Automations, Inc.), for the loan of the DC detector and for technical assistance in its operation and to M. Alper (ES Industries) for the loan of the TENF column.

LITERATURE CITED


Quantitative Determination of Partially Hydrolyzed Polyacrylamide Polymers in Oil Field Production Water

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Partially hydrolyzed polyacrylamide (PHPA) can be determined in a concentration range of 1 ppm to 100 ppm in dirty oil field water with a precision of ±1% and a lower limit of detection of 10 ppb. Solutions of high molecular weight PHPA are analyzed by high-performance size exclusion chromatography with 100 Å pore size, diol bonded phase silica columns eluted with a 0.1 M sodium perchlorate and 0.005 M pentanesulfonic acid paired ion reagent solution. UV detection at 190 nm wavelength is used for quantitation. Polymer solutions must be shear degraded to prevent column plugging. Analyses of water produced by both polymer and polymer plus sulfonate surfactant floods are illustrated.

Partially hydrolyzed polyacrylamide (PHPA) is commonly used for mobility control in surfactant-based enhanced oil recovery processes (1) and for polymer augmented water floods. A fast, reliable analytical method for measuring PHPA is needed to monitor these processes. Unfortunately, the necessary measurement of trace levels of polymer in complex oil field fluids has not been a simple analytical problem because these samples normally contain materials which show serious interference when using previously reported procedures (2–9). While the amide function of PHPA strongly absorbs UV light, \( \lambda_{max} = 185 \text{ nm} \) (10), a direct spectrophotometric method is possible if the polymer could be isolated. We have found that high molecular weight PHPA normally used in oil recovery processes can be separated from nearly all interferences by high-performance size exclusion chromatography. As a result, we have developed and field tested a simple chromatographic procedure which can measure PHPA in oil field waters with a precision of less than 1% relative standard deviation in a range of 1 ppm to 100 ppm with a lower limit of detection of 10 ppb. No interferences have been observed.

The method is relatively insensitive to the carboxylate function of hydrolyzed polyacrylamides.

EXPERIMENTAL SECTION

The chromatograph consisted of a Spectra Physics Model SP8770 isocratic pump, a Hewlett-Packard Model 1040A scanning diode array spectrophotometric detector, a Spectra Physics Model SP4270 integrator with an external events cartridge, and a Valco Model EC10W electronically operated sample injection valve fitted with a 26-µL sample loop. The column was Synchronpak GPC 100, 250 mm \( \times 4.6 \text{ mm i.d.} \) packed with diol bonded phase 10-µm silica particles (Synchron, Inc.). The column was eluted at a flow rate of 1 mL/min at ambient temperature. The solvent was 0.1 M NaClO4 (GFS Chemicals Catalog no. 92) and 0.005 M n-pentanesulfonic acid (Waters Associates Catalog no. 84198) prepared with high-purity water (Burddick & Jackson). Absorption at a wavelength of 190 nm was selected for quantitation. The instrument was standardized with dilute solutions of the polymer in 0.1 M NaClO4 and preserved with 0.1% NaN3. A high-speed homogenizer (Tekmar Co. SDT Tissumizer) was used to shear and disperse the polymer for these preparations.

Emulsion samples were extracted with chloroform (Burddick & Jackson) and the separated aqueous phases were used for analysis. For convenience, 10 mL of sample was shaken with 10 mL of chloroform, CHCl3, in a 6-dram vial with a Polyseal cap. Sonication of the mixture often speeds up the phase separation. Because very high molecular weight polymers will plug high-performance columns (11), all polymer samples must be mechanically sheared. Normally, polymers which occur in production water will not plug the columns. Sheared samples were then filtered through a Sep-PAX C18 cartridge (Water Associates part no. 5190) followed by a 0.45-µm membrane type filter (Gelman Acro LC3A).

DISCUSSION AND RESULTS

Because the amide function of PHPA strongly absorbs UV light molar absorptivity \( \epsilon = 2900 \) at 192.5 nm wavelength (10), a direct spectrophotometric method is possible if the polymer could be isolated from UV absorbing interferences. Since
polymers normally used for enhanced oil recovery are very large molecules and most interfering species are relatively small molecules, size exclusion chromatography (SEC) is an attractive technique. Previous attempts to use SEC, however, have failed for several reasons. Columns tend to become plugged by polymer adsorption and entrapment (11). Adsorption also causes broad, tailing peaks which are difficult to integrate. Older UV detectors could not be operated at the short wavelengths necessary to detect acrylicamide polymers.

Herman, Field, and Abbott (12) reported excellent recovery of pentanesulfonic acid solution, normally used for paired-ion chromatography (PIC), gave much sharper peaks which could be used for quantitation, Figure 3.

