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Improved measurement of formaldehyde in water-soluble polymers by high-performance liquid chromatography coupled with post-column reaction detection

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Abstract

An improved methodology for the analysis of free formaldehyde in water-soluble polymers used for industrial water treatment is reported. Previously, derivatization prior to HPLC or colorimetric techniques has been used. The data generated by these approaches are suspect in that the derivatizing agent can react with the polymer or other sample components to produce high results. Post-column reaction derivatization is applied after separation of the free formaldehyde from the product interferences. The type of polymer product analyzed influences the choice of column(s). The degree of high bias of the commonly used 2,4-dinitrophenylhydrazine pre-column derivatization is reported and the results are compared to those with the post-column reaction for two polymer products. This method, being more selective, should be applicable to any polymer containing formaldehyde.

Keywords: Derivatization, LC; Formaldehyde; Polymers; Dinitrophenylhydrazine; Nash reagent

1. Introduction

Formaldehyde is a raw material for many water-soluble polymers used in industrial water treatment. Some are condensation polymers where formaldehyde is a monomer [1,2], while others use formaldehyde for polymer backbone modification [3]. Residual formaldehyde values must be below 1000 ppm in the product or US Environmental Protection Agency warning labels must be attached on the product container and on the Material Safety Data Sheet [4]. Levels greater than 1000 ppm pose potential health hazards. It is important, then, that the analytical method used for these measurements be highly accurate, otherwise the product could be either a health hazard or unnecessarily be labeled as one.

Previously, formaldehyde has been measured by a variety of approaches: titration [5], colorimetry [6], and NMR [7]. For trace amounts in the ppm or ppb range, HPLC or GC must be applied. For chromatography, formaldehyde must be derivatized to enable sensitive detection. The most common derivatizing agents are dinitrophenylhydrazine (DNPH) [8] and the Nash reagent [9], because they are well-characterized reactions and provide a highly sensitive chromaphore for ultraviolet or fluorescence detection.

This work set out to achieve selective detection of free formaldehyde in water-soluble polymers and to avoid reaction of derivatizing agents with active polymer or impurities. Many analytical aldehyde derivatizations for chromatography are carried out prior to injection, because minimal instrumentation is

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needed to perform the analysis and aldehydes are more easily separated in the form of derivatives. Pre-column derivatizations, however, can produce high-biased results if the reagent also reacts with the aldehyde bound in components of the product. Post-column detection of formaldehyde by the Nash reaction in the presence of antimicrobials has been previously reported [10], but achieving significant retention of formaldehyde is difficult due to its neutrality and high polarity. A modified approach presented here is to retain the formaldehyde-incorporating components of the product and allow the free formaldehyde to be eluted and detected in or near the void volume. Comparative analyses between this Nash post-column scheme and pre-column DNPH will be presented for two water-treatment polymers to illustrate the selectivity enhancements.

2. Experimental

2.1. Chemicals

Standards of aldehydes/ketones and hydrogen-sulfite adducts were available commercially. Formaldehyde (37% in water/methanol), acetaldehyde, propionaldehyde, and butyraldehyde (Aldrich, Milwaukee, WI, USA), acetone (EM Industries, Gibbstown, NJ, USA) and hydroxymethanesulfonic acid and aminomethanesulfonic acid (Aldrich) were used as received. 2,4-Dinitrophenylhydrazine (DNPH, Aldrich) was recrystallized in acetonitrile prior to use. Pentanedione (Aldrich), ammonium acetate (EM) and glacial acetic acid (EM) were used as received. HPLC analyses were performed with HPLC-grade water (Millipore, Bedford, MA, USA) and acetonitrile (EM). Buffer solutions were made from reagent-grade dibasic sodium phosphate, sodium sulfate, and concentrated phosphoric and sulfuric acids (EM).

Samples of polymer products were available at Nalco and consisted of experimental batches of the condensation polymer of formaldehyde and dicyandiamide (Gamus PL100) and experimental and production lots of Prism brand polymer. All polymers were dissolved 1 g per 100 mL in deionized water and filtered through 0.1-μm Millex VV filters (Millipore).

