

Spectrophotometric Determination of Substrate-Borne Polyacrylamide

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Polyacrylamides (PAMs) have wide application in many industries and in agriculture. Scientific research and industrial applications manifested a need for a method that can quantify substrate-borne PAM. The N-bromination method (a PAM analytical technique based on N-bromination of amide groups and spectrophotometric determination of the formed starch–triiodide complex), which was originally developed for determining PAM in aqueous solutions, was modified to quantify substrate-borne PAM. In the modified method, the quantity of substrate-borne PAM was converted to a concentration of starch–triiodide complex in aqueous solution that was then measured by spectrophotometry. The method sensitivity varied with substrates due to sorption of reagents and reaction intermediates on the substrates. Therefore, separate calibration for each substrate was required. Results from PAM samples in sand, cellulose, organic matter burnt soils, and clay minerals showed that this method had good accuracy and reproducibility. The PAM recoveries ranged from 95.8% to 103.7%, and the relative standard deviations ($n = 4$) were $<7.5\%$ in all cases. The optimum range of PAM in each sample is 10–80 μg . The technique can serve as an effective tool in improving PAM application and facilitating PAM-related research.

KEYWORDS: Substrate-Borne Polyacrylamide; N-bromination method; spectrophotometric determination

INTRODUCTION

Polyacrylamides (PAMs) are among the most widely used synthetic polymers. They are frequently used in diverse fields such as water treatment, papermaking, petroleum recovery, mineral processing, soil conditioning, etc. Determining PAM concentration is an important factor for its successful application, since properties of PAM solution, such as rheology, adsorption, and flocculating ability, are highly concentration dependent (1). Many techniques have been developed to quantify PAM in aqueous solution (2, 3). These methods involved a great variety of analytical approaches, such as viscosity measurement, turbidimetry, polarography, colloid titration, flocculation, size exclusion chromatography, radioactive labeling, total organic carbon, N-bromination of amide groups followed by starch–triiodide complex measurement, conversion of amide groups to amines which are then determined by fluorescence spectrometry, and amide hydrolysis with ammonia detection. An extensive review on this topic was published by Taylor and Nasr-El-Din (4).

Besides the quantification of PAM concentration in aqueous solution, scientific research and industrial applications sometimes require a method that can quantify substrate-borne PAM. For example, in the fast-growing PAM soil conservation technology (5, 6), knowing the PAM distribution along with the soil depth after application helps to determine the appropriate

PAM application rate, effective conditioning depth, and its environmental impact. In the papermaking industry, direct measurement of adsorbed amounts of polymeric additives (most commonly used are PAMs) on cellulosic fiber is highly relevant for describing the action of these additives (7). Methodology to determine sorbed-state PAM will also greatly facilitate research on the interaction mechanisms between PAM and clay minerals, which are critical for explaining flocculation, swelling, and dispersion phenomena in water treatment and mining industries.

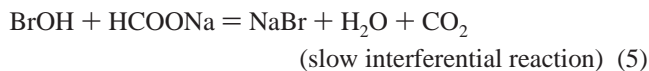
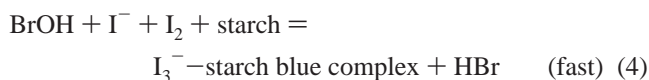
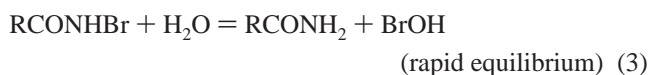
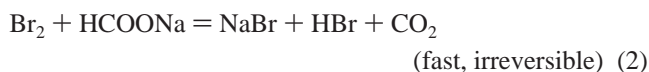
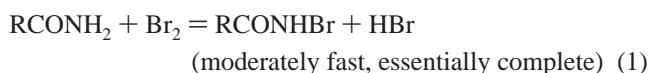
Determination of substrate-borne organic chemicals, such as soil-sorbed pesticides, usually can be done after extraction with organic solvents (8). Unfortunately, it is almost impossible to extract sorbent-sorbed PAM from its sorbent because (1) PAM is highly soluble in water and insoluble in most common organic solvents, such as methanol, diethyl ether, esters, hydrocarbons, and nitrobenzene (9) and (2) no or very low desorption of PAM occurs after its sorption into the soil or clay minerals (10). PAM binds to the soil or other sorbents by a multisegment sorption mechanism (11). It is unlikely that all of the segments of the polymer can be simultaneously detached from the surface and remain so sufficiently long for the polymer chain to move away from the surface into the bulk solution. Any method proposed for quantification of sorbent-sorbed PAM should be able to detect PAM on its sorbed state. Since all of the aforementioned methods were developed for PAM quantification in aqueous samples, none of them can be applied to analyze substrate-borne PAM directly.

