Spatial Variation of Organic Sulfur in Coal

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INTRODUCTION

Spatial variation of organic sulfur concentration in coals has been generally known for years. The high resolution of the transmission electron microscope permits that variation to be measured more precisely than is possible by bulk techniques; variations may be measured over distances less than 1 μm.

Measurement of organic sulfur content using the transmission electron microscope requires use of ultra thin films or very fine powders. We typically use foils less than 1 μm thickness or powders ground to a few μm. The organic sulfur content is proportional to the ratio of the count rate for the sulfur Kα line to the count rate for the background radiation measured over some convenient energy interval. The proportionality constant is determined using sulfur standards. The technique is highly reliable for sulfur, as is shown in earlier publications (1-3). The PIXE method for heavier elements also utilizes the background radiation to permit absolute numerical concentrations to be derived.

This paper reports a particular application of the TEM method to determination of the spatial variation of organic sulfur, both within a given maceral and among maceral types. Some of the observations report measurements on powdered specimens, others on foil specimens prepared from bulk coal.

SPATIAL VARIATION

We have reported several measurements of the spatial variation of organic sulfur in coal. We cite two new measurements here. The variation in organic sulfur content of a sporinite maceral embedded in a larger vitrinite maceral in an Illinois #5 coal is shown in Fig. 1. Several features are evident. A considerable variation exists across a maceral, but an even larger variation exists between the two macerals. The sporinite maceral has a much higher concentration of organic sulfur than of the vitrinite. In contrast, resinite commonly has a lower organic sulfur content than vitrinite in a particular coal. This is evident from the data in Fig. 2 for a resinite maceral embedded in vitrinite in a block of Illinois #6.

MEASUREMENTS ON WHOLE COALS

Many measurements have been made of the organic sulfur content of whole coals, both to find the spread in sulfur content and to determine the average organic sulfur content. A number of these coals have been from the Argonne Premium Coal Bank. We show in Fig. 3 the sulfur distribution obtained for seven of these coals. The concentration varies widely for each of the coals. We have not separated these coal into maceral types, so we do not know the variation by maceral type. We have reported measurements on other bituminous coals separated into maceral fractions, though, and report such an observation in the next section.

Measurements on individual particles of a coal have considerable variation as the data of Fig. 3 show, but the average over a number of independent measurements has been found to be very close to the average organic sulfur content of that coal determined by bulk methods. A comparison made between eight coals measured in the TEM and the reported organic sulfur content measured by ASTM methods independently shows good agreement, Fig. 4.

ORGANIC SULFUR CONCENTRATION FOR SEPARATED MACERALS

Variation in organic sulfur concentration can easily be made for maceral fractions separated by density. We have measured several such fractions separated by Dyrkacz (4,5). Results for an Indiana block coal, a high volatile bituminous (PSOC 106) are shown in Fig. 5. There the organic sulfur concentration is plotted as a function of the density of the separated macerals. Approximate boundaries between exinite, vitrinite and inertinite for this coal are shown in the figure. One sees a smooth variation of organic sulfur concentration with density, rising from the inertinites through the vitrinite, peaking at a density near 1.20 g/cc and falling off toward the lighter fractions. The peak at 1.20 corresponds to the maceral-type sporinite.

We have repeated this measurement for four other coals and find the same pattern, the curve being shifted up or down in accordance with the average organic sulfur content (2). We find, as did Raymond earlier (6), that the average sulfur content of the whole coal is about that of vitrinite.

The purpose of this paper is not to emphasize the average organic sulfur concentration of coal or of separated macerals, but to examine the variation of organic sulfur from particle to particle within a particular maceral type. We show this in two steps.

First, measurement of the organic sulfur concentration of the major maceral groups of the Indiana Block Coal (PSOC 106) shows wide variation. The measurements are shown in Fig. 6. One sees wide variation, especially for the exinite.

