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Fate of superabsorbents in the environment

Analytical techniques

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ABSTRACT

The Analytical and Environmental Committees of the Institute of Polyacrylate Absorbents (1330 Connecticut Avenue, N. W., Washington, DC 20036, U.S.A.), of which Dow is a member, requested the development of specific and sensitive analytical techniques to monitor the movement of soluble polyacrylates through soils. Three analytical techniques are explained that can be used to monitor effluents from columns or in studies where batch extraction of the soils are conducted. Concentrations of polyacrylic acid were studied from the ppm range for nuclear magnetic resonance spectroscopy and size-exclusion chromatography to the sub-ppm range for derivatization pyrolysis–gas chromatography. The soils under study were a sandy soil, a londo soil, and a clay type of soil. The investigation explained in this report was conducted with batch extractions. Included in this report is a soil adsorption capacity study that showed behavior opposite to what was expected to be the adsorption capacity of the soils. Also included are pH studies of the soils.

INTRODUCTION

The increased use of disposable diapers containing polyacrylate superabsorbents and their disposal in landfills has focused attention on the possible movement of the soluble polymer fraction and its penetration of soils. In the past, there have been reports[1,2] of studies designed to understand the dynamics of the movement of the soluble fraction of superabsorbent polymers. These studies were conducted with ^{14}C-tagged polyacrylate polymers, which made the study very expensive. Another study[3] used a Total Organic Carbon analyzer to monitor the effluent of a column loaded with soil to determine the movement of soluble polymer. The need to make this type of study more specific and available to investigators with limited resources prompted an investigation that resulted in the development of techniques that are specific and very sensitive.

The techniques investigated included size-exclusion chromatography (SEC) de-

rivatization pyrolysis–gas chromatography (Py–GC) with dual-column chromatography[4,7] and nuclear magnetic resonance (NMR) spectroscopy. Difficulties associated with the movement of polyelectrolytes through solids and the interactions these polymers will exhibit when contacted with water and soils have been explained before[5,6]. To add to these difficulties it was requested that the procedures developed be sensitive enough to detect the soluble fraction of the superabsorbent polymer at the sub-ppm level.

EXPERIMENTAL

Size-exclusion chromatography

Instrumentation. Column, 1 TSK G1000 PW; eluent, 0.3 *M* NaCl, 0.34 *M* Na_2HPO_4, pH adjusted to 6.8 with 3% H_3PO_4 and then filtered through a 0.1-μm filter; flow-rate, 1 ml/min; injection volume, 200 μl; detector, Waters differential refractometer Model 410; software, Nelson X-Chrom v. 7.1.

Sample preparation. The soluble polyacrylic acid was added to the soil in three different ways. (a) Linear polyacrylic acid (mol. wt. *ca.* 243 000 and 0% neutralization; Scientific Polymer Products, Ontario, NY, U.S.A.) was added directly to the soil and allowed to equilibrate for up to 4 h. (b) The same linear polymer was prepared by adding it to water and then contacting it with the soil. (c) soluble polymer was extracted with 0.9% NaCl from commercially available DRYTECH® (Dow Chemical, Midland, MI, U.S.A.) superabsorbent polymer which is partially neutralized. The soluble polymer in 0.9% NaCl was then contacted with the soils.

A 10-g amount of soil containing the polyacrylic acid was extracted with 100 ml of Millipore-filtered water in the case of sample a, a 10-g amount of soil was extracted with Millipore-filtered water containing soluble polyacrylic acid in the case of sample b, and a 10-g amount of soil was extracted with 100 ml of 0.9% NaCl containing the soluble polymer fraction in the case os sample c. The extraction was performed by shaking in a flatbed shaker for 16 h.

The samples were then placed in a centrifuge for 1 h with a relative centrifugal force of 1000 *g*.