Stock standard solutions of the aldehydes and acetone were made to concentrations of 1000 ppm in water. Serial dilutions in water were made from the stock solutions in the concentration ranges of 1 to 100 ppm. The Nash reagent was prepared by dissolving 154 g of ammonium acetate in roughly 500 mL of deionized water, followed by 2.5 mL of glacial acetic acid and 2 mL of pentanedione. After vigorous mixing, the solution was transferred to a 1-L volumetric flask, followed by 450 mL of water. The pH of the solution was adjusted to 5 with glacial acetic acid, and the mixture diluted to the mark with water and filtered through a 0.45-μm HV filter.

2.2. HPLC conditions

Liquid chromatography for the pre-column analyses was performed with a Waters (Milford, MA, USA) 600E quaternary gradient pump, an Alcott (Norcross, GA, USA) 708 autosampler, a Waters 996 photodiode-array UV detector, and a Waters Millennium 2010 data system. The columns were a Hypersil (Bellefonte, PA, USA) ODS (5 μm), 25 cm×4.6 mm and a guard column. The mobile phase was mixed by pump from initially acetonitrile–water (35:65) to acetonitrile–water (75:25) with a linear gradient. Solvents were filtered through 0.45-μm HV before use. The injection volume was 100 μL and primary detection was at 360 nm.

For post-column analyses, two Shimadzu (Kyoto, Japan) LC-10AD pumps, an Alcott 708 autosampler, an Applied Biosystems (Ramsey, NJ, USA) 520 post-column reactor, a Shimadzu SPD-6A UV detector, and a Shimadzu RF-530 fluorescence (FL) detector were used. The columns used were Zorbax SCX and SAX (Agilent Technologies, Wilmington, DE, USA) and Whatman Particil 5 ODS-3 (Clifton, NJ, USA). Mobile phases were buffers made from dibasic sodium phosphate and filtered through a 47-mm, 0.45-μm HV membrane (Millipore).

2.3. Pre-column derivatization

The reaction was performed by mixing 1 g of the polymer dilution in water with 4 g of 0.05 *M* (pH 1.8) sodium phosphate buffer and 5 g of DNPH solution (0.1 g in 100 mL acetonitrile). After reaction at ambient temperature for 10 min, the mixture was filtered through a 0.45-μm HV filter before injection.

2.4. Post-column derivatization

The post-column reaction was carried out in a 0.5-mL PTFE reaction coil thermostatted at 70°C. The derivatizing reagent was mixed with mobile phase at a flow ratio of 0.8 to 1.0 mL/min in a mixing tee ahead of the reaction coil.

3. Results and discussion

3.1. Post-column reaction detection

A block diagram of the configuration of the post-column reaction (PCR) HPLC instrumentation for this work is shown in Fig. 1. The apparatus consisted of two parallel pumps, with one delivering chromatographic mobile phase and the other supplying reagent to the post-column reactor. After separation of the sample mixture by the analytical column, a UV detector first monitored elution of the polymeric components. Formaldehyde was eluted in the void volume of the system and was detected as a single fluorescence peak after reaction with Nash reagent. The fluorescence detector may be substituted with another UV detector, but fluorescence was used here for increased selectivity and sensitivity.

For this approach to be effective, careful selection of the analytical column used to separate the active polymer and impurities must be made. This can be thought of as an automated solid-phase extraction where the impurities are retained to allow elution of the analyte. Prior knowledge of the chemical composition of the polymer product is vital to the success of the analysis. As will be seen later, more than one column type in series might be necessary for the measurement to be successful. Since the majority of water-soluble polymers for industrial water treatment are charged, ion-exchange columns are the most useful. In the event, however, that uncharged compounds might interfere with formaldehyde, reversed-phase columns may also be employed in series.

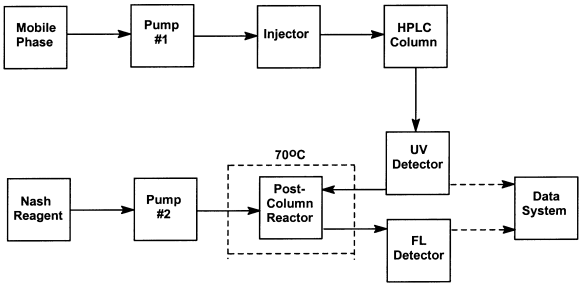

Fig. 1. Block diagram for the configuration of the HPLC post-column detection system used in this work.

