

SEPARATION OF COAL MACERALS*

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INTRODUCTION

As coal science progresses the need for pure coal macerals becomes increasingly obvious. The chemical and physical properties of the various macerals are known to differ substantially(1), but a large portion of the work is based on European coals. Furthermore, separated macerals used for previous studies were not always of high purity. Little attention has been given to the actual procedures for separating the macerals. We are currently involved in a program to define the parameters necessary for efficient separation of macerals using differences in density and to build up stocks of macerals for additional analyses. Our technique is based on density gradient centrifugation (DGC) rather than the often used sink-float procedures. As we will show, DGC has much more latitude for separation control and has the advantage of superior resolution in less time than previous methods, *e.g.*, sink-float.

EXPERIMENTAL

Coal Samples

All coal samples used in this study were obtained from the Pennsylvania State University data bank.

Microscopic Analysis

Petrographic analysis of the fine ground coal was performed in both incident blue light and white light at 1200x. The exinites autofluoresce in blue light making them more visible. Standard procedures were used for mounting, polishing, and analyzing the coal materials.

Grinding

The grinding of the coal was performed in two steps. Initial grinding of the coal to below 200 μm particle size was performed using a planetary ball mill. The resultant ground coal from the ball mill was then used as a feed for fine grinding in a Sturtevant Micro-nizer fluid energy mill. This type of jet mill has no moving parts; the coal is fed into a high velocity gas stream of nitrogen moving in a circular pattern where it self-grinds. In addition, the mill is to some degree self-classifying; therefore, a narrow particle size distribution is produced.

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In the case of PSOC-297 coal, one pass through the fluid energy mill produced particles which were $<6 \mu\text{m}$ in size. This size range gave particles which were largely homogeneous with respect to a given maceral. In the case of PSOC-124 coal, two passes through the mill, followed by demineralization, six freeze-thaw cycles between liquid nitrogen and 80°C , and then a final pass through the mill was required to reduce the particle size to $<6 \mu\text{m}$.

Demineralization

After fine grinding, the coal was demineralized chemically using standard procedures(2). Both coals still had $\approx 2.6\%$ mineral matter present after chemical treatment.

Density Gradient Centrifugation (DGC)

DGC techniques were used for all separations. Linear density gradients were used throughout this work, and were pre-formed using a commercial density gradient former (ISCO, Model 380 or 382). Aqueous CsCl was used to form all gradients. The coal was dispersed with either Brij[®] 35 (polyoxyethylene-23-lauryl ether) or dodecyltrimethylammonium salt (8 g/L) added to all solutions. Two separation systems were used: analytical DGC and preparative DGC. In the analytical mode, 5-50 mg of coal was dispersed into a low density solution by mild ultrasonic treatment, layered on a 40-45 ml gradient (≈ 1.0 to 1.5 g/cc), and then centrifuged at 12,000 rpm ($\approx 16,000 \times g$) in a Beckman J-21C centrifuge for 30 minutes. After this period the centrifuge was stopped and the contents of each of the tubes were forced out with a dense chase solution of fluorinert[®] FC-43. The contents leaving the centrifuge were then passed through an absorbance monitor and into a fraction collector. The density of each fraction was found by measuring its refractive index.

Large scale amounts of coal (2-3 g) were separated using a commercial zonal centrifuge rotor (Beckman, model JCF-2) which holds a 1.6 L density gradient. After loading and centrifuging, the contents were again pumped out with the high density chase solution and collected in 30 ml fractions. Each fraction was filtered through a $1 \mu\text{m}$ pore diameter nuclepore[®] membrane filter. The resultant residue was washed with both room temperature and hot water to remove CsCl and surfactant, dried in a vacuum at 80°C and stored under nitrogen. Selected fractions were then microscopically analysed.

Atomic ratios for some fractions were measured using a microwave plasma detector (Applied Chromatography Systems, model MPD850) equipped with a solid probe.

