

**DENSITY SEPARATION OF CHEMICALLY MODIFIED COAL MACERALS.
A TWO DIMENSIONAL SEPARATION METHOD FOR MORE HOMOGENEOUS MACERALS.**

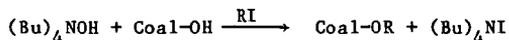
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INTRODUCTION

That coal is a very physically and chemically heterogeneous substance is one of the few facts about coal that has not been contested in the long history of coal research. However, the extent and nature of that heterogeneity is not at all clear. Coal heterogeneity is due to several elements: The varied diagenesis and catagenesis of the original organic plant constituents, specific associations and interactions of macerals from different paleo-environments, and the different mineral constituents of coal. Even though the heterogeneity is practically self-evident and is a major obstacle to defining the structural elements of coal, remarkably little work is directed toward exploring methods to reduce the heterogeneity prior to structure elucidation. Density gradient centrifugation (DGC) appears to be one of the most effective separation methods for reducing the heterogeneity of coal by separating the three maceral groups, and concomitantly provides some idea of the range^{1,2,3} of physical and chemical variation that exist within a coal sample. However, this still represents only a first order separation. We rarely can resolve the individual macerals that make up the maceral groups because their density distributions overlap. The maceral density ranges may overlap so closely, that no matter how finely we fractionate a density gradient, we will not resolve the various species. Thus, some additional treatment or separation method is necessary to resolve individual macerals or sub-maceral species.

Chemical modification of the coal maceral particles coupled with density gradient centrifugation is one approach to higher maceral resolution. For this two dimensional type of treatment to be useful, we must use a reaction which exhibits selectivity towards the macerals, and can cause an observable change in the density of the product. For our initial efforts, we felt that the reaction should be mild and not extensively alter the maceral particles, since petrographic analysis was needed to understand any changes in the separations. O-alkylation of the coal appeared to meet our requirements. The alkylation reaction utilizes tetrabutylammonium hydroxide and an alkyl iodide to alkylate hydroxyl groups⁵:



This reaction is carried out under mild conditions and is relatively non-destructive towards the coal. Since we know that at least the maceral groups have different oxygen contents and probably³ hydroxyl contents, this reaction system seemed most appropriate to our needs.

EXPERIMENTAL

Alkylation

The alkylation conditions were slightly modified from that indicated by Liotta.⁵ Under nitrogen, the sample (~20 mg) was stirred in 5 ml of THF for 10 minutes and then 50 μ l of 40% aqueous tetrabutylammonium hydroxide was added. After an hour, the alkyl iodide was added, and the solution stirred for seven days. The solution was neutralized with HCl and the volatile organics removed on a rotary evaporator at 60°C. Water was added and the mixture dispersed in a sonication bath. The solid was collected on 0.8 micron polycarbonate filter and washed with 50% aqueous methanol. The alkylated coal was dried under vacuum at 64°C.

Density Gradient Centrifugation

The density gradient centrifugation procedures in aqueous CsCl/Brij-35 solutions devised by Dyrkacz and co-workers were used as described.¹⁻³ Each coal was ground to less than 10 microns, and chemically demineralized before any further separation or chemical modification. The preparative level separations were done either on two gram levels (Preparative I) or on maceral sink-float concentrates (Preparative II). Analytical density gradient runs of the alkylated coal maceral fractions (1-25 mg) were done in 50 ml centrifuge tubes. The amount of coal at various densities in the analytical runs was inferred from the absorbance response at 660 nm in a flow through cell when the gradient was being fractionated.

Each density distribution has been normalized to the highest peak.

RESULTS AND DISCUSSION

Two high volatile A bituminous coals, PSOC-732 and 726, obtained from Pennsylvania State University were used in this study. The elemental and maceral analyses are shown in Table 1. All the data that will be presented is based on the chemically demineralized coals. This is necessary to maximize the resolution of the macerals.

Figures 1 and 2 present the DGC separations for the untreated, methylated and n-butylated coals. In the unalkylated coals, the lowest density band is the exinites and the mid-density band is the vitrinite. The highest density inertinite band is obvious in PSOC-732, but not in the PSOC-726 coal. For both inertinites the density at which there is 50% vitrinite and 50% inertinite is close to 1.31 g cm⁻¹. Relative to the untreated coals, all the alkylated coals exhibit a shift in their density distributions to lower densities, which is in accord with previous findings.⁶ We also see that the butylated coal density patterns are shifted more than the methylated coal; this is expected from molecular volume considerations.^{2,7} Looking at the density distributions in more detail, we see rather complex changes are occurring with alkylation. If each of the maceral groups were responding in the same way to alkylation, we would expect that the overall density pattern would not change. Maceral analyses of the density fractions confirmed the

notion that the macerals are changing density in a manner too complicated to follow easily by just petrographic analysis.

