Spectrophotometric Determination of Polyacrylamide in Waters Containing Dissolved Organic Matter

J. H. Lu and L. Wu*

Department of Environmental Sciences, University of California, Riverside, California 92521

Using polyacrylamide (PAM) to reduce soil erosion in irrigated land has increased rapidly in recent years. A simple and reliable method to measure the PAM concentration in waters containing dissolved organic matter (DOM) is of great importance in assessing the fate and efficiency of PAM application. In this research, an analytical method to determine the PAM concentration of waters with correction for DOM interference was developed and tested. The method is based on a combination of determining the total concentration of amide groups by the N-bromination method (NBM) and determining the DOM content spectrophotometrically. The total concentration of amide groups of both PAM and DOM was determined by NBM at 570 nm. The DOM moiety, which is proportional to DOM concentration, was determined by spectrophotometry using a UV 254-nm wavelength. The actual PAM concentration of a water sample (soil extract containing PAM in this study) was obtained from NBM readings subtracted by the interferential DOM contribution using a correction curve. Analysis of PAM in two soil−water samples showed that the recoveries ranged from 94 to 100.3% for the 2 mg/L PAM sample and from 98.4 to 101.4% for the 10 mg/L PAM sample with various DOM concentrations. The coefficients of variation were <6% in all cases.

Keywords: *Polyacrylamide; N-bromination method; UV spectrophotometry; dissolved organic matter*

INTRODUCTION

Application of polyacrylamide (PAM) to irrigation water to enhance infiltration, stabilize soil structure, and minimize erosion has been a rapidly expanding practice in recent years (*1*). It has been shown that the technology is effective, nonintrusive, and economical in the western United States (*2*). Numerous studies have been conducted to optimize the method of PAM application and to evaluate its function and mechanism of action (*1*). Concerns on the fate and environmental impact of PAM after its application, on the other hand, are also increasing. The current methods of analyzing PAM concentration in water are not sensitive at low concentrations (0.1−10 mg/L) and/or are vulnerable to the interference of both dissolved organic matter (DOM) and salts. Thus, it is difficult to estimate the concentration distribution of PAM downstream of the furrows, the potential of PAM losses to the tail water, and the PAM partition between soil solution and soil matrix. A simple and sensitive method to determine PAM in waters containing DOM (e.g., soil solution, soil extract, irrigation tail water, and surface runoff water, etc.) will greatly facilitate research work concerning the fate and impact of PAM application.

A survey of the literatures shows that several methods have been employed to quantify aqueous PAM concentrations: (1) total organic carbon (TOC) content method (*3*, *4*); (2) N-bromination of amide groups followed by starch−iodide complex measurement (*5*, *6*); (3) conversion of amide groups to amines, which are then determined by fluorescence spectrometry (*7*, *8*); (4) amide hydrolysis with ammonia detection (*9*, *10*); (5) colloid titration (*11*, *12*); (6) turbidimetric method (*13*, *14*); (7) viscosity method (*15*, *16*); (8) polarography method (*17*, *18*); (9) flocculation-based method (*2*); (10) radioactive labeling (*19*, *20*); and (11) size exclusion chromatography (*21*, *22*). Nevertheless, only a few of these methods are suitable for quantifying PAM in waters containing DOM.

Often, chemical methods are sensitive and have low detection limits, but they are not selective for PAM in the presence of DOM and are therefore unsuitable. Fluorescence spectrometry and the TOC method are not reliable due to the relatively low PAM concentration and high inherent background caused by DOM. Methods based on colloid titration, turbidity, viscosity, and polarography are not sensitive enough to measure PAM at <10 mg/L, as is typically observed in irrigation application. Furthermore, these methods are vulnerable to the interference of both salts and DOM. Radioactive labeling is a sensitive and reliable method for laboratory analysis if clean isotope-labeled PAM could be obtained, but the method is not feasible in field experiments. Size exclusion chromatography is a promising method only if separation between DOM and PAM can be achieved, which still needs to be proven. A flocculation-based method, proposed by Lentz et al. (*2*), is a practical method for estimating low PAM concentrations (0.1−10 mg/L), but the method needs to be tested before being used in water samples containing high DOM and salts that affect the flocculation process.

Salts and DOM are two major factors that interfere with the measurement of PAM concentration in water samples. A reliable method must overcome such interferences. Of all the methods noted above, the N-bromination method (NBM), which is simple and robust enough to overcome the salt interference, was selected as the basic PAM measurement method in this paper. It was originally developed for PAM analysis in oil-

* Corresponding author [telephone (909) 787-4664; e-mail Laowu@mail.ucr.edu].

