EPA-560/13-79-013

SAMPLING AND ANALYSIS OF SELECTED TOXIC SUBSTANCES
TASK I: ACRYLAMIDE

BY

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425 Volker Boulevard
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Contract No. 68-01-5017
December 1979

Tom Kopp
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Office of Toxic Substances
U.S. Environmental Protection Agency
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NOTICE

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SECTION 1

SUMMARY

The purpose of this program is to provide sampling and analysis capabilities to Environmental Protection Agency's (EPA) Office of Toxic Substances, so that the levels of suspected toxic substances in air, water, soil, and sediment at designated locations throughout the United States can be determined. The first task involved sampling and analysis for acrylamide (AA).

Methods for the determination of acrylamide in water and in polyacrylamide were validated. Water samples were reduced in volume by evaporation and analyzed by GC using a nitrogen selective thermionic detector. The detection limit was determined to be $\sim$ 1 µg/liter. Polyacrylamide samples were extracted with 80% methanol/20% pH 3.75 water for 3 hr. The extracts were analyzed by HPLC with a UV detector set at 200 nm. The monomer limit of detection was $\sim$ 0.5 µg/g.

One potable water treatment plant was sampled at pre- and post-flocculation points. MRI tap water was analyzed for comparison. No acrylamide above the detection limit was found in any of the samples.

Thirty-two polymers were analyzed for residual acrylamide. When not obscured by interferences, the observed acrylamide ranged from 0.5 to 600 µg/g.

SECTION 2

INTRODUCTION

Acrylamide is the most important chemical in the acrylamide group, being produced at an estimated rate of 63 million pounds per year as of 1976.[1] By 1978, all production should be based on catalytic hydration of acrylonitrile. The major producers of AA are American Cyanamid, Dow Chemical, and Nalco Chemical. The principal use of AA (∿ 80%) is in the production of water soluble polymers, commonly called polyelectrolytes, flocculants, coagulants, thickening agents, retention aids, and drainage aids. Polymer production consumes nearly all AA production, much of it captively.

Acrylamide release to drinking water could occur from the use of polyacrylamide flocculants in water treatment facilities. Residual monomer from the polymers could migrate into the water being treated. The extent of the problem would be influenced by the actual level of residual monomer in the flocculents. The Research Request called for MRI to determine the monomer level in polymers approved for water treatment and to determine the monomer level in water treated by these polymers.

The remainder of this report describes the experimental methods employed, including the validation of the sampling and analysis protocol, the selection of sampling sites and polymers, and a discussion of the monitoring results.

SECTION 3

SAMPLING AND ANALYSIS PROTOCOL

SAMPLING PROTOCOL

Water Sampling

Water samples were collected at various points in the water treatment process using 1 gal., silanized brown glass bottles with Teflon cap liners. After collection and during storage, the samples were kept at 4°C.

Polyacrylamides

The polyacrylamides were directly requested from the producer. The request included a full explanation of their intended use.

ANALYSIS PROTOCOL

Water Analysis

Sample Preparation--

Duplicate 500-ml aliquots were taken from each sample. Each aliquot was then reduced in volume to less than 5.0 ml by rotary evaporation at 50°C under reduced pressure. The reduced aliquots were then transferred to graduated centrifuge tubes and allowed to stand at 4°C for 1 day to allow particulate matter to settle. The supernatant fluid was drawn off, transferred to graduated centrifuge tubes, and further reduced to about 1.0 ml by evaporating at 50°C under a stream of prepurified nitrogen. Silanized glassware was used throughout. The reduced aliquots were then stored at 4°C pending analysis.

Sample Analysis Conditions--

The samples were analyzed by gas chromatography/thermionic selective detection (GC/TSD). The conditions were as follows:

Column: 3 ft x 1/8 in. ID, glass
Packing: 80/100 Chromosorb 101
Injector Temperature: 210°C
Detector Temperature: 250°C
Oven Temperature: 180°C

Carrier: 30 ml/min prepurified nitrogen
H_2 Pressure: 17.5 psi
Bead Current: 4.5 amp

Quality assurance was generated by spiking 500-ml aliquots of each sample and a water blank with 1.0 to 2.0 µg acrylamide. All were prepared and analyzed as above.

Polyacrylamide Analysis

Sample Preparation--

Duplicate 5-g samples of each polymer were weighed and transferred to 4-oz bottles. The liquid samples were stirred with a glass rod before sampling to minimize layering. Fifty milliliters of 80% methanol/20% pH 3.75 water was added to each bottle. The bottles were capped with polyethylene lined caps and placed on a wrist action shaker for 3 hr. A blank was prepared by adding 50 ml of the extracting solution to an empty 4-oz bottle fitted with a lined cap. This was also shaken for 3 hr. (The blank showed no interfering peaks.) Approximately 2 to 3 ml of the supernate from each polymer was transferred to a centrifuge tube and spun for a minimum of 10 min. For most of the polymers, this produced a clear solution ready for injection onto the HPLC. However, the five Nalco liquid samples formed emulsions that could not be filtered or spun down. The clear solutions obtained by centrifuging were transferred to capped 2-dram vials and taken to the HPLC lab for analysis.

Standards were prepared in 80% methanol/20% pH 3.75 water at concentration levels of 0.1 ppm, 0.5 ppm, 1.0 ppm, 5.0 ppm, 10.0 ppm, 50.0 ppm, 100.0 ppm, and 500.0 ppm.

Sample Analysis--

The HPLC assay parameters are listed below.

Instrument: Altex Model 100 pump, Waters' Model U6K injector, Schoeffel Model 770 variable wavelength absorbance detector, Heath Model 255B single pen recorder
Column: Whatman, Inc., Partisil-10 ODS-2, 4.6 x 250 mm
Solvent: H_2O adjusted to pH 3.75 with H_2SO_4
Flow: 2 ml/min
Detection: UV at 200 nm - attenuated as needed
Chart: 10 min/in
Injection: 20 µl using 80% methanol/20% water at pH 3.75

Injections of the Nalco liquid samples caused severe degeneration of the HPLC column. Therefore, before the final assay could be performed, the column needed to be cleaned thoroughly with DMF and then methanol. This rejuvenated the system to the original level of sensitivity.

SECTION 4

METHOD DEVELOPMENT FOR SAMPLING AND ANALYSIS

LITERATURE STUDY

Following receipt of Research Request No. 1, a survey of the literature was made to determine the state-of-the-art sampling and analysis techniques for the assigned tasks, i.e., residual acrylamide monomer in polymer and trace level acrylamide in potable water. Since MRI had recently completed a project involving analysis of acrylamide in water, this part of the literature study consisted of updating the information.

