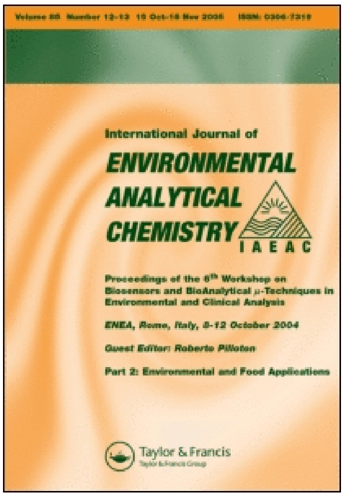

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# Fused Silica Capillary Column Gas Chromatography with Tandem Flame Ionization-Photoionization Detection for the Characterization of *In Situ* Coal Gasification By-Products†

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A photoionization detector (PID) is relatively more sensitive to aromatic than aliphatic compounds, whereas a flame ionization detector (FID) responds sensitively to all hydrocarbons. Their simultaneous use in a tandem arrangement provides a means of differentiating between aliphatic and aromatic hydrocarbons separated by gas chromatography. Employed in combination with fused silica columns having superior separation properties, this detector system provides a powerful tool for the characterization of complex mixtures of volatile organic compounds. This application requires a special PID which is gas-tight and has a low volume. Such a system is described for the characterization of organic by-products of *in situ* coal gasification.

KEY WORDS: Photoionization detector, coal gasification by-products, gas chromatography.

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†Presented at the Workshop on the Chemistry and Analysis of Hydrocarbons in the Environment. Barcelona, November 1981.

## INTRODUCTION

One of the more challenging tasks confronting analytical chemists associated with the emerging synthetic fuels industry is the detection and characterization of potential pollutant organic by-products from processes such as coal gasification. This is particularly true of *in situ* (underground) coal gasification. This process, which has the potential of increasing utilizable coal by as much as four-fold by enabling extraction of the fuel value of coal that cannot be mined by conventional means, consists of partial combustion and gasification of coal between two linking wells drilled into the coal seam, and withdrawal of combustible gas from one of the wells.[1] Concurrent pyrolysis of the coal yields a number of organic chemical by-products, including phenols, aliphatic and aromatic hydrocarbons, and sulfur and nitrogen hetero compounds.[2] A large fraction of these compounds stays underground, posing a potential threat of water pollution.[3,4] Combined gas chromatography–mass spectrometry has been used to identify literally hundreds of compounds produced as by-products of *in situ* coal gasification,[5] but is too expensive and sophisticated to employ for routine monitoring and analysis.

Modern chromatographic techniques provide a less expensive, simpler alternative to gas chromatography–mass spectrometry for the analysis of many organic compounds, such as those produced as by-products of *in situ* coal gasification.[6] In particular, very sensitive gas chromatographic detectors selective for various classes of compounds can be employed to give detection limits superior to those of conventional gas chromatography–mass spectrometry, along with a surprising degree of compound selectivity. An especially useful detector system for the characterization of hydrocarbon by-products consists of a photoionization detector (PID) followed in tandem with a flame ionization detector (FID). The PID functions through the formation of conducting ions produced by the action of high-energy UV light on hydrocarbons, and is more sensitive to aromatic than to aliphatic compounds at an excitation energy of 10.2 electron-volts. The FID is a sensitive detector for all hydrocarbons. Simultaneous use of a PID and FID enables differentiation of aromatics and aliphatics, which is an important capability in the characterization of organic by-products of *in situ* coal gasification.[6] In order to use these two detectors in tandem, it is necessary to employ a gas-tight PID. Such a detector, with a particularly low volume for use as a detector for capillary gas chromatography, has been fabricated and is described in the literature.[7]

The relatively recent introduction of flexible fused silica capillary columns, in part the result of “spin-off” from fiber optics technology, has provided columns that give excellent chromatographic performance with a high resistance to breakage.[8] Use of a low volume PID enables application of these columns to a gas chromatograph employing tandem PID/FID detection to yield a powerful chromatographic tool for the characterization of complex hydrocarbon mixtures. This paper describes such a system and its application to the analysis of complex coal tar by-products of simulated and pilot studies of *in situ* coal gasification.

