decreased with time without the increase at one week. In contrast, the D series containing glyphosate (Figure 11) shows a noticeable increase in acrylamide monomer levels within one week, then decreased throughout the study. As previously described, this increase was the result of the poor inversion finally reaching complete inversion.

This study indicates that glyphosate interacts with the polymer during the inversion process, which is a time-dependent process, thus rapid inversion is not achievable. Poor inver-

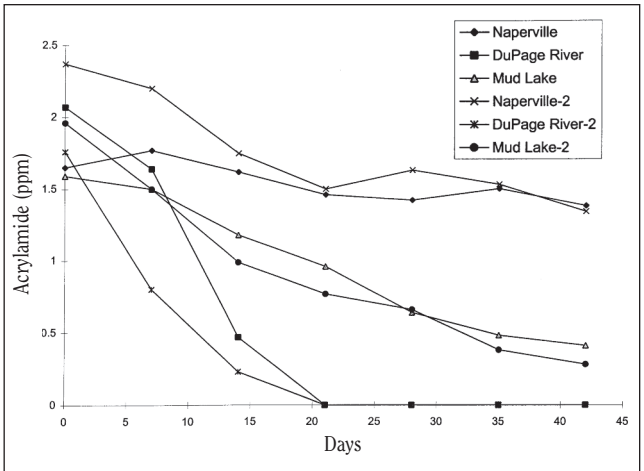

Figure 10. Comparison of acrylamide monomer levels over the 6-week study for the three water types and polymer using the Nalco method.

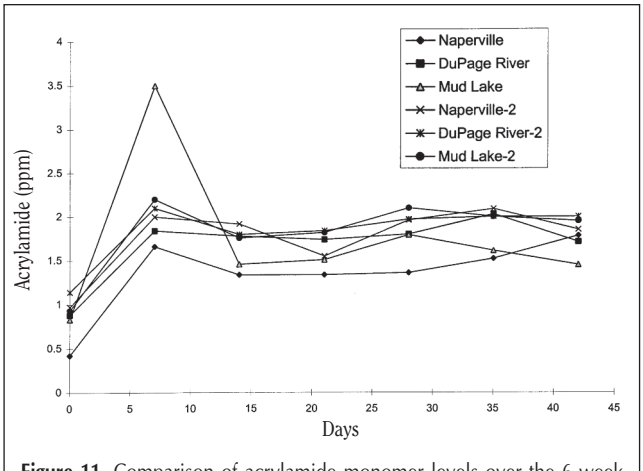

Figure 11. Comparison of acrylamide monomer levels over the 6-week study for the three water types, glyphosate, and polymer using the Nalco method.

sion of a polymer can produce varying residual concentrations throughout a time study until complete inversion occurs. This is mostly noted when the samples are allowed to sit undisturbed for a period of time, as in this study. This conclusion is also noted in the previously published method (17–19).

The poor inversion theory was also proven using a variable-speed mixer with a caged blade impeller at 900 rpm. This technique is considered the industry standard for inverting a latex polymer. Table VI contains the results of this stirring technique for water–polymer and water–GH–polymer sample series. The results show that the acrylamide levels vary slightly throughout the stirring, but this variation is within the error of the method. After 300 min of stirring, the samples were placed outside with the other samples. Over the three-week time period, the water–polymer sample shows a greater decrease in the amount of acrylamide monomer than the water–polymer–GH sample. This is consistent with the concept that the GH hinders the degradation of acrylamide monomer. Additionally, the acrylamide monomer level did not increase during this study, thus indicating a complete inversion.

Other uses for the Nalco method

Since this new technique has been used in our laboratory, over 25,000 samples have been analyzed, and this study was one out of many projects. Solution, latex, and dispersion polymer species have been analyzed with average values ranging from ~ 2–2500 ppm of residual acrylic acid and acrylamide monomers with corresponding standard deviations of 0.045 to 17 ppm for nine degrees of freedom, respectively. These standard deviations were used to calculate the method precision for this method ranging from 0.14 ppm for the sample containing less than 100 ppm residual monomer to 60 ppm for those greater than 2500 ppm.

An advantage of this procedure in comparison with other methods is the ease of analysis. The samples did not require any form of derivatization and are only diluted with mobile phase, filtered, and injected into the HPLC system.

