INSTRUMENTAL METHODS FOR THE DETERMINATION OF PAH IN COAL AND COAL DERIVED MATERIALS

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I. HISTORICAL ASPECTS

Coal is the world's major carbonaceous fuel resource. Active investigation of the polycyclic aromatic hydrocarbons (PAH) present in coal and coal-derived materials has been conducted for approximately 70 years (1). During this period, dozens of analytical techniques have been used to determine PAH in these materials. This manuscript will briefly review some instrumental methods that provide the most useful, reliable, and detailed analytical information concerning the occurrence and distribution of PAH in coal and coal-derived materials.

There are many reasons for studying the PAH present in coal. The aromatic portion of coal extracts is usually the largest fraction, ranging approximately from 40 to 60 weight percent of the extract. Detailed characterization of this fraction is therefore extremely important in helping to elucidate the chemical constitution and geochemical origins of coal and in improving our understanding of the chemistry associated with the coalification process that converted plant debris to coal. Investigating the occurrence and distribution of PAH in coal should lead to a better understanding of their possible health effects. Coal workers' pneumoconiosis, "black lung," (2,3) can develop after accumulation of respirable coal dust in the lungs. Engineering, as well as environmental, concerns are the main reasons for investigating the PAH in coal-derived materials. The advent of energy shortages has focused attention on increased use of products from the liquefaction and gasification of coal. Since the aromatic portion of coal liquefaction products usually comprises from 20 to 60 weight percent, detailed examination of this fraction has received considerable attention by both process development and environmental scientists.

During 1958, the first use of gas chromatography for the analysis of PAH from coal products was reported by F. Dupire and G. Botquin from the Research Laboratory S. A. Carbochemique in Belgium (4). Their work is a hallmark in gas chromatographic methods development for the analysis of PAH. The gas chromatographic instrument was completely constructed by these investigators and consisted of a thermal conductivity detector, column oven, and injection port heated resistively by wire wrapped around the front of the column. The glass column measured 2.5 m x 6-8 mm and was packed with crushed and sieved (60-80 mesh) refractory brick coated with 30% by weight Dow Corning high vacuum silicone grease. The separations were performed isothermally at temperatures between 185°C and 295°C, depending on the boiling point range of the fraction of the coal tar being analyzed. Identifications were made by comparing the retention characteristics of the chromatographic peaks in the unknown with those of standards. Dupire and Botquin also noticed that there was a linear relationship between the log of the retention time of the PAH and their boiling points. The results of this investigation were so promising that in the years that followed, hundreds of investigators have used gas chromatography for PAH analysis of samples derived from coal and other products, and a new frontier in the analytical chemistry of PAH was opened.

Helmut Pichler published a manuscript, the contents of which represent a milestone in analysis of coal carbonization products (5). Although Liberti (6) were the first to use capillary gas chromatography to separate PAH, Pichler was the first to apply high resolution capillary gas chromatography to the analysis of

PAH from a coal product. The aromatic fraction of a coal carbonization tar was analyzed by gas chromatography employing wall-coated open-tubular columns (WCOT) and packed columns. Individual constituents in the mixtures were identified using co-chromatography with authentic reference compounds. In cases where reference compounds were not commercially available, they were synthesized. The Kovats retention indices were calculated for all of the identified compounds (7). In addition, verification of these identifications was obtained by collecting the compounds and comparing their ultraviolet (UV) spectra with those of standards. The separation was achieved using a 100 m by 0.25 mm column coated with polypropyleneglycol, and N_2 carrier gas. Although high molecular weight PAH were not present in this distillate aromatic fraction, volatile PAH, including naphthalene, methylnaphthalenes, dimethylnaphthalenes, and acenapthylene, were present.