The samples were then filtered through several filters. The filtration started with a 0.8-μm nylon plain filter (47 mm, Cat. No. N08SP04700 MSI) followed by a 0.45-μm nylon plain filter (47 mm, Cat. No. N04SP04700 MSI), then a 0.22-μm nylon plain filter (47 mm, Cat. No. N02SP04700 MSI), and, finally, a 0.1-μm nylon plain filter (47 mm, Cat. No. N01SP04700 MSI), all filters were obtained from Fisher Scientific (Midland, MI, U.S.A.).

The samples were then concentrated by freeze-drying to obtain the desired sensitivity.

Derivatization pyrolysis–gas chromatography

GC conditions. Instrument, Hewlett-Packard 5890 GC dual-column system; columns, (1) stainless steel, 6′ × ⅛″ I.D., packed with 0.1% SP-1000 Carbopack C and (2) 60 × 0.25 mm, 0.25 μm film tickness, capillary column DB-wax; temperatures, initial 50°C for 4 min, oven ramp 6°C/min, final 220°C for 40 min, injection 200°C, and flame ionization dectector 220°C; helium flow-rate, 16 ml/min.

Sample derivatization. The sample was prepared as explained in the *Size-exclu-*

sion chromatography section. A 250-μl aliquot of Methyl-8® [dimethylformamide (DMF) dimethyl acetal] was added. The sample was heated at 160°C for 16 h. Residual solvent was evaporated with a heat lamp under a nitrogen purge. Methanol, 0.5 ml, was added to dissolve the residue.

Sample analysis. The instrument was a CDS 120 pyrolyzer equipped with coil probe. The probe was placed in the GC interface and pyrolyzed under the following conditions: ramp, off; time, 20s; pyrolysis temperature, 700°C; interface temperature, 200°C. A 4-μl sample was placed in a quartz pyrolysis boat, the boat was placed in the CDS pyrolysis coil probe and the solvent was flashed off.

NMR analysis

Instrumentation. Instrument, IBM AF300 NMR spectrometer; spectrometer frequency, 300.132 MHz; sweep width, 5000 Hz; offset frequency, 5000 Hz; data size, 32K; acquisition time, 3.277 s; pulse width, 2.0 μs; receiver delay, 0.0 s; receiver gain, 40; apodization, 2–10 Hz[a].

Scans. Linearity (polyacrylic acid): 300–3700[b]. Soils (blank, spike): 1133[a].

Sample preparation. After the water was removed by free-drying as explained in the *Size-exclusion chromatography* section, the samples were dissolved in ^2H_2O and poured into 5-mm NMR tubes.

pH Determination. To 10 g of soil 100 ml of Millipore-filtered water was added. The samples were stirred for 10 min at a low-speed setting to avoid CO_2 absorption and the pH was determined using a pH meter.

RESULTS

Size-exclusion chromatography

In order to establish a limit of detection, the samples were analyzed after concentration. It was found that the Borden sand sample did not show any interferences with polyacrylic acid at the 0.5-ppm level. The Londo soil and the clay samples showed interferences ranging from 3 to 7 ppm. Humic acid naturally present in soils did not interfere with the analysis by SEC as shown in Fig. 1. Included in Fig. 1 are typical SEC traces of the extracted soils. Studies to determine the capacity of the soil to adsorb polyacrylic acid were conducted and they are shown in Tables I–IV. It was found that when the soil was extracted with water and the polymer was not neutralized, the Borden sand showed a greater capacity than the other soils to adsorb the polymer. When the solvent used was 0.9% NACl and the polymer was partially neutralized, the clay showed greater capacity as shown in Table III.

pH determination

The pH values of the soils were determined and the results can help explain the affinity of the polymer for the sand. The pH of the Borden sand sample (9.6) is higher than the other two soils, (Londo soil, pH 7.6; Fox Sandy Loam, pH 6.9).

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[a] The number of scans and apodization was held constant for the blank and polyacrylic acid spiked soils.

[b] 39-ppm standard 3700 scans; 190-ppm standard, 1729 scans; 371-ppm standard, 313 scans.

