

**A Ranking Tool for Potentially Carcinogenic  
Polynuclear Aromatic Compounds in Synfuel Products\***

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**ABSTRACT**

This paper describes the use of a screening procedure to rank the content of polynuclear aromatic (PNA) species in synfuel samples. The ranking procedure is based on a cost-effective and rapid screening technique based on synchronous luminescence spectroscopy. The use of the screening procedure as a basis for screening of complex mixtures will be discussed.

**INTRODUCTION**

An important class of organic pollutants are PNA compounds because some of them are known to be converted by metabolic activation to ultimate carcinogens (1,2). Consequently, it is important to monitor PNA compounds in synfuel samples on a routine basis. A variety of analytical procedures have been developed to determine the concentrations of specific PNAs. High-performance liquid chromatography (HPLC) and gas chromatography/mass spectrometry (GC/MS) have been used to provide detailed analyses for a variety of PNAs in environmental samples (3,4). In many monitoring situations, the precise determination of various specific PNAs may be unnecessary and a prescreening phase is required to reduce the cost of environmental analysis.

This presentation describes the use of a ranking methodology that can be used to screen synfuel samples for their PNA content. The technique of synchronous luminescence (SL) is applied to fluorescence and phosphorescence measurements for establishing a ranking index (RI) for PNA species.

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## EXPERIMENTAL

The Luminescence Screening Technique

The screening procedure evaluated in this study is based on the synchronous luminescence technique (5,6). In conventional luminescence spectroscopy, only one of the two spectral wavelengths,  $\lambda_{em}$  (emission) or  $\lambda_{ex}$  (excitation), is scanned while the other remains fixed. For complex samples, the resulting spectra obtained with this conventional procedure are often poorly resolved and featureless because of the spectral overlays of the emissions from individual components. However, by scanning both  $\lambda_{em}$  and  $\lambda_{ex}$  synchronously with a constant interval between the two wavelengths ( $\lambda_{em} - \lambda_{ex} = \Delta\lambda$ ), the luminescence spectrum becomes more resolved with sharp peaks that are more readily identified.

The synchronous excitation technique can be applied both to fluorescence, i.e., synchronous fluorimetry (SF), and to phosphorescence, i.e., synchronous phosphorimetry (SP). For SF, the optimum value of  $\Delta\lambda$ , usually set at 3 nm, is determined by the Stokes Shift, i.e., the wavelength difference between the 0 to 0 bands in emission and absorption. For SP, the optimal value of  $\Delta\lambda$  is determined by the singlet-triplet energy difference of PNA species to be monitored by room temperature phosphorimetry (RTP) (7-9).

The RTP technique is characterized by the simplicity and versatility of its methodology and consists generally of four steps: (1) substrate preparation (optional pretreatment with heavy-atom salts); (2) sample delivery; (3) drying; and (4) spectroscopic measurement. Three microliters of sample solution were then spotted on the paper circles using microsyringes with a volume of 3 microliters. Since moisture can quench the RTP emission, predrying was achieved with infrared heating lamps. Continued drying during the measurement was accomplished by blowing warm, dry air through the sample compartment. Phosphorimetric measurements were conducted with a commercial Perkin-Elmer spectrofluorimeter (Model 43A) equipped with a rotating phosphoroscope. Details on the measurement procedures have been described elsewhere (7,9).

The presence of heavy atoms in the immediate environment of the molecule can significantly enhance the population of the triplet state (external heavy-atom effect) and, therefore, the phosphorescence intensity. For PNA compounds, a large variety of heavy atom salts such as thallium and lead acetate have been found to be very efficient in enhancing the phosphorescence quantum yields. The detection limits for most PNA compounds investigated can be lowered, in some cases, by several orders of magnitude and are in the subnanogram range. It is also possible to selectively enhance the phosphorescence emission of a given compound (or group of compounds) in a complex mixture. Selective triplet emission enhancement considerably extends the specificity of the RTP technique in multicomponent analysis.