In 1963, K. Ōuchi and K. Imuta published two manuscripts (8,9), which were to become cornerstones of our knowledge of the occurrence and distribution of PAH in coal. Until these manuscripts were published, very little was known with certainty about the PAH content of coal. The first manuscript describes the benzene extraction of Yūbari coal and the preparative liquid chromatographic fractionation of the extract. Two crystalline substances were isolated and shown to be 4,11-dimethylpicene and a dimethylchrysene. The second manuscript describes the detailed analysis of the aromatic and other fractions from the coal extract. The analysis of the aromatic fraction was performed using preparative packed-column gas chromatography, followed by ultraviolet and infrared spectroscopic identification of the isolated components. The column was operated isothermally at various temperatures depending on the fraction being analyzed. The gas chromatographic techniques used were state-of-the-art for that time. Some of the compounds identified by Ōuchi and Imuta had been previously identified in coals (10,11,12,13,14). However, in this investigation many PAH were positively identified for the first time, and the following major conclusions were drawn. 1. A considerable portion of the organically-bound oxygen in coal is present as furanic species. 2. Phenanthrene and alkylphenanthrenes were present in coal in 5 to 10 times greater concentrations than anthracene and alkylanthracenes.
3. Cata-condensed PAH were common in coal, while peri-condensed PAH were rare.

In an elegant investigation, reported in a series of papers (15,16,17,18,19,20), Jarolim and co-workers, using various chromatographic and crystallization methods, isolated over thirty compounds (some of which were PAH) from the benzene extract of North Bohemian brown coal. The structures of the isolated compounds were assigned based on the results of infrared, ultraviolet, nuclear magnetic resonance, and mass spectrometric analyses of the pure compounds isolated. The PAH identified by these methods are listed in Table 1.

A notion of the complexity of just the aromatic fraction from a coal extract can be gained by viewing the high resolution gas chromatographic profile in the article by White and Lee (21). Isolating sufficient amounts of pure compounds from such a mixture for NMR and other spectroscopic measurements is extremely difficult. In some cases, isolation of the pure compounds, and analysis by a variety of spectral techniques, did not provide sufficient information to positively identify the compounds. Their investigation has helped to elucidate the chemical reactions that occur during the coalification process.

II. CURRENT STATE-OF-THE-ART

H. G. Franck (22) has estimated the number of compounds present in bituminous coal tars to be 10,000. Mixtures of similar complexity are found in coal extracts and in liquefaction and gasification products and by-products. It is, therefore,

imperative that prior to detailed qualitative analysis by GC or GC-MS, the sample be fractionated to provide a clean aromatic fraction. Because the aromatic fractions of coal extracts and other coal products consist of hundreds, possibly thousands, of compounds, it is necessary that the gas chromatographic columns used be of the highest possible efficiency, inertness, selectivity, and thermal stability. These criteria are best met by wall-coated open-tubular (WCOT) glass or fused-silica capillary column gas chromatography. A comprehensive discussion of the effect of column dimensions and stationary phase film thickness on efficiency, capacity, and elution temperatures of PAH appears in the review article by Lee and Wright (23).

Identification of chromatographic peaks is best accomplished using co-chromatography of clean aromatic fractions with authentic PAH standards, followed by mass spectral information on the same chromatographic peaks to confirm the assignments. Unfortunately, many laboratories lack the necessary reference standards of PAH for analysis of samples by co-chromatography. This problem has been partially solved by the development of the PAH retention index system (PAHRIS) (21,24,25). The PAHRIS is based on the use of four PAH--naphthalene, phenanthrene, chrysene, and picene--as bracketing standards rather than the use of normal paraffins for bracketing. The development of the PAHRIS and its application to the analysis of complex mixtures of PAH isolated from a coal liquefaction product have been previously described (21). The PAHRIS was developed for linear-programmed-temperature, glass capillary analysis of PAH using SE-52 as the stationary phase and employing Equation 1 initially suggested by Van Den Dool and Kratz (26):

$$I = 100 \left[n + \frac{X - M_{(n)}}{M_{(n+1)} - M_{(n)}} \right] \qquad 1)$$

Retention indices were calculated for over 200 PAH standard compounds based on their comparison with these standards using the above equation. In Equation 1, I is the retention index, and n refers to the number of rings in the standard compound eluting just prior to the compound of interest. The designations X, $M_{(n)}$, and $M_{(n+1)}$ are the measured retention times of the compound of interest and of the standard aromatic that elutes just prior to the compound of interest and of the standard aromatic that elutes just after the compound of interest, respectively. The average 95% confidence limits for 3 to 8 measurements for each of 12 PAH ranging from naphthalene to perylene were $\pm$ 0.25 index units. A manuscript describing all of the results and experimental details has been published (25).

