Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Laboratory Scale Separation of Coal Macerals

Gary R. Dyrkacz[a]; C. A. A. Bloomquist[a]; E. Philip Horwitz[a]
[a] CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

To cite this Article Dyrkacz, Gary R. , Bloomquist, C. A. A. and Horwitz, E. Philip(1981) 'Laboratory Scale Separation of Coal Macerals', Separation Science and Technology, 16: 10, 1571 — 1588
To link to this Article: DOI: 10.1080/01496398108058316
URL: http://dx.doi.org/10.1080/01496398108058316

SEPARATION SCIENCE AND TECHNOLOGY, 16(10), pp. 1571-1588, 1981

Laboratory Scale Separation of Coal Macerals

GARY R. DYRKACZ, C. A. A. BLOOMQUIST, and E. PHILIP HORWITZ

CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY,
9700 SOUTH CASS AVENUE, ARGONNE, ILLINOIS 60439

ABSTRACT

A laboratory scale procedure for separation of the maceral constituents of coal has been developed. This procedure is a modification and scale-up of our earlier density gradient centrifugation method. The technique enables us to separate larger quantities and to obtain higher density resolutions of individual coal macerals than was previously possible. The procedure involves an initial sink-float separation on finely ground chemically demineralized coal using a high speed centrifuge to obtain large quantities of single maceral groups (*i.e.*, exinite, vitrinite, or inertinite). The maceral concentrate, 15-20 g in quantity, rather than the entire coal serves as the feed for the DGC separation. Efforts to apply continuous centrifugation techniques as an alternative to the sink-float separation to concentrate maceral groups were only partially successful.

INTRODUCTION

The authors have recently described a procedure for separating small amounts of maceral constituents from coal (1,2). The procedure is based on density gradient centrifugation (DGC) with commercially available equipment. Macerals of 90% (by volume) or greater purity were obtained in some fractions with a single centrifugation run. In addition, information on the

maceral density and the range of densities of each maceral type is obtained. The procedure can also produce a fairly rapid visual representation of the proportion of the various macerals within the coal.

One of the major limitations of our maceral separation procedure is the small amounts of material that are obtained in a single DGC run. (Two grams of demineralized coal are used as feed.) An important requirement in the DGC procedure is that the coal particles must be completely dispersed in the centrifuge rotor. If the concentration of coal in the rotor exceeds a certain limit, the coal particles will aggregate causing an inefficient separation. A possible way to overcome this problem is to extend the density gradient over a much larger volume so a sharp peak such as vitrinite may be spread over a greater net volume (3). Thus the total sample size applied to the centrifuge rotor can be increased, and the procedure should result in a more narrow density range for each fraction. However, under these conditions the fixed capacity of our rotor (1.9 L) is insufficient to separate an entire coal into its constituent maceral groups, and the coal must therefore be 'pre-separated' into several density regions which correspond to those occupied by each maceral group. Thus three regions are adequate for most coals.

The purpose of this work was two-fold: 1. To investigate a sink-float type procedure to separate the macerals into three fractions using a continuous flow system which is made for our specific equipment. 2. To use density gradient centrifugation (DGC) to optimally separate the macerals from one another in larger yields than was previously done.

Continuous flow techniques have the advantage of allowing much larger amounts of material to be processed relative to the traditional sink-float method which utilizes simple centrifuge tubes. Continuous flow centrifugation has been used before

to separate the maceral groups, but utilized quite different equipment than was available to us (4). We wished to utilize our available equipment, even though this equipment is not strictly designed for continuous flow separations of highly concentrated particulate slurries.

EXPERIMENTAL

Coal

The coal used in this work was a high-volatile B bituminous coal obtained from Pennsylvania State University (PSOC-106). It was found to have a maceral composition consisting of 20.1% exinite, 35.2% vitrinite, and 45.3% inertinite. Ultimate analysis (daf): C, 79.09; H, 4.16; N, 120; S, 1.06; O (diff.) 13.4; ash, 14.6.

As described in (2), the coal was prepared by fine grinding in a fluid energy mill (FEM), followed by HF/HCl demineralization. Final particle size averaged 3 microns.

Density gradient separations, both on an analytical and a preparative scale, were performed as described in (2). For analytical density gradient runs, 2-5 mg of sample from a separation were applied to a 42 ml density gradient (1.0-1.5 g/cc) formed in a 50 ml centrifuge tube. The absorbances for each run were normalized to the highest peak within that run. This technique allowed us to examine the effectiveness of a particular separation within a relatively short period (∿3 hr). For preparative experiments the standard JCF-Z zonal rotor with a zonal core was used with preformed non-linear gradients. After separation of the macerals the gradient was fractionated into ∿30 ml fractions.