In order to understand the behavior of the macerals in the alkylation/DGC separation, we approached the separation from the opposite sense. We first density separated the unalkylated coal by DGC, alkylated the individual macerals and then DGC separated this new material. The results are shown in Figures 3-5. In each case a single density gradient derived fraction, covering approximately a 0.01 g cm^{-1} range, was methylated or butylated and then separated on an analytical density gradient. The maceral density fractions that were used in these studies are at least 95% pure in a single maceral group by petrographic analysis. From analytical data the amount of alkylation per 100 carbons increases in the order: inertinite < exinite < vitrinite.

In the case of the alkylated exinites, for PSOC-732 the expected shift to lower density occurs as the size of the alkyl group increases (Figure 3). However, the methylated PSOC-726 exinites material shows a higher density distribution, while the butylated material shows a lower density relative to the untreated coal fraction. The reason for this behavior is not clear. It could be due to extraction of a highly aliphatic material from the exinite, which is more than compensated for by the molecular volume added by butyl groups, but cannot be compensated by the smaller molecular volume of the methyl groups. Alternatively, the alkylation reaction may be opening up pores which were closed to the density gradient solution in the original coal. Another possibility is that the alkylation alters the surface of the the exinites and changes the behavior of the particles in the complex density solution.

The alkylated vitrinite macerals from both coals show the expected behavior of shifting to lower density upon alkylation. However, all four alkylated vitrinites show broadening of the band. In the case of the butylated PSOC-726 there is even a distinct shoulder present. The exinites also show this behavior which implies that there may be subspecies of maceral particles which have different reactivities towards alkylation.

The alkylated inertinites show some remarkable changes in density distribution relative to the original maceral density distribution. All the alkylated inertinites show large band broadening and, in the case of the butylated materials, show the presence of multiple bands. It should be held in mind that particularly in the case of the alkylated inertinites, we have found that the relative absorbance that is plotted versus density does not necessarily reflect the true weight distribution of material; this is because of a complex relationship between absorbance and particle size for these altered materials.⁸ Nevertheless, the overall character of the patterns is still correct. Not only do the alkylated inertinites show a band broadening compared to the original material, but particularly in the butylated inertinites we see the development of new bands. The fact that specific bands emerge upon alkylation can be explained if there are classes of inertinite particles in the untreated maceral fraction with quite specific reactivity towards alkylation. The precise identity of these particles is not clear. They may represent monomaceral inertinite particles such as semi-fusinite, fusinite or micrinite within the inertinite group. On the other hand, they may represent a chemically different sub-species of an individual maceral.

To try and understand the nature of these new bands, several further experiments were done. In the case of the PSOC-732 inertinite fraction, the three bands were separated from several small scale analytical separations. The C, H, N analysis were done on the original fraction and the three new bands. Using the original data as a base, the bands contain: 3.0, 1.7 and 0.3 butyl groups per 100 carbon atoms, as a function of increasing density. In addition, FT-IR spectra of the three inertinite density bands show large increases in the aliphatic C-H stretching band in accordance with the increase in butyl groups. These results suggest that the differences in the density pattern are definitely related to selective chemical modification of different species.

CONCLUSIONS

Although we do not yet understand the nature of the species that have been separated, there is little doubt that we have achieved a higher level of separation than possible with density gradient techniques alone. The presence of new bands can only indicate that there are at least several specific classes of particles that have quite specific behavior towards alkylation.

The two dimensional separation of coal, consisting of density gradient separation and chemical modification, represents a new approach to resolving the heterogeneity of coal and possibly other maceral sub-species that may not be petrographically identifiable. It should be obvious that this approach can be used with any mild chemical treatment, O-alkylation being only one example. Even further maceral resolution might be achieved by chaining various functional group selective reactions with density gradient separation to do a multi-dimensional separation.

ACKNOWLEDGEMENTS

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2. Dyrkacz, G.R., Bloomquist, C.A.A., Ruscic, L. Fuel 1984, 63, 1166.
3. Dyrkacz, G.R., Bloomquist, C.A.A., Ruscic, L. Fuel 1984, 63, 1367.
4. In a few rare cases alginites or resinities can sometimes be separated from sporinite in the exinite maceral group, because of a very large difference in density between the constituents.
5. Liotta, R., Fuel, 1979, 58, 724.
6. Liotta, R., Rose, K., Hippo, E.J., Org. Chem., 1981, 46, 227.
7. Van Krevelen, D.W., "Coal", Elsevier, New York, 1961.
8. The alkylation reaction in some cases leads to fragmentation of some particles so that the original fairly narrow particles size distribution becomes larger. It is also possible there is selective swelling of certain maceral particles. Thus, the new material does not necessarily have a uniform size throughout the density band.