Two examples from work performed recently in our laboratories will serve as illustrations of the current state-of-the-art of PAH analyses made on coal products or by-products.

An example of PAH determinations using combined GC-MS can be taken from a project whose goal was to develop an analytical method to measure PAH in workplace atmospheres around coal liquefaction plants. Briefly, workplace air samples were collected on Tenax-GC, extracted from the solid sorbent with pentane, concentrated, and analyzed. Individual PAH were identified by full scan mass spectrometry and quantitated using Selected-Ion-Monitoring (SIM) combined with the method of standard addition. A SIM profile appears in Figure 1, while some of the SIM peaks are identified and quantitated in Table 2. A more complete description of experimental details appears elsewhere (24). Another project is concerned with comparing combustion product emissions from synthetic fuels and petroleum. Briefly, a fuel is combusted in a 20-hp boiler, and organic combustion emissions are collected from the exhaust duct using a modified Jones Adsorbent Sampler. The sample was

recovered from the solid sorbent used in the sampler, XAD-2, by methylene chloride extraction. The bulk of the methylene chloride was removed using Kaderna-Danish evaporation, and the sample was analyzed by high resolution gas chromatography and combined GC-MS. The high resolution gas-chromatographic profiles of the collected combustion effluents from three fuels appear in Figure 2, while the numbered chromatographic peaks are identified in Table 3. As can be seen from the chromatographic profiles, the combustion effluents of the fuels are distinctly different, although many of the same compounds are found in all three effluents. Interestingly, the combustion effluents from SRC-II and No. 2 Fuel Oil contain a significant portion of unburned fuel. Complete experimental details appear elsewhere (27). In both projects, capillary columns coated with SE-52 were used for separation of the unfractionated sample. In the case of the first project, glass columns were used as stationary phase supports, while in the second case, fused-silica columns were used. The columns ranged in length from 15 to 30 m and had inside diameters ranging from 0.20 to 0.30 mm.

III. TECHNIQUES ON THE HORIZON

Over the decades, many analytical methods have been developed for the determination of PAH in coal and coal-derived materials. In the last twenty years, there has been an amazing improvement in existing analytical techniques, and recently several revolutionary analytical methods and techniques for qualitative and quantitative analysis of PAH have been developed. The remaining portion of this manuscript will briefly highlight some analytical methods currently under development that have shown great promise in differentiating and, thus, determining specific isomeric PAH in coal and its products. These include low-temperature luminescence and room-temperature phosphorimetry. The following descriptions are not meant to be exhaustive theoretical descriptions of the techniques but rather an introduction to their application for the analysis of PAH in coal and related products.

Electronic spectra of PAH in fluid media are often broad. Thus, spectral overlap of individual PAH is a severe problem in mixture analysis. These problems are partially overcome at low temperature when some PAH are frozen in crystalline Shpol'skii host solvents -- most often n-paraffins. Under these conditions, some PAH exhibit well-resolved sharp line luminescence emission spectra. When dilute solutions of PAH are frozen in Shpol'skii host solvents, the solute molecules are separated enough to eliminate or minimize intermolecular interaction of the solute molecules. The PAH solute molecules are held in the frozen n-alkane matrix in oriented positions, which promotes sharp line spectra and enhances resolution of fine structure, thereby reducing spectral overlap between PAH present as mixtures. This is the Shpol'skii effect (28,29,30). Spectral definition is a function of how well the molecular dimensions of the Shpol'skii host solvent (n-alkane) fit the dimensions of the solute (PAH).

Several variations of the use of the Shpol'skii effect have been developed to characterize PAH in coal extracts, coal maceral extracts, and coal-derived materials. The variations primarily exist in the excitation source used, in the host solvent, and in whether or not the sample was separated to yield an aromatic fraction prior to analysis.