Nash reagent was chosen as the derivatizing agent for this work. While many other reactions could be used [11], the Nash reaction was found to be highly selective for formaldehyde with ammonium acetate as the amine source. No other aldehydes were found to respond under these PCR conditions. The optimum pH for the reaction at pH 5 was also close to the chosen mobile-phase pH for both cationic and anionic exchange so that changes in the reaction buffer capacity did not occur. Another attractive feature is that Nash reagent does not form a fluorescent species until it reacts with formaldehyde, and this contributes a low background and high sensitivity.

For any analysis of formaldehyde, the chemical form of the aldehyde detected in the analysis must be clarified. While a standard formalin solution is listed as being 37% (w/w) formaldehyde in water and methanol, the formaldehyde exists in its hydrated form, methylene glycol, and polymethylene glycol with up to seven formaldehyde units [7]. It is generally accepted that derivatizing agents like DNPH and Nash reagent react to completion with methylene glycol and polymethylene glycol, and it is assumed, therefore, that the term ''free formaldehyde'' refers to monomeric formaldehyde, methylene glycol, and polymethylene glycol. An example of the output of the PCR HPLC system is shown in Fig. 2, showing overlaid chromatograms of the PCR and UV signals for a formaldehyde standard. The tracings are offset by roughly 1 min, so that the formaldehyde peak actually occurs at the labeled void time (t_0) of the UV plot. No other peaks are observed with the PCR signal, and it is assumed that all formaldehyde species are eluted concurrently.

3.2. Cyanoguanidine–formaldehyde polymer

The first example presented is the cyanoguanidine–formaldehyde polymer. The synthesis scheme of the polymer [2] (Fig. 3) shows a

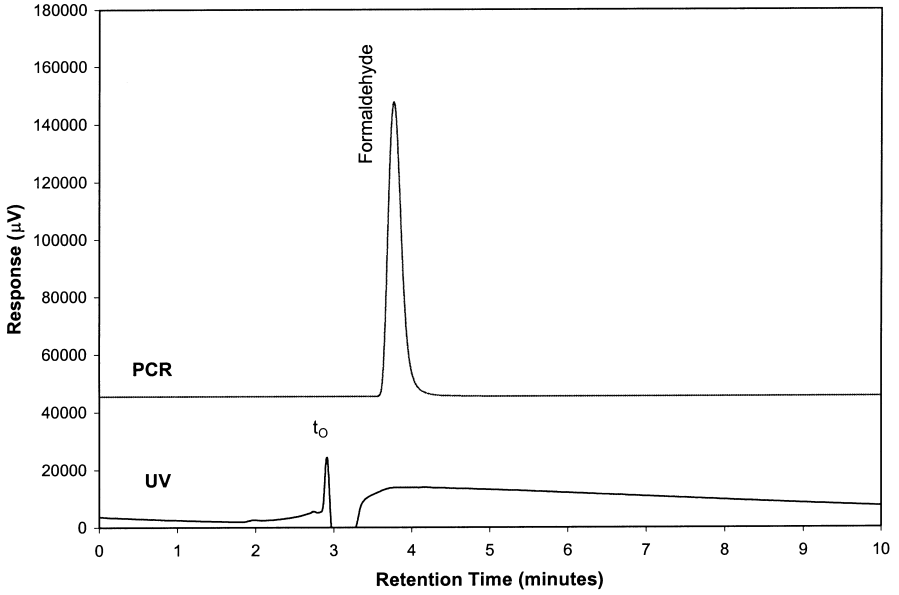

Fig. 2. Overlaid HPLC chromatograms of the Nash post-column reaction and direct UV signals for a 50 ppm formaldehyde standard. Analytical column, Zorbax SCX, 25 cm×4.6 mm; mobile phase, 0.05 *M* sodium phosphate (pH 6); flow-rate, 1.5 mL/min; injection volume, 100 μL. Detection (upper trace) post-column reaction, (lower trace) direct UV at 205 nm.

cationic backbone with pendent methylol groups that might react with derivatizing reagent. Except for the methylol groups released to give free formaldehyde, no material other than cationic polymer should be present in the product. A cation-exchange column was therefore chosen for this analysis to remove the polycation from the free formaldehyde.

