

COMPUTER ENHANCED SEPARATION OF COMPOUND CLASSES IN FUEL MIXTURES  
USING A COMBINED LC-MS APPROACH

Barbara L. Hoesterey, William H. McClennen, Willem Windig and Henk L.C. Meuzelaar

University of Utah, Biomaterials Profiling Center  
391 S. Chipeta Way, Suite F, Research Park  
Salt Lake City, Utah 84108

INTRODUCTION

Liquid Chromatography (LC) methods play an important role in coal liquid analysis both as pre-separation techniques for further analytical studies as well as coal liquid characterization methods in their own right. Among the many different LC separation methods for coal liquids, those described by Farcasiu (1) and Dark *et al.* (2) have gained relatively wide acceptance. A modified version of an open column silica gel separation method developed by Rubin *et al.* (3) was described by McClennen *et al.* (4) and adapted for GC/MS as well as direct low voltage MS studies. This modified technique involves the use of four increasingly polar eluents: namely pentane, pentane/benzene (8:1), benzene/ether (4:1) and benzene/methanol (1:1). Low voltage MS analysis of the four subfractions obtained from coal tars produced by a range of different liquefaction methods consistently reveals the following compound categories: (1st subfraction) aliphatic, naphthenic and aromatic hydrocarbons; (2nd subfraction) polynuclear aromatic hydrocarbons; (3rd subfraction) hydroxyaromatics; and (4th subfraction) polyfunctional and nitrogen compounds (4,5).

In most instances, the first (pentane) fraction is still too complex for a useful degree of compound class quantitation since this fraction contains a variety of aliphatic compound series as well as alicyclic, hydroaromatic and aromatic series. On the basis of elementary LC principles, however, it can be predicted that the various hydrocarbon compound classes will elute at slightly different points in time. In view of the broad range of molecular sizes as well as structures involved it would be unrealistic to expect a complete separation, even when using sophisticated HPLC methods, therefore considerable overlap will occur among the various compound series. Nevertheless, combination with MS techniques opens up the possibility of achieving numerically enhanced separation between incompletely resolved chromatographic peaks. This approach is widely used in combined GC/MS techniques. However, whereas on-line GC/MS instrumentation is widely available, on-line LC/MS methods are still under development and require expensive, dedicated equipment. In contrast, off-line LC/MS procedures can be carried out with relatively simple LC and MS equipment as demonstrated by Meuzelaar *et al.* (5). Preliminary results of such an off-line LC-MS approach as applied to the pentane LC fraction of a heavy coal pyrolysis tar, will be reported here.

EXPERIMENTAL

The pentane LC fraction of a heavy pyrolysis tar produced by a pilot plant scale Lurgi retort run of a Blind Canyon seam (Wasatch Plateau field, Utah) coal was prepared according to the method described by McClennen *et al.* (4). Subsequently, this pentane fraction was subfractionated over a 0.7 cm dia. X 29 cm long glass column packed with activated 120/200 mesh silica gel (Baker analyzed reagent) using hexane (pesticide grade) as the eluent. Approximately 0.7 g of the pentane LC fraction (a viscous liquid) were layered on the silica gel column. Thirty ml of hexane were used to elute the tar fraction. The first ten fractions were collected every 0.5 to 0.75 ml. Fractions 11 to 17 were collected every 1 to 1.5 ml. Fractions 18 and 19 were collected every 2 ml. Fractions were evaporated with a flow of nitrogen gas to between one half and one fourth volume.

The nineteen subfractions were analyzed by low voltage (12 eV) mass spectrometry using a heated inlet and capillary tube sample introduction procedure as described by McClennen *et al.* (5). Eight hundred scans over the mass range  $m/z$  20 to 260 were summed for each subfraction. Data analysis was performed using the factor analysis routine of the SPSS program package (6) in combination with factor rotation methods developed by Windig *et al.* (7).