The most impressive example, to date, of the potential analytical power of Shpol'skii spectrometry to analyze PAH in coal-derived materials has been published by Yang and co-workers (31). This group has used laser-excited Shpol'skii spectrometry (LESS) employing tunable dye lasers to selectively excite the sample. No preseparation of the sample was performed. A 0.1 gram sample of an SRC-II coal liquefaction product was appropriately diluted with purified n-octane, and the luminescence spectra were recorded at 15°K. The technique can also be used to obtain quantitative data on individual PAH present in coal-derived materials.

Room temperature phosphorimetry (RTP) is another relatively new analytical technique that is showing promise of being able to analyze complex mixtures of coal-derived materials for specific PAH. The technique is being developed by T. Vo-Dinh and coworkers for analysis of PAH in coal products (32,33,34). Phosphorimetry has conventionally been conducted at cryogenic temperatures so that collisional triplet quenching can be minimized while the sample is in a rigid matrix. This same effect can be achieved at room temperature by adsorption of the sample onto a support.

A major limitation of RTP for the analyses of multicomponent PAH mixtures has been the occurrence of major interferences due to overlap of other phosphorescent compounds in the sample. The RTP spectra of PAH are usually of a broad structureless nature. Thus, the selectivity of conventional RTP is poor with respect to any single PAH. Nevertheless, the selectivity of RTP for individual PAH can be improved by using synchronous excitation, which employs the specificity of energy differences, Δ_{ST}, between the phosphorescence emission band ($T_1 \rightarrow S_o$) and absorption bands ($S_1 \leftarrow S_o$ or $S_N \leftarrow S_o$) (34). Analysis of a coal liquefaction product for a specific PAH is the acid test. The synchronous RTP spectrum of pyrene was obtained on an unseparated crude extract of a coal liquefaction product. This is certainly an impressive achievement and indicates that synchronous RTP could become a valuable analytical technique for analysis of coal products for select PAH. It should be noted that synchronous RTP has recently been used to tentatively identify and quantitate pyrene and other PAH in coal liquefaction products.

In the last twenty years, significant analytical developments have been made for the analysis of complex mixtures of PAH from coal and its products, and the next twenty years will produce even further advances. The biggest advance has come in the development and application of laser-excited Shpol'skii spectrometry (LESS) (31). In the future, the use of LESS for analysis of PAH from coal and other products will increase dramatically, rivaling and possibly supplanting the use of GC-MS for PAH analysis.

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Table 1.-Some aromatic compounds isolated from Bohemian brown coal.

	Compound	Formula	Structure
1	octahydro-2,2,4a,9-tetramethylpicene	$C_{26}H_{30}$	
2	tetrahydro-1,2,9-trimethylpicene	$C_{25}H_{24}$	
3	tetrahydro-2,2,9-trimethylpicene	$C_{25}H_{24}$	
4	1,2,9-trimethylpicene	$C_{25}H_{20}$	
5	23,25-bisnormethyl-2-desoxyallobetul-1,3,5-triene*	$C_{28}H_{40}O$	
6	23,24,25,26,27-pentanormethyl-2-desoxyallobetul-1,3,5,7,9,11,13-heptaene*	$C_{26}H_{28}O$	

* Although the naming system used for these compounds is obscure, these are the names used by Jarolim and co-workers.

10-8-80 L-17894

TABLE 2. CONCENTRATION OF PAH IN A WORKPLACE ATMOSPHERE FROM A COAL LIQUEFACTION PLANT.

Compound	PPB
Naphthalene	3.5
2-Methylnaphthalene	3.2
1-Methylnaphthalene	0.3
2-Ethylnaphthalene	0.4
2,6- and/or 2,7-Dimethylnaphthalene	0.5
1,3- and/or 1,7-Dimethylnaphthalene	0.06
Acenaphthene	0.06
Fluorene	0.04
Phenanthrene	0.08

TABLE 3. SUMMARY OF GC-MS DATA OBTAINED FROM SYNFUEL COMBUSTION EMISSIONS COLLECTED ON XAD-2.