## EXPERIMENTAL SECTION

### Coal gasification by-products

Five by-product samples were analyzed. Two of these were from laboratory-simulated *in situ* coal gasification using an apparatus described in the literature.[3,6,9] Basically, the process consisted of gasification of granular Hanna, WY, subbituminous coal in a silica tube through which a stream of humid oxygen was passed. The stream of combustible gas produced by the action of a hot flame front in the tube was passed through cooled traps containing cyclohexane. Initiation of a flame front by external heating at the downstream end of the column results in movement of the gasification reaction flame in a direction counter to the flow of gas in the column, leaving a column of char residue. This mode of gasification is designated as a laboratory reverse burn. When the flame front is initiated at the upstream end of the column, the flame proceeds in the same direction as the gas flow, leaving an ash residue; this is called a laboratory forward burn. For reasons that have been discussed,[6] the compositions of the tar by-products of these two modes of gasification are quite different. In addition to these two samples, three samples were extracted from water collected at the site of the USDOE Laramie Energy Technology Center's *in situ coal gasification* experiment conducted near Hanna, WY, in 1979, designated the Hanna-IV experiment. The Hanna-IV reverse sample consisted of tar-water collected during a reverse burn used to establish linkage between two wells in the coal seam. The sample denoted Hanna-IV forward was the last available sample of tar-water collected during the forward (production) burn at the Hanna-IV site. The Hanna-IV water sample was a composite groundwater sample taken from a test well at the Hanna-IV gasification site. The Hanna-IV reverse and forward samples were diluted 1/25 and extracted with an equal volume of cyclohexane prior to sample fractionation; the Hanna-IV water sample was treated identically, except that it was not diluted. The cyclohexane extract was centrifuged to remove insoluble material, and the cyclohexane-soluble material was saved for further fractionation.

## Sample fractionation

The samples were separated into neutral, acidic, and basic fractions using a modification of a scheme developed for the determination of individual organic compounds in shale oil.[10] The procedure is outlined in Figure 1. Only the cyclohexane soluble constituents were separated. As noted previously, these consisted of samples collected directly from the laboratory gasification studies and those extracted from water contaminated by the field operations. A 5-ml portion of the sample in cyclohexane was extracted once with 5 ml of 1 N aqueous NaOH to remove acids. Five drops of benzene were then added to the cyclohexane layer. Bases were then extracted from the cyclohexane layer with 1 × 5 ml 1 *N* $H_2SO_4$, which was subsequently neutralized with 1 *N* NaOH and extracted with 2 × 5 ml benzene to give the basic fraction in a benzene solution. Since a previous study showed minimal basic components in

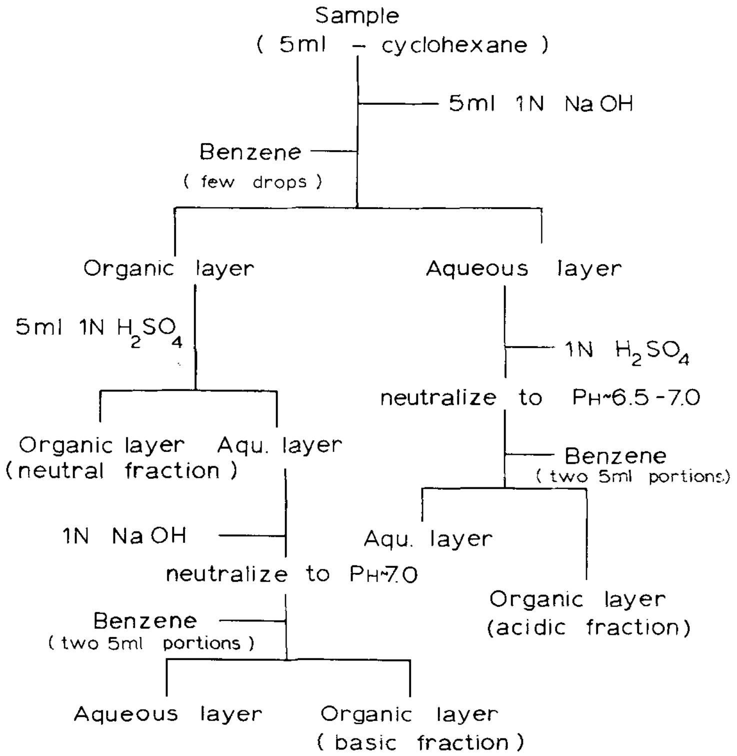

FIGURE 1 Separation scheme employed for *in situ* coal gasification by-products.

these coal gasification by-products,[6] the basic fraction was not further analyzed in this study.