## RESULTS AND DISCUSSION

The low voltage mass spectra of the original Lurgi tar and its pentane LC fraction, shown in Figure 1, illustrate the effectiveness of the LC procedure in separating hydroxyaromatic series (e.g., phenols and indanols) which appear in the benzene/ether fraction (49% yield; not shown) from the hydrocarbon components. Moreover, although some three and four ring aromatic hydrocarbons, e.g., phenanthrene/anthracene and pyrene, appear in the pentane fraction (Figure 1b) their relative abundance is decreased in comparison with the spectrum of the whole tar (Figure 1a). This is due to the fact that polynuclear aromatic hydrocarbon series are concentrated in the second (pentane/benzene) fraction (not shown; see reference 8) which accounts for 9% of the total tar.

When evaluating Figure 1, it should be pointed out that not all of the Lurgi tar was vacuum distillable (residue at 400°C -5%; see reference 8). Therefore, Figure 1a represents a combined evaporation/pyrolysis mass spectrum. Moreover, some of the higher boiling tar components (e.g., vacuum distillable between 200°C and 400°C) may have been lost by condensation in the mass spectrometer inlet. To a lesser extent, a similar problem may exist with the pentane fraction in Figure 1b. Furthermore, it should be pointed out that the chemical identities of the ion species outlined in Figure 1, as well as in subsequent figures, are tentative only since these were based on prior experience with other coal tars (4,8,9) rather than on positive identification by combined GC/MS (4) or MS/MS (10) techniques.

Figure 2 shows that the expected separation of hydrocarbon compound classes during elution with hexane (or pentane) from the silica gel column does indeed take place. Subfractions 1 (Figure 2a), 11 (Figure 2b) and 19 (Figure 2c) are found to contain primarily aliphatic hydrocarbons, cyclic terpenoids and alkylsubstituted aromatics, respectively. The aliphatic pattern in Figure 1a exhibits the familiar alkane/alkene/diene triplets up to  $C_{18}$  (probably continuing beyond the recorded mass range) illustrating that good quality aliphatic hydrocarbon spectra are obtained under the low voltage electron ionization conditions used in this experiment. Through subsequent fractions the relative contribution of the alkane components diminishes in favor of the olefinic compound series (not shown) until isoprenoid-type spectral patterns appear in fractions 10 and 11. The terpenoid pattern in fraction 11 (Figure 2b) is dominated by the characteristic rearrangement-type fragment ion series from decalins and higher terpanes at  $m/z$  82, 96 and 110 as well as equally characteristic fragment ions at  $m/z$  163 ( $C_{12}H_{19}^+$ ) and 191 ( $C_{14}H_{23}^+$ ). The fragment ion at  $m/z$  191 is often used in GC/MS studies of hydrocarbon fractions of geochemical origin to identify cyclic terpanes and terpenes (including sesqui-, di- and triterpanes and -terpenes) (11,12,13) although it is also a major fragment ion of the acyclic isoprenoid pristane (14). A closer inspection of the sesquiterpenoid molecular ion region of the spectrum in Figure 2b reveals the expected peaks at  $m/z$  208 (sesquiterpanes) and 206 (sesquiterpenes). Upon following the evolution of these patterns through subsequent hexane fractions (e.g., 12 and 13; not shown) a gradual shift towards more unsaturated sesquiterpenoids (e.g., at  $m/z$  204 and 202) can be observed, finally cumulating in the jump to  $m/z$  198 (cadalene) at the start of the alkylnaphthalene series in the last four fractions (see fraction 19 in Figure 2c).

The foregoing discussion illustrates that at least three (aliphatics, naphthenics and aromatics), and perhaps as much as five (alkanes, olefins, alicyclics, hydroaromatics and aromatics), compound classes can be seen to elute in consecutive fashion and, thus, can be evaluated qualitatively. However, significant problems are encountered when trying to obtain a quantitative estimate of the relative abundances and yields of these compound classes by means of selected ion intensities. Whereas  $m/z$  191 and 156 are found to provide good elution profiles for the terpenoid and two ring aromatic fractions, respectively (see Figure 3), no completely satisfactory fragment ion signals are found for the aliphatic components, due to strong overlap with the alicyclic and aromatic compound groups, as shown in Figure 4.

