

**NEW APPLICATIONS OF ANALYTICAL TECHNIQUES TO FOSSIL FUELS**  
Introduction to the Symposium

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The "New Applications of Analytical Techniques to Fossil Fuels" symposium was envisioned as a forum for researchers to describe (1) new twists to established techniques, (2) techniques only recently applied to fossil fuels, and (3) potentially useful techniques that have not as yet been applied to such materials. The response to our call for papers was overwhelming, the result being a four-day symposium consisting of thirty-six technical presentations. The podium will be shared by speakers from industrial, government, and university laboratories. We are pleased to acknowledge participation by three countries -- Canada, United Kingdom, and the United States -- all of which have well-established, on-going fossil fuel programs.

**ORGANIZATION OF THE SYMPOSIUM**

We resisted the urge to organize the papers into sessions according to analytical technique by structuring the symposium so as to place primary focus on the materials examined and the type of information obtained. Thus, one session is devoted to coal or coal macerals as total (unseparated) materials, while other sessions emphasize analyses for particular functional groups. Another session deals with compound identification, while others address process-oriented analysis and measurements of dynamic processes. Logistical consideration dictated that the three invited magnetic resonance papers be organized into a single session.

Most of the symposium papers deal with instrumental methods of analysis. This was not unexpected because applications of modern instrumental techniques have experienced phenomenal growth since their introduction in the mid- and late-1940's. Figure 1 depicts historically the introduction of a few such techniques into the coal research programs at the Pittsburgh Energy Technology Center; the timetable of Figure 1 closely parallels that for other fossil fuels research organizations located throughout the world. The large number of techniques that will be described during this symposium suggests that periodic updates of such plots are appropriate at relatively short intervals. Among the many techniques included in the symposium are laser induced fluorescence, inverse gas chromatography, ultraviolet resonance Raman spectroscopy, and zero field nuclear magnetic resonance, as well as many of the hyphenated techniques, such as TGA-FTIR, GC-FTIR, and LC-MS. Classical wet methods, nonetheless, are not ignored.

## SOME THOUGHTS FOR THE FOSSIL FUEL ANALYST

The current role of the fossil fuel analyst in the research environment is one in which he functions as an integral member of the research planning team. The analyst faces a number of technical challenges that require a very broad scientific knowledge covering a number of different disciplines. The lack of such knowledge may very well leave the fossil fuel analyst vulnerable to a variety of "perils and pitfalls" that in some cases are unique to the fossil fuel area. The following thoughts are given (with perhaps a degree of "tongue in cheek") to draw attention to several of these.

### Perils and Pitfalls

**Thou shalt have many samples before thee, and no one shall be considered sacred** is, for example, good advice for the coal analyst. In a study of sixty-four vitrains from coals originating from nine countries, a quite viable explanation for the electron spin resonance (ESR) characteristics of the samples was presented (1,2). Despite the large number of samples and the wide geographical distribution, a more recent study revealed "unusual" coals that do not adhere to the correlations established during the earlier study (3). Needless to say, such findings often lead to new research opportunities and improved understanding of coal structure.

In a similar vein, **Thou shalt have a variety of analytical methods before thee, and again, no one shall be considered sacred**. This statement is motivated by results from an extensive laboratory study of five methods that are commonly used for the determination of asphaltenes (4,5). In their initial study, which was confined to a coal-derived liquid, Schultz and Mima found (not unexpectedly) that the results were dependent on the method that was used (4). The method dependency was further confirmed (again, not unexpectedly) in their second study, which extended the testing of the methods to a coal-derived solid (5). Subsequent analysis of the data for both samples (Figure 2) revealed a sample dependency in addition to the method dependency, thus precluding the use of a constant factor to compare the results of analyses performed by the different procedures (6).

With respect to the coal analyst's need for a broad knowledge of a variety of scientific disciplines, it is well that **Thou shalt remember thy physics and honor its relevance**. Drawing again from the ESR literature, it has been shown that misleading  $g$  values and spectral intensities may result from the lack of attention given to the physical bases that underlie both the ESR phenomena and the microwave techniques employed to observe the resonances (7).

Fossil fuel analysts should no longer permit themselves to be viewed as conveyers of data, and they must **Recognize that "data, however fascinating, is not insight"** (8). The present authors feel that coinage of the phrase "data base" is unfortunate in that it fails to communicate that it is the storage of information or the translation of data into useful information that should be emphasized.

Analysts, in general, strive to achieve results of high precision. It is our feeling that a more appropriate goal is to strive for that precision

necessary to solve the problem at hand. It is important that analysts **Know thy data and thy precision, and use both wisely.** Some recent work undertaken in our laboratory to respond to a challenge of the doublet state free radical interpretation of the ESR behavior of coals (9) serves to illustrate this point. Careful reanalysis of the data from reference 9, the results of which are summarized in Table 1, showed no reason to choose a model that includes both doublet and triplet states over the Curie law model, which is, in part, the basis for the doublet state free radical interpretation (10).

Fossil fuel analysts often face the problem of long-term storage instability of samples. Although the problem has been well documented (11-13), it is appropriate to remind analysts that they should **Honor thy sample, for its integrity (or lack thereof) may very well reflect upon their own.** Long-term sample stability is but one of many concerns. Certainly, analytical results on second-hand samples are suspect, and those on samples of questionable origin should be rejected outright. Additionally, short-term sample stability has received little attention despite a study that showed measurable changes in spectral properties of coal within a few hours after removal from the mine atmosphere (14). The lack or improper use of sampling protocols is yet another problem that often confronts the fossil fuel analyst. Unless he asserts himself as a member of the research team, the problems associated with improper sampling are likely to be ignored.