The literature search was performed by computer and was limited to Chemical Abstracts, 1977 to 1979 (Vol. 90, No. 6), since the earlier literature had already been obtained. The search strategy was based on a Boolean AND of the terms in Columns 1 (items 1-15) and 2 (items 17-24) shown below. The number in parentheses indicates the number of hits for that particular term.

Column 1		Column 2	
1	(54374) ANALYSIS	17	(435) RN=79-0601
2	(68608) ANAL?	18	(0) RN=44170-53-8
3	(76810) DET?	19	(2161) ACRYLAMIDE
4	(0) DETN? S CHROMATOG?	20	(0) SY=ACRYLAMIDE
5	(56943) DETN?	21	(0) 2-PROPENAMIDE
6	(12176) SPECTROM?	22	(2) PROPENAMIDE
7	(14467) HYDROL?	23	(0) 2(W)PROPENAMIDE
8	(0) SOLVEL?	24	(0) MF=C3-H5-N-O
9	(0) DISTN?S SAMPL?	25	(2301) 17-24/OR
10	(8361) ADSORP?	26	(604) 16*25
11	(15098) ABSROP?	27	(360) 26/ENG
12	(14680) CROMATOG?		
13	(8992) SOLVEN?		
14	(2240) DISTIN?		
15	(4761) SAMPL?		
16	(158870) 1-15/OR		

The combination of lines 16 and 25 gave 605 hits. When limited to articles in English, 360 hits were made. This list was then printed out, manually inspected, and relevant articles were then obtained.

The most promising methods found in the literature search for the determination of residual acrylamide in polymers are summarized in Table 1. Various polarographic techniques were found but they lack the necessary specificity to be of value.

No methods for trace acrylamide in water other than what was used in the previous study[2] were found in the literature study.

ANALYTICAL METHODS

Water Analysis

In the previous project on acrylamide,[2] protocols for GC analysis and GC/MS confirmation were developed and evaluated. The sample was prepared for analysis by evaporation and then analyzed by GC/Hall detection or by GC/high resolution mass spectrometry. For this project, the use of a new generation thermionic bead detector, from Varian, was tested as a replacement for the Hall electrolytic conductivity detector. The nitrogen-phosphorus selective thermionic bead detector had comparable sensitivity for nitrogen but much better stability.

The precision of the chromatographic analysis was determined by replicate injections (3-5) of 1 and 10 ppm solutions of acrylamide in water. The relative standard deviations were 11% and 35% at 10 and 1 ppm, respectively.

There was concern about the stability of acrylamide in potable water treated with chlorine. A limited study was run at 4°C with 25 ppm chlorine and was designed to include the effect of time on stability. The conditions and results are summarized in Table 2.

Although there was some difference in the initial concentrations, there was no significant change in any of the three samples over the 6-day test period. Therefore, it can be concluded that chlorine has no effect on acrylamide stability, and the addition of $Na_2S_2O_3$ is unnecessary.

Polyacrylamide Analysis

Development of Instrumental Procedure--

The analysis procedure as outlined by Skelly and Husser in Analytical Chemistry (Vol. 50, No. 14, p. 1959) was used as a basis for this development.

TABLE 1. LITERATURE METHODS FOR DETERMINATION OF RESIDUAL ACRYLAMIDE MONOMER IN POLYMERS

Citation	Sample preparation	Analysis method	Limit of detection	Recovery, precision (spike level)	Application, comments
E. R. Husser, et al. Anal. Chem. 49, 154(1977)	1. Nonaqueous dispersed polymer				
	Ten grams of polymer are batch extracted with 50 ml methanol for 2 hr and centrifuged. Benzamide added as internal standard.	Column: Partisil 10 PAC (250 x 4.6 mm) Mobile phase: 15% methanol, 85% methylene chloride at 1 ml/min Detector: UV at 240 nm Volume: 6 µl external sample loop	10 ppm (0.001%)	99 ± 4%	-
	2. Aqueous dispersed polymer				
	Five grams of polymer are dropped into a stirred mixture of 10 ml methylene chloride, 40 ml water, and 0.5 ml conc. HCl. After 30 min stirring, the sample is centrifuged, the supernatant removed, and reduced to 10 ml.	Column: Dowex 50 W-X4 (250 x 4 mm) Mobile phase: 0.01 N H_2SO_4, 0.7 ml/min Detector: UV at 225 nm Volume: 500 µl injection	0.1 ppm (0.00001%)	86 ± 13% (1 ppm) 102 ± 12% (20 ppm)	Ethyl acrylate based polymer Ethyl acrylate based acrylonitrile modified polymer Butyl acrylate based acrylonitrile modified polymer
F. J. Ludwig, Sr., et al. Anal. Chem. 50, 185 (1978)	Four to six grams of polymer emulsion or solution are added dropwise to stirred acetone (or methanol). After stirring 15 min the suspension is filtered. Benzamide is added as an internal standard.	Column: Partisil 10 PAC (250 x 4.6 mm) Mobile phase: 10% methanol, 90% methylene chloride at 1 ml/min Detector: UV at 240 nm Volume: 10-15 µl injection	40 ppm (0.004%)	~90% (300 ppm), aqueous polyacrylamide ~94% (200 ppm), cationic emulsion ~99% (3 ppt), anionic emulsion	Acrylamide elutes on solvent tail
N. E. Skelly, et al. Anal. Chem. 50, 1959(1978)	Fifty milliliters of 80-20 methanol water is added to 5 g polyacrylamide and stirred 4 hr.	Column: Partisil 10 ODS-2 (250 x 4.6 mm) Mobile phase: Water at 2 ml/min Detector: UV at 206 nm Volume: 200 µl injection	0.1 ppm (0.00001%)	3.7% relative standard deviation at 177 ppm sample	Results agreed with ion exclusion method of Husser above, with 20 polymers

TABLE 2. STABILITY STUDY OF ACRYLAMIDE

Sample test conditions		Acrylamide, mg/liter			
Chlorine	$Na_2S_2O_3$[a/]	Initial	24 hr	48 hr	144 hr
No	No	0.85	1.04	0.91	0.79
25 ppm	No	0.58	0.40	0.49	0.54
25 ppm	430 ppm	0.82	1.16	0.71	0.96

a/ The $Na_2S_2O_3$ was added to the mixture of acrylamide and chlorine.

However, substantial difficulty was encountered when MRI tried to duplicate the chromatographic method. The instrumentation used at MRI included an Altex Model 100 pump, a Waters U6K injector, a Shoeffel Model 770 variable wavelength absorbance detector and a Heath Model 255B recorder. This equipment is equivalent to the instrumentation used by Skelly. A Whatman Inc., Partisil-10 ODS-2, 4.6 x 250 mm reverse phase column was used to duplicate the C_{18} loading and subsequent acrylamide retention volumes. Standards were prepared in 80% CH_3OH as directed. An outline of the development follows:

1. The instrumentation listed above was set up using a Whatman guard column (2.1 x 60 mm) with 100% H_2O from the Milli-Q water system as the eluant (2 ml/min). The detector was set at 208 nm 0 → 0.01 setting. Although Skelly and Husser reported a retention time of 5.2 min for acrylamide in this system, at MRI no peaks eluted in 30 min.

