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A Density Gradient Centrifugation Method for Separation of Peat

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ABSTRACT

The conditions necessary for a laboratory—scale separation of the premaceral constituents of peat (i.e., the precursor to coal) are investigated. The method used is an isopycnic density centrifugation (DGC) technique aimed at isolating pure premacerals. This method, which is based on known density differences of various macerals, has been used successfully in coal separations but never with peats. The technique involved grinding the peats in a planetary ball mill to an approximate 10 μm average particle size and conducting dispersion tests using NaCl, $Ca(NO_3)_2$, CsCl, and TBE as solvents coupled with numerous surfactants. The density gradient centrifugation technique was run with both an aqueous and organic gradient using plain milled peat, demineralized peat, and demineralized methylated peat. The best separations were achieved in a single run if the peat was demineralized

and dispersed with a wetting agent in an organic gradient. Analytical-scale separations were used to choose the most responsive peat to be used in a preparative-scale separation. A low and high density weight fraction, analyzed by flash pyrolysis, revealed distinctly different chromatograms, indicating that the peat had reached a reasonable degree of separation. Four peats of differing constitution are reviewed.

Key Words. Peat; Coal; Density gradient centrifugation; Dispersing agents; Pyrolysis

INTRODUCTION

Scientific investigators in the biological fields have long been interested in separating and identifying the individual constituents composing complex natural mixtures to better understand their combined properties. The application of these biological separation techniques in other fields has led to a variety of experimental strategies to isolate individual constituents composing various mixtures. For example, a number of investigators have used either late zonal or isopycnic gradient centrifugation (DEC) to identify the clay minerals in soils (1–3). This method involves layering a sample on a continuous density gradient and centrifuging until each component reaches its isopycnic point (the point at which the material reaches its own density). The effectiveness of this procedure is dependent on the material from which the gradient is made, method of gradient formation, and the use of a compatible dispersing agent (surfactant). Both density gradient and continuous flow centrifugation have been used to separate colloidal organic particles in water (4, 5). Since these particles are very small (molecular weight less than 10^{-6}), the characteristics thought to be most important in a successful separation are banding density, sedimentation rate, particle size and shape, and the concentration range.

Recently, density gradient separation techniques have been modified to separate macerals from coals or separate organic matter from other sedimentary rocks (6–14). Coal has proven to be especially difficult to analyze because it consists of a complex assortment of ingredients (macerals) that can be naturally welded together into a solid, which does not easily break into its individual components. However, recent advances in sink/float methods, zonal centrifugation, and continuous flow separation using density gradients have greatly refined the separation technique (15–19).

The development of a method for separation of a peat sample into its physicochemically distinct components (premacerals) can have several important practical applications. Some of these include: 1) greatly enhanc-

ing our understanding of the coalification process by allowing petrographic and chemical comparisons of like ingredients of peats and coals; 2) increasing our basic knowledge of the chemical composition of peats and thus allowing us to predict or improve their economic or industrial properties; and 3) improving our ability to better characterize specific peat types for the purpose of investigating their capacity to extract hazardous substances from contaminated waters (20). This study was thus undertaken to try to develop a DGC technique that would separate the premacerals found in peats. Several peats that are distinctly different were chosen for testing.

MATERIALS AND METHODS

Selection and Characterization of Peat Samples

Four peat samples representing a wide range of physical, chemical, and botanical compositions (Table 1) were obtained from the University of South Carolina's peat sample bank. Standard coal tests, including proximate and ultimate analysis and calorific value, were obtained for the peat samples as were various wet chemical and spectrochemical analyses of the organic and inorganic components (21). Botanical composition, fiber content, porosity, and birefringence were all measured from microtome sections of peats, prepared according to the method described in Cohen and Spackman (22) and Cohen (23), using a Leitz Orthoplan microscope.

Maceral Separation Techniques

The initial step in the separation procedure began by wet grinding the four peats. A 50-g wet weight sample of each peat type, along with 50 mL

TABLE 1
Peat Types, Source Locations, and the Botanical Composition of Peat Samples Tested (Me. = Maine; Oke. = Okefenokee; Sph. = *Sphagnum*; Tax. = *Taxodium*; Nym. = *Nymphaea*)

Sample designation	Location	Dominant botanical componants
Me. Sph.	Maine	*Sphagnum*
Oke. Tax.	Okefenokee Wildlife Refuge, GA	*Taxodium* (cypress) and *Persea* (bay)
Oke. Nym.	Okefenokee Wildlife Refuge, GA	*Nymphaea, Sagittaria,* and grass-sedge
Snuggedy Swamp	Green Pond, SC	*Myrica, Persea*

of deionized water, were placed in a planetary ball mill (Alfred Fritsch & Co.). The peats were ground for 5 minute intervals until a 30-minute milling period was reached. This amount of grinding was sufficient for the peats to pass through a 1.0-mm screen. The samples were put into amber bottles, bubbled with nitrogen, and sealed.