#### A Closing Thought

The final thought that we would leave with the audience is that analytical methods that have been applied successfully to other materials frequently are not directly transferable to the analysis of fossil fuels. Rare is the coal analyst who has not on occasion identified with Figure 3. We offer this closing thought for consideration by the speakers as we open this symposium.

#### ACKNOWLEDGMENTS

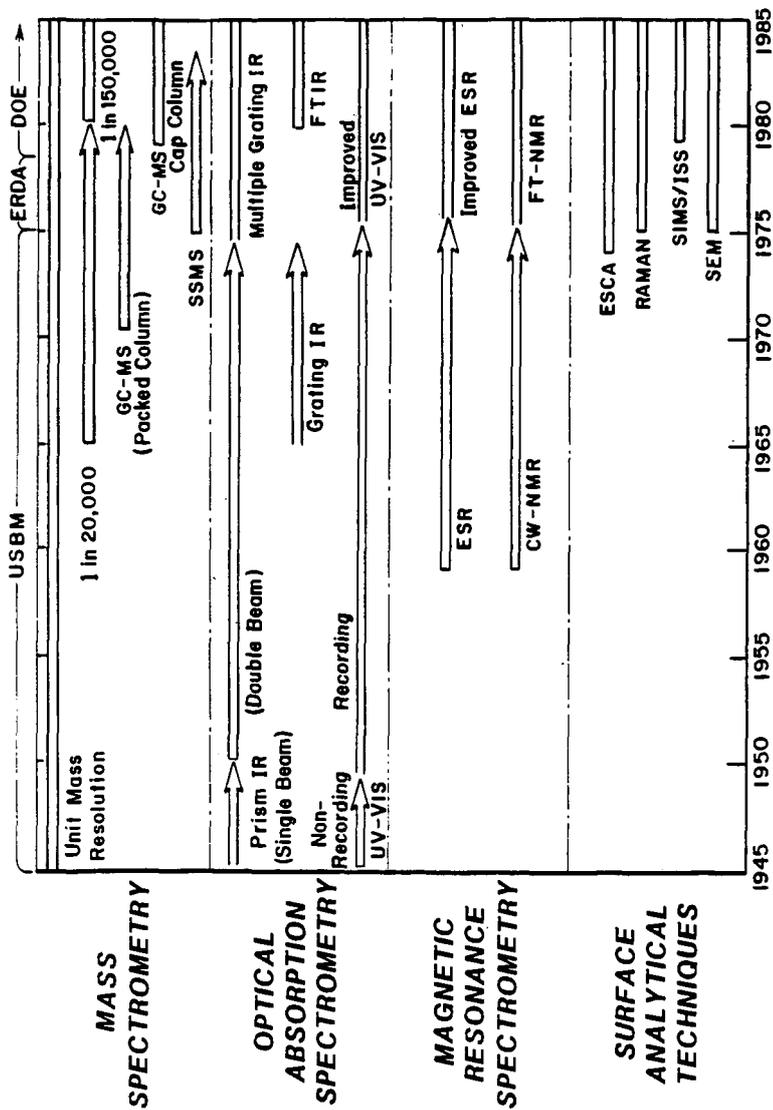
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Table 1. ESR Intensity-Temperature (IT) Behavior for a Single Coal

Temperature Range, K	126	to	264
IT (Measured), Arbitrary Units	23.4	to	28.95
IT (Measured) - IT (Predicted) (CURIE LAW MODEL)	-0.45	to	0.25
IT (Measured) - IT (Predicted) (CHARGE TRANSFER MODEL)	-0.47	to	0.37

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**FIGURE 1. Spectrometric Instrumentation at PETC  
(Partial Historical overview)**

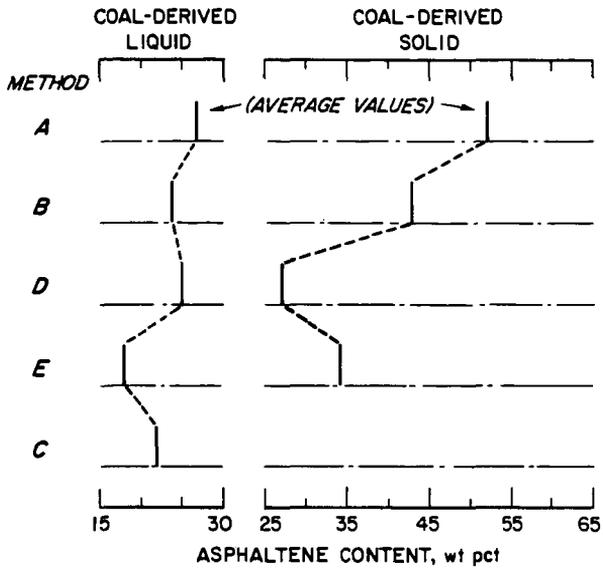


FIGURE 2. Comparison of Methods for the Determination of Asphaltenes in Liquid and Solid Products from Coal Liquefaction

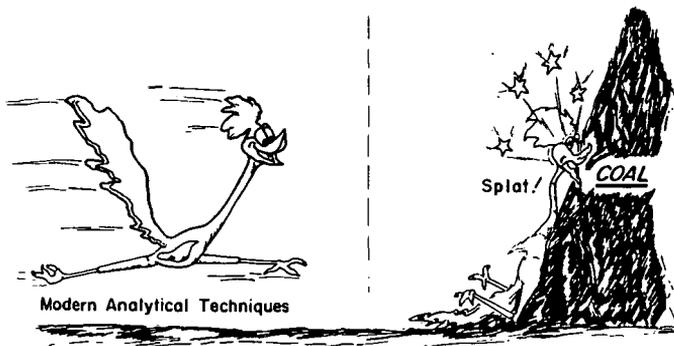


FIGURE 3. The Study of Coal Structure