The acidic components were extracted from the aqueous base layer by neutralization with 1 *N* $H_2SO_4$ and extraction with $2 \times 5$ ml benzene. This fraction was subsequently analyzed for phenolic compounds.

The compound recoveries obtained with the separation scheme were checked using seven model compounds at 100 ppm cyclohexane.

## Gas chromatographic conditions

A flame ionization detector was mounted in tandem with a gas-tight, low-volume photoionization detector fabricated at the University of Missouri. A 10.2 eV UV lamp (HNU System, Inc.) was used as an excitation source for the PID. The detectors were mounted on a Tracor Model 560 gas chromatograph equipped with a split-splitless injector and a 10-meter flexible fused silica column coated with SE-54 (Quadrex Corp.). Nitrogen carrier gas was used. A split ratio of 1:25 was employed with a column flow of approximately 2 ml/min. Make-up gas at 25 ml/min was introduced before the FID. The flow rates of hydrogen and air to the FID were 30 and 200 ml/min, respectively.

All aromatic and aliphatic hydrocarbon standards were obtained from Aldrich Chemical Co. (Milwaukee, WI). The phenolic standards were obtained from Theta Corp. (Media, PA).

## RESULTS AND DISCUSSION

The fractionation scheme shown in Figure 1 was tested for percent recovery with model compounds, with the results shown in Table I. Although methylene chloride was tried as an extracting solvent, it was found that benzene gave about 10% better recoveries. With benzene,

TABLE I
Fractionation of model compounds

| Model compd. | Amt. added (mg) to 5 ml cyclohexane | Amt. recov. (mg) | % recovery |
|---|---|---|---|
| Naphthalene | 0.49 | 0.47 | 96 |
| Tetradecane | 0.52 | 0.52 | 100 |
| Anthracene | 0.50 | 0.50 | 100 |
| 2, 3, 5-Trimethyl phenol | 0.37 | 0.31 | 84 |
| 2-Naphthol | 0.45 | 0.39 | 87 |
| Quinoline | 0.75 | 0.70 | 93 |
| Trimethyl pyridine | 0.61 | 0.53 | 87 |

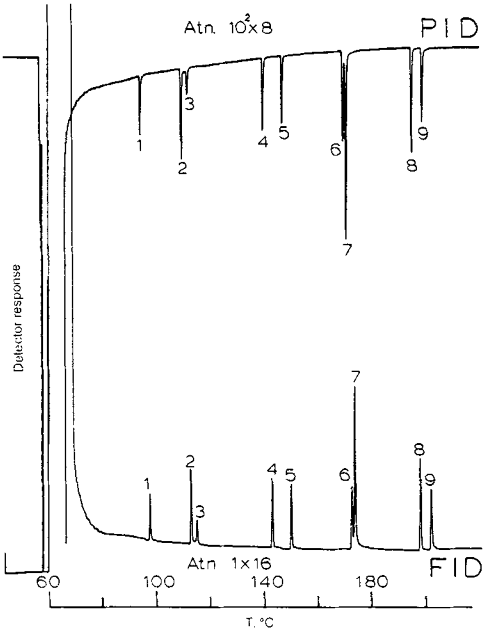

FIGURE 2 Photoionization and flame ionization detector responses of aromatic hydrocarbons: (1) naphthalene, (2) 2-methyl naphthalene, (3) 1-methyl naphthalene, (4) dimethyl naphthalene, (5) acenaphthene, (6) phenanthrene, (7) anthracene, (8) triphenyl methane, (9) terphenyl.

recoveries ranging from 84 to 100% were obtained; repeated benzene extractions did not improve recovery.

Comparisons of PID and FID responses have been used to distinguish classes of organic compounds separated by gas chromatography[11] in a study that used packed columns for the chromatographic separations, in contrast to the present study, which employed a flexible fused silica column. The PID-FID responses of aromatic and aliphatic hydrocarbon standards (5 ng aromatic, 10 ng aliphatic, split ratio 1:25) are shown in Figures 2 and 3. Under the conditions given, the PID/FID response ratios were ca. 50 for the aromatic compounds and ca. 10 for the aliphatic standards. The response of an analyte in a PID depends on the energy of the exciting photons, the source intensity, the background current with associated noise, and the ionization potential of the analyte molecule. If the instrumental parameters are held constant, as is the case in the routine application of PID, the response of the analyte molecule is determined predominantly by its ionization potential. In general, the probability of ionization for multiple (*n*-fold) ionization processes at energies slightly