RESULTS AND DISCUSSION

Two bituminous coals were used in this study, PSOC-297 and -124. PSOC-297 is a cannel-like coal, and PSOC-124 is a true cannel coal. The composition of these two coals is shown in Table I. These coals were chosen for their large inertinite and exinite concentrations; PSOC-297 was also interesting because of its high mineral matter content. We expect that any separation difficulties with mineral matter would be most evident in this coal.

Scheme I shows the sequence of procedures used to obtain separated macerals. The first and one of the most important aspects in maceral separation is the grinding stage. The initial grinding step (using a planetary ball mill) is necessary to reduce the particle size below 200 μm , which is required for the feed to the fluid energy mill. The average particle size after grinding in the fluid energy mill is 2.6 μm , with 95% of the material below 6 μm . After grinding, the coal is demineralized. We have found that demineralization is a necessary step for the two coals investigated in order to achieve a good maceral separation.

The density gradient separations were carried out using a maximum and minimum density of 1.5 and 1.0 g/cc, which encompasses the range of maceral densities. All gradients were linear (by volume). CsCl was used to form the gradients because of its relative inertness to coal, convenience in handling, and maximum density of 1.9 g/cc. However, the hydrophobic nature of coal presented a problem in dispersing the fine particles in a hydrophilic medium. In fact, very little maceral separation can be achieved without the use of surfactants to improve the dispersibility of the coal in CsCl solution. We tested three classes of surfactants: anionic, cationic, and nonionic, for their ability to disperse the two coals in aqueous density gradients. Quaternary ammonium salts, particularly dodecyltrimethylammonium bromide, and the nonionic Brij[®] 35 (polyoxyethylene-23-lauryl ether) were found to improve the wetting properties of the aqueous medium. However, Brij[®] 35 was used for all runs because it has good solubility in aqueous CsCl, is readily available, and was found to be better than the quaternary ammonium salt in regard to the stability of the dispersion of PSOC-124.

Figure 1 presents the combined results of analytical DGC runs for the two coals. All densities are solution densities corrected to 25°C. The absorbance scale can be taken as a measure of the relative amount of coal at a particular density, but the curves have not been normalized; thus direct comparison of yields per fraction between the two coals is not possible. As would be expected for such dissimilar coals, the curves are quite distinct and reflect at least crudely the proportion of the various maceral groups, with the exception of inertinite. From Dormans *et al.* (3), we expect the densities for the various macerals to be: exinites \sim 1.2, vitrinites \sim 1.3, and inertinites \sim 1.4 g/cc. It is interesting to note that the fractograms do not show peaks where inertinite is expected to appear.

Figures 2 and 3 show the results of preparative DGC runs on PSOC-297 and PSOC-124. The top curves in each set compare very well with the analytical runs. The lower graphs show the corresponding volume percent of the three maceral groups for selected fractions. It can be seen that for both coals many fractions are better than 90% pure with respect to a maceral constituent. In the case of alginite many particles apparently split out of the coal as single entities during grinding and could be identified from other exinites by their morphology. The actual yield of alginite is probably higher but smaller particles were counted as alginite only if they exhibited the morphological characteristics of alginite.

The inertinites present an interesting case because they seemingly exhibit high concentrations in more than one density region.

This can be seen more clearly in Figures 4 and 5, where we have plotted the data in a different manner. The ordinate is the weight of coal in each equal volume fraction collected. The percentage of each maceral in a density fraction was multiplied by the weight of that fraction. The weight of vitrinite was divided by 10 in Figure 4 for convenience of plotting. We have neglected the difference between vol. % and wt. % because of the difficulty of accurately calculating wt. % from a volume distribution. Neglecting the difference in vol. and wt. % only affects the results where there is an overlap of two or more macerals, but not significantly enough to change the overall results. Note that there seems to be multiple inertinite peaks with both coals. The reason for this behavior was revealed by microscopic examinations, which showed that the low density inertinite consisted of micrinite particles bound to other macerals.