10.1021/jf010430o CCC: $20.00
Published on Web 08/04/2001

Table 1. Textural and Chemical Properties of the Six Test Soils

soil	clay %	sand %	silt %	OM[a] (%)	pH (saturated paste)	EC[b] (S/m)	SP[c] (%)
Fiddletown silt loam	16.4	22.6	61.0	6.36	5.96	0.702	45
Palouse silt loam	18.1	32.2	49.7	5.45	5.88	0.0742	40
Linne clay loam	33.0	30.2	36.8	3.88	7.14	0.168	43
Imperial silty clay	42.5	10.8	46.7	2.46	7.48	0.664	49
Arlington loamy sand	8.7	87.5	3.8	1.93	7.06	0.868	27
Hanford sand	3.6	95.6	0.8	0.575	7.54	0.0591	21

[a] Organic matter content (OM %) was measured by combustion method. [b] EC is electrical conductivity and measured in extracts of saturated pastes. [c] SP is saturation percentage.

containing samples by Scoggins and Miller (*23*) and later modified and automated to a flow injection analysis method by Taylor (*24*). In this method, the amide groups of PAM are converted to *N*-bromo amides by reaction with bromine. Excess bromine is removed by the addition of sodium formate. Finally, the *N*-bromo amides are used to quantitatively convert iodide ions to iodine in the presence of starch−CdI_2 reagent. The iodine concentration is measured in the form of starch−triiodide blue complex. Detailed information of the method was described by Scoggins and Miller (*23*). Taylor (*6*) showed the method had a PAM detection limit of 0.1 mg/L with a coefficient of variation (CV) of <1.5% in the linear range from 0.1 to 60 mg/L. Ions such as Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, CO_3^{2-}, NO_3^-, and Br^- did not affect PAM measurement as long as the salt concentration was not high enough to cause polymer to precipitate. For Cl^- <0.05 mg/L, no detectable effect was observed. For Cl^- >0.05 mg/L, a small and monotonic suppression of near-blank readings was observed. This error could be easily corrected by inclusion of NaCl in the calibration standards (*6*). Nevertheless, this method again does not exclude the DOM interference.

DOM in soil water samples typically has a concentration range of 0−300 mg/L in terms of TOC. It can be measured separately by spectrophotometry at a 254-nm wavelength (*25*). The objective of this research was to develop a sensitive, simple, and reliable method to measure the concentration of PAM in water samples containing DOM by determining the total concentration of amide groups using the NBM and DOM using spectrophotometry.

MATERIALS AND METHODS

Preparation of Soil Extracts. Soil extracts (water containing DOM) were obtained by equilibrating soils with deionized (DI) water. Six soils from the western United States, a Fiddletown silt loam (Loamy-skeletal, mixed, mesic Pachic Xerumbrepts), a Palouse silt loam (mixed, superactive, mesic Pachic Haploxerolls), a Linne clay loam (mixed, thermic Calcic Pachic Haploxerolls), an Imperial silty clay (semectitic, calcareous, hyperthermic Typic Torrifluvents), an Arlington loamy sand (mixed, thermic Haplic Durixeralfs), and a Hanford sand (mixed, superactive, nonacid, thermic Typic Xerorthents), were selected to obtain a wide range of textures and organic mater contents. All samples were collected from the upper 10 cm layer of the profiles, air-dried, and ground to pass through a 1-mm sieve. Their textural and chemical properties are presented in Table 1. Six levels of water/soil (mass/mass) ratios ranging from 2 to 50 were used for each soil sample to get a range of DOM concentrations as might be observed in field conditions. After 24 h of shaking in a reciprocal shaker, the suspensions were centrifuged and the supernatants were passed through 0.22-μm membrane filters (Millipore Corp., Bedford, MA) to remove possible suspended particles. The soil extracts were stored at 4 °C before analysis (~2 days). The DOM concentrations of the samples (reported in terms of TOC in solution) were measured in a DC-80 Dohrmann carbon analyzer (Xertex, Santa Clara, CA) using potassium hydrogen phthalate as a carbon standard.

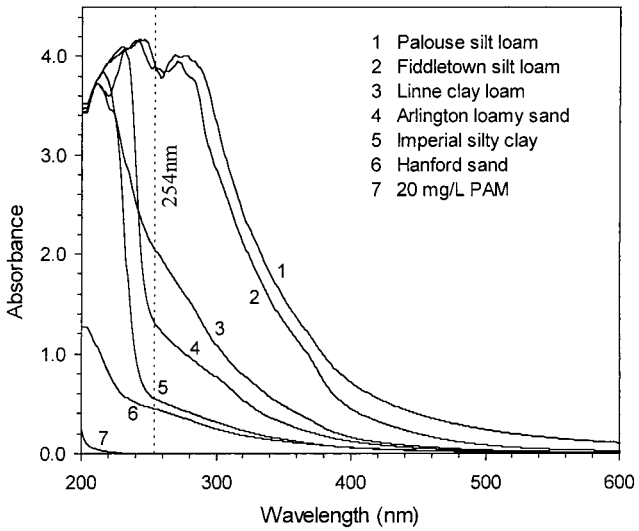

Figure 1. UV−vis absorbance spectra of soil extracts (water/soil ratio is 2) and PAM (20 mg/L).