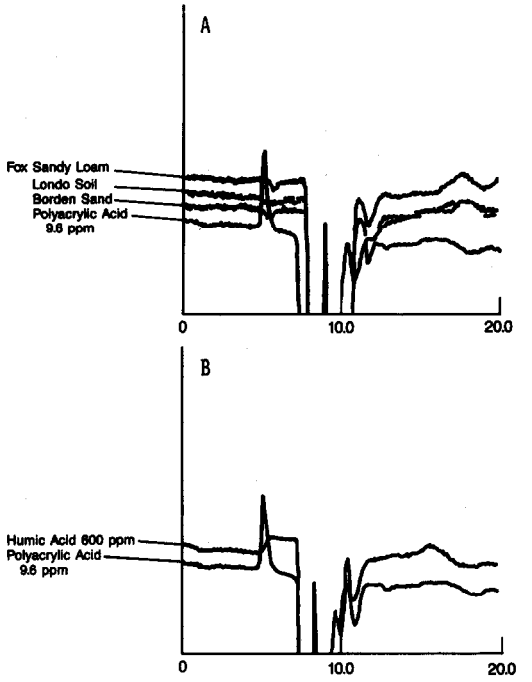

Fig. 1. SEC traces of (A) standard and soils (B) standard and humic acid. Horizontal axis represents time in minutes.

TABLE I

SOIL CAPACITY

Polymer was applied to the soil and the soil was extracted with water.

Soil type	*Polymer added* (μg)	*Recovery* (%)	*Lost* (%)	*Capacity* (μg/g)
Borden sand	400	0	100	>40
Londo soil	400	0	100	>40
Fox Sandy Loam	400	0	100	>40

TABLE II

SOIL CAPACITY OF BORDEN SAND

Polymer was applied to the soil and the soil was extracted with water.

Sample No.	*Polymer added* (μg)	*Recovery* (%)	*Lost* (%)	*Capacity* (μg/g)
1	400	0	100	> 40
2	1230	0	100	>120
3	2040	0	100	>200

TABLE III

SOIL CAPACITY

Soil type[a]	*Polymer added (μg)*	*Recovery (%)*	*Lost (%)*	*Capacity (μg/g)*
Borden sand[b]	14 000	70	30	460
Borden Sand	11 200	87	13	150
Londo soil	11 200	70	30	370
Fox Sandy Loam	11 200	24	76	850

[a] Polymer was added in 0.9% NaCl.
[b] Polymer was added in 0.7% NaCl.

Surface area

The surface areas of the three soils were determined following the BET Nitrogen Test with the following results: Borden sand, 0.3 m^2/g; Londo soil, 1.63 m^2/g; Fox Sandy Loam 8.78 m^2/g.

Derivatization pyrolysis–gas chromatography

In order to maximize the sensitivity of the method, the sample must be carefully concentrated and dried before derivatizing the polyacrylic acid. This was done by freeze-drying the extract in a 100-ml vial as explained before. The vial was washed with 5 ml of water which were then transferred to a 5-ml Reacti-vial. The sample was then evaporated to dryness by blanketing the sample with a stream of nitrogen and heating with an infrared heat lamp. Once the samples were dried, 250 μl of Methyl-8 were added and the vial was heated at 130°C for 16 h. After derivatization, the sample was again dried and the residue was redissolved in 0.5 ml of methanol. This second drying step was incorporated into the method because the derivatized polymer is not soluble in the methylating agent. A spin bar was used in the vial to aid in dissolution of the polymer. Using a 10-μl syringe the solution was then transferred to a quartz boat for pyrolysis. A quartz boat was used in favor of a platinum ribbon since the

TABLE IV

SOIL CAPACITY

Polymer was added to the water and extracted with water.