In the case of PSOC-297 the micrinite is bound to exinites and vitrinites, whereas with PSOC-124 the micrinite is bound only to exinite. In both unground coals the micrinite is highly dispersed throughout the coal rather than localized in definite regions, and thus does not seem to selectively split out of the coal on grinding. For PSOC-297 this does not constitute a major problem, but for PSOC-124 a large fraction of the inertinite is obtained as composite particles. However, these composite materials prevent us from seeing the true distribution of a particular maceral, and therefore we modified our counting procedure. If the crosslines (of the microscope) fell on a particle which contained more than 10% of a second maceral, then we described that maceral under the crosslines as being bound. The error in such a counting procedure is high ($\sim 10\%$), especially where the macerals are generally of a fine nature, but for our purposes the error was not a severe problem. This procedure allows us to effectively eliminate, albeit in an artificial manner, mixed maceral particles and only observe the distributions of pure constituents. Figures 6 and 7 show this data. It is an easy task to read off from Figures 6 and 7 the maceral distribution and density peaks. For PSOC-297 coal: alginite, 1.06 g/cc; sporinite, 1.19 g/cc; vitrinite, 1.29 g/cc; and inertinite, 1.35 g/cc. Alginite constitutes only 2% of PSOC-297 and yet we achieved an excellent separation, which shows the effectiveness of the density gradient method. For the PSOC-124 separation, the alginite was present as a shoulder (1.0 to 1.1 g/cc) on the concentration profile of the exinites (see Figure 3), but was not counted because the fluorescence was not as distinctive as in the case of PSOC-297. The exinite distribution in Figure 7 shows a rather asymmetric shape. We believe this asymmetry represents two different types of exinite material, possibly different spore types; one showing higher fluorescence than the other. Vitrinite has a peak density of 1.25 g/cc and inertinite, 1.30 g/cc.

Figure 8 is a plot of the H/C and S/C for selected PSOC-297 fractions. An almost linear dependence of H/C on density is exhibited in the early fractions (< 1.35 g/cc); however, the inertinite fractions show little change. The H/C behavior in the exinite-vitrinite region may be explained according to Van Krevelen's correlation between density and atomic ratios (1). However, we cannot explain the H/C independent region (> 1.35 g/cc) at this time.

CONCLUSIONS

We feel the density gradient technique offers significant advantages over previous methods of maceral separation. It provides a rapid method of measuring the overall density ranges of the various macerals and of separating macerals having any density range desired. Of course, the smaller the fraction cuts, the less coal per fraction. Our current fractions range between 0.007-0.010 g/cc. To obtain the same range using sink-float techniques would require over 40 separate stages. As the results show, we have had good success with PSOC-297 and -124 coal samples using the DGC technique, although micrinite presents some problems. In the case of PSOC-297, the micrinite contribution does not drastically affect the material in which it is mixed, *e.g.*, vitrinite is still over 90% pure. In the case of PSOC-124 much more exinite material is contaminated by micrinite inclusion, undoubtedly because of the very high micrinite concentration initially present.

Two important points can be made from this study. First, the broad distribution of densities for exinite and inertinite and the corresponding large drop in H/C ratio for the exinites suggests large changes in chemical structure must be occurring. Thus, caution must be used in studying the properties of exinites and inertinites to insure that structural information is based on narrow range density fractions. In fact, this is probably why in the past the properties, both chemical and physical, have much broader limits for exinites and inertinites(1). Second, the density range for vitrinites is relatively narrow in both coals, suggesting that the properties of vitrinite should be generally less erratic and therefore considerably more predictable.

ACKNOWLEDGMENTS

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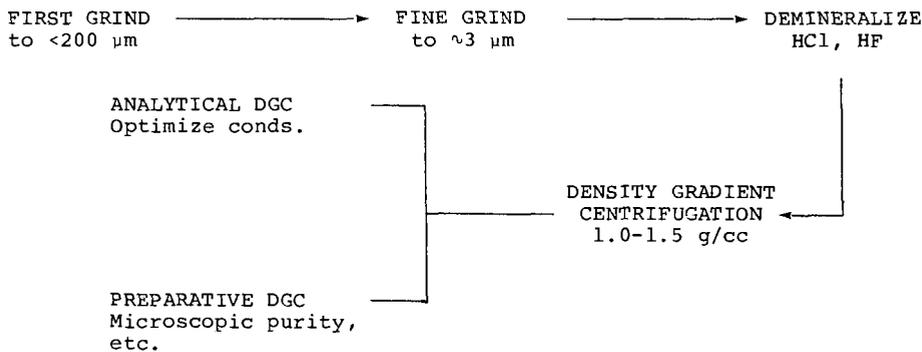
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TABLE I. Composition Data for Coals