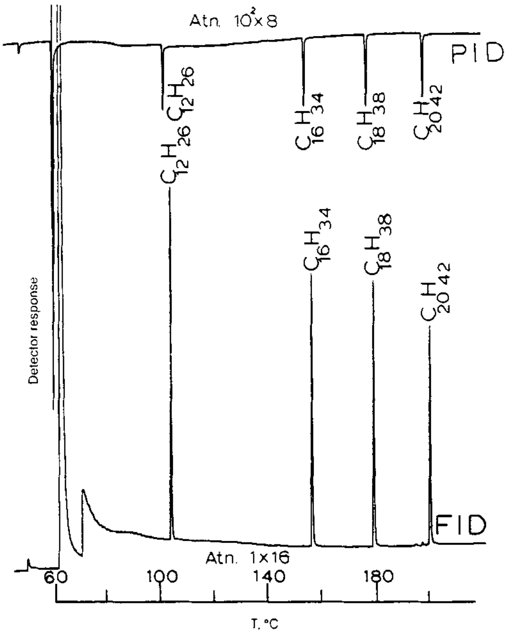

FIGURE 3 Photoionization and flame ionization responses of aliphatic hydrocarbons.

above the ionization threshold (as in the present case) is given by the following expression:[12]

$$P(E) \propto (V - V_c)^{n-1} \tag{1}$$

In this expression $P(E)$ is the ionization probability, $V$ is the photon energy and $V_c$ is the ionization potential. Thus, for single ionization processes ($n = 1$) the relation gives a zero-order function and molecules can be ionized easily with photon energies just above the threshold. However, the photoionization efficiencies of alkanes do not rise sharply with increases in photon energy compared to aromatics.[13] This phenomenon accounts for the appreciably greater response of aromatic compounds compared to aliphatics at a PID photon energy of 10.2 eV. This difference in response makes feasible the differentiation of aromatic and aliphatic components of complex mixtures using a series configuration of PID and FID; unlike the PID, the response of the FID for most organics depends primarily upon the mass flow rate of carbon. Thus, the use of a tandem PID/FID detector system combined with capillary chromatography offers a relatively simple, yet useful, means of characterizing complex organic mixtures.

Various forward- and reverse-burn samples fractionated by the above scheme were analyzed. The chromatograms of the neutral fraction components are shown in Figures 4–7. Despite the complexity of the chromatograms, a clear difference in the response traces for PID and FID can be observed. The chromatograms in Figures 4–7 were obtained with the same attenuation settings as those of the standards shown in Figures 2 and 3. Therefore, on the basis of a visual examination, peaks with about the same response in both PID and FID may be tentatively designated as aromatics. Likewise, peaks with PID/FID response ratios of 0.2 to 0.3 may be designated as aliphatics. The neutral fraction from the laboratory forward burn shows several peaks with stronger FID response (Figure 4), while the peaks from the neutral fraction of the laboratory reverse burn products (Figure 5) shows peaks of comparable response in the two detectors. Thus, the products of the laboratory forward burn are rich in aliphatic hydrocarbons, whereas those of the reverse burn are aromatic-rich. Obvious aromatic-type compounds may be spotted easily in Figure 6; examples are peak numbers 16, 25, 54, and 59; aliphatics are 27, 56, 60, 68, and 72. In Figure 7 the obvious aromatic components are those of peak numbers 1, 5, 8, 36, and 40; aliphatics are peak numbers 37 and 51.