Soil type	*Polymer added (μg)*	*Recovery (%)*	*Lost (%)*	*Capacity (μg/g)*
Borden Sand	12 000	0	100	>1200
	24 300	0	100	>2430
	30 400	0	100	>3040
Londo Soil	12 000	0	100	>1200
	24 300	14	86	2100
	30 400	16	84	2540
Fox Sandy Loam	12 000	0	100	>1200
	24 300	3	97	2360
	30 400	30	70	2100

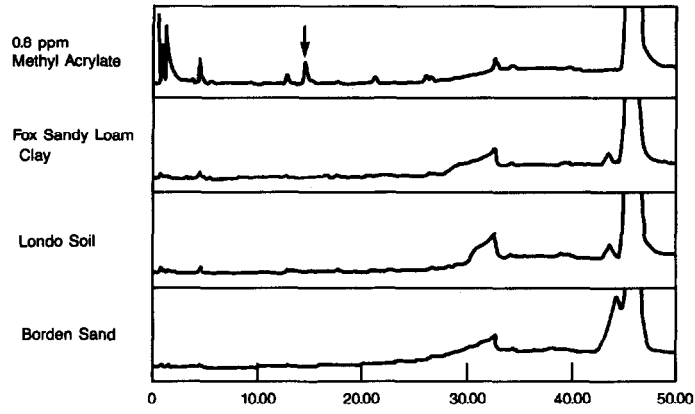

Fig. 2. Py–GC traces of an 0.8-ppm standard and soil samples using the packed column. Horizontal axis represents time in minutes.

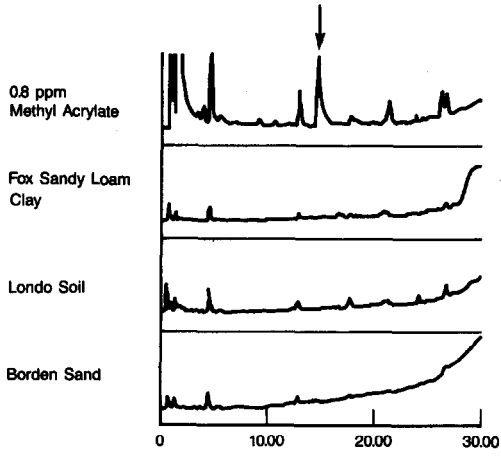

Fig. 3. Py–GC traces of an 0.8-ppm standard and soil samples using the packed column as in Fig. 2, but magnified electronically five-fold. Horizontal axis represents time in minutes.

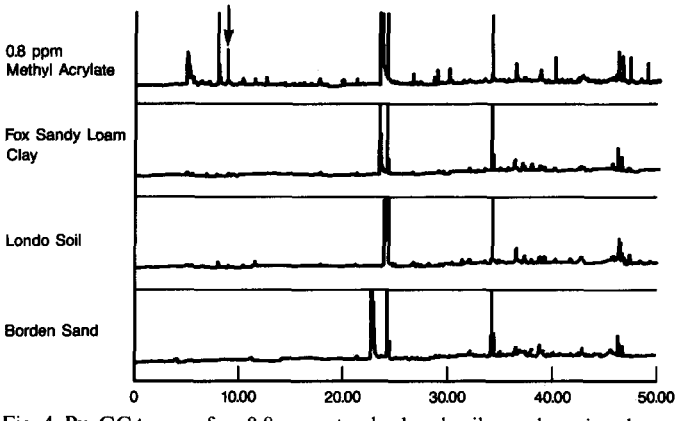

Fig. 4. Py–GC traces of an 0.8-ppm standard and soil samples using the capillary column. Horizontal axis represents time in minutes.

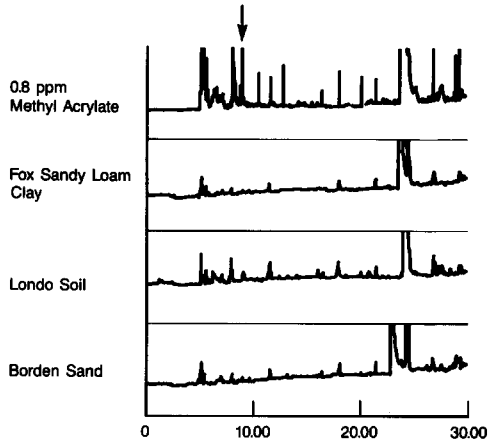

Fig. 5. Py–GC traces of an 0.8-ppm standard and soil samples using the capillary column as in Fig. 4, but magnified electronically five-fold. Horizontal axis represents time in minutes.

sample could contain salts. Rather than contaminating a ribbon with the salt, a boat was used which could be readily cleaned with acidified methanol.