Fig. 4 illustrates the stacked post-column reaction and direct UV chromatograms of the cation-exchange analysis. The PCR tracing in Fig. 4a shows a large formaldehyde peak and smaller peaks after 7 min. A C_{18} column was also tried for this polymer, but no change was observed in the formaldehyde or the polymer peaks. Upon comparison of PCR retention times with the UV tracing in Fig. 4b it was concluded that the small peaks in the PCR could have originated from the polymer, which does not exhibit a significant response to Nash reagent. Since the formaldehyde levels for this material are high (>2000 μg/g), this analysis could conceivably be

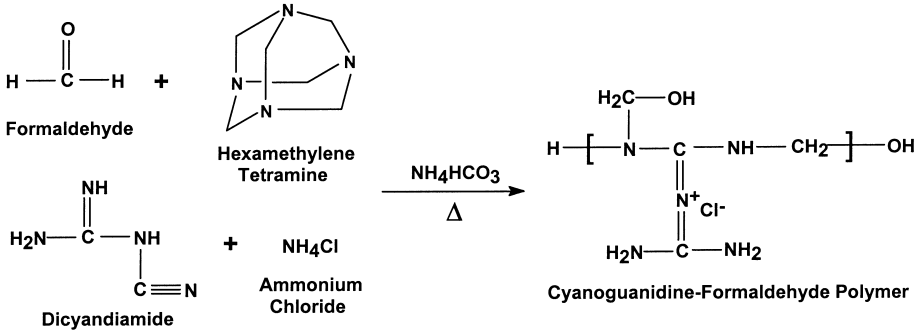

Fig. 3. The synthesis of cyanoguanidine–formaldehyde condensation polymer.

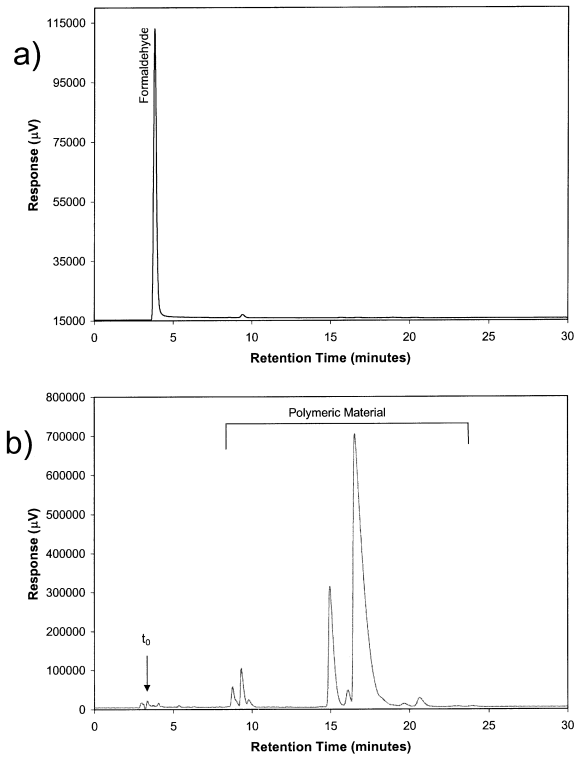

Fig. 4. Stacked HPLC chromatograms of (a) the Nash post-column reaction and (b) direct UV signals for an experimental batch of cyanoguanidine–formaldehyde polymer. Conditions are the same as in Fig. 2.

performed in pre-column mode without greatly interfering with the result. Should this polymer be made to a higher monomer-to-polymer conversion, however, the formaldehyde content would be lower and the polymer response would then become significant.