Continuous Flow Procedure

The first approach to achievement of scaled-up maceral separations was to use the Beckman model JCF-Z rotor with the

standard capacity continous flow (CF) core (*i.e.*, with 660 ml of usable liquid volume remaining in the rotor after core installation). Centrifugation was performed in a Beckman model J-21C high speed centrifuge.

The standard Beckman CF core is designed to facilitate large-scale separations by pelleting out the heavy material (sink) against the rotor wall, while the remaining material contained in the supernatant is pumped out of the rotor and collected externally (float). Four radial channels have been cut across the top flange of the core (annular or edge passage) for effluent flow, and openings exist at the core bottom which lead internally diagonally back to the central passageway (for input flow). As recommended, the flow of liquid through the rotor was through the center passage to the bottom of the core, up the core side, and out through the annular or edge passage accross the upper flange (3). In the case of the separation of exinite the sample was run through the rotor at such a flow rate that the vitrinite and inertinite particles would have time to deposit on the rotor wall during the time required for the feed mixture to move from the bottom of the core to the edge passage. The exinite supernatant should then flow up to the flange and exit the rotor through the edge or annular passageway.

The rotor was loaded with solution, at an input rate of 20 ml/min while spinning at 2000 rpm (2K) with the vacuum and refrigeration both on. The centrifuge was then accelerated to 5K rpm at the same flow rate, and the evacuated rotor chamber was brought to atmospheric pressure. Once all of the coal feed solution had been pumped through, the apparatus was allowed to come to a complete stop without braking, the rotor lid was carefully opened, and the rotor supernatant was siphoned off so as not to disturb the rotor wall deposit. The solid deposit on the rotor core was collected, as was the rotor wall solid deposit. Sample sizes ranged from 20-90 g coal in 0.5-1.0 L volumes of feed mixture.

Modified Zonal Core

A second approach to the CF separation technique was tried using a modified zonal core. The vanes of this core were cut to half the standard length. Thus the new input holes on the vanes were positioned up approximately one-half the distance from the floor of the rotor to the lid surface. Plumbing connections for this modification were connected as for zonal runs (5), and the same procedure was used as with the CF core. The liquid flow with this configuration was into the middle of the rotor through the four core vane passages and out through the center holes at the top of the core.

The total rotor volume with the modified zonal core used in the CF mode was 1.9 L (6). The feed solutions consisted of mixtures of 20-66 g coal in 0.5-1.0 L CsCl solutions of density 1.27 g/cc having Brij-35® surfactant concentrations of 8 g/L. The rotor was prefilled (at 2K rpm with rotor chamber vacuum and refrigeration turned on) at an input flow rate of approximately 50 ml/min. The rotor speed was then increased to 5K rpm and the slurry pumped into the middle of the rotor at 20 ml/min flow rate. The feed slurry could not be successfully pumped into the rotor at 20 ml/min unless the vacuum was turned off. Refrigeration under these conditions was at best only partly effective. At completion of slurry input approximately 0.5 L of density 1.27 g/cc CsCl + Brij-35® rinse solution was pumped through the apparatus and collected with the combined effluent. The centrifuge was braked to 2K rpm, and finally allowed to come to rest without further braking. As before, the rotor lid was removed, the supernatant siphoned out, and the two deposits removed.

Sink-Float Procedures: Pre-separation of Macerals

We used a Beckman model JA-10 fixed angle rotor, having a 6 x 500 ml capacity, for all sink-float experiments. A sink-float separation of exinite from vitrinite plus inertinite was

performed using a feed consisting of 20 g/L of coal suspended in 3 x 400 ml portions of CsCl/Brij-35® solution. Dispersion of the coal in this mixture was assured by ultrasonic pretreatment as described in (2). The slurry was then centrifuged for 45 min at 8K rpm and the top 300 ml of float supernatant from each bottle was carefully suctioned off, leaving the sink material deposited on the polycarbonate centrifuge bottle walls and bottom. Both float and sink fractions were isolated by filtration through 0.8 micron Nuclepore® polycarbonate membranes.

A final SF separation was performed on the combined vitrinite and inertinite sink fraction. The sink fraction was redispersed in a CsCl/Brij-35® solution having a density of 1.35 g/cc and the SF procedure repeated.

RESULTS AND DISCUSSION

Coal

The coal used for this study (PSOC-106) was chosen because of a nearly equal content of each of the three major maceral groups (Fig. 1).