The polyacrylic acid was derivatized to methylacrylate because the main pyrolysis products of the acid are carbon dioxide and water. Only a small amount of the monomer was produced under the pyrolysis conditions listed. By derivatizing the acid to methylacrylate, the main pyrolysis products are methanol and methylacrylate both

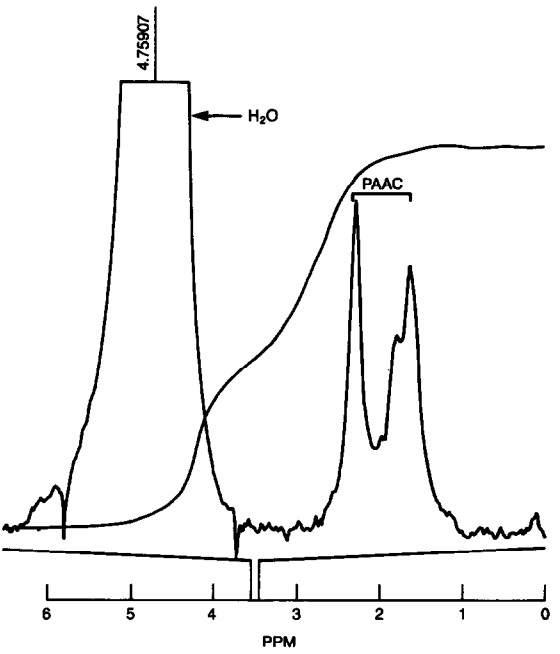

Fig. 6. NMR spectrum of 190 ppm polyacrylic acid (PAAC) in ^2H_2O.

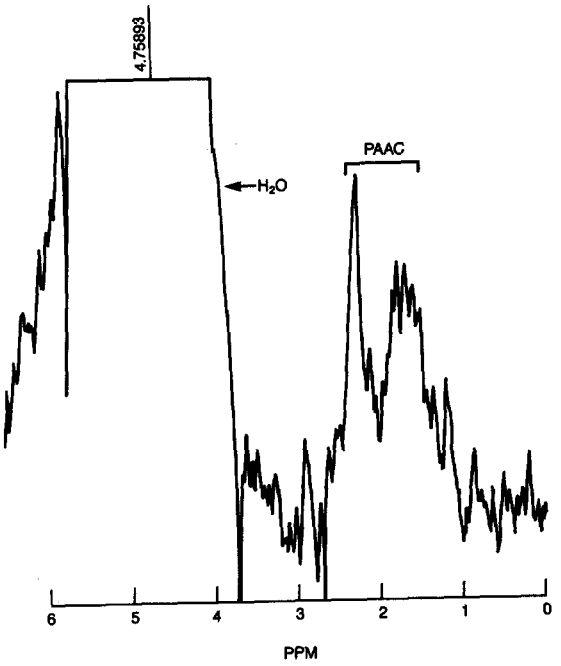

Fig. 7. NMR spectrum of 39.1 ppm polyacrylic axid (PAAC) in ^2H_2O.

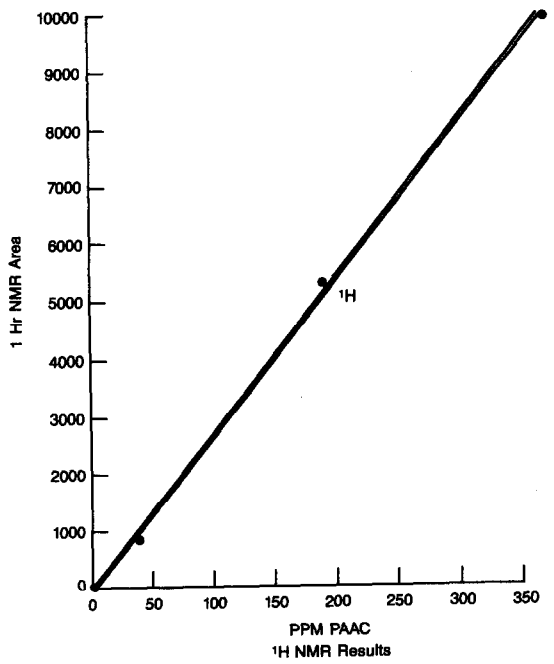

Fig. 8. Plot of the total area response for the polyacrylic acid (PAAC) backbone hydrogens *versus* PAAC concentration by NMR.