Selection of Wavelength for DOM Measurement. The estimation of DOM in natural water by spectrophotometry is a widely accepted method (*26*). However, the wavelengths used to measure DOM vary among laboratories. For example, Dobbs et al. (*27*) and Mrkva (*25*) used 254 nm; Traina et al. (*28*) used 280 nm; De Haan et al. (*29*) and Moore (*30*) used 330 and 350 nm; Bloom and Leenheer (*31*) used 465 nm; and Lawrence (*32*) used a combination of several wavelengths to measure DOM by spectrophotometry. Our preliminary test showed that the UV−vis absorbance of the soil extracts from the six selected soils increased considerably as the wavelength decreased, especially when the wavelength was <300 nm (Figure 1). The PAM solution, however, had no detectable absorbance until the wavelength was <240 nm. For high sensitivity, 254 nm was selected in this study for the DOM concentration measurement.

Preparation of PAM Standard Solution. Granular anionic polyacrylamide, with an average molecular mass of 10−15 million g/mol, 21% NH_2 group substituted by OH group, was provided by the Celanese Corp. (Louisville, KY). The standard solutions were prepared by dissolving PAM in DI water and aged (25 °C, dark) for 1 week to obtain a uniform solution before use. Various PAM concentrations of the water samples containing DOM were obtained by spiking the PAM standard solution into soil extracts, mixing them thoroughly, and then allowing them to age for 2 days before analysis.

Preparation of the Reagents for NBM. The NBM used in this study is based mainly on methods found in earlier references (*6*, *23*, *24*). To make it suitable for analyzing PAM concentrations in water samples, the concentration and volume of the reagents needed for analysis were optimized to make the method more robust and easier to operate. The sampling volume for each assay was reduced to 2−4 mL from the 30 mL reported in the references. All of the chemicals used were of analytical grade or higher.

(1) Preparation of the 1 M HOAC−NaOAC buffer solution (pH 3.5) is accomplished by transferring 28.9 mL of glacial

acetic acid into 300 mL of DI water, adjusting the pH of the solution to 3.5 by the addition of 1% NaOH solution, adding 6 mL of oxamide solution (50 mg/L), and then diluting to 500 mL with DI water. Oxamide is added to eliminate the nonzero intercepts in calibration curves, thereby improving the sensitivity of the method (*24*). Oxamide can be substituted by any primary amide, such as acetamide or benzoamide, but the optimum amount added to the buffer solution may be different from that specified in this paper.

(2) Preparation of the 0.04 M bromine water solution is performed by adding 3.20 g of liquid Br_2 to 300 mL of DI water, stirring until complete dissolution, then bringing the volume to 500 mL.

(3) Preparation of the 0.08 M sodium formate solution is done by dissolving 2.72 g of sodium formate into 500 mL of DI water.

(4) Preparation of the 0.25% starch−0.03 M CdI_2 solution is accomplished by weighing 1.25 g of water-soluble linear starch, wetting it with 5 mL of DI water, then adding it to 300 mL of boiling DI water, with constant stirring until the solution becomes clear. After the solution has cooled to room temperature, 5.49 g of CdI_2 is added and stirred to dissolve, the volume is brought to 500 mL, and then the mixture is filtered by fine filter paper (such as Whatman No. 5 or No. 42) to remove any insoluble particles. The solution must be stored in a brown glass bottle.

Analysis Procedure. Two milliliters of a water sample is pipetted into a 20-mL glass bottle, 1 mL of HOAC−NaOAC buffer solution is added and mixed in, 1 mL of bromine water solution is added and mixed thoroughly, and the mixture is allowed to react for 40 min at room temperature. After that, 1 mL of sodium formate solution is added and mixed; 5 min later, 1 mL of starch−CdI_2 solution is added to develop a blue complex. Ten minutes later the absorbance of the solution is measured at 570 nm versus a reagent blank. The absorbance of the starch−triiodide blue complex remains stable for at least 90 min. The maximum absorbance wavelength may change in the range of 540−650 nm, depending on the type of starch used. For the linear potato starch provided by Allied Chemical (New York, NY) for iodometry, a maximum absorbance at 570 nm was found.