3.3. Prism polymer

The second example is that of a sulfomethylated polyacrylate, or Prism brand polymer [3], where product impurities are the source of high bias. As seen in Fig. 5, formaldehyde, hydrogensulfite ion, and ammonia are engaged in an equilibrium with hydroxymethanesulfonic acid (HMSA) and aminomethanesulfonic acid (AMSA) [12]. Primary amide groups on the polymer become transamidated by AMSA to produce secondary sulfomethylated amides. When an excess of hydrogensulfite is present in the product, the equilibrium is forced to the AMSA side and consumes the formaldehyde to maximize transamidation. Despite the excess hydrogensulfite, though, formaldehyde, hydrogensulfite, HMSA, and AMSA exist in equilibrium with each other in the product. At an HPLC mobile-phase pH of 6, AMSA would be in a neutral net charge zwitterionic state and would be eluted in the void volume of an anion-exchange column. Therefore, it was necessary to combine both a reversed-phase C_{18} column with anion exchange to resolve AMSA and HMSA (as well as polymer) from formaldehyde.

Fig. 6 shows the stacked post-column reaction and direct UV chromatograms of the C_{18}/anion-exchange analysis. The PCR tracing in Fig. 6a shows the resolution of formaldehyde and AMSA near the labeled UV void time in Fig. 6b and the later elution of HMSA. After injection of HMSA and AMSA standards, no UV response was detected while no PCR response is evident for the polymer components of the product. Depending on the specific application, the lengths of the C_{18} and anion-exchange

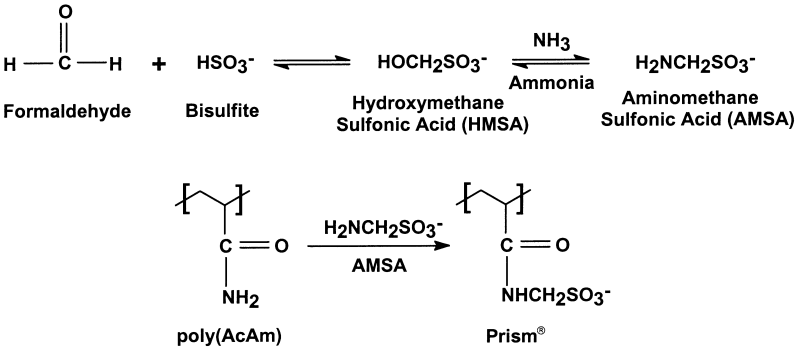

Fig. 5. The transamidation of polyacrylamide polymer to produce Prism polymer.

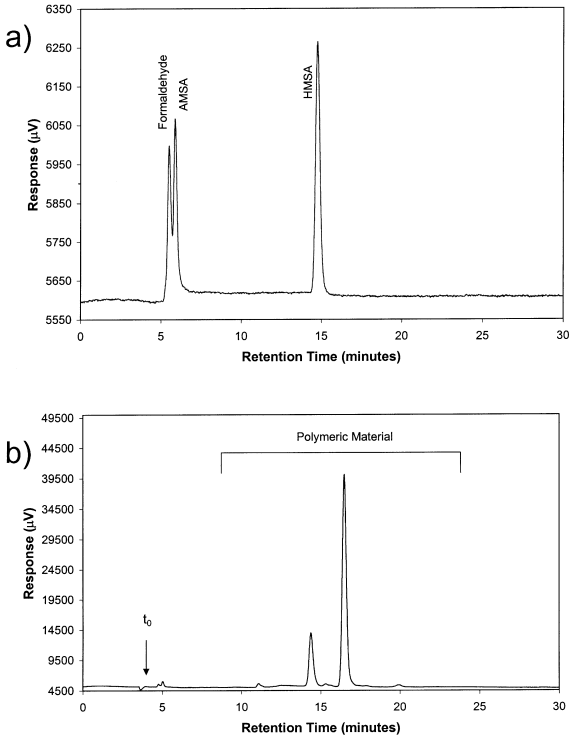

Fig. 6. Stacked HPLC chromatograms of the Nash post-column reaction and direct UV signals for an experimental batch of Prism polymer. Analytical columns: Whatman Particil 5 ODS-3, 10 cm×4.6 mm, plus Zorbax SAX, 25 cm×4.6 mm. Mobile phase, 0.01 *M* sodium phosphate, pH 6; flow-rate, 1.5 mL/min; injection volume, 100 µL. Detection: (a) post-column reaction, (b) direct UV at 205 nm.