TABLE 1. Analytical Data for Coals.

Coal	C	H	N	S	O	Ash	
	% wt (daf)					(dry)	
PSOC-732	84.5	4.72	1.65	0.82	8.2	18.7	
PSOC-726	87.5	5.20	1.30	0.65	5.3	4.8	
Pet. Anal.							

Coal	Sp	Re	Cu	Bi	Vit	S-fus	Mi	Fus	Id
	% volume ^a								
PSOC-732	10.2	0.4	0.0	1.5	63.0	27.9	3.1	2.8	3.7
PSOC-726	10.6	1.4	0.5	0.0	50.4	10.9	3.8	2.6	7.2

a. Sp = sporinite; Re = resinite; Cu = cutinite; Bi = bituminite;
 Vit = vitrinite S-fus = semi-fusinite; Mi = micrinite; Fus = fusinite;
 Id = inertodetrinite.

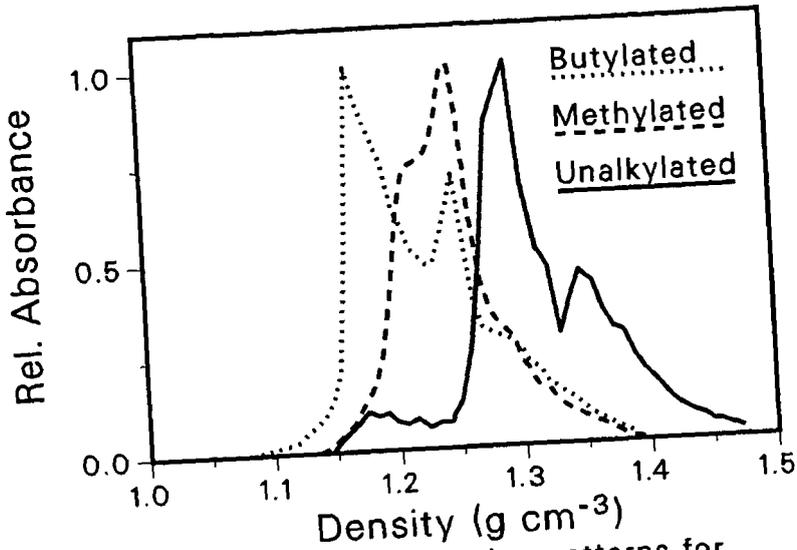


Figure 1. Density distribution patterns for alkylated and unalkylated PSOC-726; 25° C.

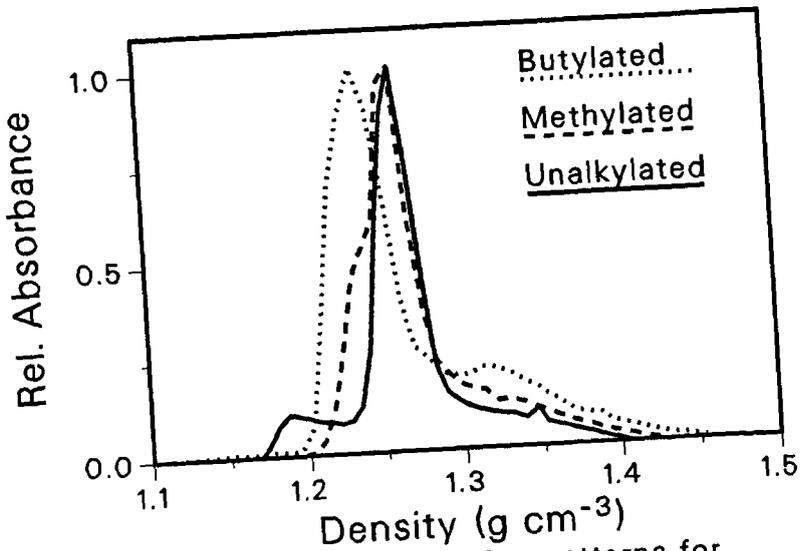


Figure 2. Density distribution patterns for alkylated and unalkylated PSOC-732; 25° C.