Second, measurement has been made of the variation of organic sulfur concentration for each of the separated density fractions plotted in Fig. 3. Three of the measurements are shown in Fig. 7 one for each of the major maceral groups. The range of sulfur concentration for the inertinite and vitrinite macerals of density 1.42 g/cc and 1.30 g/cc is again small. But for the fraction at 1.18 g/cc (sporinite) the range is still enormous. Is this a result of maceral impurity, or do pure macerals of the exinites have an intrinsic variation of sulfur content which is very broad?

To make sure that this pattern was not peculiar to coals separated by this gravity-centrifuge process, we have made measurements in situ for 4 macerals of an Illinois #5 coal (7). Those measurements are plotted in Fig. 8, where they are compared to measurements on separated macerals of an Illinois #5 coal. The agreement is satisfactory.

DISTRIBUTION OF ORGANIC SULFUR IN FINELY SEPARATED MACERALS

A laboratory for separating coals into submaceral types by the density gradient method has been established by Professor Crelling at SIU. By pushing the techniques of Dyrkacz to the extreme, he can prepare powdered macerals of even higher purity. He has supplied us with specimens from a bituminous coal #SIU 647 J, an Indiana paper coal. We have measured the organic sulfur content of four of those specimens and show the distributions in Fig. 9.

The organic sulfur content of specimen #1, a cutinite, is a narrow distribution with an average value of about 0.45 wt%, Fig. 9a. The distribution is a single mode. That of specimen #2, also a cutinite with a somewhat lower density, is also a single mode except for 4 isolated points at a much higher organic sulfur concentration, Fig. 9b. Including all points, the average organic sulfur concentration is 0.57 wt%, neglecting the 4 highest points it is about 0.49. It is possible that specimen #1 has a few macerals of another subtype with a higher organic sulfur concentration.

That same trend continues for maceral type #3, a sporinite with a specific gravity about 1.16. One hundred measurements were made for this coal, yielding a bimodal distribution shown in Fig. 9c. It would appear that two maceral subtypes may be present, one with an organic sulfur content near 0.4 wt%, the other near 1.3 wt%. This same biomodal distribution is shown for the density fraction near 1.21, near the edge of the vitrinites, Fig. 9d. A maceral type with organic sulfur content near 0.40 must again be mixed with a maceral with organic sulfur content slightly above 1.0.

These measurements seem to show that macerals separated on a density basis may not be "pure". Thus the broad ranges of data in Figs. 4 and 5 may demonstrate that macerals separated by density techniques may contain two or more submaceral fractions. If one considers the data of Figs. 9c and 9d, the values for the individual modes among this bimodal distribution show a variation of not more than ±20%, a value not much different from the variations seen in Fig. 1 for the in-situ macerals, which are assuredly a more pure type, at least locally.

Chlorine Distribution in Coal

The Indiana bituminous coal, PSOC 106, also contains chlorine. We have measured the spatial variation of chlorine in the separated macerals; measurements are shown in Fig. 10. The average chlorine content of this coal is relatively small, about 0.35 wt%. In vitrinite and inertinite the range is relatively small, from about 0.15 to about 0.55 wt%. For the exinites again, the chlorine content is much larger on the average and the spread is much higher, nearly a factor of 10. We have not measured the chlorine distribution in the macerals separated on a finer scale, but it would be easily feasible.

Organic Iron in Coal

We occasionally observe x-ray lines for iron in regions of the foil in which these are not observable precipitates, nor x-ray lines of any other element. We have concluded that these x-rays must show the presence of organic iron. An example is shown for Illinois #5 coal in Fig. 11. The quantity is quite small, less than 0.1 wt%. No variation among the three major maceral groups was observed. Of course, one always worries that fine oxide particles may be present; but they must be less than perhaps 3 nm in size or we could detect their presence.

SUMMARY

The TEM method for measuring organic sulfur concentration is most valuable when its fine scale spatial resolution can be utilized. We have demonstrated that the variation of organic sulfur is about ±10% of the average when measured over distances separated by 1 m. The technique also has value in showing the organic sulfur variation in minute particles of separated macerals. Apparently, it is very difficult using density techniques to obtain pure maceral types.