Aqueous stock solutions of 1 M sodium chloride (NaCl) and calcium nitrate [$Ca(NO_3)_2$] along with several different densities (from 1.2 to 1.7) of cesium chloride (CsCl) solutions were prepared. Also, organic stock solutions with densities between 1.2 and 1.7 $g \cdot cm^{-3}$ density of 1,1,2,2 tetrabromoethane (TBE) mixed with ethanol (EtOH) were prepared. These stock solutions were put into 4 mL test tubes along with 0.015–0.01 mL of milled peat and 0.01–24.0 g/L of various surfactants. In the organic studies the milled peat solutions were filtered through a polycarbonate filter and washed with acetone and ethanol prior to loading into the test tubes. The test tubes were shaken, and the dispersion and settling rates of the peat constituents were visually observed to determine which gradients and surfactants worked best prior to analytical separation.

Analytical-scale separation (using 0.5 mL of different peat types) used targeted density gradients of aqueous CsCl and organic TBE media that were pre-formed using a commercial gradient maker (Dialagrad 380 or 3822, Instrumentation Specialty Co.). Two stock solutions representing the high (1.7) and low (1.2) densities of the gradient were prepared. The gradients were formed in 50 mL polycarbonate (for aqueous gradients) and Teflon (for organic gradients) centrifuge tubes over a 20-minute period. The milled peat samples were added to 2 mL of low density solution in a 10-mL beaker. To disperse the particles completely, the beaker was placed under a micro-tip sonicator horn and subjected to gentle intermittent cycles (10% duty) for a few seconds. The milled peats were also chemically demineralized with acids (HF and then HCl) and prepared for separation runs as stated previously. Portions of the milled peats were also methylated using diazomethane. This involved filtering the samples through a 0.8-μm polycarbonate filter and drying the remaining sample overnight in a low temperature (65°C), nitrogen-filled vacuum oven. The samples were washed with acetone and dispersed with a vortex mixer before centrifuging. This was completed three times with acetone and then repeated with ethanol. The samples were filtered with a 0.2-μm polycarbonate filter and dried overnight as explained previously. Samples were washed with methanol in the same fashion as stated above prior to methylation. Methylated samples were prepared for separation runs in the same manner as the parent and demineralized milled peats.

The slurry was carefully layered on the prepared gradient and centrifuged (Beckman Instruments Inc., J2-21C) with a slow acceleration/dece-

leration (30 minutes each) rate and swinging bucket rotor at 25°C for 2 hours at 10,000 rpm. After centrifugation the centrifuge tubes were pumped out to a fraction collector using a dense chase solution (Fluoinert FC-43 or 2.0 density TBE solution for the organic gradients) pumped in at the bottom of the tube. Simultaneously, the optical density of the peat solution was measured at 660 nm with an absorbance monitor with a 2-mm path length flow cell (UA-5, ISCO).

Preparative-scale separation (using 3 mL of milled peat dispersed in the low density gradient solution) was carried out in a refrigerated Beckman JCF-Z zonal rotor, which has a capacity of 1.6 L (24). Since the standard Noryl core of this rotor was destroyed by the solution, a custom made, high molecular weight polyethylene core was used in later separations. An organic TBE gradient was loaded while the rotor was spinning at 2000 rpm. The peat suspension consisted of 3 mL of peat solution in 100 mL of the low density gradient solution that was subjected to intermittent cycle sonication (10% duty) for three 4-minute periods. After loading, the system was accelerated to 12,000 rpm for 60 minutes, the rotor was decelerated to 2000 rpm, and the contents were pumped to a fraction collector using a 2.0 density TBE chase solution. The density of each fraction was measured with a DMA-45 densitometer. Each fraction was filtered using a Teflon (0.8 μm) membrane filter and washed with 1500 mL of ethanol (95%). This procedure is described in greater detail in Dyrkacz and Horwitz (8).

Analytical Pyrolysis

The flash pyrolysis technique used was that published by Kotra and Hatcher (25) and Bates et al. (26). Using a Chemical Data System Pyroprobe 1000, approximately 1 mg of sample was loaded into a quartz capillary tube, and this tube was placed inside the coils of the pyroprobe. The probe and sample were then inserted into the injection port (temperature maintained at 280°C) of a Varian 2700 gas chromatograph, and the sample was pyrolyzed. The residue was first thermally desorbed at 300°C for 30 seconds and the gas chromatograph cycled to elute these volatiles from the column. The samples were then pyrolyzed. Flash pyrolysis was conducted at a temperature of 610°C for 10 seconds with a heating rate of 5°C/ms. The pyrolyzate was cryotrapped with liquid nitrogen prior to being chromatographed on a 25 m × 0.25 mm i.d. J & W DB-17 capillary column. The GC was temperature programmed from 30 to 280°C at 4°C/min. The effluent was swept into the source of a DuPont 490B mass spectrometer fitted with a Teknivent Vector/One data system for detection and compound identification. Compounds were identified by a combination of

methods, which included comparison of mass spectra to the NBS/Wiley library, to published mass spectra, and to authentic standards whenever possible.