When a water sample is suspected to contain DOM, an ultraviolet (UV) absorbance at 254 nm is used to make the correction for PAM analysis. The water sample containing DOM is pipetted to fill up approximately two-thirds of the quartz cuvette to measure absorbance at 254 nm, using DI water as blank. In this research, absorbance was measured on a Beckman 50 UV−vis spectrophotometer (Beckman Instruments, Fullerton, CA) in 1-cm path length cuvettes. When the absorbance was >2.5, samples were diluted before measurement to eliminate the nonlinear portion in high concentration zones. In this study, all of the measurements were duplicated or triplicated.

For samples with a PAM concentration ranging from 5 to 30 mg/L, a 2-mL sampling volume keeps the final absorbance readings in an appropriate range of 0.5−2.5. When the PAM concentration is <5 mg/L, inasmuch as the final absorbance reading is <0.5, doubling the sampling volume (4 mL) is recommended to increase the accuracy of the assay.

RESULTS AND DISCUSSION

Linearity of DOM Concentration and UV 254-nm Absorbance. For clarity, the UV 254-nm absorbance curves of soil extracts for the three low-DOM soils (Figure 2A) were plotted separately from those of the high-DOM soils (Figure 2B). The three low-DOM soils are the Imperial silty clay, Arlington loamy sand, and Hanford sand, which have a DOM concentration range of 2−80 mg/L in their extracts. The high-DOM soils are the Fiddletown silt loam, Palouse silt loam, and Linne clay loam, which have a DOM concentration range of 8−300 mg/L. It is obvious that for each soil, the 254-nm absorbance of its extracts is linearly proportional

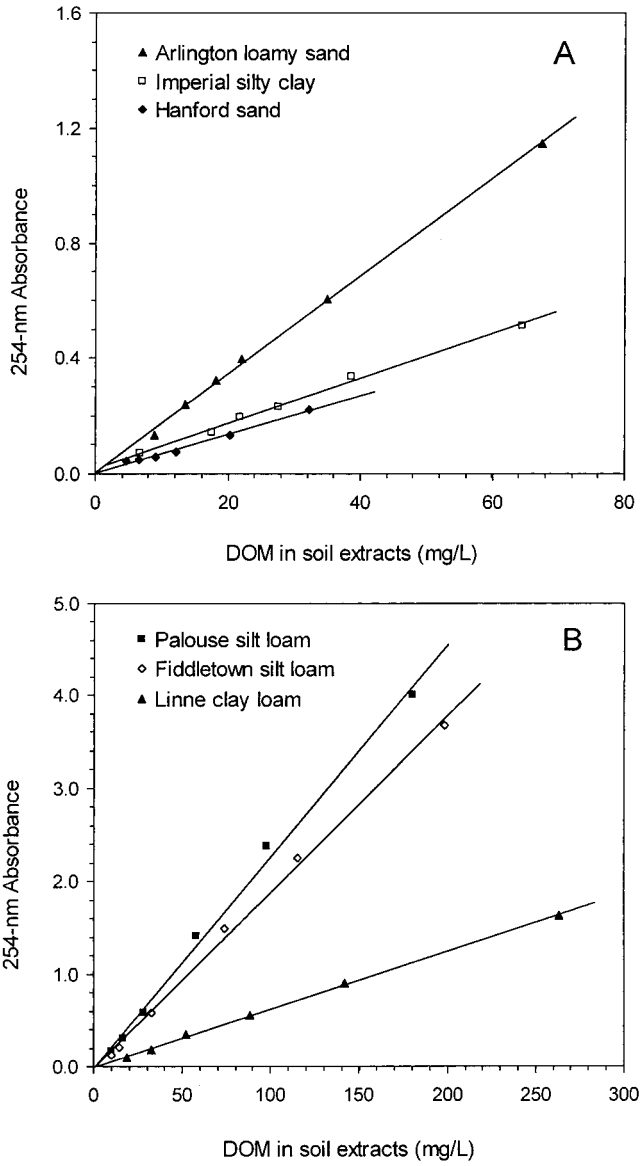

Figure 2. UV 254-nm absorbance curves of soil extracts with different DOM concentrations.

to its TOC concentration, because all of the $R^2 > 0.992$. This result agrees well with earlier studies, which recommended that 254 nm be used for measuring organic matter content in natural water (*25*, *27*). The slopes of the 254-nm absorbance lines differed with soil type (Figure 2), indicating different 254-nm absorbances at the same DOM concentration. These differences are attributed to the various amounts of organic matter components and their unique molecular structural characteristics in each soil.