Table V. Acrylic Acid Levels During the Study

	Acrylamide (ppm)*						
Sample	Day 0	Day 7	Day 14	Day 21	Day 28	Day 35	Day 42
Naperville A	nd†	(3.67)	nd†	na‡	na‡	na‡	nd†
Naperville B	2.99	1.86	nd†	na‡	0.82	nd†	nd†
Naperville B2	3.68	3.20	1.49	na‡	0.18	nd†	nd†
Naperville C	nd†	nd†	nd†	na‡	na‡	na‡	nd†
Naperville D	2.43	2.93	2.11	na‡	2.29	nd†	2.15
Naperville D2	3.86	3.10	2.86	na‡	2.20	nd†	2.99
DuPage River A	nd†	nd†	nd†	na‡	na‡	na‡	nd†
DuPage River B	3.85	0.20	1.23	na‡	nd†	nd†	nd†
DuPage River B2	3.71	0.10	nd†	na‡	nd†	nd†	nd†
DuPage River C	nd†	nd†	nd†	na‡	nd†	nd†	nd†
DuPage River D	3.49	4.10	3.22	na‡	2.63	nd†	2.94
DuPage River D2	4.45	3.10	2.83	na‡	3.11	3.14	3.38
Mud Lake A	nd†	(0.83)	1.17	na‡	na‡	na‡	nd†
Mud Lake B	3.39	0.06	nd†	na‡	nd†	nd†	nd†
Mud Lake B2	3.18	1.20	nd†	na‡	nd†	nd†	nd†
Mud Lake C	nd†	(2.0)	0.64	na‡	na‡	na‡	nd†
Mud Lake D	3.84	3.50	2.40	na‡	2.35	2.53	2.57
Mud Lake D2	2.87	3.90	2.73	na‡	2.55	3.06	2.92

* Using the Nalco HPLC method. A, water; B, water–polymer (stirred); B2, water–polymer (blended); C, water–glyphosate; D, water–polymer–glyphosate (stirred); D2, water–polymer–glyphosate (blended).
† nd, nondetectable.
‡ na, not analyzed.

Table VI. Caged Blade Impeller Stir Test

	Acrylamide (ppm)										
	0 min	30 min	60 min	120 min	180 min	300 min	Average	Range	7 days	14 days	21 days
Water–polymer	2.71	2.54	2.83	2.32	2.84	2.47	2.24	2.32/2.84	2.5	2.24	2.14
Water–polymer–GH	2.47	2.69	3.24	2.36	2.72	3.54	2.43	2.36/3.54	2.47	2.5	2.29

Conclusion

This paper presents a new and efficient method for the determination of residual acrylamide and acrylic acid in latex, dispersion, and solution polymers. The new method effected the separation of the monomers from interfering components and proved robust enough to handle over 2000 polymer injections without substantial column degradation. In addition, the method is easy to set up and operate and does not require time-consuming column switching, extraction, or derivatization procedures.

The new technique was successfully used in a study, revealing that polyacrylamide does not degrade to acrylamide monomer in the presence of sunlight and glyphosate. Additionally, glyphosate appears to interact with either the acrylamide monomer or polymer, decreasing the rate of monomer degradation.