RESULTS AND DISCUSSION

The initial step of the study was to determine the compositional characteristics of four distinctly different peat types. The peats choosen were a Maine *Sphagnum*, Okefenokee *Nymphaea*, Snuggedy Swamp, and Okefenokee *Taxodium*. The Maine *Sphagnum* peat is composed predominantly of one plant species (*Sphagnum* moss). Its constituents are well preserved (i.e., it has high fiber content—about 80%), and it has a relatively moderate pH (4.29), a low ash content (<1.00 dry wt%), and a low sulfur content (0.10 wt%). The Okefenokee *Nymphaea* peat is composed predominantly of *Nymphaea oderata* (white water lily) tissues, with some additional debris from other floating and submerged aquatic plants. It has a moderate amount of fiber (about 50.0%), has a moderate pH (4.53), an intermediate ash content (12.0 dry wt%), and low sulfur content (0.40 dry wt%). The Snuggedy Swamp peat is composed of woody debris derived from a variety of shrubs [*Persea borbonia* (red bay), *Myrica cerifera* (wax myrtle), and *Cyrilla racemiflora* (titi)]. It is moderately to highly decomposed (<33.0% fiber), has a moderate pH (4.70), an ash content of 8.10 wt%, and a sulfur content of 1.00 wt%. The Okefenokee *Taxodium* peat is composed mainly of woody material from *Taxodium* and *Persea* trees. It is highly decomposed (fiber content of 18%), has a low pH (3.14), an ash content of 12.7 dry wt%, and a sulfur content of 0.29 dry wt%. Table 2 gives some additional characteristics of these peats that can be correlated with the proportion and type of premaceral.

TABLE 2
Selected Characteristics of Peat Samples

Sample designation	Location	Birefringence (area %)	Volatiles (dry wt%)	Fixed carbon (dry wt%)
Me. Sph.	Maine	78.0	71.8	28.0
Oke. Nym.	Okefenokee Swamp, GA	54.0	62.2	27.0
Oke. Tax.	Okefenokee Swamp, GA	20.0	59.2	26.0
Snuggedy Swamp	Green Pond, SC	—	64.0	36.0

The botanical and "premaceral" compositions of the peat types used in this study have been described in several publications (27–29). "Premacerals" are the organic components in the peats which, due to their color, opacity, shape, and fluorescence, can be interpreted as the probable progenitors of specific macerals in coals. Peats with the highest proportions of birefringent premacerals tend to have the highest volatile matter (Table 2). Peats with a dominance of premacerals in the light yellow to red range tend to have a higher volatile matter and a lower fixed carbon content compared to those that have a high amount of brown and black ingredients (preinertinites). The Maine *Sphagnum* and Okefenokee *Nymphaea* peats tended to have the highest previtrinites while the Okefenokee *Taxodium* and Snuggedy Swamp peats had the highest prephlobaphenites (and precorpocollinites) and also the highest preinertinites (premicrinites, prefusinites, and presclerotinites).

Wetting and Dispersion Studies

The DGC studies were designed to determine if any of the techniques that had been used with coal maceral separation could be used to separate the premacerals in peats. A number of possible choices were available as the medium for routine laboratory density separation of macerals. NaCl and $Ca(NO_3)_2$ were chosen because they are cheap to acquire, and CsCl because it is the standard used in coal maceral separation. $Ca(NO_3)_2$, although cheap, has viscosity problems that reduces its maximum working density range to <1.45 g·cm^{-3}. The density of NaCl would also not be appropriate for density work but it does provide a similar inexpensive substitute to slurry with surfactants.

Dyrkacz (7) demonstrated that the addition of a wetting agent (surfactant) greatly enhanced the total amount of liptinite recovered from three sink–float cycles. Also, the purity of the liptinite was much higher when a surfactant was present. The number of surfactants available is even larger than that for gradient media. The best surfactant for use in coal maceral separation was determined to be Brij 35 (polyoxyethylene-23-lauryl ether). Therefore, an obvious important question was: Which surfactant would work the best with peats.