The rationale for ranking the samples for luminescence spectroscopy is based upon the fact that the majority of PNA species, especially the polyaromatic hydrocarbons, fluoresce and/or phosphoresce. Luminescence is known as two of the most sensitive techniques to detect these compounds. Provided that all the spectral interferences are accounted for, the screening procedure can be based on the principle that the higher the total intensity of the SL bands, the more concentrated the samples are in PNA content.

## APPLICATIONS

Screening Profiles of Coal Liquid Samples

Figure 1 shows the synchronous fluorescence spectra of five synfuel products collected at different locations of a synfuel production facility. In order to test the capability of the rapid screening procedures, no prior attempt had been made to analyze these samples and obtain compound-specific information about the individual components. All of the five samples were diluted in ethanol by serial dilution ( $10^3$ ,  $10^4$ ,  $10^5$ , and  $10^6$  dilution factor). A wavelength interval of  $\Delta\lambda = 3$  nm was used in the synchronous fluorescence measurements. With the use of the  $\Delta\lambda$  value, the resulting synchronous fluorescence peaks correspond approximately to the 0,0 band emissions of most PNA compounds. The synchronous profile, therefore, is not just a spectral fingerprint, but contains useful information about the nature and PNA composition of the samples.

The main relationship between the size of the benzenoid structure of a polyaromatic hydrocarbon and its fluorescence emission is the dependence of its 0,0 band upon the number of benzene rings (5). The wavelength position of the 0,0 band of a high-number, linear fused-ring size cyclic compound generally occurs at longer wavelengths than that of a lower number ring-size compound.

Synchronous fluorescence measurements were conducted with the five products at various concentrations. The results indicated that the SF profile remained unchanged when the samples were diluted to  $10^4$  fold or less. This indicated that spectral interferences did not occur at these concentration levels for the products investigated. Without any identification and quantification procedure, a rapid examination of the synchronous fluorescence profiles of the five synfuel products A, B, C, D, and E at  $10^5$  fold dilution levels can readily provide the following conclusions (Figure 1). A rapid comparison of the SL profiles first indicates that product C should contain the least amount of PNA compound. The compound that contributes to the peak at 285-290 nm in sample C is a monocyclic aromatic species and it is also present in similar amounts in other samples (A, B, D, and E). The intensity of the peak at about 305 nm is approximately 10-fold less intense in sample C than in the other samples. Besides a weak shoulder at about 325 nm, no other band was detected in sample C at wavelengths longer than 320 nm.

In order of increasing PNA content, product D is the next sample to consider. The peak at 305 nm is about 10-fold more intense than that of sample C. A rapid examination of the SL profile of sample A also shows that this product is similar to product B. Product B, however, contains slightly more PNA compounds that have 0,0 bands at 346 nm, 382 nm, 402 nm, and 442 nm. Although the general structure of the spectra for products A and D are similar, these spectral differences are still noticeable. Finally, the synchronous profiles show that the PNA content of products B and E are similar. These two samples contain more PNA compound with 3-5 rings than samples A, C, and D as indicated in Figures 1b and 1e.

Another example of the screening procedure by RTP is the characterization of another series of coal liquids produced by a synfuel production process. The results of this screening procedure are shown in Figure 2. All the samples were diluted in ethanol by serial dilution ( $10^{-2}$ ,  $10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$ , and  $10^{-6}$ ) and spotted on filter paper (Schleicher and Schuell, No. 2043A) treated with a mixture of thallium acetate and lead acetate. The excitation used to obtain the RTP spectra was 315 nm. This wavelength was used to excite most of the PNA compounds having 3 to 5 fused rings. The samples shown in this figure were  $10^{-6}$  fold diluted. Without any identification and quantification procedure, it is possible to rank these

samples as follows: B > A > D > C. Note that sample C exhibited stronger intensity at approximately 600 to 650 nm where pyrene and other 4- to 5- ring PNA compounds mainly emit.

The above examples show that it is possible to obtain a preliminary ranking of coal products after a rapid synchronous scanning procedure. All the samples were screened without any prior prefractionation or precleaning process. Each SL and RTP measurement was conducted in less than five minutes, after the appropriate concentration range had been selected. Recently the SL technique has been developed for measuring important biomarkers including PNA metabolites and PNA-DNA adducts produced by human exposure to PNA pollutants (10,11).