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The N-bromination method (NBM) is a spectrophotometric method that was originally developed to determine acrylamide copolymers in surface waters and oil field brines (12, 13). Recently, a modification was made to correct the interferences from dissolved organic matter by an additional spectrophotometric determination at 254 nm, which extended its applicability to soil solution and irrigation runoff waters (3). The method has a detection limit of 0.2 mg/L and a linear range from 0.2 to 60 mg/L. Nevertheless, since PAM binds irreversibly on substrates and is hard to extract, this method needs to be modified before being used to quantify substrate-sorbed PAM.

The objectives of this research were to modify the NBM to quantify substrate-borne PAM and to ascertain the precision, sensitivity, and applicability of the method. The technique can serve as an effective tool in improving PAM application and facilitating PAM-related research.

Modification of NBM for Substrate-Borne PAM. (A) *Mechanisms of NBM.* To explain the modifications made to the analytical procedure, a brief description of the mechanisms of NBM (12) is necessary. This method is based on the measurement of the amounts of amide groups in PAM. Amide groups in PAM are first N-brominated with bromine to form *N*-bromo amide (reaction 1). Excess bromine is removed by reaction with sodium formate (reaction 2). The *N*-bromo amide then oxidizes iodide to iodine, which is then detected spectrophotometrically as the starch-triiodide complex (reactions 3 and 4). During the removal of excess bromine by sodium formate, a slow competing reaction between the *N*-bromo amide and sodium formate occurs, which lowers final absorbance of the starch-triiodide complex (reaction 5).



This method is unaffected by most of the common ions, such as Na^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , CO_3^{2-} , NO_3^- , and Br^- (2). However, the presence of primary and secondary amides or iodide ion in aqueous samples (4) or incomplete depletion of bromine by sodium formate in the analysis process can cause significant positive interference.

(B) *Problems and Modification of NBM.* Preliminary experiments showed that the bromination reaction of amide groups (reaction 1) also occurs and proceeds to completion for sorbed-state PAM, which suggests the possibility of quantification of PAM in its sorbed state. A substrate-borne PAM sample of known weight is first mixed with deionized (DI) water to form a suspension and then analyzed by a procedure similar to NBM for water-borne PAM samples (see Materials and Methods section). The quantity information of sorbed-state PAM is ascertained by the concentration of the starch-triiodide complex

in aqueous solution that is then measured by spectrophotometry. However, two major problems arise, leading to some modifications:

(1) Sorption of reagents and reaction intermediates on substrate: Supplementary experiments showed that the reagent of bromine water and the critical intermediate BrOH strongly sorbed onto the substrate, especially montmorillonite. The sorption of BrOH requires that starch-iodide reagent (to develop the blue starch-triiodide complex) must be added before the separation of substrate particles from the solution. Therefore, a fraction of the formed starch-triiodide complex may also sorb onto the substrate, which somewhat lowers the sensitivity of the method. The sorption of bromine on the substrate slows down the reduction process of excess bromine by sodium formate. To ensure the depletion of bromine by sodium formate, a lower concentration of bromine water than that in NBM for aqueous samples must be used. The much higher concentration ratio of sodium formate to bromine than stoichiometry causes more efficient reduction of substrate-sorbed bromine. However, it also facilitates the disadvantageous side reaction (reaction 5). Furthermore, to compensate for the negative effects of the lower concentration of bromine water, longer reaction time for bromination of amide groups is needed, which prolongs the time required for analysis.