Our early test-tube studies involved testing as many surfactants as possible with the three media stated previously within the time frame of the experiment. The range of surfactant concentrations varied depending on their individual characteristics, but each was tested between the lowest and highest possible concentrations until their separation potentials were determined. The majority of these aqueous dispersion tests showed rapid aggregation between a period of a few minutes and 1 hour (Table 3). Sev-

TABLE 3
List of Surfactants Studied and Their Resulting Dispersion Characteristics for the Peats Studied[a]

	Surfactant	Origin	Solvents	Observation
1	Polyethylene glycol	JT Baker Co.	1, 2	A
2	Polyoxyethylene 10 lauryl ether (Brij 36T)	Sigma	1, 2, 3	A
3	Polyvinyl alcohol crystalline type II	Sigma	1, 2	A
4	Brij 78	Aldrich	1, 2, 3	DA
5	Dinonyl naphthalene sulfonic acid	Pfaltz & Bauer	1, 2	A
6	Polyoxyethylene sobitan monostearate	Sigma	1, 2	A
7	Metrizamide	Aldrich	1, 2, 3, 5	DA
8	Brij 35	Aldrich	1, 2, 3	DA
9	Hexadecyltrimethyl ammonium chloride	Eastman	1, 2	A
10	*p*-Heptylphenol	Eastman	1, 2	A
11	Polyoxyethylene sorbitan monolaurate	Sigma	1, 2	DA
12	*n*-Octadecyl disodium sulfosuccinate	Pfaltz & Bauer	1, 2	NA
13	Dodecyltrimethyl ammonium chloride	Eastman	1, 2	A
14	Dodecylbenzene sodium sulfonate	Pfaltz & Bauer	1, 2	DA
15	Dodecyl sulfate sodium	Aldrich	1, 2, 3	A
16	Lauryldimethylnaphthyl ammonium chloride	Pfaltz & Bauer	1, 2	A
17	Dodecylbenzene sulfonic acid	Sigma	1, 2, 3	DA
18	Dextrin	Sigma	1, 2	A
19	1-Octadecanol	Aldrich	1, 2	A
20	Sucrose	Beckman	3	DA
21	Polyvinylpyrilodone (PVP K-30)	Aldrich	1, 2, 3, 4	D

[a] A = samples aggregate within a 1-h time period. NA = solution was not acceptable for DGC. DA = samples dispersed for 2–3 h, then began to aggregate. D = samples stayed dispersed over 5 h. 1 = NaCl; 2 = $Ca(NO_3)_2$; 3 = CsCl; 4 = TBE; 5 = H_2O.

eral of the CsCl dispersion tests, however, resulted in the peat particles remaining dispersed close to the 5 hours that are needed for an analytical-scale separation. A 5-hour time period is approximately the time it takes to run an analytical-scale separation from start to completion. The best surfactants of the eight that showed dispersion were Brij 78, Brij 35, PVP, and metrizamide.

Since none of the aqueous dispersion tests surpassed this time period, an organic medium composed of TBE plus EtOH was tested with the surfactant PVP. Dispersion tests were run at 0.2 density increments between 1.2 and 2.0 containing 10% by weight PVP. All the densities experienced dispersion for more than the 5-hour time period. More important was the fact that upon going from low density to high density, the dispersion gradually went from a small amount of sink to a small amount of float. The organic TBE medium and PVP surfactant along with the four best surfactants in a CsCl medium were used in the analytical-scale separation studies.

Density Gradient Separation

The initial analytical DGC runs using CsCl and Brij 78, Brij 35, PVP, and metrizamide surfactants showed small amounts of aggregation in the banding of premacerals. This was despite favorable results from the aggregation studies. Increasing the concentrations of the surfactants from 8 to 10 g/L for Brij 78 and Brij 35, and from 10 to 15% w/w (weight per unit-volume-weight) for PVP and metrizamide did not resolve the problem. However, the band did shift to a higher density. The focus of the study then turned to the organic TBE gradient. The first run used treated peats; one set was demineralized with HCl and HF and the other was methylated to cap the hydroxyls. Methylation of the peats was intended to effectively change their surface properties and promote better dispersion. Samples were run using 5% w/w PVP. The methylated sample produced all sink while the demineralized samples had some small bands, with the majority showing up as a wide range density band. The demineralized milled peats were used for all remaining separation runs. A second organic run, using 10% w/w PVP, had good banding and correlations between similar peat types. Figure 1 shows the absorbance of two peats, Maine *Sphagnum* (Fig. 1A) and Okefenokee *Nymphaea* (Fig. 1B). The density distribution curves are similar to one another, which may be expected based on the botanical composition of the peats. Also, both of these peats have high fiber content (i.e., are very little decomposed). Likewise, the two woody peats, Okefenokee *Taxodium* and Snuggedy Swamp (Figs. 2A and 2B, respectively) produced similar density distribution curves. Additional DGCs using 5, 15, and 20% PVP were also tried. Only the Okefenokee *Taxodium* peat seemed to have a broader density range in premaceral separation using 20% PVP (Fig. 3).

Analytical separation using 20% PVP was repeated two more times with similar results. Okefenokee *Taxodium* peat was then chosen for the 2 g preparative-scale separation.