of which can be readily chromatographed and detected. The advantages of derivatizing the sample also include the fact that the pyrolysis products can be ratioed to each other, and when compared to a standard will indicate the presence of any interferences in the analysis. By using a dual-column system with columns of differing polarity or retention mechanisms, determination of the retention times of the main pyrolysis products becomes almost a definitive means of identifying the polymer present in the sample as polyacrylic acid. In Fig. 2 are shown Py-GC traces of an 0.8-ppm standard and soil samples using the packed column. In Fig. 3 are shown the same traces only magnified electronically five-fold. In Fig. 4 are shown the pyrograms of an 0.8-ppm standard and soil samples using the capillary column. In Fig. 5 the same traces are shown magnified electronically five-fold.

NMR spectroscopy

The spectra acquired for polyacrylic acid–^2H_2O solutions of 190 and 39.1 ppm are given in Figs. 6 and 7, respectively. The assignments for the polyacrylic acid backbone hydrogens and the residual hydrogens from the undeuterated water are included in the spectrum. A plot of the total area response for the polyacrylic acid backbone hydrogens versus concentration is given in Fig. 8. Although the signal-to-noise ratio in the spectrum given in Fig. 7 is not high, a reasonable estimate of the detection limit of the NMR experiment is approximately 20–40 ppm polyacrylic acid in ^2H_2O. The NMR spectrum of the polyacrylic acid standard spiked in ^2H_2O is given in Fig. 9. The area of the polyacrylic acid backbone hydrogens corresponds to approximately 128 ppm of polyacrylic acid. The spike was prepared to contain ap-

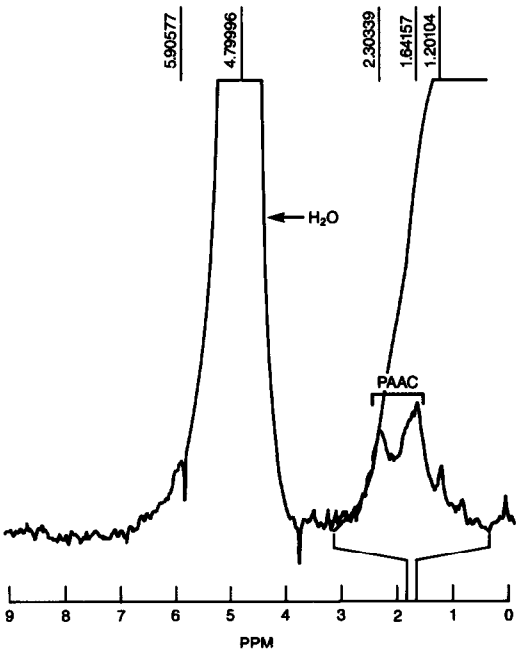

Fig. 9. NMR spectrum of the polyacrylic acid (PAAC) standard spike in ^2H_2O.

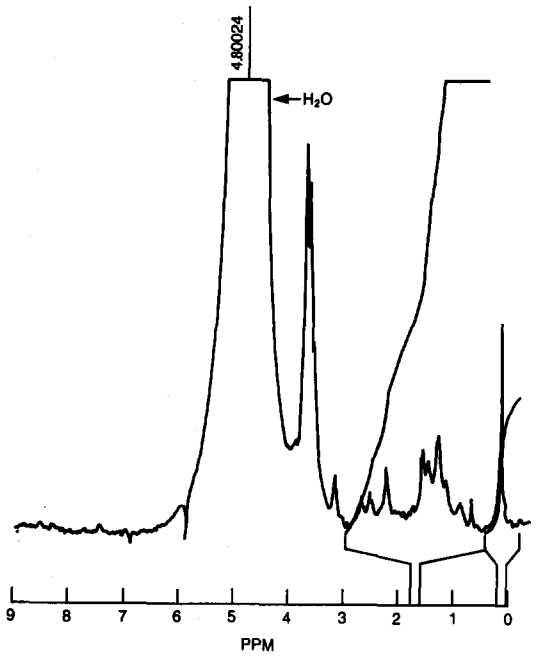

Fig. 10. NMR spectrum of a Fox Sandy Loam blank in ^2H_2O.