	Volume %	
	PSOC-297	PSOC-124
Sporinite	16.4	51.7
Resinite	0.4	1.5
Cutinite	0.4	1.7
Alginite	2.0	1.6
Vitrinite	63.0	14.6
Micrinite ^a	17.0	27.4
Semi-fusinite	0.8	1.0
Fusinite	0.4	0.4
M.M (wt. %)	22.8	10.7
% C (dmmf)	82.17	84.99
% H (dmmf)	5.62	7.20

^aIncludes: micrinite, inertodeterinite, and macrinite.

SCHEME I



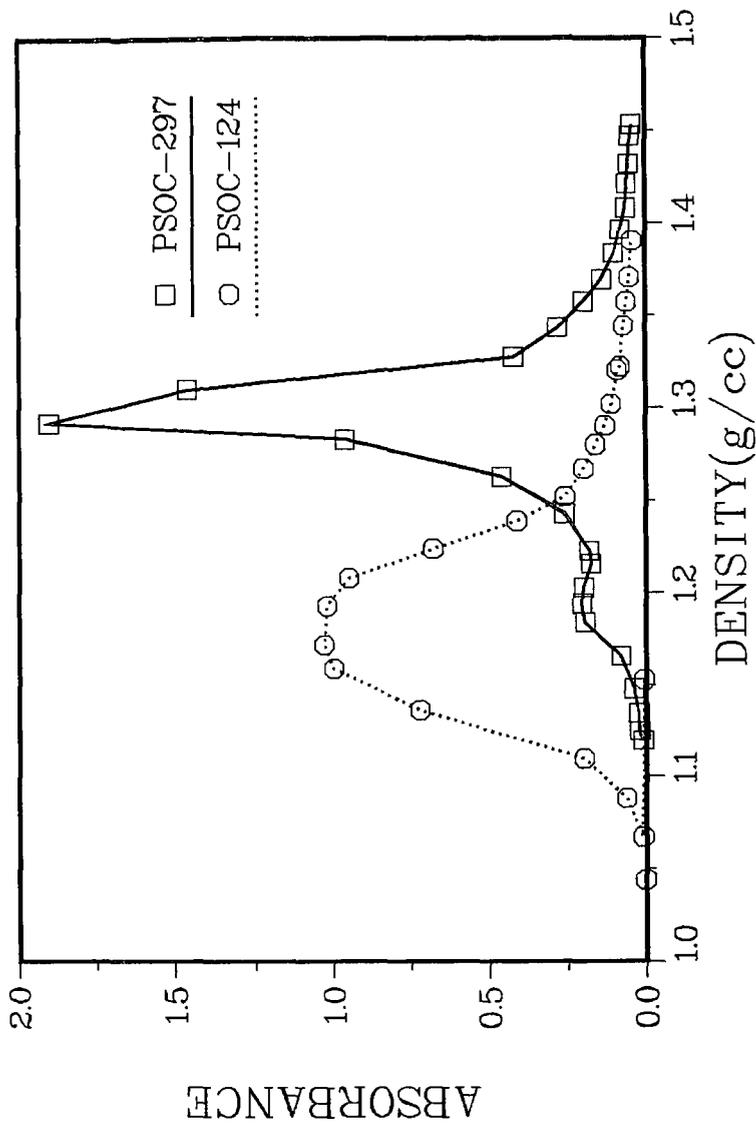


Figure 1. Analytical Density Gradient Separations for Two Coals.

Figure 2. Preparative Density Gradient Separation and Maceral Analysis of PSOC-297.