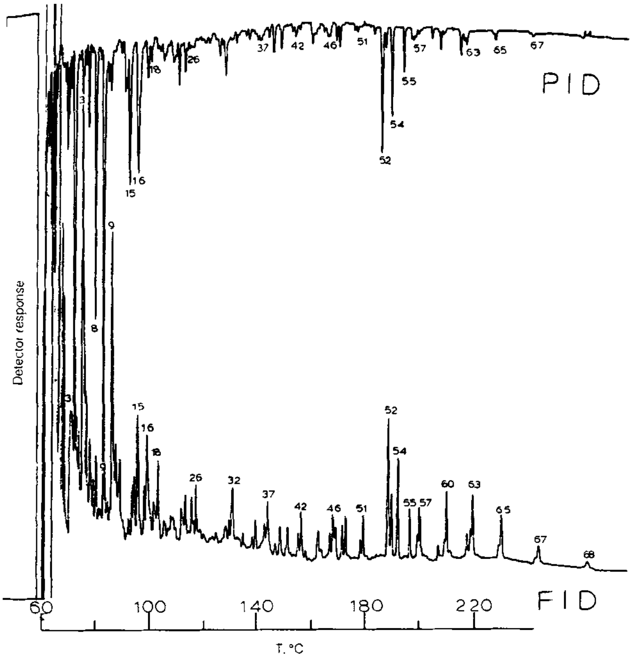

FIGURE 4 Chromatograms of the neutral fraction of a laboratory forward burn.

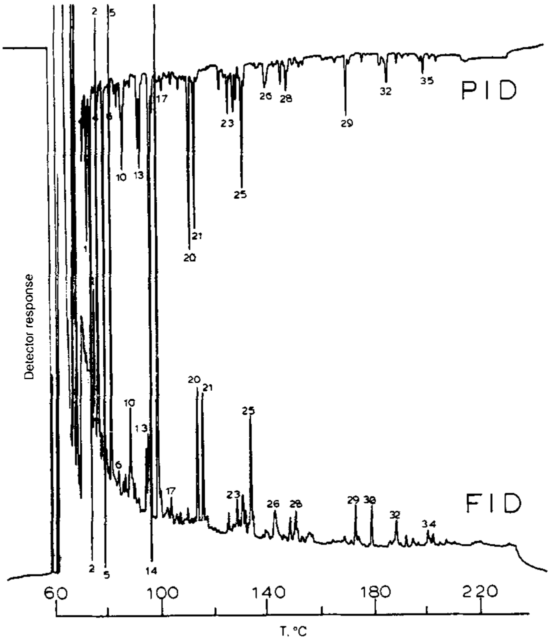

FIGURE 5 Chromatograms of the neutral fraction of a laboratory reverse burn.

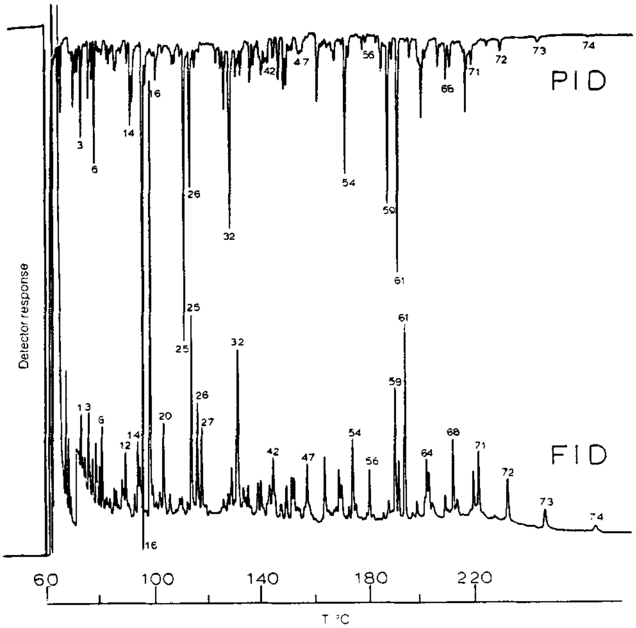

FIGURE 6 Chromatograms of the neutral fraction of the Hanna-IV forward burn.

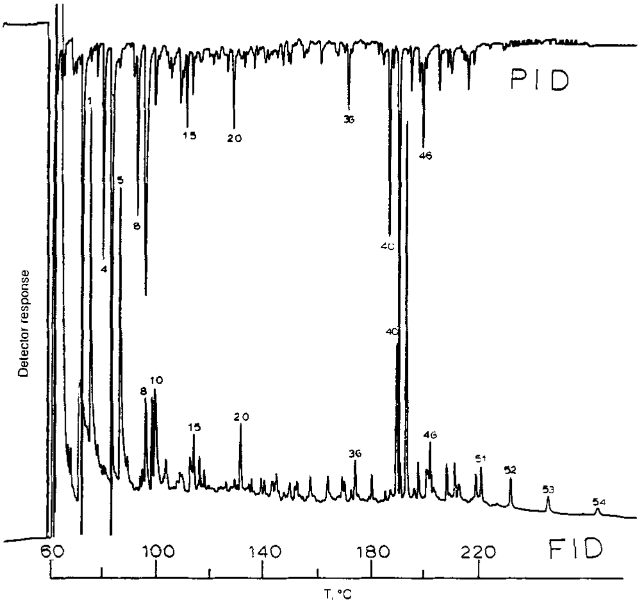

FIGURE 7 Chromatograms of the neutral fraction of the Hanna-IV reverse burn.