Continuous Flow Experiments

Initially we attempted to use the standard continuous flow core supplied by Beckman Instruments for the model JCF-Z zonal rotor. This rotor is the heart of our separation system, and has several types of cores (among which are the continuous flow and the zonal cores) which can be used for different types of separations. In all cases our adaptations of this rotor involved the use of a single density medium. For example, in the case of the exinite enrichment the intent was to pellet the combined vitrinite and inertinite fractions against the rotor wall, with the exinite fraction exiting the rotor in the supernatant.

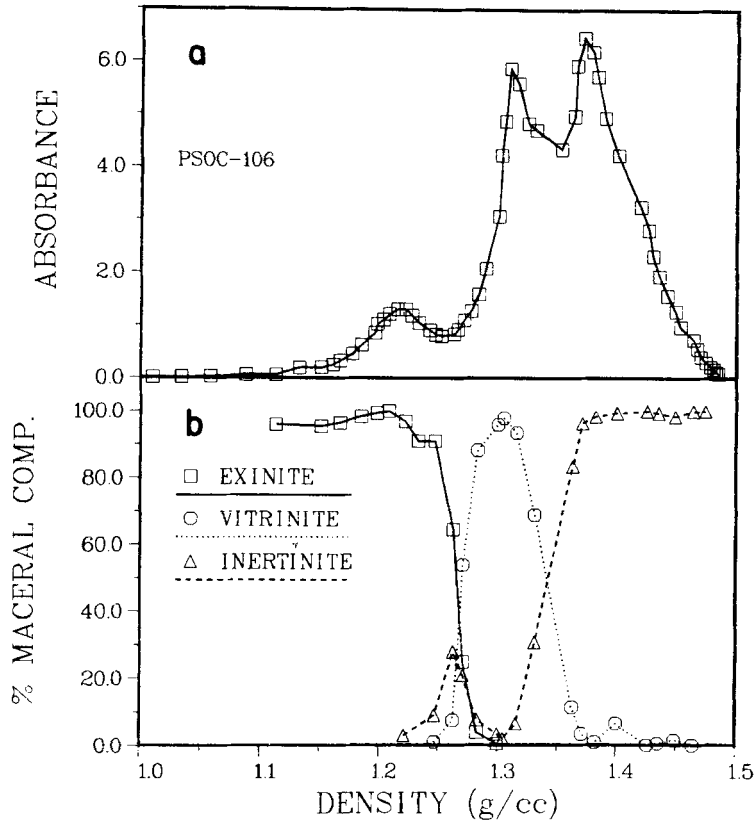

FIGURE 1. Preparative separation of PSOC-106 using a linear gradient. Maceral comparison by % by volume. All densities are at 25°C. Absorbance is roughly proportional to mass of material at a particular density (1).

Figure 2a and Table 1 show analytical scale density gradient centrifugation results obtained from samples of effluent, core solid, and rotor contents obtained from the best separations of exinite from vitrinite and inertinite using the continuous flow (CF) core. Figure 2b shows the data for the corresponding fractions obtained for the follow-up vitrinite from inertinite separation. From the data it was clear that a problem existed with the core. The separation is not as effective as we had