We have not determined the exact reason for this improvement. Presumably the sulfonic acid either deactivates residual polar sites on the column packing or it simply adsorbs, creating a negative charged surface which should repel the negative carboxylate groups on PHPA. On the other hand, negative carboxylate groups on PHPA. On the other hand, the highest molecular weight PIC reagent gave much sharper peaks which could be used for quantitation, Figure 3.

We have not determined the exact reason for this improvement. Presumably the sulfonic acid either deactivates residual polar sites on the column packing or it simply adsorbs, creating a negative charged surface which should repel the negative carboxylate groups on PHPA. On the other hand, it could be altering the hydrodynamic volume of the polymer in solution so that polymer permeation into the 100-A pores does not occur. Inferior results were obtained when methane, ethane, propane, and butanesulfonic acids were substituted for the pentanesulfonic acid PIC reagent. Likewise, potassium dihydrogen phosphate, KH₂PO₄, also gave inferior results. We have not tested other solvent modifiers. So long as the samples are mechanically sheared and filtered, we have not had column plugging problems.

Analyses of samples prepared from serial dilutions of a standard polymer solution indicated a nearly linear response from 5 ppm to 100 ppm with a precision of better than ±1% relative standard deviation, Table I. All the polymers we have analyzed do not permeate the 100-A pores with the PIC solvent. Even a sample extensively sheared for 3 h in a high-speed 20000 rpm tissue homogenizer would not permeate the pores. As previously mentioned, we have found that high molecular weight polymers must be mechanically sheared in order to prevent column plugging and that either blending or homogenizing the samples is an important part of the procedure. On the other hand, we found that dilute hydrogen peroxide readily degrades PHPA into fragments small enough to permeate the pores. The chromatogram of a sample partially degraded with hydrogen peroxide, Figure 4, demonstrates a typical size exclusion mechanism. Both the total exclusion and the total permeation volumes are clearly defined.

RESULTS

A few illustrations with real samples should demonstrate the utility of the procedure and also point out typical problems encountered.

**Table I. Calibration and Response**

<table>
<thead>
<tr>
<th>polymer concn, ppm</th>
<th>taken</th>
<th>found</th>
<th>std dev</th>
<th>% error</th>
</tr>
</thead>
</table>
| 0.10              | 0.091 | ±0.0046 | -9.0
| 4.00              | 4.01  | ±0.044  | +0.25   |
| 20.0              | 19.7  | ±0.16   | -0.05   |
| 40.0              | 32.9  | ±0.13   | -0.15   |
| 150               | 144   | ±0.26   | -4.0    |

*Average response factor = 42.068 counts/ppm. Relative standard deviation = ±0.383%. Average of 10 runs, results based on the following calibration: 100 ppm solution run 10 times.*

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RESULTS

A few illustrations with real samples should demonstrate the utility of the procedure and also point out typical problems encountered.
The first sample was produced by a typical polymer flood. The oil and water phases were clearly separated with no evidence of emulsions. The yellow water phase, however, contained sulfides in addition to the usual treating chemicals. Upon exposure to air, the sample developed a milky gray turbidity caused by the oxidation of sulfides to elemental sulfur. An aliquot was prepared for analysis by simply filtering through a Sep-PAK C18 cartridge. The chromatogram, Figure 5, shows a large well-defined peak corresponding to 66 ppm polymer. This same sample was also analyzed by a Chlorox bleach turbidity method (2) and 150 ppm polymer was found. The high value for the turbidity method is caused by the sulfides which must be removed, not always an easy task. On the other hand, sulfides do not interfere with the chromatographic procedure. A similar sample with a much higher sulfide content and no detectable polymer spiked with 10 ppm polymer gave 9.96 ppm by the chromatographic procedure.

A second sample produced from the same flood but a different well was run and showed about 0.6 ppm polymer, Figure 6. Note sensitivity changed to 0.05 absorbance units full scale. No polymer was detected, <10 ppm, by the turbidity method. Because this sample did not contain sulfides, both methods should give comparable results.

The third example is derived from a viscous emulsion produced by a sulfonate surfactant/polymer flooding project. The water phase was separated by extracting the emulsion with an equal volume of chloroform. Interestingly, we have found that sonication speeds the phase separation in the extraction. The water phase was then filtered through a Sep-PAK cartridge. Although the water still contained hydrophobic sulfonates, the chromatogram, Figure 7, indicated no interference for the polymer and that this sample contained either very little or no polymer. The original emulsion was spiked with 50 ppm polymer and the procedure repeated. An excellent response was obtained, Figure 8, demonstrating that low levels of polymer can be determined in an extremely complex sample with this simple procedure.