Linearity of DOM Concentration and NBM Readings. When exposed to bromine during analysis, the primary amide groups both in DOM and in PAM respond to N-bromination reaction and contribute to the final 570-nm absorbance. On average, the magnitude of the 570-nm absorbance value for a 50 mg/L DOM is comparable to that of a 3 mg/L PAM standard solution. The 570-nm absorbance of the water samples as a function of their DOM concentrations is plotted in Figure 3. Good linearity was observed for all of the soil samples (all $R^2 > 0.995$). Differences in slopes of the regression lines are due to the different contents of primary amide groups in the samples. Figure 3 shows

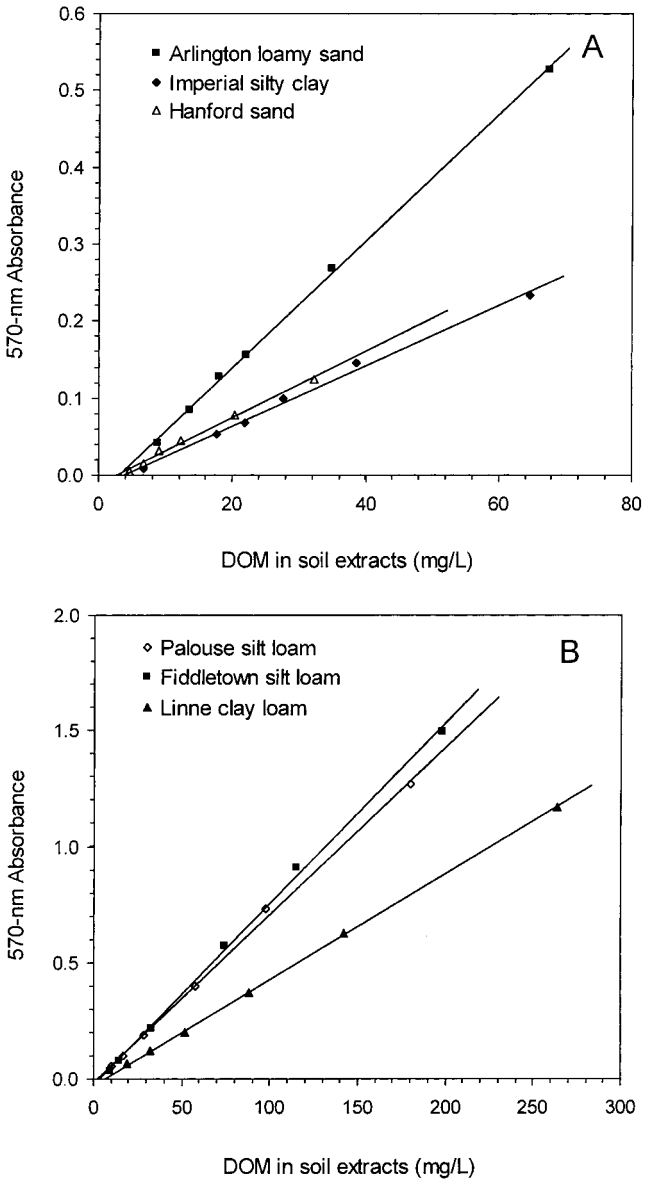

Figure 3. NBM 570-nm absorbance curves of soil extracts with different DOM concentrations.