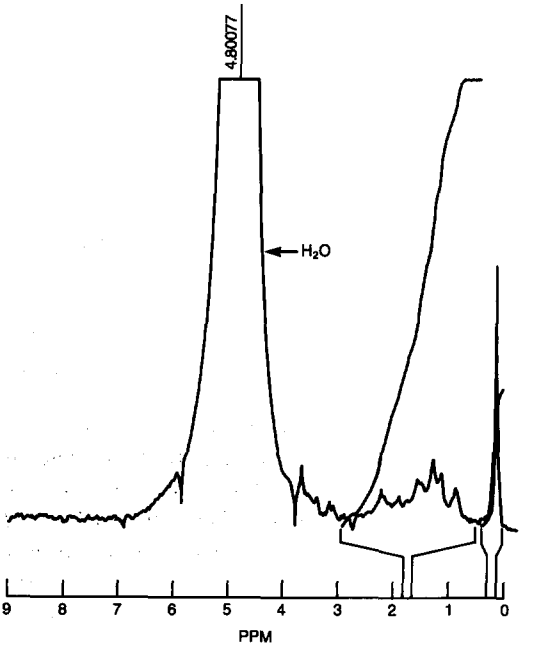

Fig. 11. NMR Spectrum of a Borden sand blank in ^2H_2O..

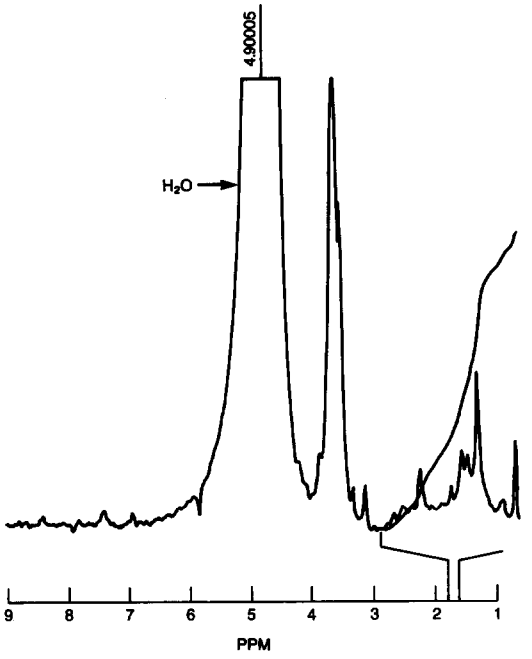

Fig. 12. NMR Spectrum of the Fox Sandy Loam soil spiked with 200 ppm polyacrilic acid in ^2H_2O.

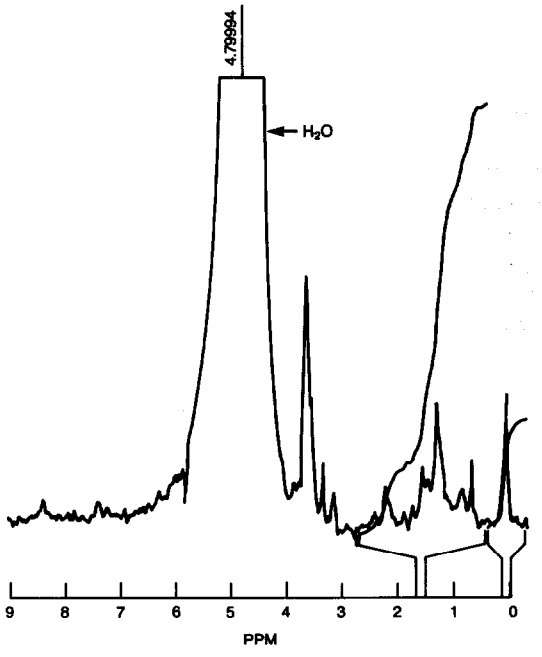

Fig. 13. NMR spectrum of the Borden sand soil spiked with 200 ppm of polyacrylic acid in ^2H_2O.