1. Naphthalene
2. 2-Methylnaphthalene
3. 1-Methylnaphthalene
4. Biphenyl
5. 2-Ethylnaphthalene
6. 2,6- and/or 2,7-Dimethylnaphthalene
7. 1,3- and/or 1,7-Dimethylnaphthalene
8. 1,6-Dimethylnaphthalene
9. 1,5-Dimethylnaphthalene
10. Acenaphthylene
11. 1,2-Dimethylnaphthalene
12. Acenaphthene
13. Dibenzofuran
14. Fluorene
15. 9-Methylfluorene
16. 2-Methylfluorene
17. 1-Methylfluorene
18. 9-Fluorenone
19. Dibenzothiophene
20. Phenanthrene
21. Anthracene
22. Carbazole
23. 1-Phenylnaphthalene
24. 3-Methylphenanthrene
25. 2-Methylphenanthrene
26. 4H-Cyclopento(def)phenanthrene
27. 9- and/or 4-Methylphenanthrene
28. 1-Methylphenanthrene
29. 2-Phenylnaphthalene
30. Fluoranthene
31. Benz(e)acenaphthalene
32. Benzo(def)dibenzothiophene
33. Pyrene
34. Retene
35. Benzo(b)fluorene
36. 4-Methylpyrene
37. 2-Methylpyrene
38. Benzo(ghi)fluoranthene
39. Benzo(a)anthracene
40. Chrysene and/or Triphenylene
41. n-Alkanes