2. The eluant was modified with 5%, 4%, 2% and 1% CH_3CN to reduce retention times. A peak did elute for acrylamide at 100 ppm and 10 ppm concentration levels at retention times of 5 to 10 min; however, the response dropped off almost geometrically instead of linearly. The 1 ppm standard could not be seen even at the lowest absorbance setting (0 → 0.01 range).

3. The monitoring wavelength was dropped to 204 nm and 200 nm and the 3% CH_3CN eluant injections were repeated. Although the 100 ppm and 10 ppm standards increased slightly in response, the 1 ppm standard could not be seen.

4. All of the work in B and C was repeated using CH_3OH as the modifying solvent. The results were similar.

5. After consulting with Skelly to insure that nothing had been overlooked, Waters Associates applications lab was contacted for additional suggestions. They recommended buffering the H_2O to an acidic pH. This presented another problem since most buffers would be opaque at 208 nm. The only choice seemed to be a nonhalide mineral acid. H_2SO_4 was added to the water pump to a pH 3.75 and the work in 2 and 3 was repeated. The baseline was very erratic and 1 ppm could not be detected. The guard column was removed with no effect.

6. To alter the approach, a system was tested that did not include any organic solvents. The standards were remade using H_2O adjusted to pH 3.75 with H_2SO_4. The eluant of the system was changed to H_2O adjusted to pH 3.75. This dramatically changed the chromatography so that standards from 100 ppm to 0.1 ppm were detectable with good linearity. The baseline was excellent even at 200 nm (0 → 0.01 range).

7. A fresh set of standards was prepared in 80% CH_3OH/20% H_2O at pH 3.75. Although these samples do not chromatograph as well as the water standards, the analysis will be possible so long as injection volume is consistent and not less than 20 µl.

Final HPLC Procedure--

Instrument: Altex Model 100 pump, Waters Model U6K injector, Schoeffel Model 770 variable wavelength absorbance detector, Heath Model 255B single pen recorder
Column: Whatman Inc., Partisil-10 ODS-2, 4.6 x 250 nm
Eluting Solvent: H_2O adjusted to pH 3.75 with H_2SO_4
Flow: 2 ml/min
Detection: UV at 200 nm - attenuated as needed.
Chart: 10 min/in
Injection: 20 µl using 80% CH_3OH/20% H_2O at pH 3.75

Twenty milliliters of each of the following standards of acrylamide were injected onto the system to test linearity.

			(Adjusted absorbance)	
Conc. in sol'n.	Peak height	Abs. range	Abs.	Abs./Conc.
0.1 ppm	11 nm	0 → 0.01	0.11	1.10
0.5 ppm	37 nm	0 → 0.01	0.37	1.35
1.0 ppm	76 nm	0 → 0.01	0.76	1.32
5.0 ppm	93 nm	0 → 0.01	3.72	1.34
10.0 ppm	181 nm	0 → 0.04	7.24	1.38
50.0 ppm	87 nm	0 → 0.4	34.80	1.44
100.0 ppm	173 nm	0 → 0.4	69.20	1.45

The calibration curve generated by these data is shown in Figure 1. Copies of typical chromatograms are shown in Figure 2.

Optimization of Extraction Procedure--

Optimum extracting solvent--Dry 5-g samples of one polymer were extracted in 4-oz bottles on a wrist action shaker using the following solvents:

50 ml	20% CH_3OH/80% pH 3.75 H_2O
50 ml	50% CH_3OH/50% pH 3.75 H_2O
50 ml	80% CH_3OH/20% pH 3.75 H_2O
100 ml	80% CH_3OH/20% pH 3.75 H_2O

The 20% and 50% CH_3OH would not wet the polymer. Fifty milliliters of 80% MeOH shook well with the least dilution.

Minimum extraction time--A 5-g sample of Celanese 295 was weighed and transferred to a 4-oz bottle. Fifty milliliters of 80% CH_3OH/20% pH 3.75 H_2O was added and the bottle was fitted with a lined cap. The sample was placed on a wrist action shaker for 3 hr. A small aliquot ($\sim$ 1 ml) was removed at 15 min, 30 min, 60 min, 90 min, 150 min and 180 min. These samples were assayed using the HPLC system outlined above. The analysis results follow:

Extraction time	Peak height
15 min	19 nm
30 min	20 nm
60 min	22 nm
90 min	22 nm
150 min	29 nm
180 min	29 nm

Figure 3 shows the chromatogram of Celanese 295. Note the peak eluting after acrylamide.

Several other observations concerning the polymer analysis procedure are:

* Propionamide, a possible internal standard, elutes in the pH 3.75 eluant at 7.0 min compared to 5.5 min for the acrylamide; however, there is interference from a peak in some of the polymers at 7.0 min. No internal standard will be used.

* Hydroacrylonitrile does not elute at selected conditions; therefore, we expect no interference. This was mentioned as a known impurity in their polymers by John E. Villaume of American Cyanamid (personal communication, 1979).