ACKNOWLEDGMENT
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LITERATURE CITED
Simultaneous Determination of Pyridoxal and Pyridoxal 5-Phosphate in Human Serum by Flow Injection Analysis

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The sequential, simultaneous, and differential-kinetic determination of pyridoxal (Py) and pyridoxal 5-phosphate (Py5P) based on the reaction of these compounds with cyanide, has not been suggested in any of the above-mentioned papers. At most they reported the manual methods (9). The determination of both species (Py and Py5P) in the same samples has not been suggested in any of the above-mentioned papers. In a previous paper (8), we suggested fluorometric methods for the determination of pyridoxal and ita phosphate (Py5P), respectively. The calibration curves cover the range of $10^{-4}$ to $10^{-3}$ M for both compounds, with sampling rates of 30 samples/h and relative standard derivation values less than ±1%. These species have been determined in serum samples at the $10^{-6}$ M level with an average error of ±10–15%.

The determination of B$_6$ vitamers and their derivatives is of great interest, especially in clinical chemistry. Among them, the determination of pyridoxal (Py) and its phosphate (Py5P) has received much attention. The most common technique for the determination of both compounds is fluorometry, involving the use of Zn–glycine (1), formation of hydrazine derivatives (2), direct fluorescence measurements of these substances after a chromatographic separation (3, 4), reductive amination with methyl anthranilate and sodium cyanoborohydride (5) or reaction with cyanide (6) to yield 4-pyridoxolactone and 4-pyridoxic acid 5-phosphate (Py and Py5P, respectively) (7). On the basis of this last reaction and by use of flow injection analysis, FIA, in a previous paper (6), we suggested fluorometric methods for the determination of both pyridoxal and pyridoxal 5-phosphate. Both are sensitive methods, with wide linear calibration ranges ($2.5 \times 10^{-8}$ to 1.0 $\times 10^{-3}$ M), good precision (relative standard deviation 0.5%), a sampling rate of 25 samples per hour, and a high tolerance level for species such as NAD, normally an interference in the manual methods (9). The determination of both species (Py and Py5P) in the same samples has not been suggested in any of the above-mentioned papers. At most they reported the determination of one of them (Py), hydrolysis of Py5P, and determination of the sum (10).

Flow injection analysis offers the chance of determining both species in a mixture without a prior separation by several methods based on the different working conditions or difference of completion of the indicator reaction with the use of a very simple manifold and a flow cell in a single detector.

The indicator reaction chosen for the development of determinative methods of these vitamers in mixtures has been the above-mentioned oxidation to 4-pyridoxolactone and 4-pyridoxic acid 5-phosphate under the catalytic action of cyanide ion. On the basis of this reaction and after checking that both products are suitably formed at a pH close to neutrality, but showing maximal fluorescence at very different pH values, a sequential method involving the use of a simple manifold with a diverting valve which provides carriers with cyanide of alternative pH’s for the determination of one or the other compound has been applied. The sample injection into each carrier provides peaks in which the contribution of one of the products is maximal and that of the other is minimal or nil. On the basis of the different oxidation rate of Py and Py5P, two methods are suggested with the use of a manifold with splitting of the flow into two channels (with different geometrical and hydrodynamic characteristics) which merge prior to arriving at the detector. At the splitting point the sample is divided into two parts which, due to the characteristics of the two channels, reach the detector at different times, yielding a two-peak diagram per sample injected. In each of these peaks the contribution of each product to the analytical signal is different. This reaction-rate difference has been taken advantage of in two different ways providing the measurement of the native fluorescence of one of the compounds (Py), which implies its maximal contribution to the first peak (short reactor and minimal dispersion) and that of the oxidation product of the other (Py5P), with which its contribution to the second peak will be higher (longer reaction time). In the differential-kinetic method the working experimental conditions have been optimized in order to make both oxidation reactions feasible, but with the maximal possible rate difference between them.

**EXPERIMENTAL SECTION**

Reagents. The stock solutions used included aqueous solutions of pyridoxal ($1 \times 10^{-3}$ M), pyridoxal 5-phosphate ($1 \times 10^{-3}$ M), phosphate buffer (0.6 M) at several pH values, 0.9 M hydrochloric acid, and an aqueous 1.000 g/L solution of potassium cyanide.

**Apparatus.** A Perkin-Elmer 650-10 S spectrofluorometer, equipped with a Hellma 176.52-QS flow cell (inner volume 25 µL) and connected to a Radiometer REC-90 recorder, was used. Gilson Minipuls-2 and Ismatec e-840 peristaltic pumps, a Tectator L100-1 injection valve, a Rhodyne 5301 three-way valve, a Tectator TM III chemilom, and the accessory instruments Radiometer PHM-82 pH meter and Selecta 382-S thermostat were also used.