PID/FID response ratios, retention times, and co-chromatography were used for tentative identification of several components of the neutral fraction, and the results are summarized in Table II. The neutral fractions of all samples except the one from the laboratory reverse burn showed essentially similar patterns, with an abundance of aliphatic species. The relative abundance of aromatics in the laboratory reverse burn has been explained by the gasification and pyrolysis conditions.[6] There is evidence of doublet peaks in the laboratory forward burn samples, implying the presence of isomers of the aliphatic compounds.

The acidic fraction of tar samples contained a variety of phenolic compounds, as shown by the chromatograms in Figures 8 and 9. In general, similar chromatogram profiles were obtained from both the laboratory, and pilot plant samples. Again, the major exception was the laboratory reverse burn sample, which contained smaller amounts of phenolic substances. Various phenolic compounds determined by retention times matched by co-chromatography are listed in Table III.

Analysis of the ground water sample from the pilot project showed little or no hydrocarbon material in the neutral fraction (Figure 10A). However, this sample did contain large amounts of phenolic compounds (Table II, Figure 10B). Such an observation is consistent with the relatively high aqueous solubilities of phenols.

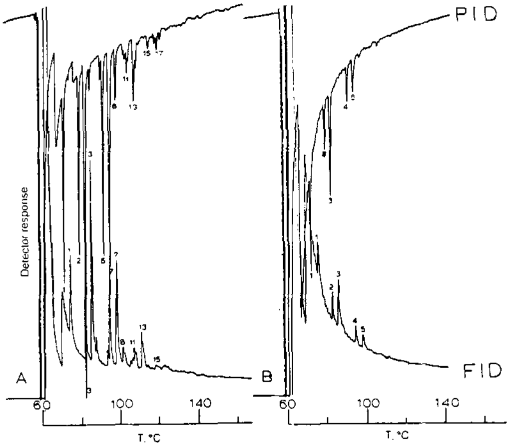

FIGURE 8 Chromatograms of the acidic fractions prepared from laboratory gasification experiments: (A) laboratory forward, (B) laboratory reverse.

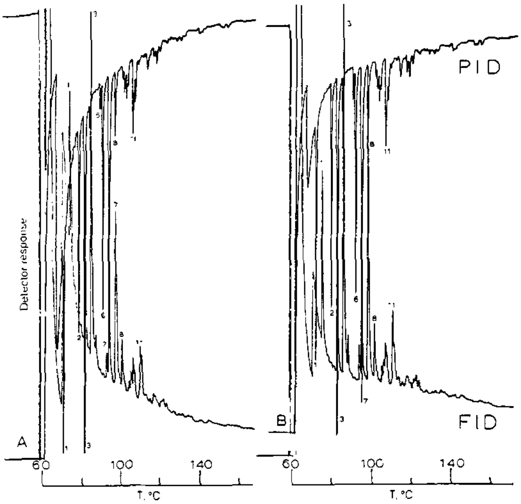

FIGURE 9 Chromatograms of the acidic fractions from Hanna-IV tar-water samples: (A) Hanna-IV forward, (B) Hanna-IV reverse.

## TABLE II

Compounds tentatively identified in the neutral fractions

| | Sample | | | |
|---|---|---|---|---|
| Compound | Lab. Forward Burn | Lab. Reverse Burn | Hanna IV Forward Burn | Hanna IV Reverse Burn |
| 2,4,6 Trimethyl Benzene | 3 | 1 | — | 1 |
| Naphthalene | 15 | 14 | 16 | 5 |
| 2-Methyl Naphthalene | 24 | 20 | 25 | 8 |
| Phenanthrene | — | 29 | 54 | 36 |
| Anthracene | — | 30 | 55 | — |
| Methyl Phenanthrene | 52 | — | 59 | 40 |
| $C_{10}H_{22}$ | — | — | 4 | — |
| $C_{11}$ | — | — | 12 | — |
| $C_{12}$ | 18 | — | 20 | 9 |
| $C_{13}$ | 26 | — | 27 | 17 |
| $C_{14}$ | 32 | — | — | — |
| $C_{15}$ | 37 | — | 44 | 26 |
| $C_{16}$ | 42 | — | 49 | 31 |
| $C_{17}$ | 46 | — | 51 | 33 |
| $C_{18}$ | 51 | — | 56 | 37 |
| $C_{19}$ | 53 | — | 60 | 41 |
| $C_{20}$ | 57 | — | 64 | 46 |
| $C_{21}$ | 60 | — | 68 | 48 |
| $C_{22}$ | 63 | — | 71 | 51 |
| $C_{23}$ | 65 | — | 72 | 52 |
| $C_{24}$ | 67 | — | 73 | 53 |
| $C_{25}$ | 68 | — | 74 | 54 |