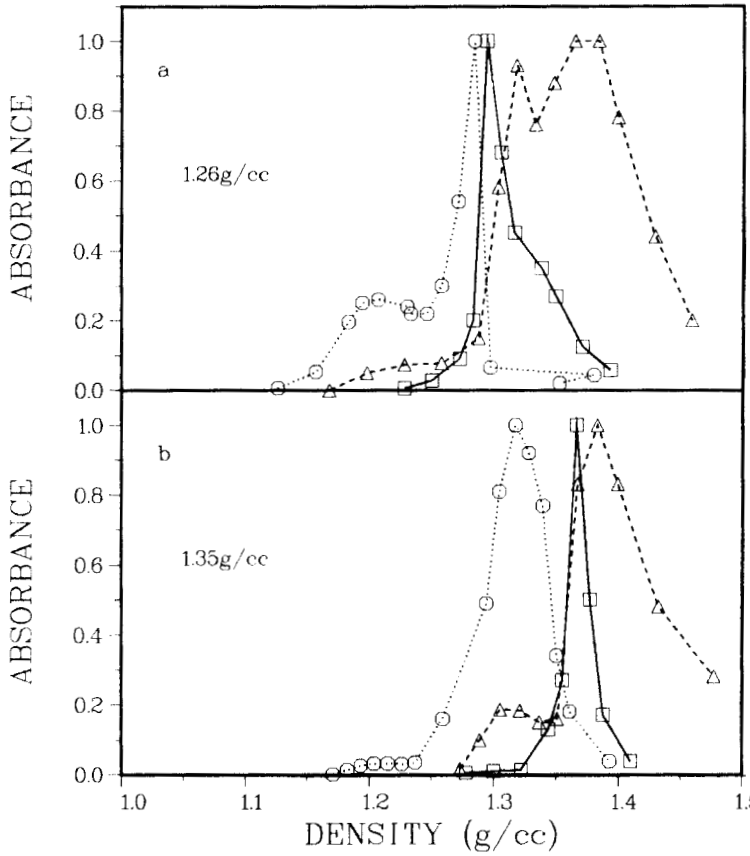

FIGURE 2. Continuous flow core experiment: Analytical density gradient of fractions. Absorbance is roughly proportional to mass of material at a particular density. a) Separation of exinites from vitrinite and inertinite at 1.26 g/cc: effluent, □; coal on core, ○; rotor wall deposit, △. b) Separation of vitrinites from inertinites at 1.35 g/cc: effluent, □, coal on core, ○; rotor wall deposit, △; [Brij-35®] = 8 g/L.

hoped. After several attempts, the overall conclusion we reached with regard to CF centrifugation was that the experimental configuration we used did not work. We found several limitations imposed on us with our particular problem. We could not operate at high enough centrifugal speeds to cleanly

TABLE 1.

Continuous Flow Separations with Standard Continuous Flow Core[a]

		Maceral Anal. (% by Vol)		
	Yield (g)	Exinite	Vitrinite	Inertinite
1.26 g/cc:				
Float[b]	4.0	60.0	40.0	--
1.35 g/cc:				
Float	14.5	3.0	75.0	22.0
Sink[c]	25.0	2.0	8.0	90.0

[a] Initial coal concentration was 45 g in 2 L of CsCl with 8 g/L Brij-35®.

[b] The float consists of the coal that was pumped out of the rotor as feed was pumped in plus material scraped off the continuous flow core.

[c] The sink fraction consists of the material found on the rotor wall and the slurry (660 ml) filling the rotor.

separate sinks from floats. At high speeds the rotor must be operated in an evacuated chamber to prevent the titanium rotor lid threads from seizing to the rotor body threads, but if we evacuated the centrifuge rotor chamber, the special seal which separates the rotating and non-rotating parts of the rotor, as well as the input and exit fluid flow routes, would invariably fail causing cross-contamination of flows and ejection of material into the centrifuge chamber. This is not a fault of the rotor since it is not primarily designed for highly loaded slurries. However, since we had little trouble with density gradient experiments, we felt we may have been able to overcome

these problems. The only way we could avoid seal failure was to operate at lower speeds under atmospheric pressure. Increasing the spring tension on the graphite seal did not help. Nevertheless, under these non-optimum conditions we still had difficulties because coal entered the rotor chamber at the rotor floor. The fine coal had a tendency to stick to the titanium rotor bottom instead of either going to the rotor wall or being entrained in the effluent. Thus most coal particles remained near the input passage holes and although some separation was effected (Fig. 2), most of the float material remained in the rotor either in the deposit at the bottom or on the core itself. In an attempt to overcome the retention of coal on the bottom of the rotor we modified a standard zonal core, normally used for density gradients, by trimming the vanes to half their original length. Since the vanes are bored to permit flow to the bottom outside wall of the rotor, we were able to pump our coal slurry into the middle of the rotor assembly (both center to wall and top to bottom). This modification eliminated the problem of coal adhering at the site of entry into the rotor cavity, but we had the same problem with the rotor seal and thus lower than optimum centrifuging speeds and atmospheric pressure were again necessary. Figure 3 and Table 2 present the data for the best run. The efficiency of the separation is low and, therefore, we have abandoned this technique with our present equipment.

Sink-Float Separation

Currently our best option for scale-up of maceral separations is the sink-float (SF) technique followed by DGC, even though the CF method has the potential for handling much larger sample sizes.