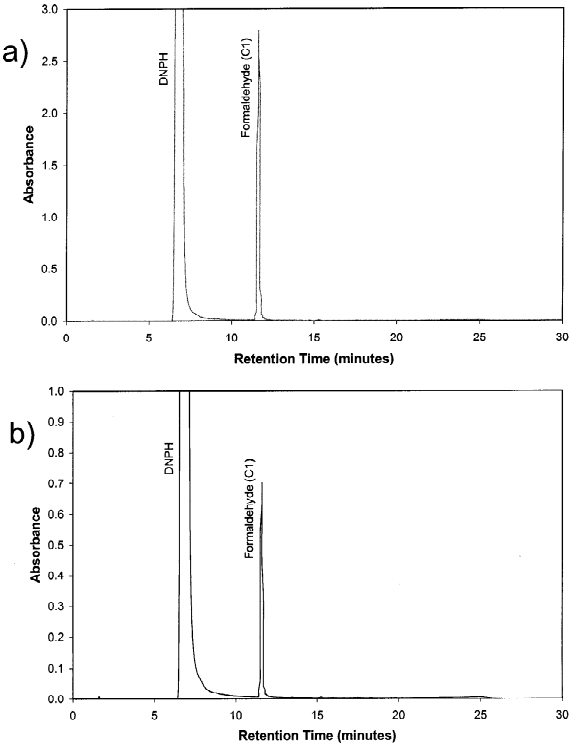

Fig. 7. Stacked HPLC chromatograms of the DNPH pre-column analysis of the polymers studied in this work. Analytical column: Hypersil ODS, 25 cm×4.6 mm. Mobile phase, acetonitrile–water (35:65) plus a linear gradient to 90:10; flow-rate, 1.5 mL/min; injection volume, 100 µL; detection, UV at 360 nm. Samples: (a) cyanoguanidine–formaldehyde polymer, (b) experimental Prism polymer.

columns could be manipulated to customize the resolution of the formaldehyde and AMSA equilibrium components. Removal of the C_{18} column from the PCR configuration, though, produces two to 10 times higher formaldehyde results due to coelution with AMSA.

3.4. Comparison of pre- and post-column analysis

To determine the impact of pre-column derivatization on the final formaldehyde results for the polymers exemplified in this work, a direct comparison was made with PCR on a common sample set. The DNPH method was chosen since it is a commonly used reagent [8]. Fig. 7 illustrates the chromatograms following the DNPH method for both the C–F and Prism polymers and shows no significant peaks other than formaldehyde. What is lost by this approach is the direct knowledge of whether the formaldehyde is free or stripped from other species in the product.

However, the polymer attack by the derivatizing agent could be estimated kinetically. Free formaldehyde under the conditions in this work completely reacts to form the DNPH hydrazone within 15 min. One could speculate that the measured formaldehyde was being stripped from the active polymer if the formaldehyde result increases significantly beyond the 10-min reaction time. This can be determined by performing duplicate injections of the same DNPH reaction products and observing whether the result after the second injection is more than 5% higher than the first. If low levels of small impurities like HMSA and AMSA are present, though, this kinetic approach would not detect them.

Table 1
Comparative results of the analysis of cyanoguanidine–formaldehyde (C–F) and Prism polymers by the Nash post-column and DNPH pre-column methods (in ppm)

Polymer identity	Pre-column	Post-column
Prism — production	600	2
Prism — experimental No. 1	2700	30
Prism — experimental No. 2	2600	60
C–F	11 000	3200
Average RSD (%)	3.0	4.5

A final summary of the comparison of the PCR and DNPH methods is presented in Table 1. For all cases, the post-column result is generally lower than that for DNPH by a factor of 3 to 300. The pooled relative standard deviation for all of the analyses is given in the bottom row of the table and is similar for both methods. Recoveries for both methods were also over 90% for the two polymer products.

4. Conclusions

Post-column reaction has been shown to provide a more selective detection of free formaldehyde in water-soluble polymers than the pre-column DNPH reaction. With the proper choice of analytical column and use of a highly selective reaction, PCR can separate formaldehyde from not only active polymer, but also from product impurities (AMSA in the case of Prism polymers). PCR yielded values three to 300 times lower than the DNPH pre-column reaction for the two polymers studied here. It is a viable alternative for the detection of residual formaldehyde in water-soluble polymer products. It could be applied to other formaldehyde-containing polymers as well.

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