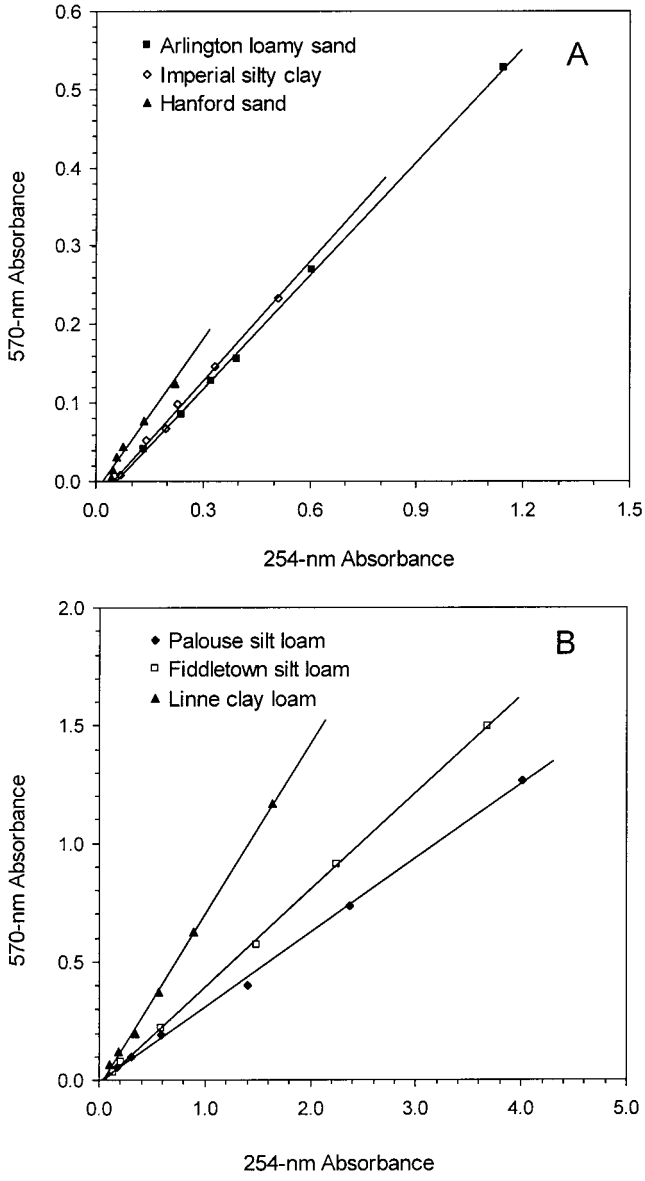

Figure 4. DOM correction curves for the NBM.

that each regression line has a minute negative intercept, which implies that when the DOM concentration is lower than a threshold value, the amount of the primary amide groups is beyond the sensitivity of the NBM. Under such circumstances, DOM has no interference on the PAM measurement.

DOM Correction Curves for NBM. By plotting the NBM 570-nm absorbance of water samples containing DOM against their UV 254-nm absorbance, DOM correction curves were obtained (Figure 4). Again, good linearity was observed as all $R^2 > 0.995$. This result is a direct consequence of the good linearity of both 254-nm absorbance and the NBM 570-nm absorbance versus DOM concentrations. The good linearity ensures that the interference from the amide groups in soil organic matter can be quantitatively corrected by using a UV 254-nm absorbance measurement during PAM determination.

Organic matter in each soil may have its unique structural characterstics, which cause different UV 254-nm absorbance and the NBM 570-nm absorbance at the same DOM concentration (Figures 2 and 3). As a result, the DOM correction curve for each soil is different (Figure 4). Therefore, individual DOM correction curves for each soil need to be established before measuring the PAM concentration in its water samples.

A DOM correction curve can be developed by (1) collecting a soil sample from the area concerned, (2) preparing water samples containing various concentrations of DOM by equilibrating soil with DI water at different water/soil ratios, (3) measuring their UV 254-nm absorbance and their NBM 570-nm absorbance separately, and (4) plotting the 254-nm absorbance against the 570-nm absorbance, as shown in Figure 4.

Examples of Sample Analysis. Once the DOM correction curve of a particular soil is established (Figure 4), the PAM concentration in water can be determined by the following procedure:

a. Determine the 570-nm absorbance by NBM, which includes the contribution of both PAM and interferential DOM.

b. Measure the DOM content in the same sample using UV 254-nm readings.

c. Obtain the DOM correction value from the plot of NBM 570-nm versus UV 254-nm for the soil (Figure 4).

Table 2. Analytical Results of PAM Concentration in Water Samples Containing DOM

soil	DOM (mg/L)	2 mg/L PAM			10 mg/L PAM		
		mean[a] ± SD	CV (%)	recovery (%)	mean[a] ± SD	CV (%)	recovery (%)
Imperial silty clay	3.4	2.01 ± 0.05	2.3	100.3	10.00 ± 0.07	0.7	100.0
	8.8	1.96 ± 0.12	6.0	97.8	10.01 ± 0.09	0.9	100.7
	11.0	1.89 ± 0.05	2.3	94.3	9.97 ± 0.14	1.4	99.7
	13.9	1.91 ± 0.05	2.5	95.7	10.05 ± 0.11	1.1	100.5
	19.3	1.88 ± 0.09	4.4	94.0	10.03 ± 0.15	1.5	100.3
	32.3	1.95 ± 0.08	4.2	97.3	9.84 ± 0.27	2.7	98.4
Palouse silt loam	5.1	1.97 ± 0.03	1.6	98.7	9.90 ± 0.06	0.6	99.0
	8.3	1.93 ± 0.12	5.9	96.7	10.14 ± 0.14	1.4	101.4
	14.2	1.89 ± 0.04	2.0	95.5	10.01 ± 0.28	2.8	100.1
	28.8	1.97 ± 0.08	4.0	98.3	9.92 ± 0.06	0.6	99.2
	48.9	1.98± 0.11	5.5	99.0	10.01 ± 0.12	1.2	100.1
	90.1	1.97 ± 0.08	4.0	98.3	9.84 ± 0.24	2.4	98.4

[a]Mean values are the average of three measurements.

d. Caculate the net NBM absorbance (*a*−*c*) and obtain the actual PAM concentration by the standard calibration curve of NBM.

To test the proposed method, one low-DOM soil, the Imperial silty clay, and one high-DOM soil, the Palouse silt loam, were selected. The PAM standard solution and their water samples with different DOM concentration levels were mixed together to test the methodology in two levels of PAM concentration (2 and 10 mg/L). After 2 days of aging, PAM concentrations in those samples were analyzed by using the procedures described above.