Data from SF runs done on a 400 ml scale, at 8K rpm, using PSOC-106 are given in Table 2. The presence of the

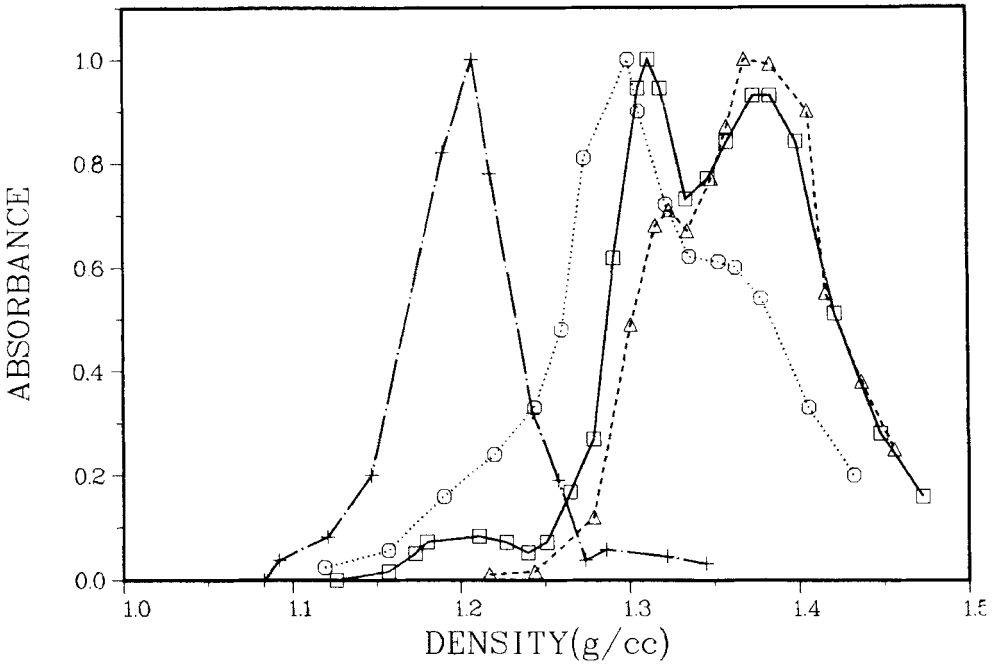

FIGURE 3. Modified zonal core for continuous flow: Analytical density gradients of various fractions. Supernatant-material found in 1.9 L that occupies rotor, □; yield 16.2 g coal; effluent, ○, yield 3.1 g; coal on rotor wall, △, yield 2.4 g; coal on core, †, yield 1.6 g; [Brij-35®] = 8 g/L.

Brij-35® surfactant in the CsCl - coal mixture and the ability to utilize high centrifuge speeds are both important keys to the efficient separations obtained.

Figure 4 and Table 3 give results of analytical DGC separations done on fractions obtained from two typical SF runs. The initial exinite from vitrinite and inertinite separation was carried out at density 1.28 g/cc and consequently did contain a portion of the low density vitrinite fraction. A better separation would have been obtained at density 1.27 g/cc. Very little exinite was carried down in the sink portion of the heavier macerals. The final vitrinite from inertinite separation

TABLE 2.

Continuous Flow Separations with Modified Zonal Core[a]

	Yield (g)	Maceral Anal. (% by Vol) Exinite	Vitrinite	Inertinite
Supernatant[b]	16.2	18.0	45.0	37.0
Core[c]	1.6	57.0	20.0	23.0
Effluent[d]	3.1	39.0	35.0	26.0
Wall[e]	2.4	1.0	38.0	61.0

[a]Initial slurry concentration was ∿25 g in 0.5 L.

[b]Coal found in the 1.9 L that occupies the rotor at any time.

[c]Coal scraped off the Noryl® rotor core itself.

[d]Coal found in the effluent as the coal slurry was pumped in.

[e]Coal found adhering to the rotor wall.

TABLE 3.

Sink-Float Separation[a]

	Yield (g)	Maceral Anal. (% by Vol) Exinite	Vitrinite	Inertinite
1.28 g/cc:				
Float	3.1	68.0	19.0	13.0
1.35 g/cc:				
Float	5.8	6.0	79.0	15.0
Sink	6.6	0.5	4.0	95.5

[a]Initial coal concentration was 13.4 g/L with 8 g/L Brij-35®.