*Numbers refer to peak numbers in accompanying chromatograms.

## TABLE III

Compounds tentatively identified in the acidic fractions

| | Sample | | | | |
|---|---|---|---|---|---|
| Compounds | Lab. Reverse | Lab. Forward | Hanna IV Reverse | Hanna IV Forward | Hanna IV Water |
| Phenol | 1 | 1 | 1 | 1 | 2 |
| O-Cresol | 2 | 2 | 2 | 2 | 3 |
| m & p/Cresol | 3 | 3 | 3 | 3 | 4 |
| 2, 4 Xylenol | — | 4 | 4 | 4 | 5 |
| o-Ethyl phenol | — | 5 | 5 | 5 | 6 |
| m-Ethyl phenol | 5 | 7 | 7 | 6 | 8 |
| 2,6 Xylenol | 4 | 6 | 6 | 7 | 7 |
| 2,4,6 Trimethyl phenol | — | 8 | 8 | 8 | 9 |
| 2,3,5 Trimethyl phenol | — | 12 | 11 | 11 | 10 |

*Numbers refer to peak numbers in accompanying chromatograms.

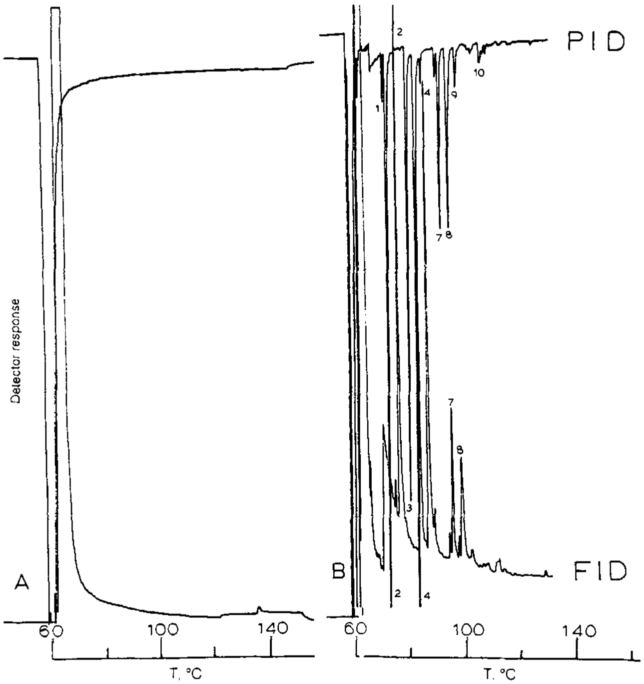

FIGURE 10 Chromatograms of Hanna-IV water samples: (A) neutral fractions, (B) acidic fractions.

No significant peaks were found in the basic fractions of the samples used in this study. Unlike shale oil products, coal liquids contain relatively small quantities of the nitrogen compounds, such as pyridines and azaarenes, which make up the basic fraction. More definitive results can perhaps be obtained by the use of a selective detector, particularly the N-P thermionic detector.

This work has demonstrated the capability of tandem PID-FID detection combined with capillary gas chromatographic separation for the characterization of a complex mixture of organic compounds produced as by-products of a synthetic fuels manufacturing process. The key to the success of this system has been the use of a specially-fabricated PID that has two essential characteristics. The first of these is that it is gas-tight, so that the effluent from it may be subjected to flame ionization detection further downstream. The second major characteristic is the low volume, essential for detection of capillary column effluents in this application. Combined with a relatively simple fractionation scheme prior to analysis, this system affords many of the capabilities of gas chromatographic–mass spectrometric analysis at a fraction of the cost and complexity.

## Acknowledgement

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