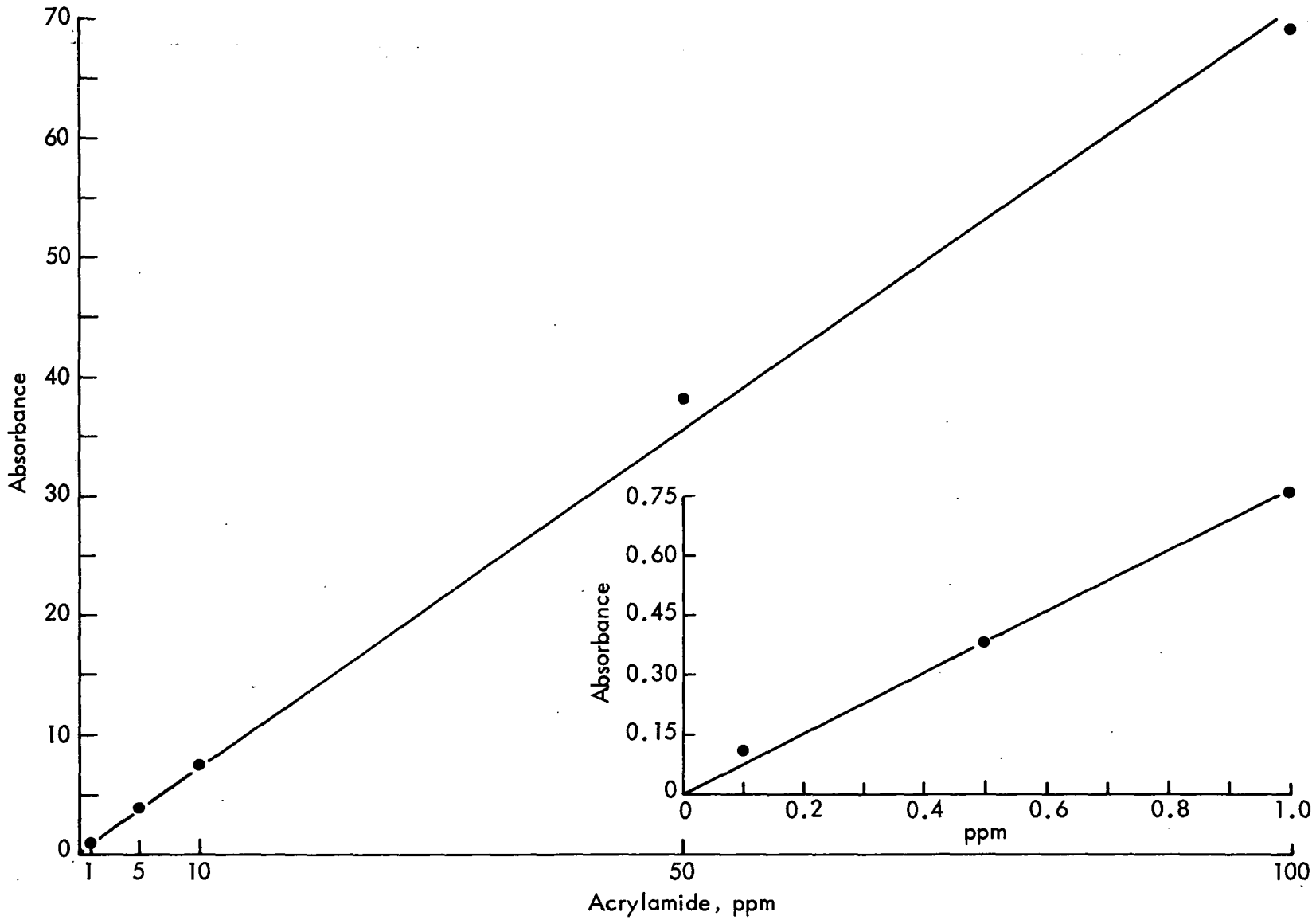


Figure 1. Calibration curve for the HPLC determination of acrylamide.

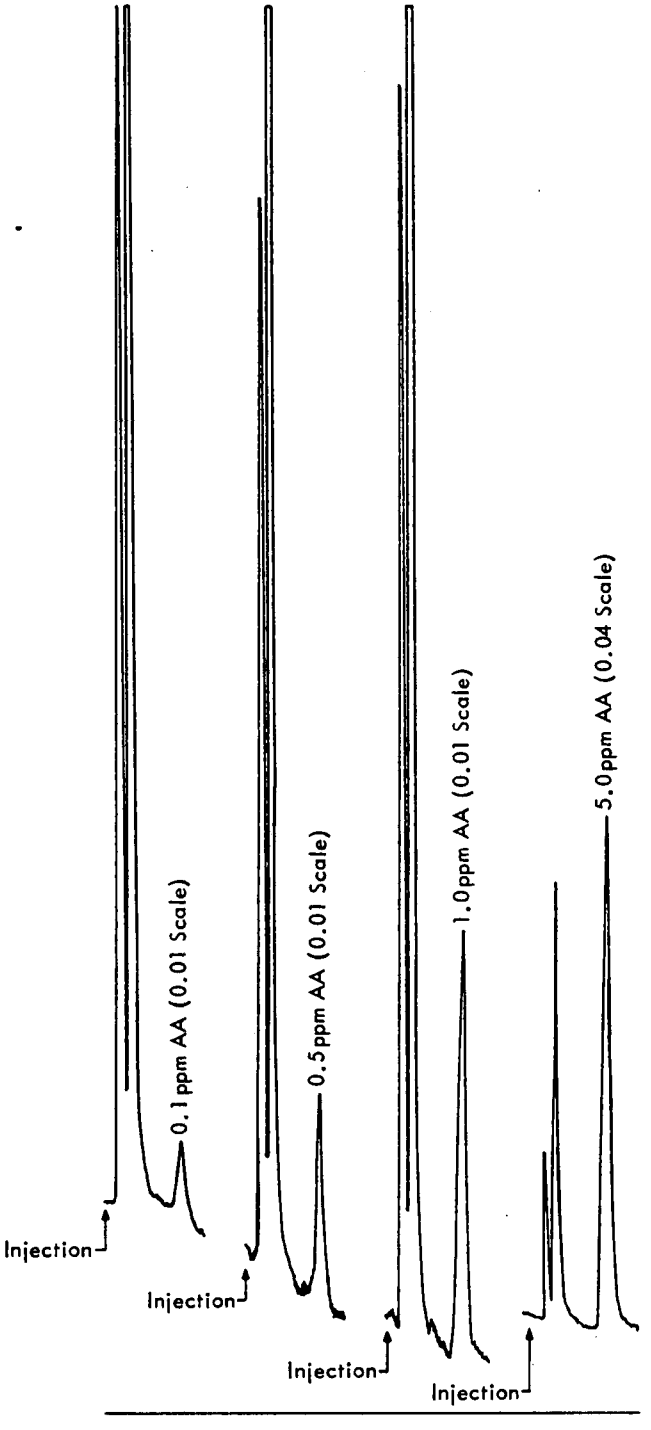


Figure 2. Chromatograms from acrylamide calibration curve.