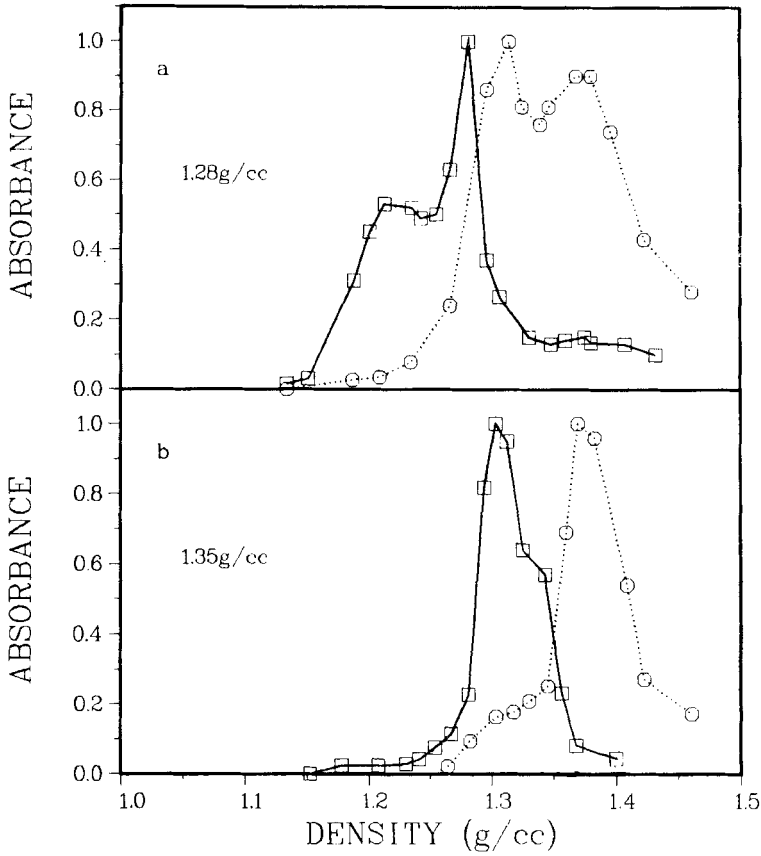

FIGURE 4. Sink-float separations: Analytical density gradients of fractions. Separation of exinites from vitrinites and inertinites at 1.28 g/cc: Floats, □, sinks, ○. Separation of inertinites from vitrinites at 1.35 g/cc: Floats, □; sinks, ○; [Brij-35®] = 8 g/L.

was done at density 1.35 g/cc and yielded an efficient split between the two macerals right at the density chosen. Table 3 presents a summary of the microscopic analyses of the three major maceral fractions obtained from these two SF separations. A comparison of Table 3 with Table 2 reemphasizes the superiority of the SF approach versus the CF method under our present experimental environment. However, sample amounts that can be sepa-

rated by SF at any one time are limited, a point in favor of the continuous flow method.

Large-Scale DG Separations of the Exinite, Vitrinite, and Inertinite Main Maceral Groups

Maceral fractions obtained from first stage separations using the standard CF core were further purified using a modified version of the density gradient centrifugation (DGC) technique described in (2). The results shown in Fig. 1 are based on density gradients that were linear with respect to volume. As stated before, to increase the yield it is necessary to have a very shallow density gradient so that a sample can be spread over many more fractions than is the case with the conventional gradient. Figure 5 is a plot of the three density gradients

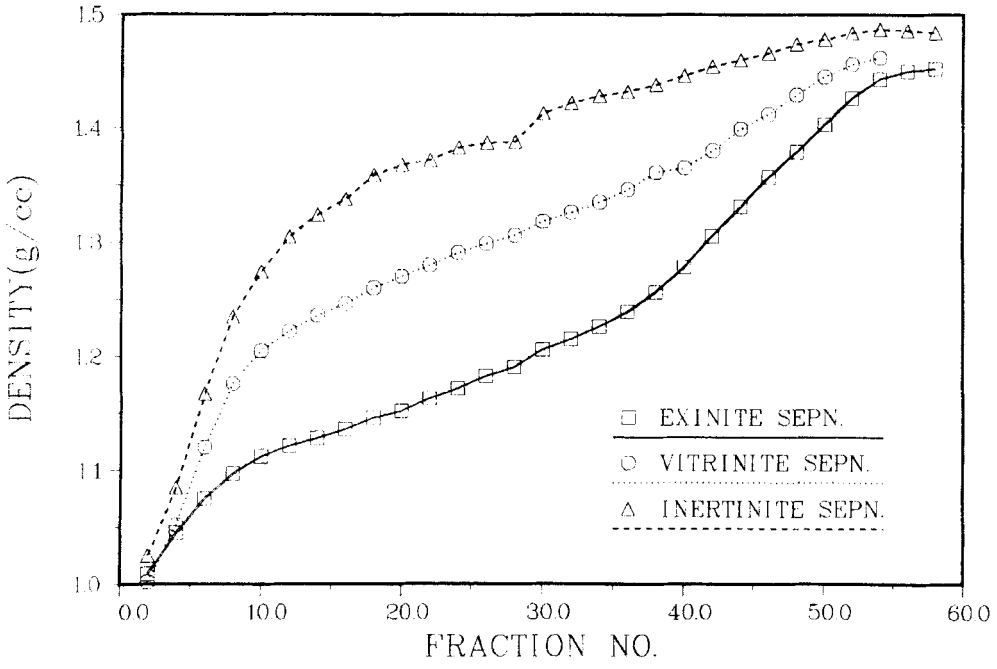

FIGURE 5. Density gradient shapes used to separate the three maceral concentrates. Each fraction is 30-31 ml. All densities are corrected to 25°C.