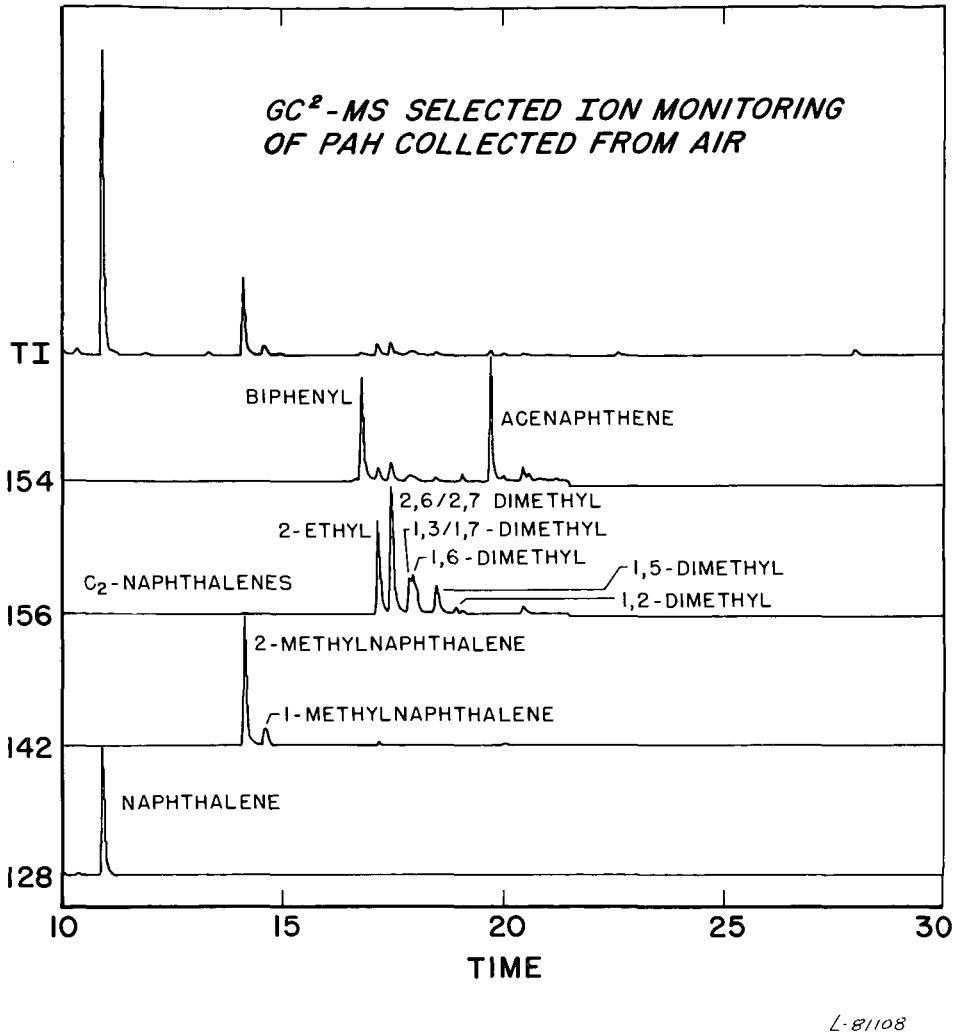

Figure 1 - Selected ion chromatograms at m/e values of 154, 156, 142, and 128 obtained on a workplace air sample collected in a coal liquefaction plant. Quantitative information on some compounds appears in Table 2.

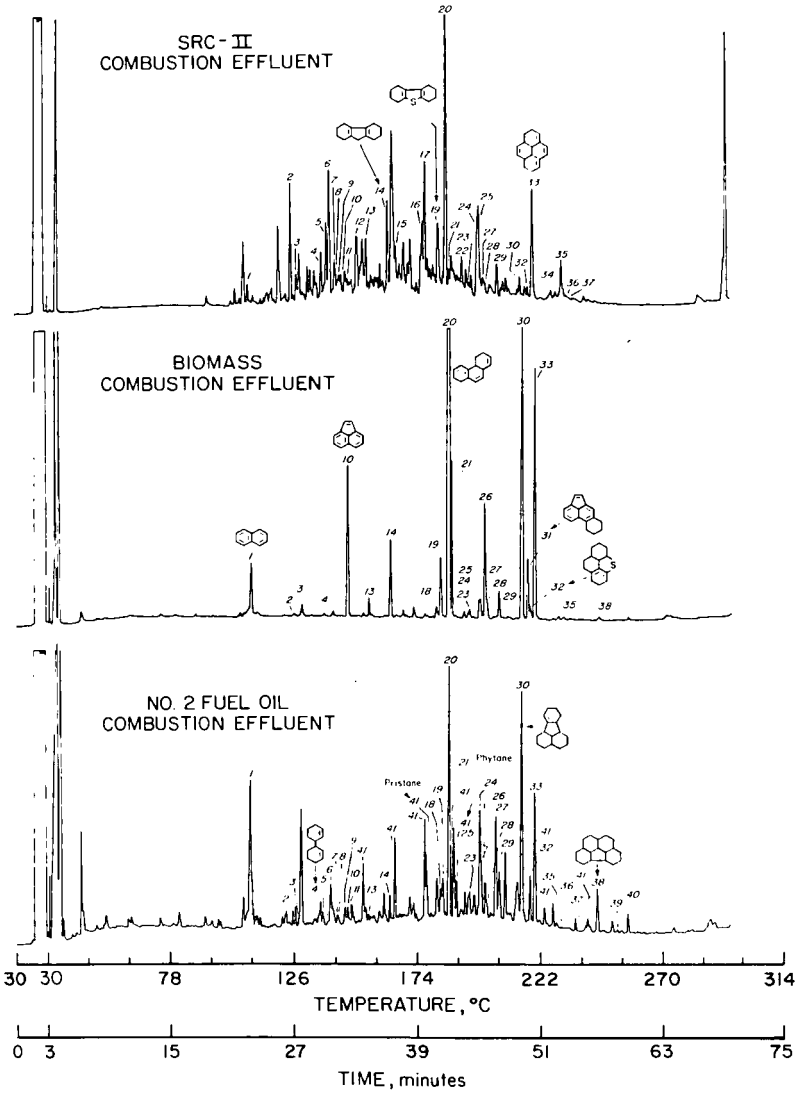

Figure 2 - Gas chromatographic profiles of combustion effluents from SRC-II, biomass, and petroleum No. 2. Separations were achieved using a 19 m x 0.30 mm SE-52 fused-silica column, with splitless injection, He carrier gas, and appropriate temperature programming. Numbered chromatographic peaks are identified in Table 3.