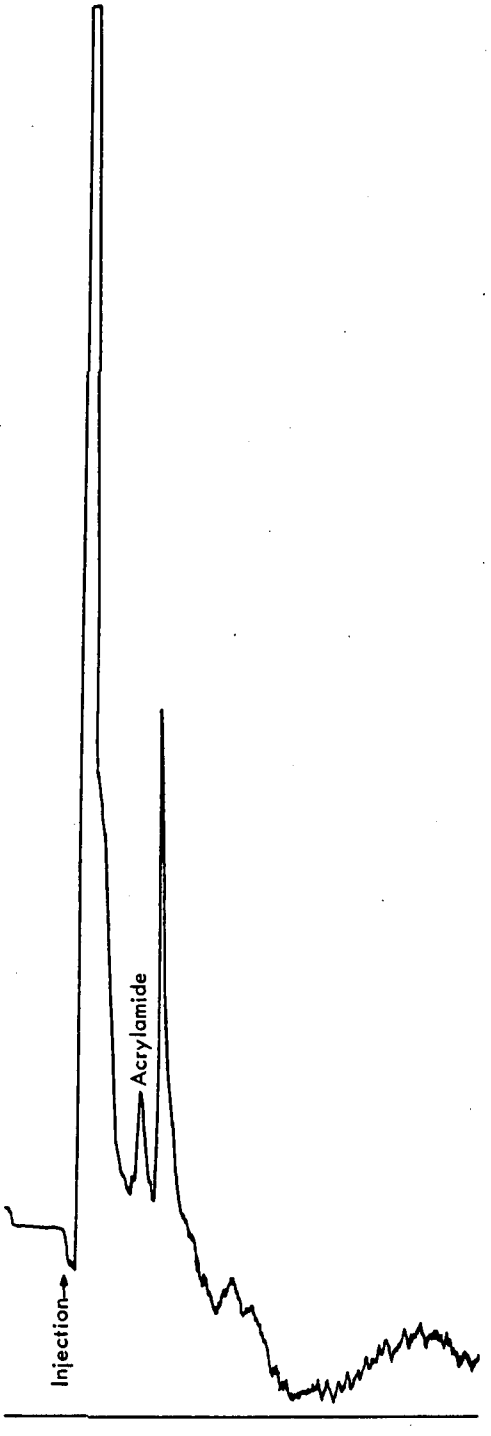


Figure 3. Chromatogram of Celanese sample 295.

* Some of the polymers are wetted into very stiff emulsions which will make sampling very difficult and the dry weight percents may be in error.

Standardizations--

Table 3 is representative of the injections of standards during the assay.

TABLE 3. RESULTS FROM ANALYSIS OF ACRYLAMIDE STANDARDS

Concentration	Date	Attenuation	Peak height	Adj. peak height
0.1 ppm	8/23	0.01	8	0.08
0.5 ppm	8/23	0.01	31	0.31
0.5 ppm	8/25	0.01	33	0.33
1.0 ppm	8/23	0.01	68	0.68
1.0 ppm	8/24	0.01	67	0.67
1.0 ppm	8/24	0.04	16	0.64
5.0 ppm	8/24	0.04	84	3.36
5.0 ppm	8/24	0.04	88	3.52
5.0 ppm	8/24	0.1	36	3.60
10.0 ppm	8/24	0.04	165	6.60
10.0 ppm	8/24	0.04	178	7.12
10.0 ppm	8/24	0.10	74	7.40
50.0 ppm	8/24	0.20	166	33.2
50.0 ppm	8/25	0.20	173	34.6
500 ppm	8/25	2.0	171	342

For these standards, the best fit curve by linear regression is:

(Adj. peak height in mm) = 0.68 (concentration in solution in ppm) - 0.006

corr. = 0.99999

SECTION 5

SELECTION OF SITES AND SAMPLES

POTABLE WATER TREATMENT PLANTS

A recent study of acrylamide use has established that about 1.3 million pounds (∿ 2.5% of yearly use) is used for potable water treatment.[1/] As part of this study a survey of 59 cities was made to establish the use pattern of polyacrylamide flocculants. A summary of the cities that responded as using polyacrylamide is given in Table 4. The cities are classified as large (population greater than 250,000), medium (population from 100,000 to 150,000), and small (25,000 to 50,000). Eleven cities are using polyacrylamides and two cities--Lancaster, Pennsylvania, and Milwaukee, Wisconsin--reported using polyacrylamides in the past.

The following is a list of potential factors for consideration as site selection criteria. Their value is discussed and, if appropriate, they are applied to the list of users.

* Probability of site having a measurable level of acrylamide,
* Size of population potentially exposed,
* Duration of exposure, and
* Source of polyacrylamide.

Probability of Finding Acrylamides

The probability that a site will have a measurable level of acrylamide is directly proportional to the level of flocculant used. The best sites by this criterion are Kansas City, St. Louis, and possibly Los Angeles. It is not clear from the survey information what flocculant Los Angeles used to reach the reported 5 ppm level. The next choices would be Las Vegas and Chicago. None of the remaining cities appear to be using enough polyacrylamide flocculant to produce a measurable level of monomer.

TABLE 4. SUMMARY OF CITIES SURVEYED FOR POLYACRYLAMIDE USE

City	Water supply	Polyacrylamide used	Use pattern	Flocculant concentration (ppm)	Amount used per year (lb)	Amount of water treated
Large Cities						
Chicago, IL	Lake Michigan	1978: Calga Catfloc A 1979: Cyanamid	Continuous use	0.24 (ave.)	590,000	1,000 MGD
Kansas City, MO	Missouri River	1978: Cyanamid Magnifloc 990N Dow Purifloc N20 Nalco and Hercufloc	Turbid conditions (6 months/year)	0.03-0.6	100,000	110 MGD
Los Angeles, CA	Owens Valley (East. Sierras) through the Mojave or Cottonwood aqueducts	Not known	Turbid conditions (6 months/year)	0.6-5[a/]	Not known	1,100 MGD(?)
St. Louis, MO	Not specified	Dow Purifloc N17 Nalco Nalcolyte 8171 Others	Continuous use	0.6 (coagulent aid)	84,000 as coagulent aid	Not known
Medium Cities						
Alexandria, VA	Reservoir, surface water	Dow Separan NP10	Experimental	0.05	Not known	Not known
Elizabeth, NJ	Upland surface water	Cyanamid 1986 N	Very cold weather only	0.01	Not known	Not known
Fremont, CA	Mostly river	Cyanamid 1986 N	Continuous use	0.012	Not known	8 MGD
Las Vegas, NV	60% Lake Mead 40% Well	Cyanamid 990 N	Continuous use	0.4	Not known	~70 MGD
Small Cities						
Bismark, ND	Missouri River	Nalco Nalcolyte 8184	Not known	Not known	~500	5.9 MGD
Fort Collins, CO	Poudry River	Cyanamid 1986 N	~5 months/year (May-September)	Not known	17 500 gal. barrels/year	11 MGD
Richland, WA	Columbia River Wells	Dow Separan NP10	~0-7 months (spring and summer)	Not known	~500	2×10^9 gal (7 months)

a/ Refers to flocculant use. Regulation presents use of polyacrylamides at greater than 1 ppm with 0.05% residual monomer.

Size of Exposed Population

All other things being equal (i.e., flocculant level, accessibility of site, etc.), the size of population potentially exposed may be used as a criterion. This is easily quantified by the size of the plant as expressed in the millions of gallons per day (MGD) of water that is treated. Considering only the sites selected above based on flocculant level, Chicago and Los Angeles are the largest and are nearly equal in size (see Table 4). Although the volume of water treated at St. Louis is not known, the quantity and concentration of polyacrylamide is similar to that of Kansas City. Las Vegas is slightly smaller than Kansas City and presumably smaller than St. Louis.

Duration

The differences in duration did not appear to be large enough to use for selection criteria.