(2) Severe interferences from organic matter: This situation is typically encountered in soil samples. Soil usually has a natural organic matter content of 5–80 g/kg, which is much higher than PAM content found in soil conservation technology. As the primary and secondary amide groups in organic matters also respond to the NBM, high background absorbance was found, which invalidates the correction method for organic matter interference by ultraviolet 254 nm measurement as in the NBM for water-borne PAM samples (3). Therefore, organic matter must be removed before the modified NBM is used. This requirement limits the application of the method on natural soils.

MATERIALS AND METHODS

PAM and Substrates. Anionic PAM, with an average molecular weight of 10–15 million g/mol, 21% NH_2 group substituted by OH group, was provided by Celanese Corp. (Louisville, KY). Six substrates, with a wide range of physical and chemical properties, were used. They were a silica sand (>98% pure SiO_2), a microcrystalline cellulose, two clay minerals, and two soils. The sand size ranged from 0.4 to 0.7 mm in diameter. The sand was thoroughly washed with DI water before use. The cellulose powder had a particle size of about 100 μm and was purchased from Sigma-Aldrich Co. (Milwaukee, WI). The two clay minerals were a well-ordered kaolinite (specific surface area of 10.05 $\text{m}^2 \text{g}^{-1}$ and CEC of 2.0 cmol kg^{-1}) and a Ca-based montmorillonite (specific surface area of 97.42 $\text{m}^2 \text{g}^{-1}$ and CEC of 120 cmol kg^{-1}). They were purchased from the Source Clay Minerals Repository (Columbia, MO). The two soils were a Hanford sandy loam (coarse loamy, mixed, superactive, nonacid, thermic Typic Xerorthents; Fresno, CA) and a Linne clay loam (fine loamy, mixed, thermic Calcic Pachic Haploxerolls; Chula Vista, CA). Soil samples were collected from the surface (0–15 cm). They were air-dried and ground to pass through a 1-mm sieve.

To quantify soil-sorbed PAM by the modified NBM, organic matter in soil must be removed, since it causes significant positive interference. In this study, the soil samples were burnt at 450 °C for 5 h (14) and cooled in open air before use. Results from thermal analysis showed that the main clay minerals in soil, such as kaolinite, montmorillonite, and illite, lose their hygroscopic water and interlayer cation-bound water under this temperature, but the loss of crystalline water, which affects their crystal structure, occurs only when temperature is above 500 °C (15, 16). Since the loss process of hygroscopic water and cation-bound water is reversible, the chemical properties of organic matter burnt soil are supposed to be similar to the inorganic component of natural soil.

However, the soil aggregate stabilized by organic matter will be destroyed during the combustion. Organic matter burnt soil is used as a close representative of natural soil.

Preparation of Standard Substrate-Borne PAM Samples. The PAM stock solution was prepared by dissolving 1.000 g of PAM in 1000 mL of DI water and aged (25 °C, dark) for 1 week to obtain a uniform solution. Solutions with lower concentrations were prepared by diluting this solution with DI water. The standard substrate-borne PAM samples were obtained by the following procedure: PAM solution was added into the substrate at a solution:substrate ratio of 2:1, and the resultant slurry was thoroughly mixed, oven-dried at 105 °C, and ground. Since PAM has very high sorptive affinity on these substrates (17–19) and all of the polymers left in solution become irreversibly bonded to soil upon drying (10), all the added PAMs are considered to be in sorbed-state on the substrates after the drying process. Samples with a PAM content range of 10–80 μg in 1.0 g of sand and soils or in 0.1 g of cellulose and clays were prepared.

Preparation of Reagents. Preparation of the reagents for the modified NBM is the same as in the NBM for water-borne PAM samples (3), except for some changes in the concentration of bromine water and sodium formate. For convenience and clarity, pertinent experimental details are restated here.

(1) *1 M HOAc–NaOAc Buffer Solution.* Transfer 28.9 mL of glacial acetic acid into 300 mL of DI water, adjust the pH of the solution to 3.5 by dropwise addition of 1% NaOH solution, add 6 mL of oxamide solution (50 mg/L), and then dilute to 500 mL with DI water.

(2) *0.02 M Bromine Water Solution.* Add 1.60 g of liquid Br₂ to 300 mL of DI water, keep stirring until completely dissolved, and then bring the volume to 500 mL.