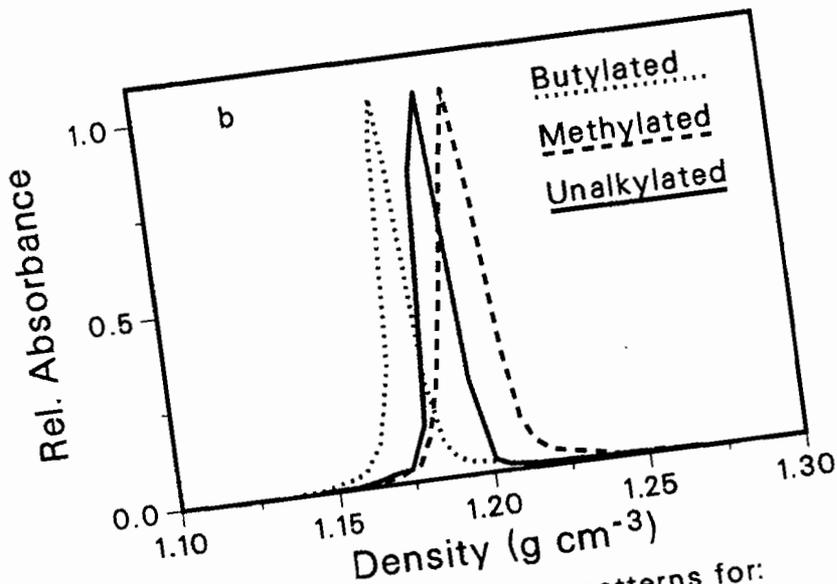
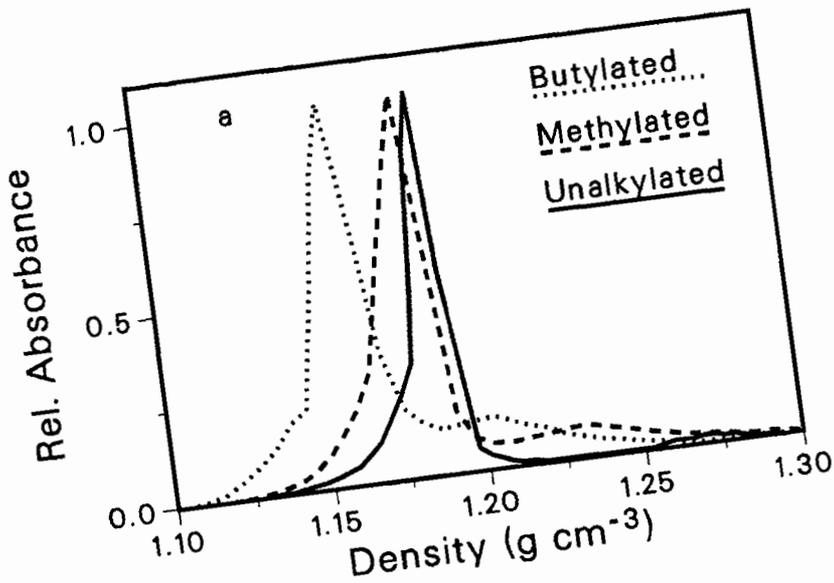


Figure 3. Exinite distribution patterns for: (a) PSOC-732; (b) PSOC-726.

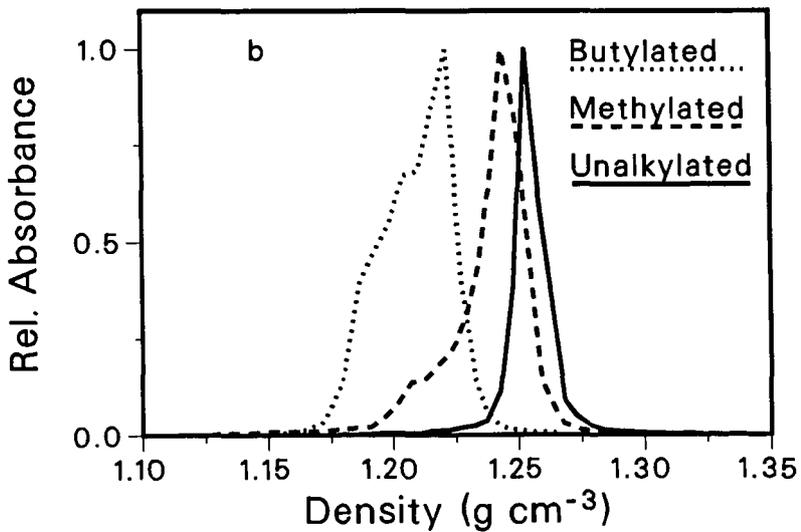
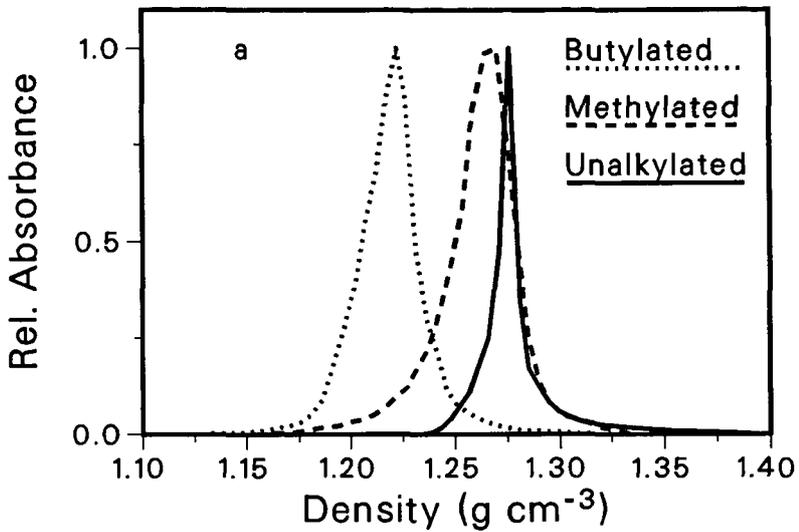