Source of Polyacrylamide

The source of the polyacrylamide was not suggested as a criterion for several reasons. Many cities use various brands singly and in mixtures, and it was not always possible to know ahead of sampling time exactly what polymer would be used. Also, all of the polymers were analyzed for residual monomer and were, in fact, not expected to be significantly different. They were expected to be generally around 0.05% since government regulations require that the residual monomer be $\leq$ 0.05% and that the added polymer level be $\leq$ 1 ppm.

Using the criteria discussed above, and giving consideration to the cost of field sampling, the recommended sites selected for sampling are listed in Table 5 in decreasing order of priority. However, this list was flexible, and before any actual sampling, each potential site was to have been contacted to confirm the information used to establish its ranking. The sites visited first were those with the highest probability of having detectable acrylamide. If no acrylamide or a low, but acceptable level of acrylamide was found, then it was planned to terminate sampling.

POLYACRYLAMIDE SAMPLES

The samples selected for polyacrylamide analysis were primarily those listed in the Research Request as being approved for treatment of potable water. Additional samples were later selected that were approved for food packaging. Table 6 lists the selected samples and their approved use.

TABLE 5. RECOMMENDED SITES FOR SAMPLING

Priority	Location	Rationale
1	Kansas City, MO	High level of flocculant (0.6 ppm) Large plant Location
2	St. Louis, MO	High level of flocculant (0.6 ppm) Large plant Closeness to Kansas City
3-4	Las Vegas, NV or Los Angeles, CA	High level of flocculant (0.4 ppm) Flocculant may be high (0.6 ppm)
5	Chicago, IL	Medium level of flocculant (0.24 ppm) Very large plant

TABLE 6. POLYACRYLAMIDES SELECTED FOR ANALYSIS

Polyacrylamide	Approved use
Calgon Coagulant Aid	
223(N)	Potable water treatment
253(A)	Potable water treatment
Cyanamid Magnifloc	
345(A)	Potable water treatment, food packaging
846(A)	Potable water treatment, food packaging
847(A)	Potable water treatment, food packaging
985(N)	Potable water treatment, food packaging
900(N)	Food packaging
990(N)	Potable water treatment, food packaging
1849(A)	Potable water treatment, food packaging
1986(N)	Potable water treatment, food packaging
Dow Purifloc	
C31	Potable water treatment, food packaging
C51	Potable water treatment, food packaging
A23P	Potable water treatment, food packaging
N17	Potable water treatment, food packaging
N20	Potable water treatment, food packaging
Dow Separan	
AP30	Potable water treatment, food packaging
NP10	Potable water treatment, food packaging
NP10PWG	Potable water treatment, food packaging
AP273 premium	Potable water treatment, food packaging
Nalco Nalcolyte	
8170	Potable water treatment, food packaging
8171	Potable water treatment, food packaging
8172	Potable water treatment, food packaging
8173	Potable water treatment, food packaging
8174	Potable water treatment, food packaging
8182	Potable water treatment, food packaging
8184	Potable water treatment, food packaging
Stein-Hall (Celanese)	
M-19	Potable water treatment, food packaging
M-295PW	Potable water treatment, food packaging

(continued)

TABLE 6 (continued)

Polyacrylamide	Approved use
Hercules Reten	
210	Food packaging
220	Food packaging
420	Food packaging
421	Food packaging
423	Food packaging
423	Food packaging

SECTION 6

DISCUSSION OF RESULTS

SAMPLING

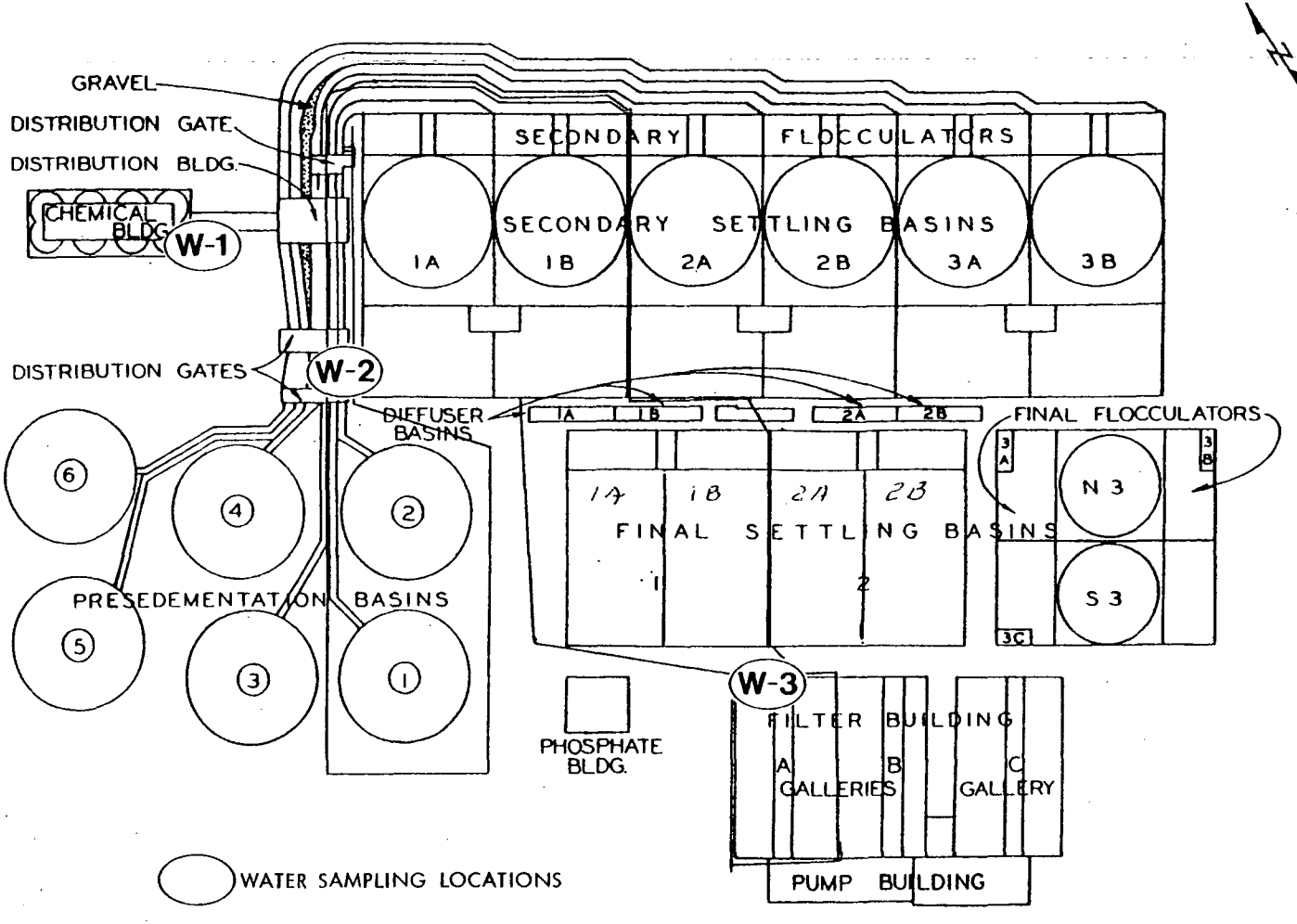
Water Samples - Kansas City, Missouri, Water Treatment Plant

Field Sampling--

Presampling survey--A presampling survey of the Kansas City, Missouri, Water Treatment Plant was conducted on July 24, 1979. The plant is located near the junction of Missouri Highway 9 and 32nd Avenue immediately north of North Kansas City, Missouri.