In view of the fact the single variables prove unsatisfactory for quantitation purposes, multivariate approaches such as factor analysis appear to be indicated in this case. Figure 5 shows a plot of the scores of the first two factors obtained on the low voltage mass spectra of 17 of the original 19 subfractions (subfractions 3 and 14 were eliminated because of aberrant behavior in the factor analysis). Together these two factors explain as much as 72.9% of the total variance in the mass spectra. In other words, the intrinsic ("true") dimensionality of the data set is close to 2. This is typical of situations where only three components dominate the behavior of the data set. The ternary mixture nature of the subfractions is further indicated by the near triangular arrangement of the data points in Figure 5 with aliphatics (alkanes + olefinics), naphthenics (alicyclics + hydroaromatics) and aromatics representing the three corner points of the triangle. As shown in previous multivariate analysis studies of mass spectra of ternary mixtures (5,7,15) the relative concentration of the components in such mixtures can be directly estimated from the factor analysis scores. The factor scores of the three component axes A, B and C representing aliphatic, naphthenic and aromatic components, respectively, are plotted in Figure 6 and show the relative concentrations of these compound classes during elution of the subfractions from the silica gel column. However, calculation of absolute concentration values requires the availability of suitable reference standards (e.g. reference mixtures obtained by repeated LC analysis of representative coal tars) and has not been attempted here.

It should be noted that the factor score plot in Figure 6 shows a numerically enhanced separation of the aliphatic and naphthenic compound classes in comparison to the selected ion intensity plots in Figure 4. Finally, it should be pointed out that the aliphatic and naphthenic compound classes in Figure 6 may each be subdivided further into at least two classes (as indicated by arrows) by using additional factor analysis data (factor III represents 12.7% of the total variance). This would result in a total of five compound classes: alkanes, olefins, alicyclics, hydroaromatics and aromatics.

#### REFERENCES

1. Farcasiu, M., Fuel 56, (1977) 9.
2. Dark, W.A., McFadden, W.H., Bradford, D.L., J. Chromatogr. Sci. 15, (1977) 454.
3. Rubin, I.B., Guerin, M.R., Hardigree, A.A., Epler, J.L., Environ. Res. 12, (1976) 358.
4. McClennen, W.H., Meuzelaar, H.L.C., Metcalf, G.S., Hill, G.R., Fuel 62, (1983) 1422.
5. Meuzelaar, H.L.C., McClennen, W.H., Final report to USAF, contract 416-84-004, "Tandem Mass Spectrometric Analysis (MS/MS) of Jet Fuels; Part II: Quantitative Aspects of Direct MS Analysis", 1984.

6. Nie, N.H., Hull, C.H.G., Jenkins, J.G., Steinbrenner, K., Bent, W.H., *tistical Package for the Social Sciences*: 2nd Ed.; McGraw-Hill: New York, 1975.
7. Windig, W., Meuzelaar, H.L.C., Anal. Chem. 56, (1984) 2297.
8. Meuzelaar, H.L.C., Hoesterey, B.M., McClennen, W.H., Hill, G.R., "Composition and Stability of Pyrolytic Tars from HVB Wasatch Plateau Coals", Proceedings of EPRI's Clean Liquid and Solid Fuels Contractors' Conference, 1985.
9. Meuzelaar, H.L.C., Harper, A.M., Hill, G.R., Given, P.H., Fuel 63, (1984) 640.
10. Meuzelaar, H.L.C., McClennen, W.H., Tomlinson, J.H., Pope, D.L. "A Multimode Curie-point MS System for Rapid Characterization of Fossil Fuels and their Liquefaction Products", Proc. Int. Conf. on Coal Science, Dusseldorf, 1981, pp. 816-821.
11. Gallegos, E.J., J. Chromatogr. Sci. 19, (1981) 156.
12. Gallegos, E.J., Anal. Chem. 47, (1975) 1524.
13. Larter, S.R., in "Analytical Pyrolysis, Techniques and Applications", ed. K.J. Voorhees, publ. Butterworth, 1984, p. 212.
14. Given, P.H., "An Essay on the Organic Geochemistry of Coal" in Coal Science, Vol. 3, eds. M.L. Gorbaty, J.W. Larsen, and I. Wender, publ. Academic Press, 1984, p. 63.
15. Windig, W., Haverkamp, J., Kistemaker, P.G., Anal. Chem. 55, (1983) 81.