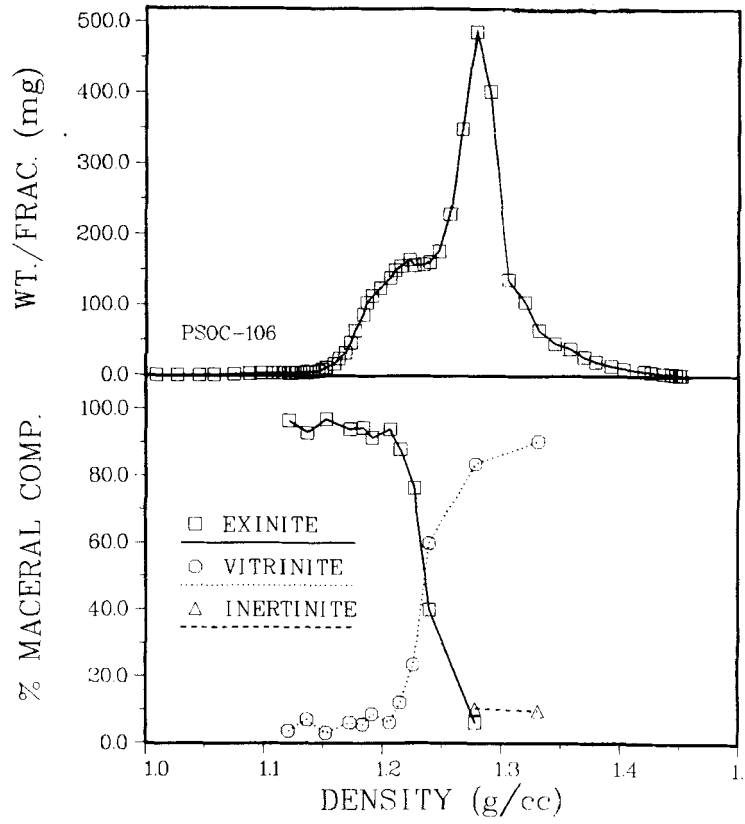

FIGURE 6. Separation of exinite concentration and corresponding maceral analysis of selected fractions (% by volume). All densities are corrected to 25°C. [Brij-35®] = 8 g/L.

generated during the three separate purification runs for each maceral concentrate. Using these gradients it was possible with the vitrinite fraction, for example, to spread out the density range of interest in ∿80% of the rotor volume as compared to ∿20% with a simple linear gradient (Fig. 1). Thus, a much larger total weight of a given maceral could be kept dispersed without causing aggregation. In the vitrinite case the initial 10% of the rotor volume holds mainly exinite material and the last 10% holds primarily the inertinite. With this gradient design we