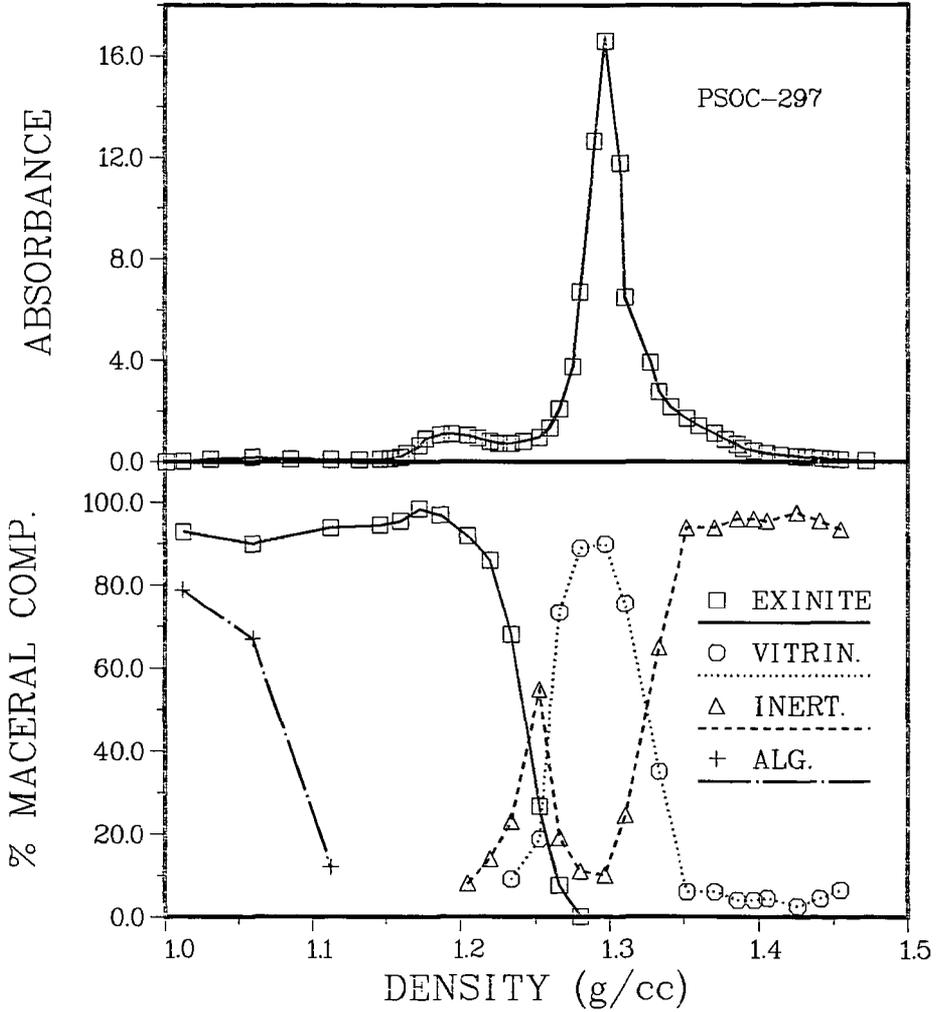
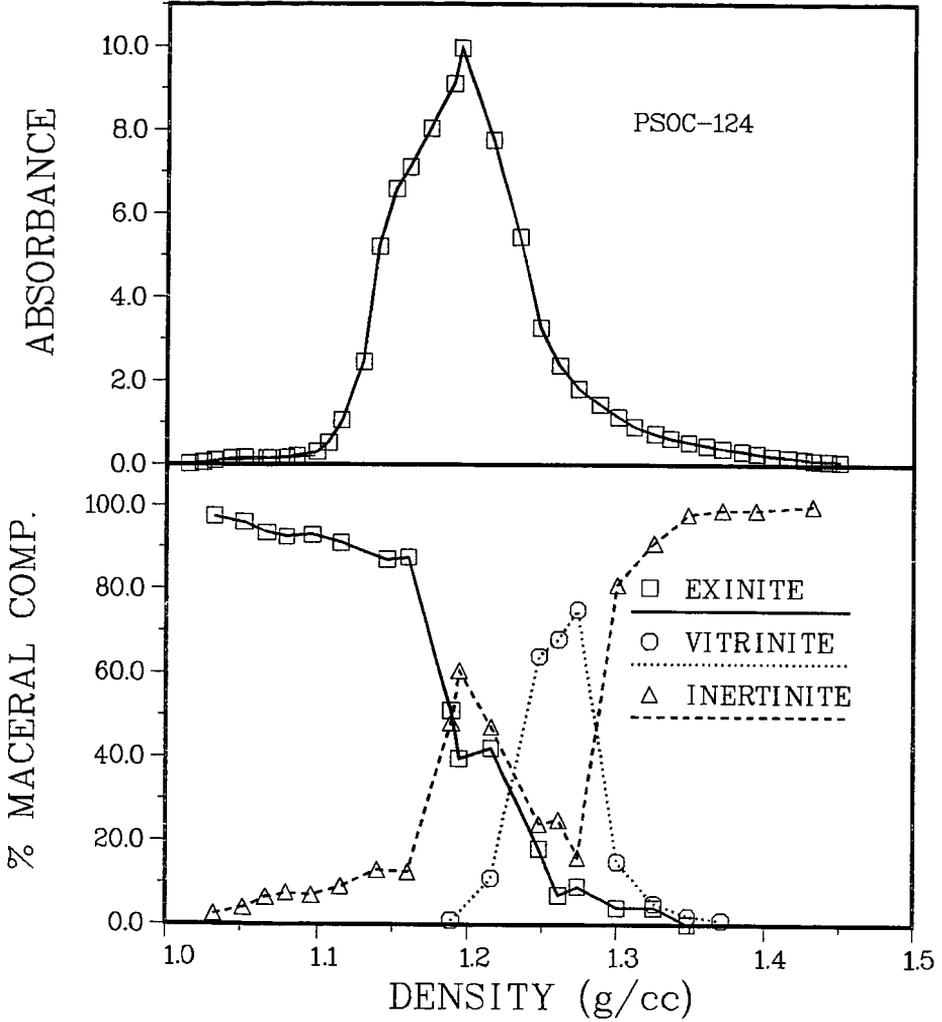