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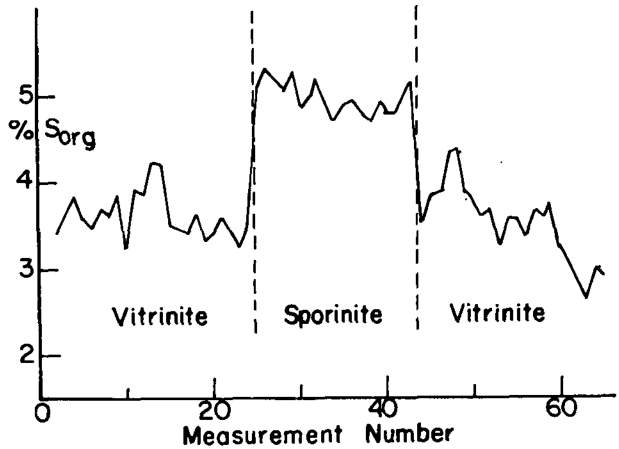


Fig. 1. Organic sulfur trace across a sporinite maceral embedded in vitrinite. Illinois #5.

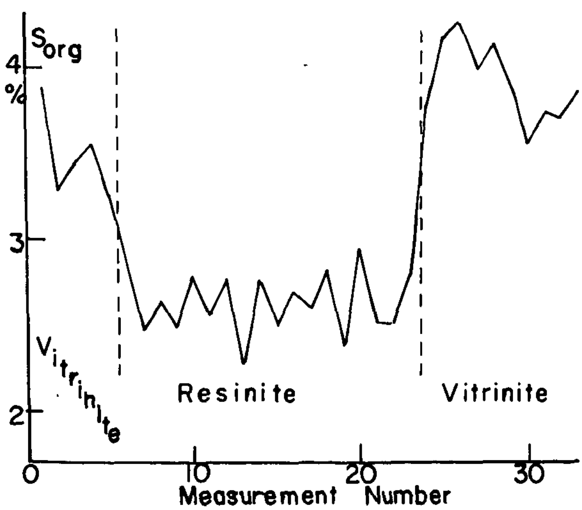
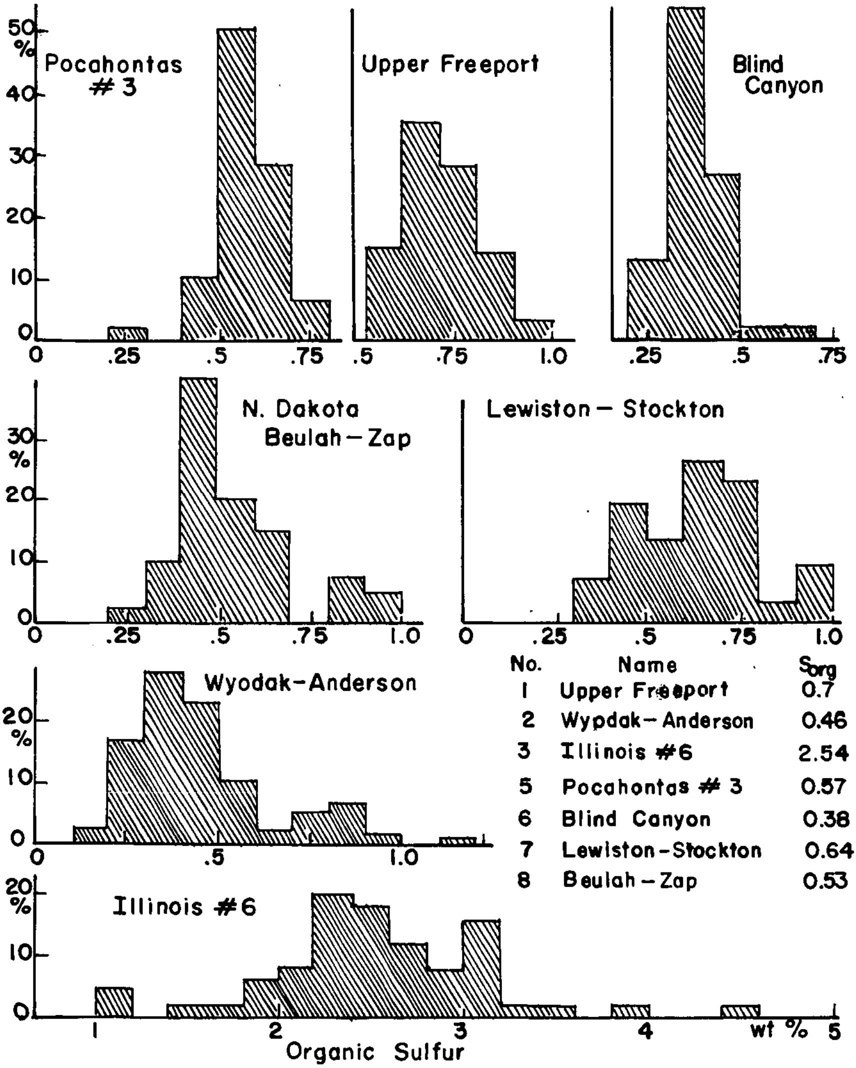