proximately 200 ppm of polyacrylic acid. The NMR result indicates a recovery of approximately 64%. The sample loss took place during the freeze-drying step and is probably due to irreversible adsorption of the polyacrylic acid to the glass of the bottle.

The hydrogen NMR spectra of the soils labeled Fox Sandy Loam and Borden sand are given in Figs. 10 and 11, respectively. There are peaks evident in the region 3–1 ppm. This is the region where the backbone hydrogens of polyacrylic acid resonate. Therefore, interferences exist in the soils which will interfere with the determination of low levels of polyacrylic acid.

The hydrogen NMR spectra for the Fox Sandy Loam and Borden sand soils spiked with 200 ppm of polyacrylic acid are given in Figs. 12 and 13, respectively Comparing these spectra with the spectra of the blank soils (Figs. 10 and 11), it is evident that very little, if any, polyacrylic acid is present in the samples. Further work is necessary to identify the components present in the soils.

DISCUSSION

The first approach was to use SEC, excluding the polymer totally to obtain a useable signal. Adsorption capacities of the soils for polyacrylic acid were obtained using this procedure. NMR spectroscopy was used as a characterization tool to verify the response obtained by SEC. Derivatization Py–GC with dual columns was then investigated. It was known that polyacrylic acids will degrade to CO_2 when heated at high temperatures for pyrolysis purposes. A derivatization procedure explained elsewhere[7] was successfully tried, and no interferences were found in any of the soils at the sub-ppm level.

The samples of soil extracts needed to be cleaned and concentrated to get the desired detection limits. The clean bottles normally used in the analytical laboratories for trace analysis were found to contain interferences in the area of elution of the polymer on the SEC system. The problem was solved by rinsing the bottles with Millipore-filtered water. Rinsing the bottles eliminated the interferences in the Borden sand sample, but the Londo soil and the Fox Sandy Loam sample still had some interferences at the 5-ppm level that were not introduced by the bottles. Humic acid naturally present in soils did not interefere with the SEC analysis. The use of batch extractions has advantages over the use of columns to study the movement of the polymer in soils. When batch extraction is used, all the intereferences that are naturally present in the soils will be present during extraction, while in the case of column studies the soil is constantly stripped of some of the components. Batch extractions monitored with SEC have been used to determine the capacity of soils which can be used to better understand the movement of polyelectrolytes through soils. As it was shown in Tables I–IV the selectivity of soils is not directly related to surface area.

Sand, which has a smaller surface area than clay (0.3 *versus* 1.63 and 8.78 m^2/g) has a greater selectivity for this type of polymers. On the other hand a decrease in particle size will increase the trapping of polymer molecules. In this case clay will perform better to stop the polymer movement. Water enhances the repulsive forces among the negatively charged carboxylic acid groups and expands the chains, increasing the hydrodynamic volume of the polymer. Salt solutions will have the opposite effect contracting the chains to their original size. The results presented in Tables

I–IV indicate that when this happens the capacity of soils to adsorb polyacrylates is enhanced when the polymer chains are at their larger volume. Concentration of the polymer under investigation is also a critical parameter, since the increase in concentration will increase the viscosity of the polymer and will affect the capacity of the soil to adsorb polyacrylates and the movement of the polymer.

CONCLUSIONS

SEC with batch extraction of the soils and NMR spectroscopy can be used to determine the capacity of soils to adsorb polyacrylates. Derivatization Py–GC with a dual-column system and a flame ionization detector or a single-column system with a mass spectrometer can be used to monitor effluents from columns or from batch extraction at the sub-ppm level.

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