(3) *0.04 M (for Sand-, Cellulose-, Soil-, and Kaolinite-Borne PAM) and 0.08 M (for Montmorillonite-Borne PAM) Sodium Formate Solution.* Dissolve 1.36 g (0.04 M) or 2.72 g (0.08 M) of sodium formate into 500 mL of DI water.

(4) *0.25% Starch–0.03 M CdI₂ Solution.* Weigh 1.25 g of water-soluble linear starch, wet it with 5 mL of DI water, then add it to 300 mL of boiling DI water, and keep stirring until the solution becomes clear. Cool the solution to room temperature, add 5.49 g of CdI₂, stir to dissolve, bring the volume to 500 mL, and then filter the solution with fine filter paper (such as Whatman no. 5 or no. 42) to remove any insoluble particles.

Analysis Procedure for Substrate-Borne PAM. Weigh accurately a PAM-containing substrate sample (approximately 1.0 g dry weight equivalent for sand and soils or 0.1 g dry weight equivalent for cellulose and clays) into a 20-mL glass vial with a screw cap. Add 2 mL of DI water and 1 mL of HOAc–NaOAc buffer solution and mix thoroughly. Add 1 mL of bromine water solution and mix again. Then mount the vial on a reciprocal shaker and allow reaction for 1 h at room temperature. After that, add 1 mL of sodium formate solution (0.04 M for sand-, cellulose-, soil-, and kaolinite-borne samples or 0.08 M for montmorillonite-borne samples) and mix thoroughly. Exactly 5 min after the addition of sodium formate, add 1 mL of starch–CdI₂ solution to develop a blue complex. Since the reactions occur between the particle surface-sorbed PAM (or its reaction intermediates) and the reagents in the solution, a vigorous mixing by a vortex mixer after addition of each reagent and continuous moderate shaking during reaction time is required to ensure complete reactions. Finally, separate the solution and the substrate particles by centrifuge and then measure the absorbance of the blue supernatant against a reagent blank at 570 nm.

Normally, in the presence of substrate, a background absorbance of 0–0.5 (depending on substrate properties) occurs due to the incomplete reduction of substrate-sorbed bromine by sodium formate. This background absorbance can be measured by analyzing the PAM-free substrate sample and should be subtracted on calculation.

Calibration curves for substrate-borne PAM were obtained by measurements of a series of standard substrate-borne PAM samples. The optimum range of PAM content in each sample is 10–80 μg . When PAM content is out of this range, adjust the sample size by double or half, respectively, to increase the accuracy of the assay.

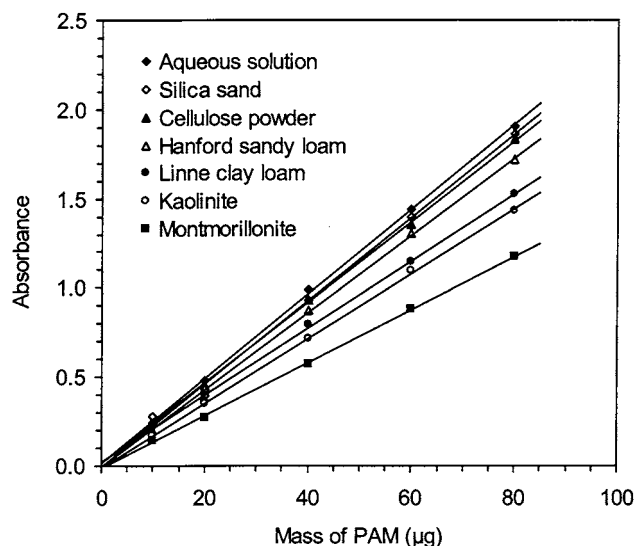


Figure 1. Calibration curves for sorbed-state PAM samples on six substrates. The mass of substrate for sand and soils is 1.0 g and for cellulose and clays is 0.1 g.