Figure 3. Preparative Density Gradient Separation and Maceral Analysis of PSOC-124.



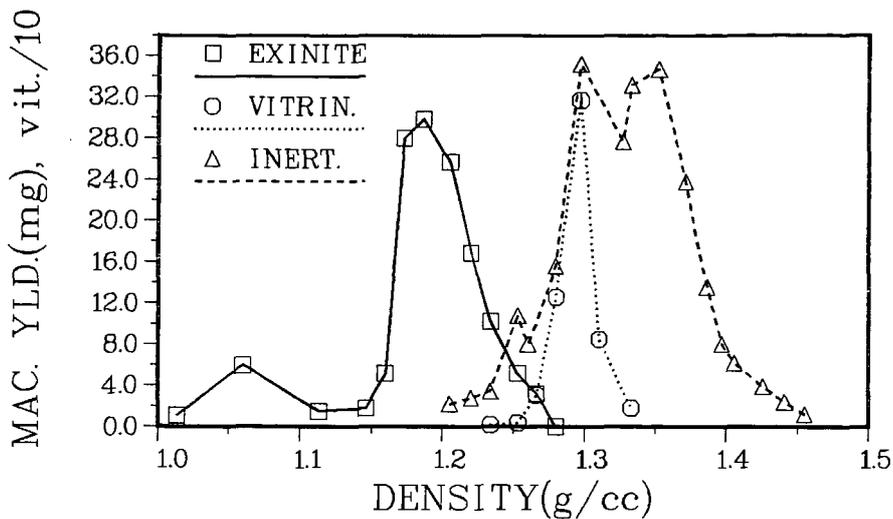


Figure 4. Amount of Each Maceral Type in Selected Density Fractions of PSOC-297.