The Kansas City, Missouri, Water Department takes its water from the Missouri River and processes about 130 million gallons per day (MGD) through six lines acting as three units. While polymer was not used at this time of year, the Kansas City, Missouri, Water Department volunteered to run Nalco 8173 through one-third of the system for 24 hr to accommodate our sampling. The use of polymer was started on July 24, 1979.

Sampling--Sampling was conducted on the morning of July 25, 1979, between 0930 and 1100 local time. Six 1-gal. water samples were taken at three locations (Figure 4) representing raw water influent (W-1), post-floc, prechlorination (W-2), and chlorinated final effluent (W-3). The water is chlorinated to provide 1 ppm residual chlorine. Additionally, a sample of the polymer mix used to treat the water and a sample of the Nalco 8173 were also obtained. The polymer mix was 0.5% by volume. The sampling locations are described in Table 7. Due to the fact that polymer was only being added to one-third of the system during a 2-day period, no tap water samples were taken.



BASIC DESIGNATION & LOCATION

Figure 4. Kansas City, Missouri, Water Treatment Plant.

TABLE 7. WATER SAMPLING DATA, KANSAS CITY, MISSOURI, WATER TREATMENT PLANT

Sample No.	Description of location of sampling points	Sample type	Sample size
W-1	Raw water valve in chemical building	Grab water	2, 1-gal.
W-2	Sluice from sedimentation basins 1 and 2, prior to chlorination	Grab water	2, 1-gal.
W-3	Valve in filter gallery A, after chlorination prior to pumping out for distribution	Grab water	2, 1-gal.

Sample Handling and Preservation--

The water samples were taken in silanized, brown glass bottles with Teflon liners and transported directly to MRI where they were stored at 4°C.

Polyacrylamides

All requested polymers that are currently available were received. Table 8 summarizes the requested and received samples.

SAMPLE ANALYSIS

Water Samples

The water samples were analyzed for acrylamide by GC/TSD using the conditions listed in Section 3. The results of the analysis plus the QA studies are summarized in Table 9. Two of the samples spiked a 1 µg/liter showed 76% recovery while no acrylamide was found in the other two samples. In these cases, however, the detection limit was extremely close to the expected acrylamide level of ∿ 0.75 µg/liter (1 µg/liter spike at ∿ 75% recovery). Two blanks, however, spiked at 2 µg/liter recovered well. All the results, taken together, indicate that the practical detection limit is more on the order of 1 µg/liter and that the samples do not contain acrylamide at or near that level.

TABLE 8. POLYMERS REQUESTED AND RECEIVED

Polymer requested	Polymer received	Lot number
Calgon Coagulant Aid		
233 (N)	233	8 B422
253 (A)	253	8 A478
Cyanamid Magnifloc		
845 (A)	845A	12885
846 (A)	846A	12937
847 (A)	847A	13081
985 (N)	985N	13123
990 (N)	990N	130109
1849 (A)	1849A	13011
1986 (N)	1986N	12993
-	900N	13141
Dow Purifloc		
C31	C31	7A12268A6N
C51	Out of production	-
A23P	A-23-P	MM 03306SI33
N17	AP10PWG	-
N20	XD-7817.00	-
Dow Separan		
AP30	AP30	MM 07078SI30
NP10	NP10	MM 02I09SII0
NP10PWG	NP10PWG	MM 02089NII0
AP273 premium	AP273 premium	MM 06II7SI32
Nalco Nalcolyte		
8170	8170	B-7251
8171	8171	G-8319
8172	8172	-
8173	8173	B-7355
8174	8173	-
8182	8182	B-9065
8184	8184	B-8305
Stein-Hall (Celanese)		
M-19	Out of production	-
M-295PW	M-295PW	-
-	540PW	-
-	361	-

(continued)

TABLE 8 (continued)

Polymer requested	Polymer received	Lot number
Hercules, Inc.		
Reten 210	Reten 210	8201
Reten 220	Reten 220	8200
Reten 420	Reten 420	7338
Reten 421	Reten 421	5651
Reten 422	Reten 422	6815
Reten 423	Reten 423	6667

TABLE 9. SUMMARY OF ACRYLAMIDE ANALYSES

Sample	Sample reduction	Results	
K.C. W-1(A)	500 → 1.5	0.4 µg/ℓ	
K.C. W-1(B)	500 → 2.0	< 0.5 µg/ℓ	
K.C. W-1 spiked at 1 µg/ℓ	500 → 1.0	< 0.5 µg/ℓ	No recovery
K.C. W-2(A)	500 → 1.0	< 0.26 µg/ℓ	
K.C. W-2(B)	500 → 0.6	0.16 µg/ℓ	
K.C. W-2 spiked at 1 µg/ℓ	500 → 1.0	0.76 µg/ℓ	76% recovery
K.C. W-3(A)	500 → 1.0	0.92 µg/ℓ	
K.C. W-3(B)	500 → 0.6	< 0.16 µg/ℓ	
K.C. W-3 spiked at 1 µg/ℓ	500 → 1.0	0.76 µg/ℓ	76% recovery
K.C. TW(1)	500 → 1.1	0.68 µg/ℓ	
K.C. TW(2)	500 → 0.8	< 0.21 µg/ℓ	
K.C. TW spiked at 1 µg/ℓ	500 → 1.0	< 0.6 µg/ℓ	No recovery
Blank spiked at 2 µg/ℓ	500 → 1.0	2.6 µg/ℓ	130% recovery
Blank spiked at 2 µg/ℓ	500 → 1.0	2.9 µg/ℓ	150% recovery
Water blank	500 → 1.0	< 0.6 µg/ℓ	

Polyacrylamide Samples

The results of the analysis for residual acrylamide monomer are given in Table 10. Note that Dow Puriflox N17 is now supplied as NP10PWG, and Dow Purifloc N20 is now XD-7817.00. All of the polymers designated for analysis by the Research Request were received and analyzed.