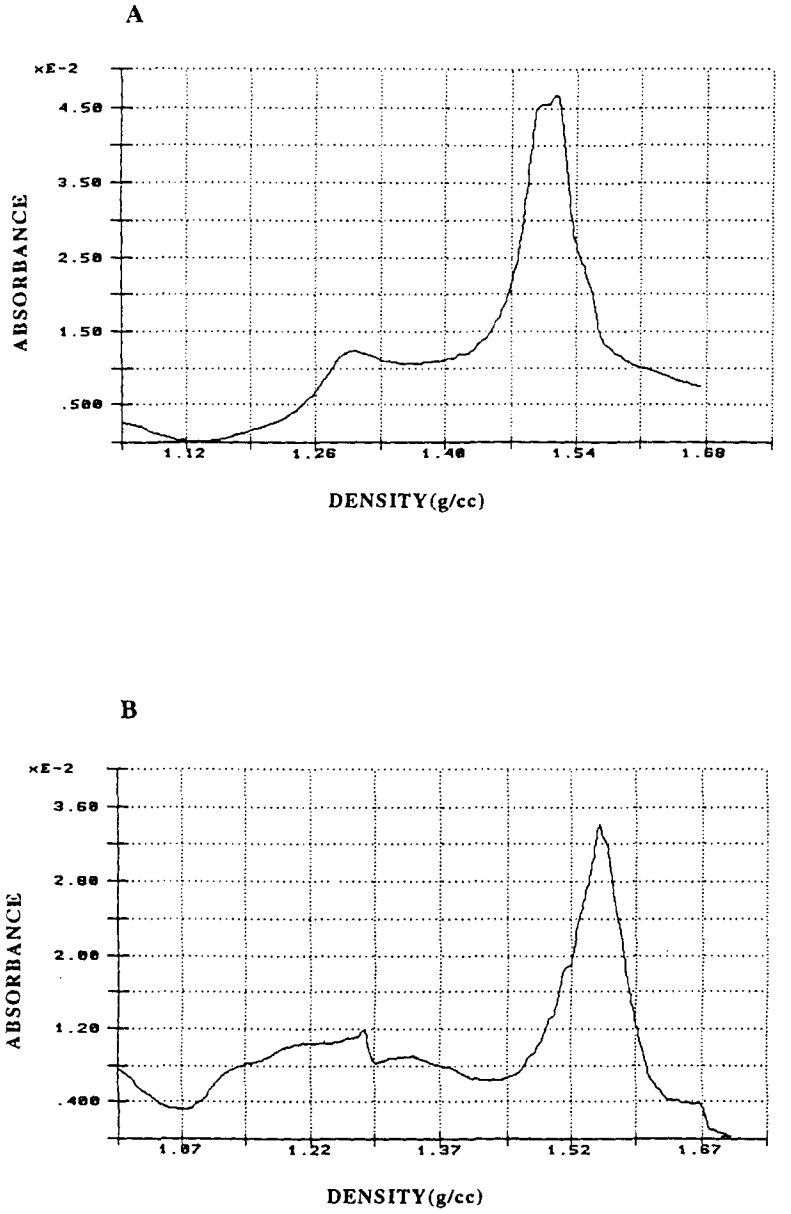

FIG. 1 Analytical density gradient centrifugation of peats using 10% PVP in a TBE medium. Absorbance is roughly proportional to the mass of the material at a particular density. All densities are at 25°C. Note the similarity of the curves for these high fiber peats. (A) Maine *Sphagnum* peat and (B) Okefenokee *Nymphaea* peat.