#### ACKNOWLEDGEMENTS

The research reported here was supported by the Electric Power Research Institute (contract RP2502-3). The Lurgi tar sample was kindly provided by Bechtel Group Inc. The invaluable help and advice of Dr. George R. Hill is gratefully acknowledged.

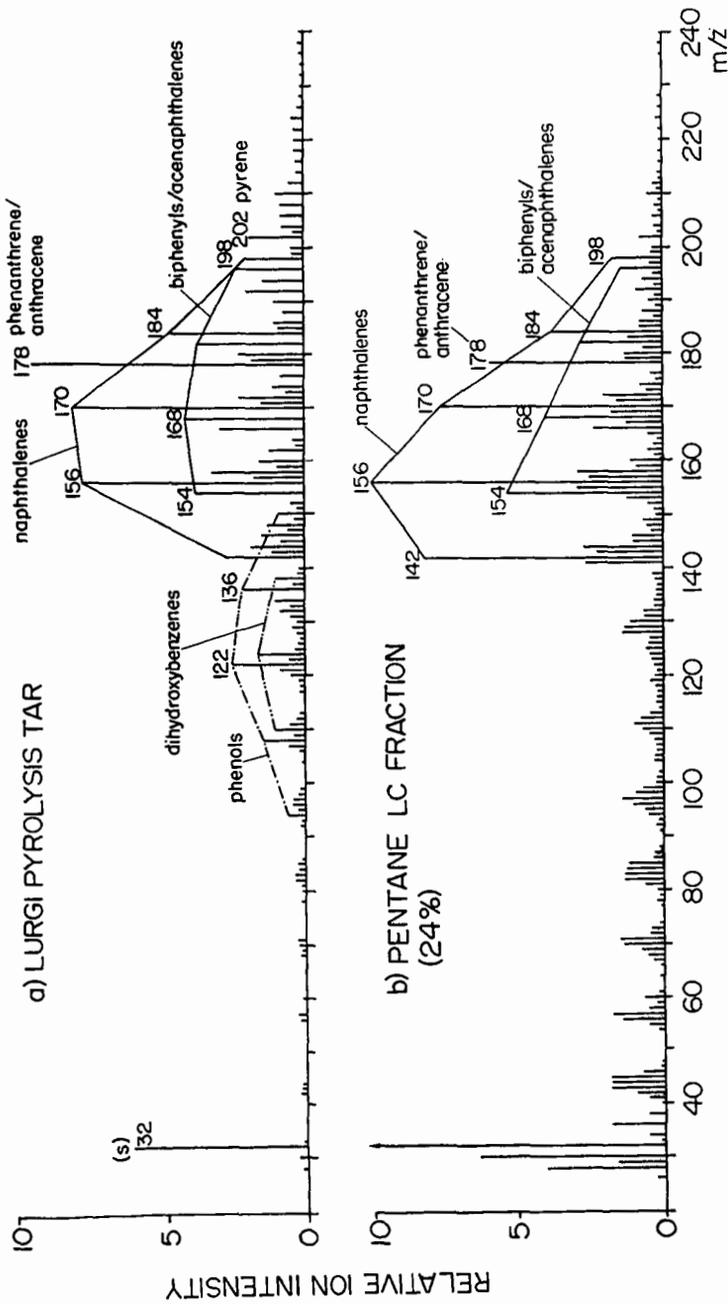


Figure 1. Low voltage volatilization/pyrolysis mass spectra of (a) the Lurgi pyrolysis tar and (b) the pentane LC fraction of the tar (24 wt. %) which was used in the subtraction procedure. Note the absence of phenols and dihydroxybenzenes in the pentane fraction.