Analytical quality assurance was achieved by spiking at three concentration levels in duplicate. In each case an aliquot of the original solution from the extraction bottle was reinjected and the response noted. A known amount of acrylamide was then added to the extract in 2 ml of 80% methanol/3.75 pH water to make up the volume taken out for the analysis. The polymer and solution was then put on the wrist action shaker for 1 hr and then was reinjected. The results follow in Table 11.

Federal regulations require that polyacrylamides used for potable water treatment have less than 0.05% (500 ppm) residual monomer. Of the 32 polymers analyzed, only one, Dow Separan NP10, had residual monomer above that level. The Nalco 8173 polymer used by the Kansas City Water Treatment Plant during MRI's sampling had a residual monomer level of 72 ppm. At this level, and considering that the maximum permissible flocculant level is 1 ppm, the maximum possible acrylamide concentration in the water would be:

$$\frac{72\ \mu g\ \text{acrylamide}}{1\ g\ \text{polyacrylamide}} \times \frac{10^{-3}\ g\ \text{polyacrylamide}}{\text{liter of water}} = 0.07\ \mu g/\text{liter}$$

This level is less than the expected detection limit and indicates that the use of polyacrylamide flocculants did not result in the addition of detectable acrylamide to potable water. In fact, in the worst case of 500 ppm residual monomer, the maximum water level would be 0.6 µg/liter.

TABLE 10. RESULTS OF ANALYSIS OF POLYACRYLAMIDE SAMPLES

Polymer requested	Polymer received	Lot number	Sample form	Acrylamide concentration (µg/g)
Calgon Coagulant Aid				
233 (N)	233	8 B422	Solid	25, 23
253 (A)	253	8 A478	Solid	19, 17
Cyanamid Magnifloc				
845 (A)	845A	12885	Solid	0.5, 0.5
846 (A)	846A	12937	Solid	6.5, 7.1
847 (A)	847A	13081	Solid	46, 49
985 (N)	985N	13123	Solid	102, 107
990 (N)	990N	13109	Solid	189, 189
1849 (A)	1849A	13011	Clear liquid	2.3, 2.4
1986 (N)	1986N	12993	Clear liquid	< 0.5, < 0.5[a]
-	900N	13141	Solid	214, 219
Dow Purifloc				
C31	C31	7A12268A6N	Dark liquid	< 50[b]
C51	Out of production		-	-
A23P	A-23-P	MM 03306SI33	Solid	< 5[c]
N17	NP10PWG		Solid	See results for NP10PWG
N20	XD-7817.00		Solid	229, 230
Dow Separan				
AP30	AP 30	MM 07078SI30	Solid	5.4, 6.5
NP10	NP 10	MM 02109SI10	Solid	608, 605[d]
NP10PWG	NP10PWG	MM 02089NI10	Solid	34, 31
AP273 Premium	AP 273 Premium	MM 06117SI32	Solid	< 5[c]
Nalco Nalcolyte				
8170	8170	B-7251	Solid	112, 112
8171	8171	G-8319	Liquid	355, 358
8172	8172	-	Liquid	184, 182[e]
8173	8173	B-7355	Solid	28, 30
		B-8340		73, 71[f]
8174	8174	-	Liquid	5.9[e]
8182	8182	B-9065	Liquid	3.2[e]
8184	8184	B-8305	Liquid	5.9[e]
Stein-Hall (Celanese)				
M-19	Out of production			
M-295PW	M-295PW	-	Solid	1.6, 1.2
	540PW	-	-	-
	361	-	-	-
Hercules, Inc.				
Reten 210		8201	Solid	14, 16
Reten 220		8200	Solid	54, 54
Reten 420		7338	Solid	197, 197
Reten 421		5651	Solid	133, 136
Reten 423		6815	Solid	20, 21
Reten 425		6667	Solid	< 200[g]

a/ Sample had no detectable response at lowest setting.

b/ Sample was a dark, honey-like liquid. Extraction was really only dilution. Sample gave a very large peak which interfered with AA quantitation. Sample solution was spiked with 20 ppm and a side-peak of 20 mm appeared. Therefore, sample concentration is given as < 50 ppm.

c/ Sample had interfering peak. A 2 mm shoulder peak could be seen at (0.1).

d/ Extraction solution is slightly yellow in color but there were no interfering peaks.

e/ Solutions would not centrifuge or filter. They were allowed to stand in centrifuge tubes and a thin layer of clear liquid formed on the surface. An aliquot of this solution was injected for the assay.

f/ Sample obtained from Kansas City Water Treatment Plant.

g/ Sample has interfering peak. An injection of this sample solution spiked at 20 ppm was detectable; therefore, sample concentration is given as < 200 ppm.

TABLE 11. RECOVERIES FROM SPIKED POLYMERS

Sample	Peak height (mm)	Atten.	Adj. peak height (mm)	Conc. (ppm)	% Recovery
No. 1 (Magnifloc 845A)	8	0.01	0.08	0.13	-
No. 1 + 0.4 ppm	38	0.01	0.38	0.57	107
No. 2 + 0.4 ppm	38	0.01	0.38	0.57	107
No. 31 (Purifloc NP10PWG)	53	0.04	2.12	3.13	-
No. 31 + 4.0 ppm	128	0.04	5.12	7.54	106
No. 32 + 4.0 ppm	124	0.04	4.96	7.30	102
No. 15 (Magniflox 900N)	142	0.2	28.4	41.7	-
No. 15 + 20 ppm	208	0.2	41.6	61.2	99
No. 16 + 20 ppm	212	0.2	42.4	62.3	101

REFERENCES

1. "Assessment of the Need for and Character of Limitations on Acrylamide and Its Compounds," Draft Final Report, EPA Contract No. 68-01-4308, July 1977.

2. "Environmental Monitoring Near Industrial Sites: Acrylamide," Final Report, EPA Contract No. 68-01-4115, March 1978.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

A sampling and analysis program was conducted to determine the level of residual acrylamide monomer in selected polymers and to determine if the use of those polymers in water treatment leads to measurable levels of acrylamide in the water.

Methods for the determination of acrylamide in water and in polyacrylamide were validated. Water samples were reduced in volume by evaporation and analyzed by GC using a nitrogen selective thermionic detector. The detection limit was determined to be ∿ 1 µg/liter. Polyacrylamide samples were extracted with 80% methanol/20% pH 3.75 water for 3 hr. The extracts were analyzed by HPLC with a UV detector set at 200 nm. The monomer limit of detection was ∿ 0.5 µg/g.

One potable water treatment plant was sampled at pre- and post-flocculation points. MRI tap water was analyzed for comparison. No acrylamide above the detection limit was found in any of the samples.

Thirty-two polymers were analyzed for residual acrylamide. When not obscured by interferences, the observed acrylamide ranged from 0.5 to 600 µg/g.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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