Figure 4. Vitrinite density distribution patterns for: (a) PSOC-732; (b) PSOC-726.

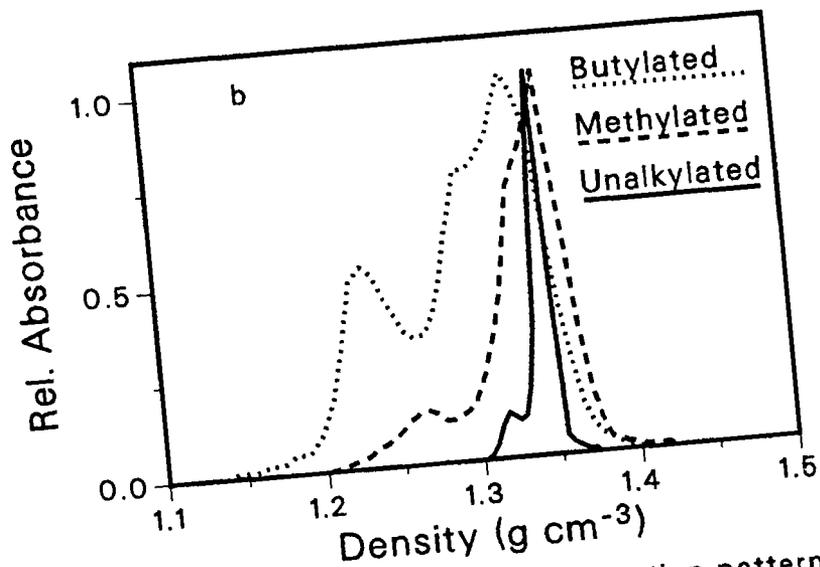
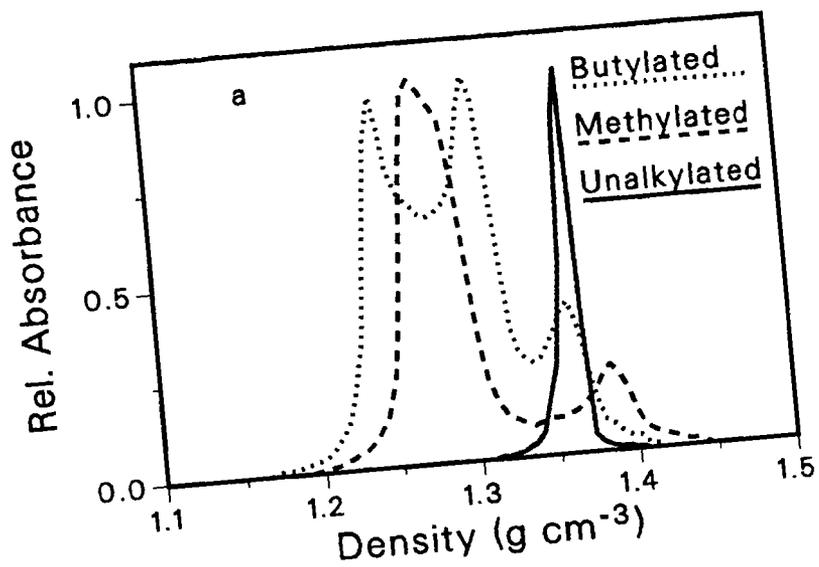


Figure 5. Inertinite density distribution patterns for: (a) PSOC-732; (b) PSOC-726.