Results are listed in Table 2. For 10 mg/L PAM, the CVs for the DOM concentrations ranging from 3.4 to 32.3 mg/L were <2.7% and the recoveries were >98.4% in the Imperial silty clay. The CVs for the DOM concentrations ranging from 5.1 to 90.1 mg/L were <2.8% and the recoveries were >98.4% in the Palouse silt loam. These results indicate that the DOM interference was effectively removed through the proposed correction method. For soil−water samples containing 2 mg/L PAM, the CVs were less than 6.0 and 5.9% and the recoveries were greater than 94 and 95% for the Imperial silty clay and the Palouse silt loam, respectively. These results indicate that the proposed method is efficacious even for PAM concentration levels as low as 2 mg/L despite high-DOM background. The somewhat low recovery in 2 mg/L PAM samples is possibly because a portion of PAM in the water was absorbed by the container walls (*7*). Nevertheless, these results suggest that the sensitivity and reproducibility of the proposed method could meet the general requirement of most research and evaluation work on PAM application in soils.

The lower detection limit of NBM is ∼0.1 mg/L with a signal-to-noise ratio of 2:1. According to the rule of propagation-of-error, the proposed method has a detection limit of 0.2 mg/L PAM.

In summary, the proposed method first determined the total concentration of amide groups (from both PAM and DOM) in water samples by NBM. Second, the DOM moiety, as proportional to the DOM concentration, was determined by spectrophotometry. The actual PAM concentration then was obtained from NBM readings after subtraction of the interferential DOM contribution by UV spectrometry measurements. For completeness of the method, we tested the effects of a range of DOM concentrations on PAM measurements. In practice, however, if the water samples have similar DOM concentrations and if the DOM has similar structural characteristics, correction for DOM can be made through a single measurement of a representative water sample by NBM at 570-nm absorbance and UV 254-nm absorbance. On the other hand, if a field exhibits heterogeneity of organic matter both quantitatively and qualitatively, an individual correction curve for each type of soil should be established.

ABBREVIATIONS USED

PAM, polyacrylamide; DOM, dissolved organic matter; NBM, N-bromination method; TOC, total organic carbon; UV, ultraviolet; DI, deionized; CV, coefficient of variation.

ACKNOWLEDGMENT

We are grateful to Dr. John Letey and Dr. Walter J. Farmer for helpful discussions and Ralph A. Strohman and Peggy Pesketo for assistance in the laboratory.

LITERATURE CITED

(1) Sojka, R. E.; Lentz, R. D. A PAM Primer: A brief history of PAM and PAM-issues related to irrigation. In *Proceedings: Managing Irrigation-Induced Erosion and Infiltration with Polyacrylamide*, May 6−8, 1996, College of Southern Idaho, Twin Falls, ID; Sojka, R. E., Lentz, R. D., Eds.; University of Idaho Miscellaneous Publication 1996, 101-96; 1996; pp 11−20.

(2) Lentz, R. D.; Sojka, R. E.; Foerster, J. A. Estimating polyacrylamide concentration in irrigation water. *J. Environ. Qual.* **1996**, *25*, 1015−1024.

(3) Aly, S. M.; Letey, J. Polymer and water quality effects on flocculation of montmorillonite. *Soil Sci. Soc. Am. J.* **1988**, *52*, 1453−1458.

(4) Lecourtier, J.; Lee, L. T.; Chauveteau, G. Adsorption of polyacrylamides on siliceous minerals. *Colloids Surf.* **1990**, *47*, 219−231.

(5) Scoggins, M. W.; Miller, J. W. Spectrophotometric determination of water soluble organic amides. *Anal. Chem.* **1975**, *47*, 152−154.

(6) Taylor, K. C. Development of a flow injection analysis method for the determination of acrylamide copolymers in brines. *J. Pet. Sci. Eng.* **1998**, *21*, 129−139.

(7) Hendrickson, E. R.; Neuman, R. D. Determination of polyacrylamide by spectrofluorometry. *Anal. Chem.* **1984**, *56*, 354−357.

(8) Arryanto, Y.; Bark, L. S. Improved and rapid method for the spectrofluorimetric determination of trace amounts of polyacrylamides in waters. *Analyst* **1991**, *116*, 1149−1153.

(9) Hawn, G. G.; Talley, C. P. Gas chromatographic determination of polyacrylamide after hydrolysis to ammonia. *Anal. Chem.* **1981**, *53*, 731−732.