Fig. 2. Organic sulfur trace across a resinite maceral embedded in vitrinite. Illinois #6.



No.	Name	S_{org}
1	Upper Freeport	0.7
2	Wypdak – Anderson	0.46
3	Illinois #6	2.54
5	Pocahontas # 3	0.57
6	Blind Canyon	0.38
7	Lewiston - Stockton	0.64
8	Beulah – Zap	0.53

Fig. 3. Distribution of organic sulfur in seven whole coals from the Premium Coal Bank. The inset Table gives the average organic sulfur concentration for each coal.

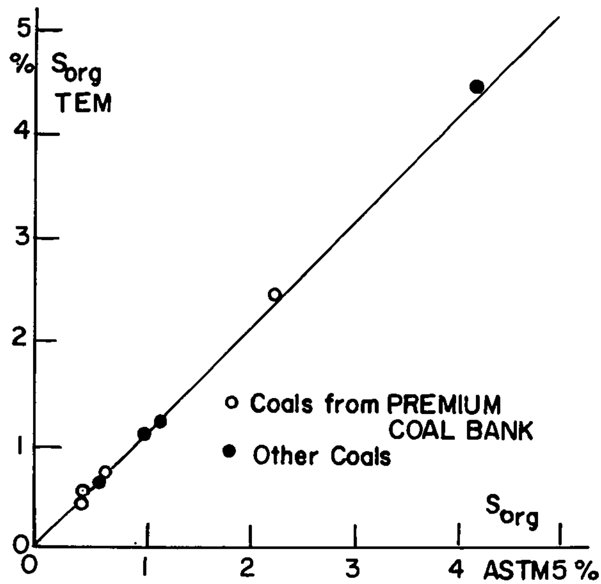


Fig. 4. Comparison of organic sulfur concentration measured by the TEM method and by the ASTM method.

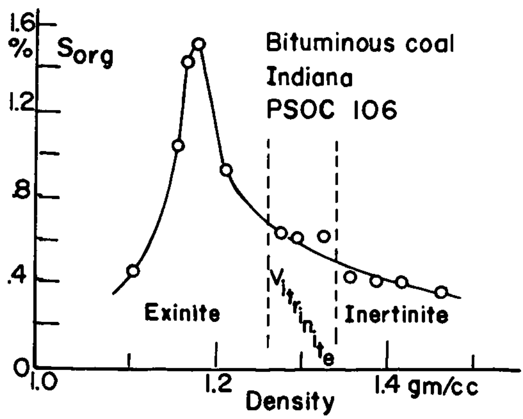


Fig. 5. Variation of organic sulfur for macerals separated by density. Indiana Block coal.