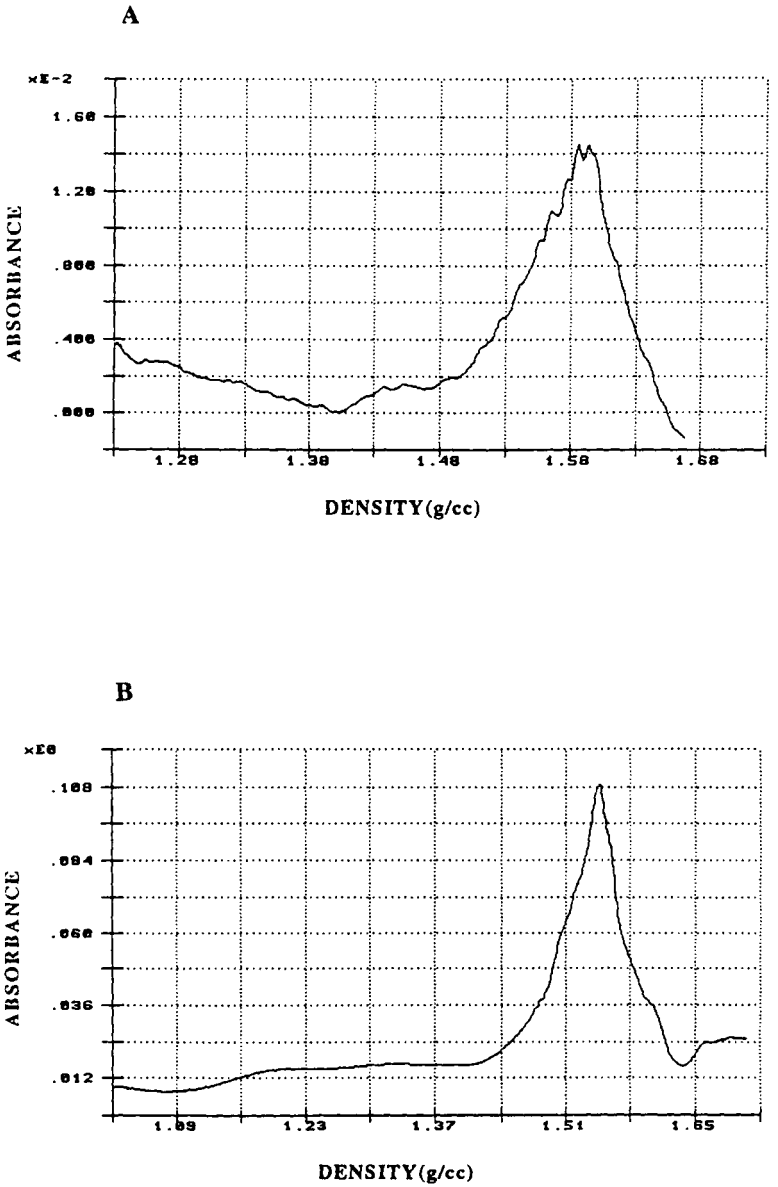

FIG. 2 Analytical density gradient centrifugation of peats using 10% PVP in a TBE medium. Absorbance is roughly proportional to the mass of the material at a particular density. All densities are at 25°C. The curves for these two woody peats are similar in appearance but are markedly different from those of the fibric peats in Fig. 1. (A) Okefenokee *Taxodium* peat and (B) Snuggedy Swamp peat.

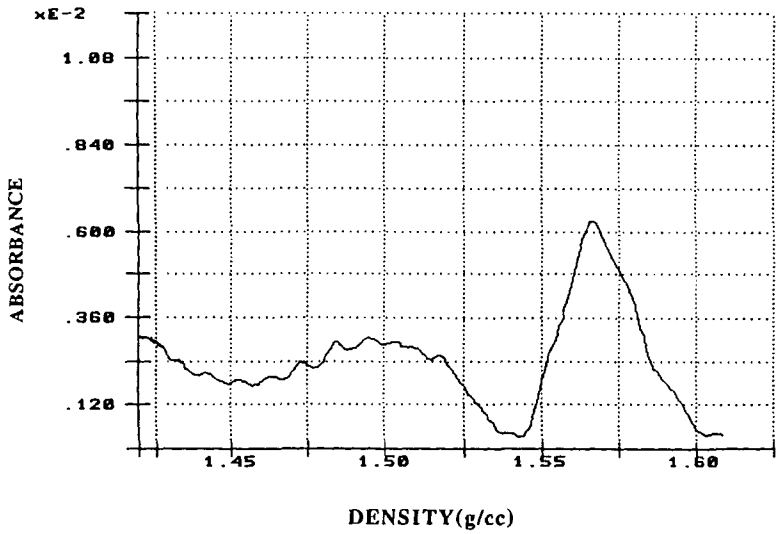

FIG. 3 Analytical density gradient centrifugation of Okefenokee *Taxodium* peat using 20% PVP in a TBE medium. Absorbance is roughly proportional to the mass of the material at a particular density. All densities are at 25°C.

The preparative separation of the Okefenokee *Taxodium* peat was split into 58 weight fractions (Fig. 4). These premaceral weight fractions had a density range from 1.38 to 1.71 with a maximum weight fraction occurring at a density of 1.58.

The flash pyrolysis data for two fractions separated by density gradient centrifugation, fractions #17 (low density) and #53 (high density), are shown in Figs. 5 and 6. Along with the total ion current (TIC) chromatogram, a specific ion chromatogram (SIC) for *m/z* 71 is shown in each figure. This SIC is specific for *n*-alkanes and *n*-alkenes.

The TIC for fraction #53 (Fig. 5) shows a series of peaks that are characteristic of peat containing a significant proportion of vascular plant remains. The major peaks are identified in Table 4 as guaiacol, 4-methylguaiacol, 4-propylguaiacol, vinylguaiacol, syringol, *trans*-isoeugenol, acetoguaiacone, vinylsyringol, allylsyringol, acetosyringone, and propiosyringone. All of these peaks are typical of those one would obtain from the flash pyrolysis of lignin (30). Another major peak observed in the TIC is that of levoglucosan. This compound is typically observed in pyrolyzates of cellulosic materials and is characteristic of the contribution of cellulosic components of peat (31). In addition to the above peaks, several