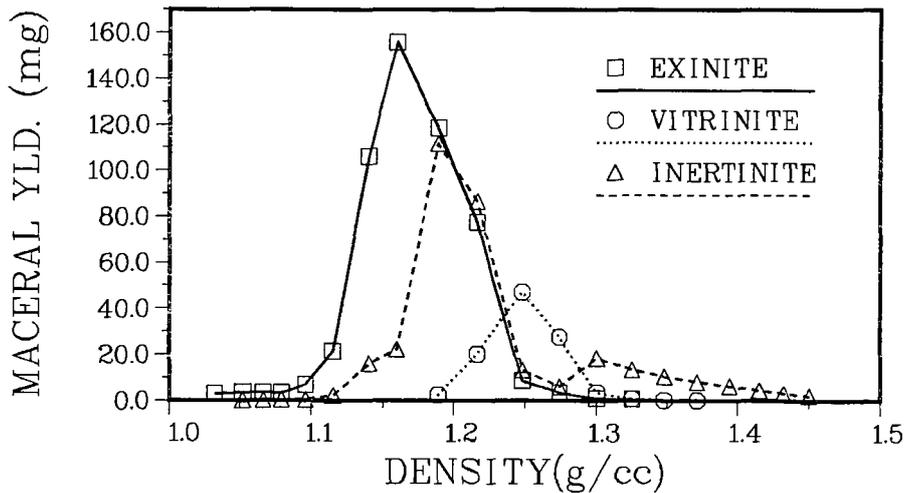


Figure 5. Amount of Each Maceral Type in Selected Density Fractions of PSOC-124.

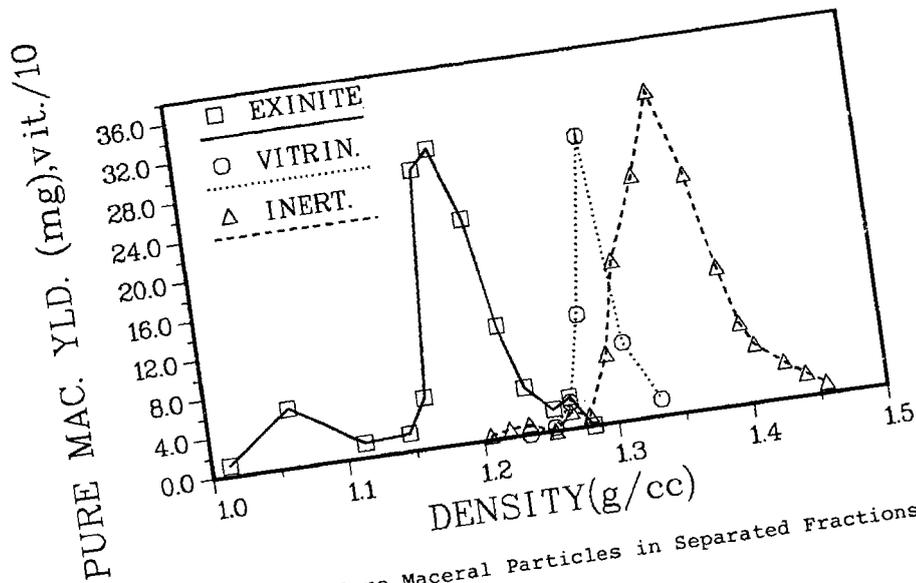


Figure 6. Yield of Pure Maceral Particles in Separated Fractions of PSOC-297.