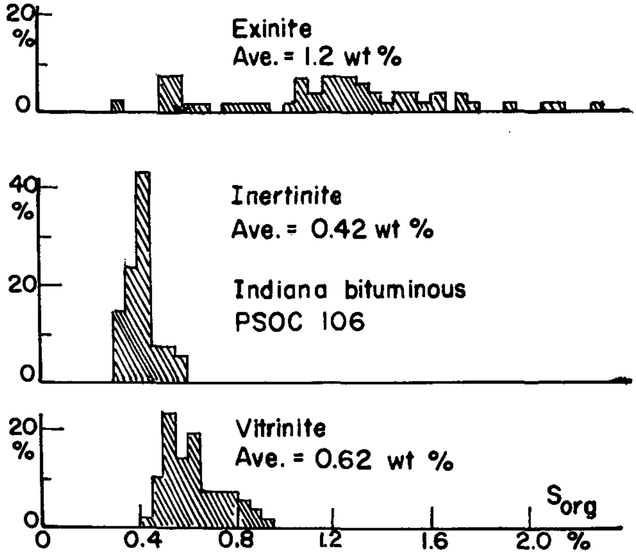


Fig. 6. Distribution of organic sulfur for the major maceral types.

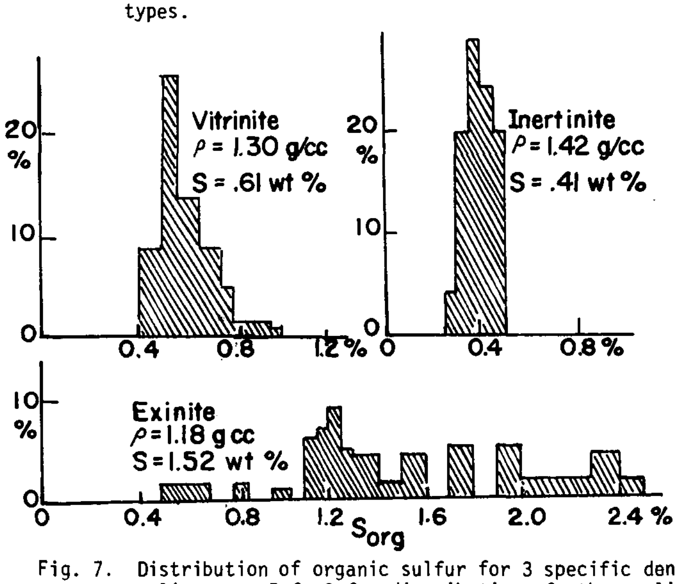


Fig. 7. Distribution of organic sulfur for 3 specific density splits, see Ref. 2 for distribution of other splits.

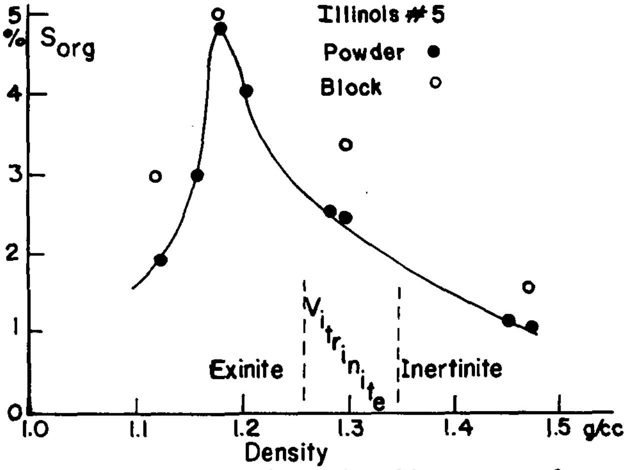


Fig. 8. Comparison of organic sulfur content of separated and in situ macerals.