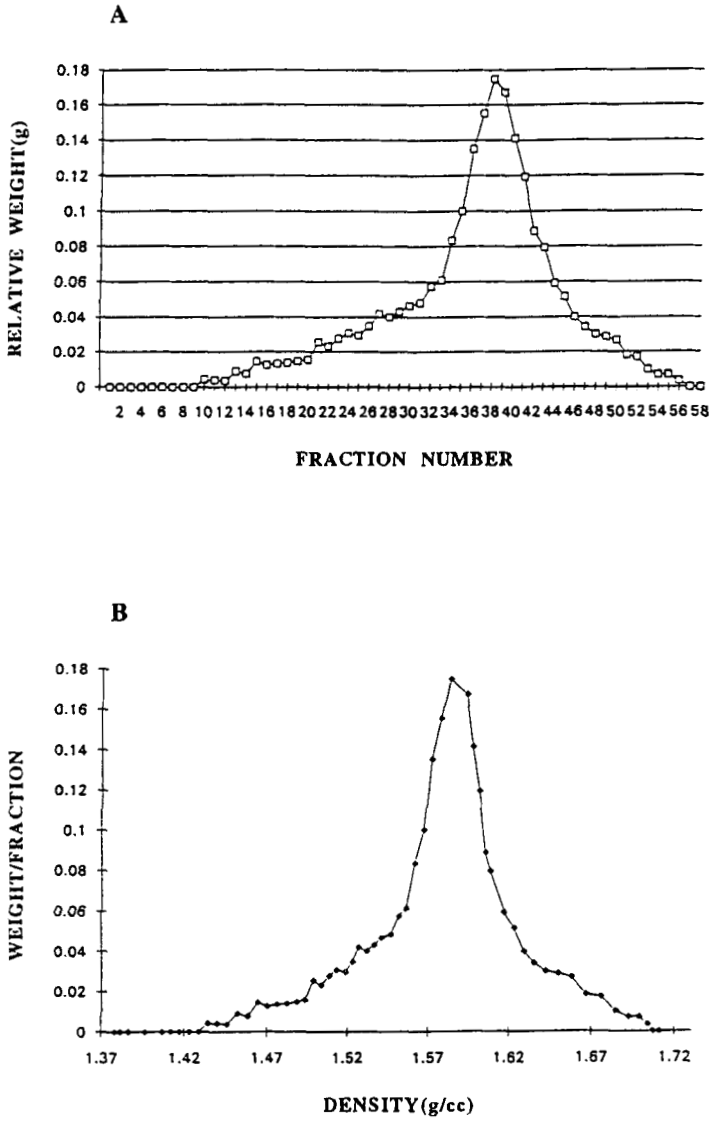

FIG. 4 Preparative separation of Okefenokee *Taxodium* peat using a linear gradient. A TBE medium was used with 20% PVP surfactant. All densities are at 25°C. (A) Number of fractions separated versus their relative weight and (B) the density of each fraction compared to its relative weight.

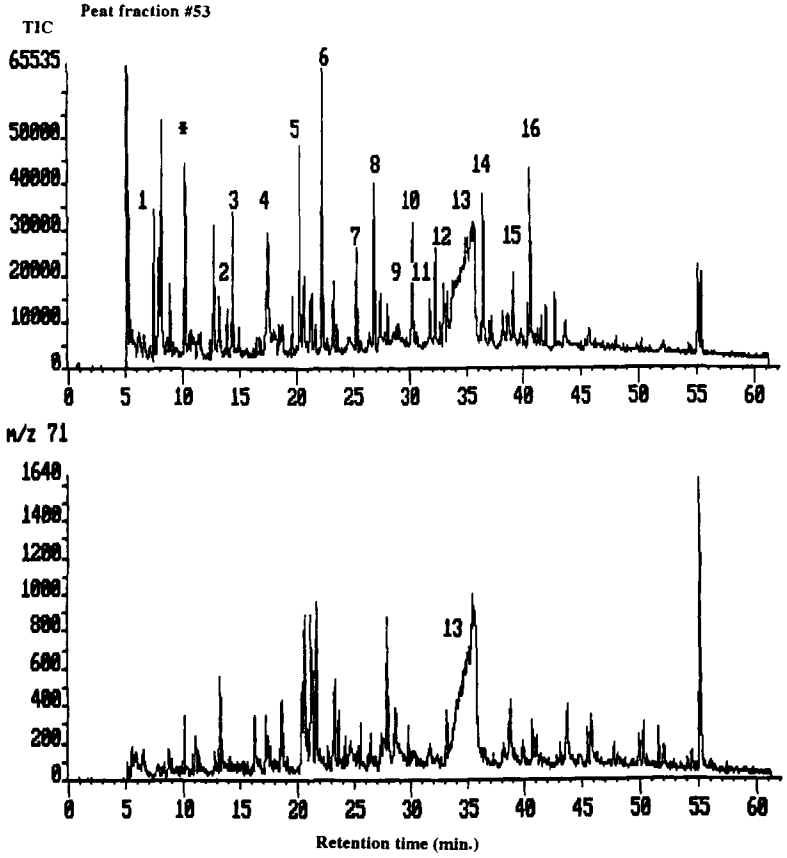

FIG. 5 Pyrograms for peat fraction #53 showing the TIC trace (upper) and the SIC for *m/z* 71 (lower). The asterisk indicates the peak due to contaminants, while the numbers refer to peaks identified in Table 3.

peaks can be identified as contaminants, introduced from the surfactant used, in this case, PVP. The SIC trace shows a large number of peaks without a regular pattern. These components are *n*-alkanes and/or *n*-alkenes of varying chain length but also include other compounds having a fragment ion at *m/z* 71. Levoglucosan displays a small peak at *m/z* 71 and is observed in the SIC.