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References

1. *Assessment of Health Risks from Exposure to Acrylamide*. Office of Toxic Substances, U.S. Environmental Protection Agency, B1-005:1-8, 1990.
2. A.M. Bollinger. Poly(ethylene oxide) polymers for industrial wastewater treatment. *Int. Water Conf.* **56:** 179–82 (1995).
3. P.E. Goodenough and J. Owen. Chromatographic and electrophoretic analyses of papaya proteinases. *Phytochemistry* **26(1):** 75–79 (1986).
4. L. Brown, M.M. Rhead, and K.C. Bancroft. Case studies of acrylamide pollution resulting from the industrial use of polyacrylamide. *Water Pollut. Control* **79:** 507–510 (1980).
5. Process for treating water-in-oil emulsions of water-soluble carboxamide polymers. *Engl. Res. Discl.* **193:** 184–85 (1980).
6. L.F. Bouse, J.B. Carlton, and P.C. Jank. Use of polymers for control of spray droplet size. *Am. Soc. Agric. Eng.* **AA-86-005:** 1–18 (1986).
7. A.K. Underwood, A. Clark, R.E. Mack, J. Thomas, J.R. Roberts, and G.C. Volgas. Dry concentrate spray adjuvants. *Proc. Fourth Intl. Symp. Adjuvants Agrochemi.* **193:** 391–96 (1995).
8. R.A. Downer, T.M. Wolf, A.C. Chapple, F.R. Hall, and J.L. Hazen. Characterizing the impact of drift management adjuvants on the dose transfer process. *Proc. Fourth Intl. Symp. Adjuvants Agrochemi.* **193:** 138–43 (1995).
9. P. Chamberlain. European patent EP506313 A1 920930, 1992.
10. D.D. McCollister, C.L. Hake, S.E. Sadek, and V.K. Rowe. Toxicologic investigation of polyacrylamide. *Toxicol. Appl. Pharmacol.* **7:** 639–51 (1965).
11. M.S. Miller and P.S. Spencer. The mechanism of acrylamide axonopathy. *Ann. Rev. Pharmacol. Toxicol.* **25:** 643–66 (1985).
12. C.A. Seybold. Polyacrylamide review: soil conditioning and environmental fate. *Commun. Soil Sci. Plant Anal.* **25:** 2171–85 (1994).
13. *Assessment of Health Risks from Exposure to Acrylamide*. Office of Toxic Substances, U.S. Environmental Protection Agency, B1-005:1-8, 1990.
14. NIOH and NIOSH basis for an occupational health standard. In *Acrylamide*. U.S. Department of Health and Human Services, PB2-133222, Chapter 2.
15. M.S. Johnson. Degradation of water-absorbing polymers used as soil ameliorants. *Arab. Gulf J. Sci. Res.* **3(2):** 745–50 (1985).
16. W. Henzelmann, S. Winteler, and R. Leidecker. Organic polymers as retention aids in the paper industry. *Tech. Mitt.* **89(3):** 157–60 (1996).
17. E.A. Smith, S.L. Prunes, and F.W. Oehme. Environmental degradation of polyacrylamides. 1. Effects of artificial environmental conditions: temperature, light and pH. *Ecotoxicol. Environ. Saf.* **35:** 121–35 (1996).
18. E.A. Smith, S.L. Prunes, and F.W. Oehme. Environmental degradation of polyacrylamides II. Effects of environmental exposure. *Ecotoxicol. Environ. Saf.* **37:** 76–91 (1997).
19. E.A. Smith and F.W. Oehme. Rapid direct analysis of acrylamide residue in polyacrylamide thickening agents by HPLC. *J. Chromatogr. Sci.* **31:** 192–95 (1993).
20. B.T. Croll and G.M. Simkins. The determination of acrylamide in water by using electron-capture gas chromatography. *Analyst* **97:** 281–88 (1972).
21. A. Hashimoto. Improved method for the determination of acrylamide monomer in water by means of gas–liquid chromatography with an electron-capture detector. *Analyst* **101:** 932–38 (1976).
22. L. Brown, M. Rhead, and K.C. Bancroft. Rapid screening technique utilizing high-performance liquid chromatography for assessing acrylamide contamination in effluents. *Analyst* **107:** 749–54 (1982).
23. F. Andrawes, S. Greenhouse, and D. Draney. Chemistry of acrylamide bromination for trace analysis by gas chromatography and gas chromatography–mass spectroscopy. *J. Chromatogr.* **399:** 269–75 (1987).
24. S.S. Cutie and G.J. Kallos. Determination of acrylamide in sugar by thermospray chromatography/mass spectroscopy. *Anal. Chem.* **58:** 2425–28 (1986).
25. N.L. Freshour, P.W. Langvardt, and S.W. Dryzga. Direct determination of acrylamide in tissue culture solution by liquid chromatography using column switching. *J. Chromatogr.* **346:** 376–81 (1985).
26. A. Tseng. Determination of residual acrylamide monomer in solution and emulsion polymers by column-switching high performance liquid chromatography. *J. Chromatogr.* **519:** 363–68 (1990).
27. G. Odian. *Principles of Polymerization*, 2nd ed. John Wiley & Sons, New York, NY, 1981, Chapter 4.
28. R. Heusch. *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A9, 5th ed. VCH, Weinheim, Germany, 1987, p 302.
29. F.E. Bailey and J.V. Koleske. *Nonionic Surfactants*, Vol. 19. Dekker, New York, NY, 1987, p 930ff.
30. P. Munk. *Introduction to Macromolecular Science*, 1st ed. John Wiley & Sons, New York, NY, 1889, p 217ff.
31. D.H. Napper. *Polymeric Stabilization of Colloidal Dispersions,* 1st ed. Academic Press, New York, NY, 1983, p 4ff.

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