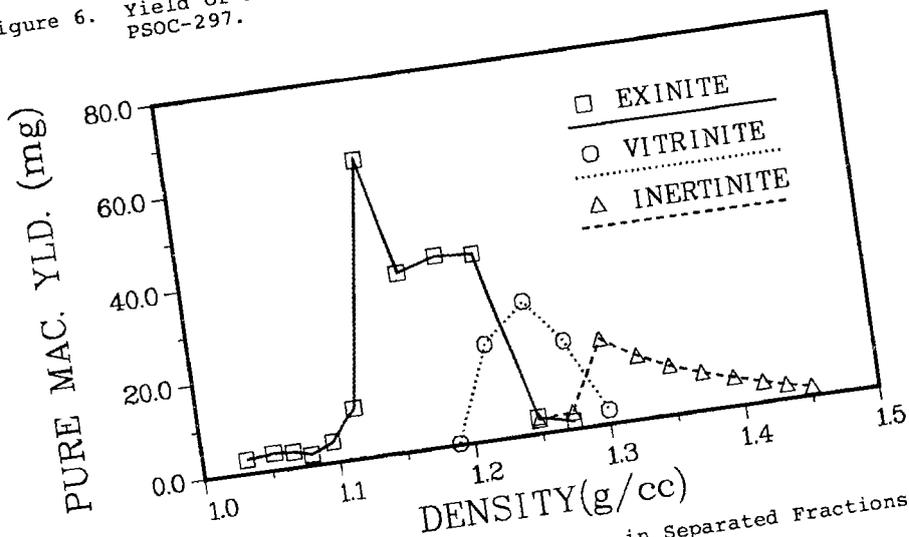


Figure 7. Yield of Pure Maceral Particles in Separated Fractions of PSOC-124.

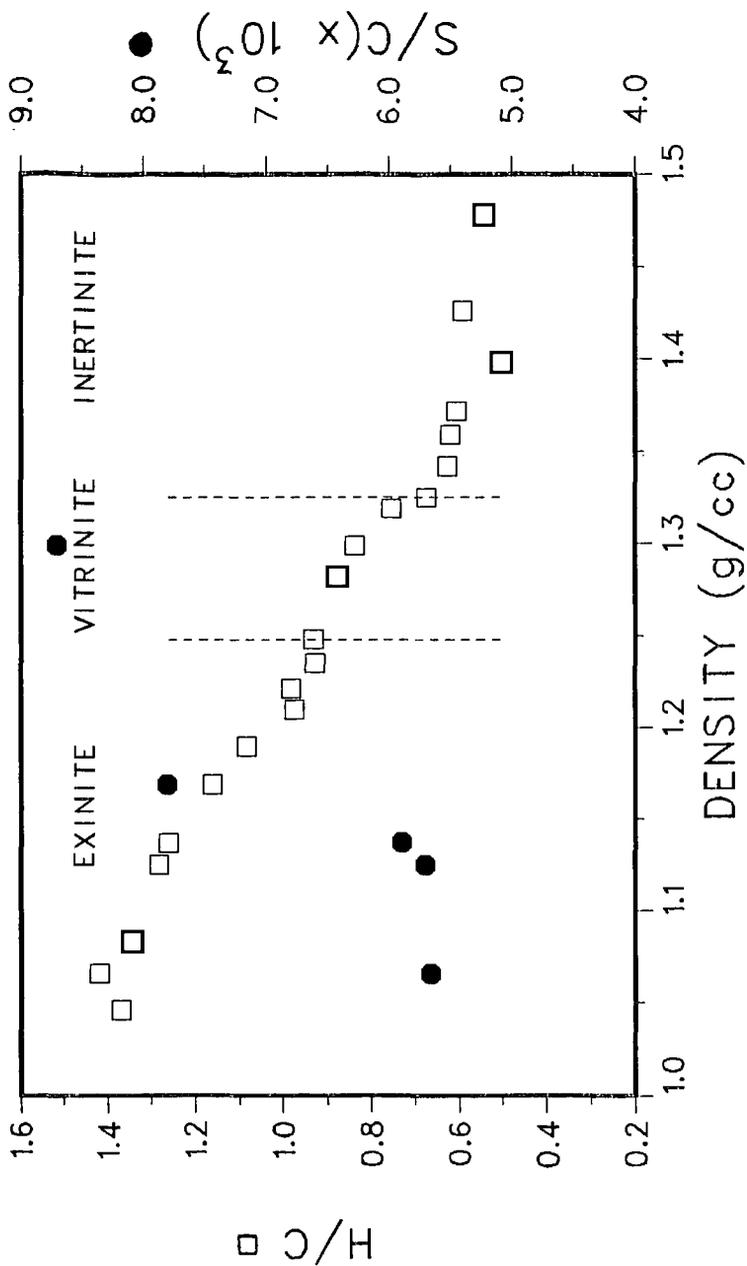


Figure 8. H/C and S/C Atomic Ratios for Separated PSOC-297 Coal.