(10) McCulley, L. Z.; Malachosky, E. A new method for the quantitative determination of the PHPA polymer content of drilling fluids and other aqueous systems. Paper 22580, presented at the 66th Annual Technical Conference and Exhibition, Society of Petroleum Engineers, Dallas, TX, 1991.
(11) Toei, K.; Kohara, T. A conductometric method for colloid titrations. *Anal. Chim. Acta* **1976**, *83*, 59−65.
(12) Tanaka, H.; Sakamoto, Y. Polyelectrolyte titration using fluorescent indicator: I. Direct titration of anionic and cationic polyelectrolyte with 10E-4N standard solution. *J. Polym. Sci. A* **1993**, *31*, 2687−2691.
(13) Crummett, W. B.; Hummel, A. The determination of traces of polyacrylamides in water. *J. Am. Water Works Assoc.* **1963**, *55*, 209−219.
(14) Kuehne, D. L.; Shaw, D. W. Manual and automated turbidimetric method for the determination of polyacrylamides in the presence of sulfonates. *Soc. Pet. Eng. J.* **1985**, *25*, 687−692.
(15) Lindstrom, T.; Soremark, C. Adsorption of cationic polyacrylamides on cellulose. *J. Colloid Interface Sci.* **1976**, *55*, 306−312.
(16) Jungreis, E. A simple microdetermination of polymer flocculants (polyacrylamides and guar) in mine water. *Anal. Lett. A* **1981**, *14*, 1177−1183.
(17) Wentzell, B. R.; Smith-Palmer, T. Determination of polyacrylamides by maximum suppression. *Can. J. Chem.* **1987**, *65*, 557−562.
(18) Smith-Palmer, T.; Wentzell, B. R.; Donini, J. C.; Jerrard, R. J. A tensammetric study of polyacrylamides including their determination. *Can. J. Chem.* **1988**, *66*, 2658−2663.
(19) Nabzar, L.; Pefferkorn, E.; Varoqui, R. Polyacrylamide-sodium kaolinite interactions: flocculation behavior of polymer clay suspensions. *J. Colloid Interface Sci.* **1984**, *102*, 380−388.
(20) Nadler, A.; Letey, J. Adsorption isotherms of polyanions on soils using tritium labeled compounds. *Soil Sci. Soc. Am. J.* **1989**, *53*, 1375−1378.
(21) Beazley, P. M. Quantitative determination of partially hydrolyzed polyacrylamide polymers in oil field production water. *Anal. Chem.* **1985**, *57*, 2098−2101.
(22) Hunt, J. A.; Young, T. S.; Green, D. W.; Willhite, G. P. Size-Exclusion chromatography in the measurement of concentration and molecular weight of some EOR polymers. *Soc. Pet. Eng. Res. Eng.* **1988**, *3*, 835−841.
(23) Scoggins, M. W.; Miller, J. W. Determination of water-soluble polymers containing primary amide groups using the starch-triiodide method. *Soc. Pet. Eng. J.* **1979**, *19*, 151−154.
(24) Taylor, K. C. Spectrophotometric determination of acrylamide polymers by flow injection analysis. *Soc. Pet. Eng. Adv. Technol. Ser.* **1993**, *1*, 130−133.
(25) Mrkva, M. Evaluation of correlations between absorbance at 254 nm and COD of river waters. *Water Res.* **1983**, *17*, 231−235.
(26) Hautala, K.; Feuravuori, J.; Pihlaja, K. Measurement of aquatic humus content by spectroscopic analysis. *Water Res.* **2000**, *34*, 246−258.
(27) Dobbs, R. A.; Wise, R. H.; Dean, R. B. The use of ultraviolet absorbance for monitoring the total organic carbon content of water and wastewater. *Water Res.* **1972**, *6*, 1173−1180.
(28) Traina, S. J.; Novak, J.; Smeck, N. E. An ultraviolet absorbance method of estimating the percent aromatic carbon content of humic acids. *J. Environ. Qual.* **1990**, *19*, 151−153.
(29) De Haan, H.; De Boer, T.; Kramer, H. A. Applicability of light absorbance as a measure of organic carbon in humic lake water. *Water Res.* **1982**, *16*, 1047−1050.
(30) Moore, T. R. The spectrophotometric determination of dissolved organic carbon in peat waters. *Soil Sci. Soc. Am. J.* **1985**, *49*, 1590−1592.
(31) Bloom, P. R.; Leenheer, J. A. *Vibrational, Electronic and High-Energy Spectroscopic Methods for Characterizing Humic Substances. II. Humic Substances*; Hayes, M. H. B., MacCarthy, P. M., Malcolm, R. L., Swift, R. S., Eds.; Wiley: New York, 1989; pp 409−446.
(32) Lawrence, J. Semi-quantitative determination of fulvic acid, tannin and lignin in natural water. *Water Res.* **1980**, *14*, 373−377.

Received for review March 30, 2001. Revised manuscript received June 22, 2001. Accepted June 25, 2001. Mention of products is for information only and does not constitute an endorsement by the University of California.

JF010430O