The TIC for the lower density peat fraction (#17) is dominated by a complex series of peaks eluting at short retention times and in the range

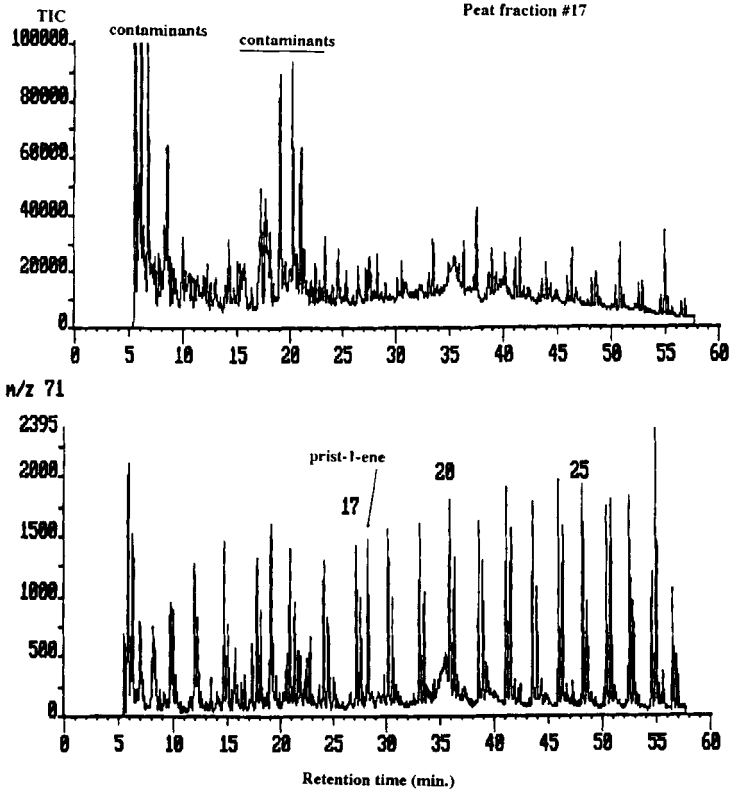

FIG. 6 Pyrograms for the peat fraction #17 showing the TIC (upper) and SIC for *m/z* 71 (lower). The numbers above select peaks refer to the carbon number for the homologous series of *n*-alkane/*n*-alkene pairs.

of 20 minutes (Fig. 6). We determined from the mass spectral characteristics that these components were primarily associated with the surfactant PVP. Their dominance in the TIC indicates that this fraction of peat is not easily rid of the surfactant during preparation. In addition to these contaminant peaks, a series of other peaks appearing as doublets was also observed. The SIC trace for *m/z* 71 shows that these doublets are assigned to an homologous series of *n*-alkanes and *n*-alkenes extending up to a chain length of 29 carbons or higher. The chromatogram was terminated slightly prematurely in this analysis; however, it is likely that additional

TABLE 4
Peak Identifications for Figure 5

Peak number	Peak identification
1	Acetic acid
2	Cresol
3	Guaiacol
4	Methyl guaiacol
5	Propyl guaiacol
6	Vinyl guaiacol
7	Syringol
8	*trans*-Isoeugenol
9	Methyl syringol
10	Acetoguaiacone
11	Propioguaiacone
12	Vinyl syringol
13	Levoglucosan
14	Allyl syringol
15	Acetosyringone
16	Propiosyryngone

peaks for higher chain-length hydrocarbons would have emerged at later retention times. The homologous series of hydrocarbons is characteristic of the highly aliphatic biopolymers associated with plant cuticles, bark, roots, and algae (32).

CONCLUSION

The flash pyrolysis data for the low and high density peat fractions from the *Taxodium* peat show clearly that some significant differences in chemistry are contained within the material from these fractions. The more dense fraction appears to be dominated by lignin pyrolysis fragments from vascular plant materials and by cellulosic material from the same vascular plants. The lower density fraction contains a homologous series of *n*-alkanes and *n*-alkenes typically associated with highly aliphatic biopolymers from a variety of vascular plant and microbial sources. Pyrolysis products derived from the surfactant are readily apparent in this low-density fraction. However, they are easily distinguishable from the peat pyrolysis products. This suggests that a density gradient technique using a TBA and EtOH gradient with a PVP surfactant has the potential to achieve reasonable separation of the premacerals in peats. However, addi-

tional work with other types of organic gradients and compatable surfactants may significantly refine the density gradient centrifugation of peats and organic soils.

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