RESULTS AND DISCUSSION

Calibration Curves. The calibration curves for sorbed-state PAM samples on the six substrates are shown in **Figure 1**. They were constructed over the range of 10–80 μg of PAM in 1.0 g of sand and soils or in 0.1 g of cellulose and clays. A calibration curve for the aqueous PAM samples subjected to the same analytical conditions with sand-, cellulose-, and soil-borne PAM samples was also included in **Figure 1** for comparative purpose. As shown in **Figure 1**, all the curves pass through the origin (within experimental error) and have good linearity ($R^2 > 0.9991$, $n = 5$).

The slopes of the regression lines in the calibration graph represent the response of the same amount of PAM in different substrates to the NBM. The smaller is the value of the slope, the lower of the sensitivity of the NBM to sorbed-state PAM on the substrate. Compared to the calibration curve for the aqueous PAM samples, the final absorbance for the same amount of PAM in substrate-borne samples was about 62–98% of that in water-borne samples, depending on the properties of the substrate (**Figure 1**). The lower response of substrate-borne PAM to the NBM is attributed to (1) incompleteness of the N-bromination reaction of amide groups in some sorbed-state PAM molecules due to possible steric hindrance and (2) sorption of the final starch–triiodide complex on substrates. For the montmorillonite-borne samples, besides these two possible reasons, the much lower slope of the calibration curve is also due to the facilitation of the side reaction which consumes the critical BrOH (reaction 5) by the higher concentration of sodium formate used for removal of excess bromine water. However, the quantification of PAM is not affected because the individual calibration curve for each substrate is established on its standard substrate-borne PAM samples.

Accuracy, Reproducibility, and Sensitivity. Substrate-borne PAM samples with two levels of content (10 μg and 40 μg in 1.0 g of sand and soils and in 0.1 g of cellulose and clays) were analyzed according to the outlined procedure in four replicates. The results are listed in **Table 1**. For the 10 μg PAM standard, the relative standard deviations were <4.8% for sand-, cellulose-, and soil-borne samples and <7.5% for clay-borne samples, and the recoveries ranged from 95.8% to 103.7%. For the 40 μg PAM standard, the relative standard deviations were

Table 1. Accuracy and Reproducibility for Quantification of Substrate-Borne PAM by the Modified NBM

substrates	recovery \pm RSD ^a (%)	
	10 μ g of PAM	40 μ g of PAM
sand	100.1 \pm 3.3	100.4 \pm 2.2
cellulose	99.2 \pm 4.8	99.5 \pm 1.8
Hanford sandy loam	95.8 \pm 3.3	100.9 \pm 2.0
Linne clay loam	101.2 \pm 4.5	96.8 \pm 2.6
kaolinite	99.6 \pm 4.2	99.6 \pm 4.8
montmorillonite	103.7 \pm 7.5	102.9 \pm 3.3

^a Relative standard deviation, calculated from four replicates.

<2.6% for sand-, cellulose-, and soil-borne samples and <4.8% for clay-borne samples, and the recoveries ranged from 96.8% to 102.9%. These results suggest that the accuracy and reproducibility of the proposed method could meet the general requirement of most research and evaluation work on PAM application.

Since the quantification of substrate-borne samples involves the process of two-phase interactions (between the particle surface-sorbed PAM or reaction intermediates and reagents in aqueous solution), the inconsistency in mixing manner and strength between samples greatly affects the reproducibility of the method. During the mixing process, attention should be devoted to minimizing these differences. Other sources of errors come from the inaccuracy in controlling the reduction time of excess bromine by sodium formate and regular gravimetric and volumetric operations.

The lower detection limit of this modified NBM method varies with the properties of substrates. Apparent loss of sensitivity of NBM occurs on clay and fine soils because of their high sorptive affinity to analytical reagents and reaction intermediates. For sand- and cellulose-borne samples, the lower detection limit is approximately 1 μ g and for soil- and clay-borne samples about 4 μ g. The optimum range of PAM content in each sample is 10–80 μ g. Limitations of this method include (1) no organic matter (more accurately, no primary and secondary amides that respond to the NBM) in substrates and (2) variation of sensitivity on substrates and degrees of hydrolysis of PAM (4). However, the method offers a considerable promise for determining particle surface-borne PAM on a variety of substrates with satisfactory accuracy and reproducibility.

ABBREVIATIONS USED

PAM, polyacrylamide; NBM, N-bromination method; DI, deionized.

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