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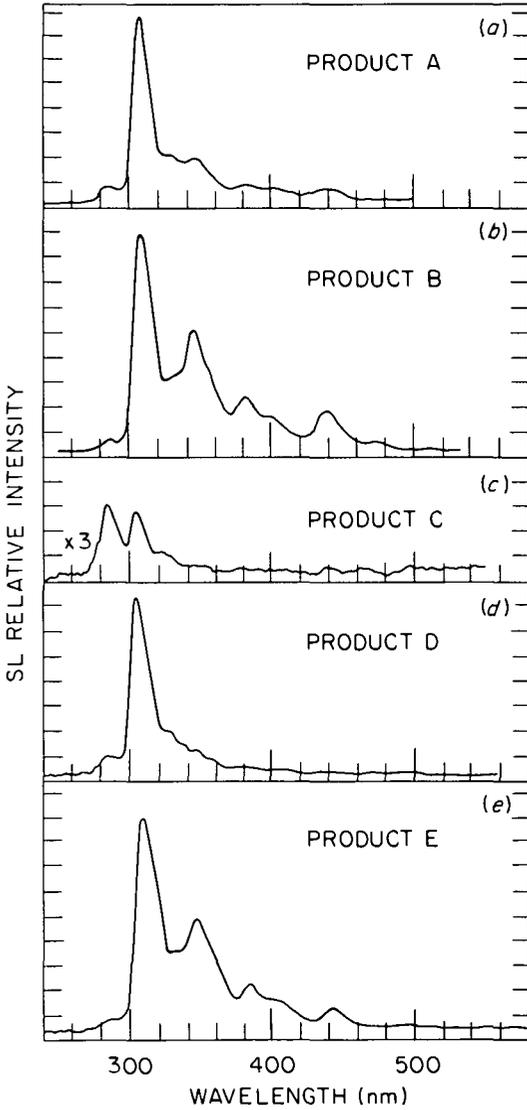


Figure 1: Ranking Procedure of several Coal Liquid Products by Synchronous Fluorescence.

RTP SCREENING OF SYN FUEL PRODUCTS

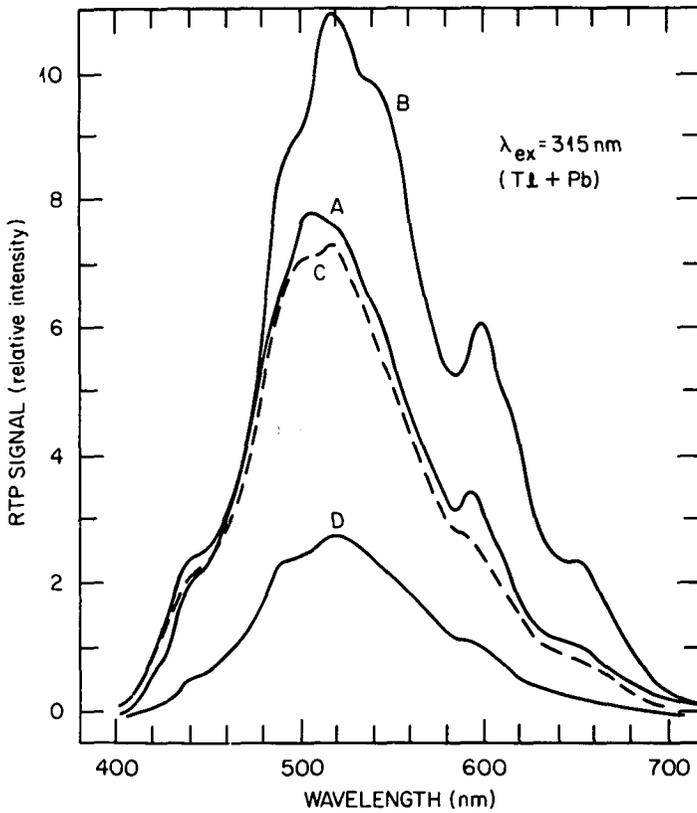


Figure 2: Ranking Procedure of Synfuels Products by Room Temperature Phosphorimetry.