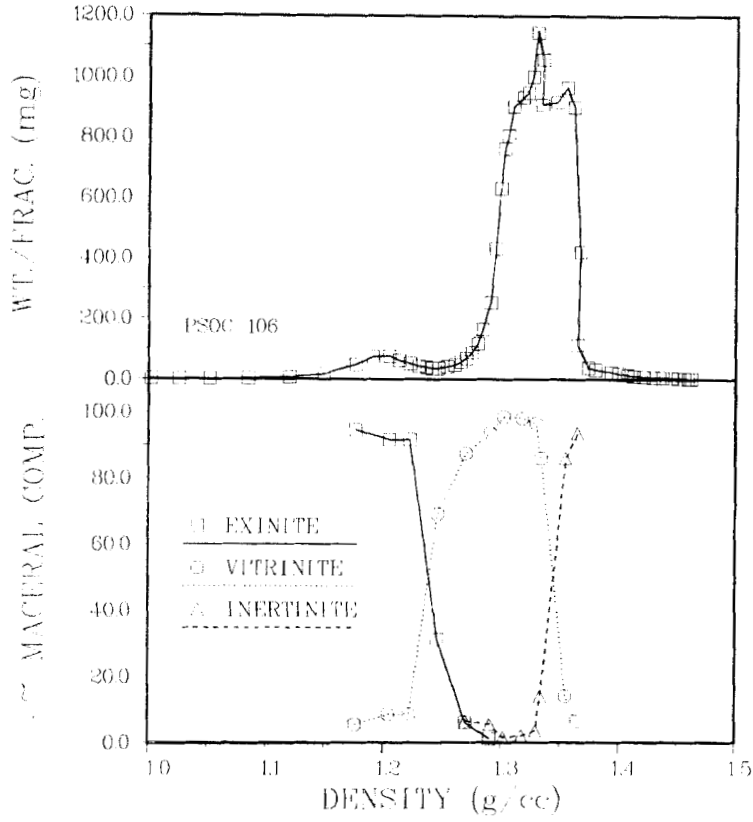

FIGURE 7. Separation of vitrinite concentrate and corresponding maceral analysis of related fractions. Conditions as in Figure 6.

do not exceed the ability of the surfactant to disperse the coal in the latter regions. If aggregation occurs, the rotor passages could be clogged. Sample sizes separated using the modified DGC technique were 3.9 g exinite, 14.3 g vitrinite, and 24.5 g inertinite. Figures 6, 7, and 8 present results of the three separation runs done on the crude major maceral fractions. The altered gradient (Fig. 5) did result in a wide spread of the major maceral densities and a corresponding significance improvement in amounts of maceral separated in a pure state.

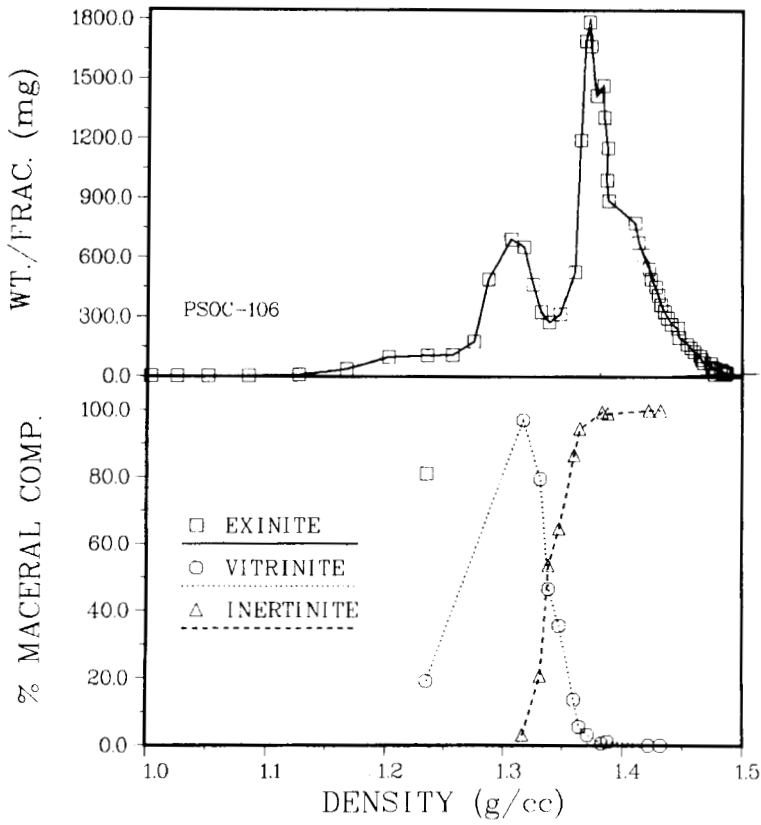

FIGURE 8. Separation of inertinite concentration and corresponding maceral analysis of related fractions. Conditions as in Figure 6.

CONCLUSIONS

With our present equipment we were unable to utilize the continuous flow system designed for our particular centrifuge. However, the sink-float technique presents no problems, and with the addition of the surfactant can result in quite pure density cuts.

We have also been able to substantially increase the amount of coal that can be applied to a density gradient. Approximately

15-20 g of an initial maceral concentrate can now be separated into fractions which have a 0.006 g/cc density range.

REFERENCES

1. G. R. Dyrkacz, C. A. A. Bloomquist, L. H. Fuchs, and E. P. Horwitz, Separation of Coal Macerals, Division of Fuel Chemistry, American Chemical Society, Vol. 25, No. 3, p. 216 (1980).
2. G. R. Dyrkacz and E. P. Horwitz, Fuel, in press.
3. T. D. Prospero, Meth. Dev. Biochem. (Ed. E. Reid), 3, (1973).
4. C. Kroger, A. Pohl, and F. Kuthe, Glückauf, 93, 122 (1957).
5. Beckman Instruction Manual JCF-Z-IM-3, November, 1975.