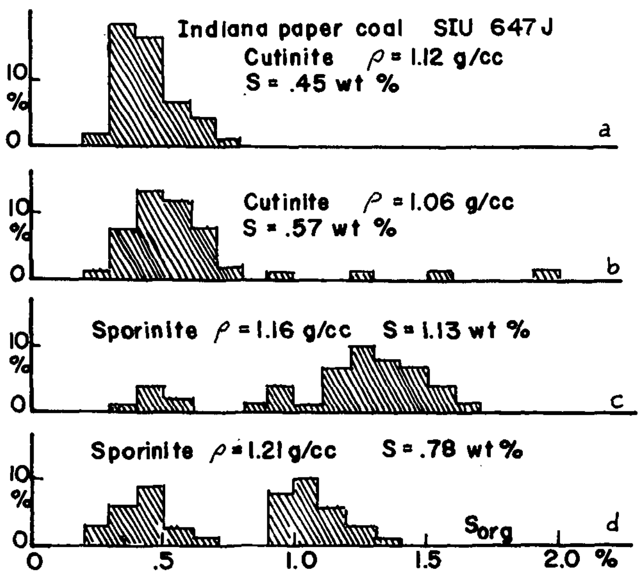


Fig. 9. Distribution of organic sulfur in fine density splits of an exinite.

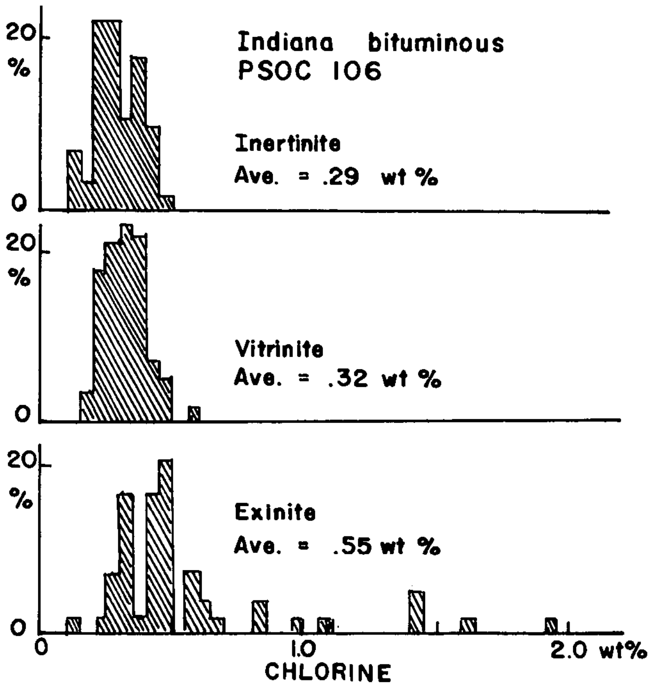


Fig. 10. Distribution of chlorine content of a bituminous coal as a function of maceral type.

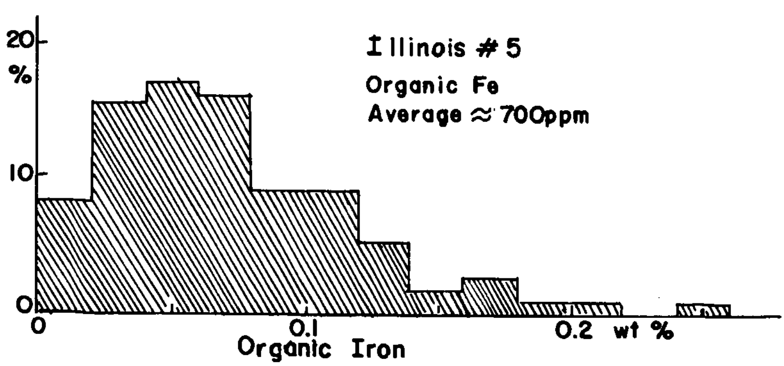


Fig. 11. Distribution of organic iron in a specimen of Illinois #5.