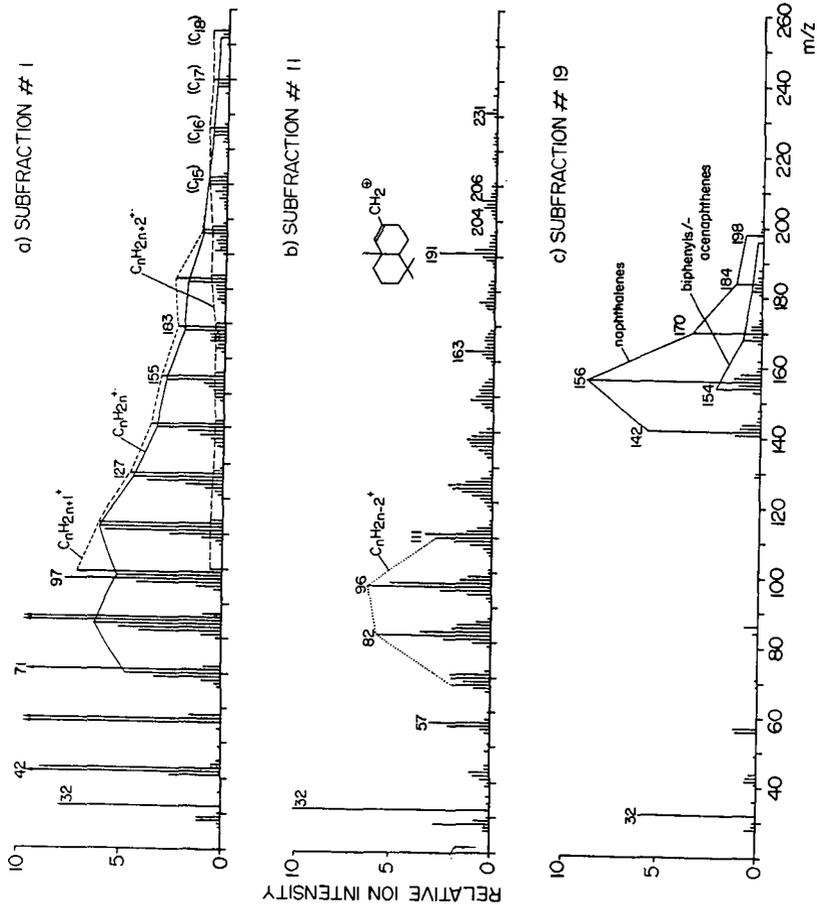


Figure 2. Low voltage mass spectra of selected subfractions of the pentane LC tar fraction. In (a) fraction 1, alkane and alkene molecular ions and fragments predominate; in (b) fraction 11, polyisoprenoid signals are evident; and in (c) fraction 19, naphthalene and acenaphthene and/or biphenyl molecular ions are present.

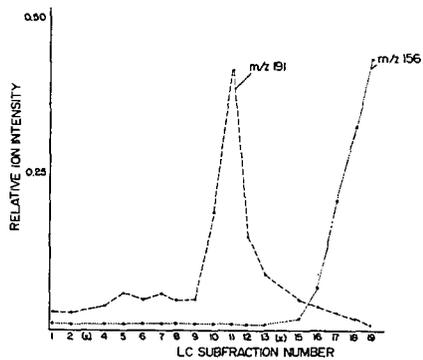


Figure 3. Relative ion intensities of selected ion intensities representing specific compound classes present in the subfractions. See text for details.

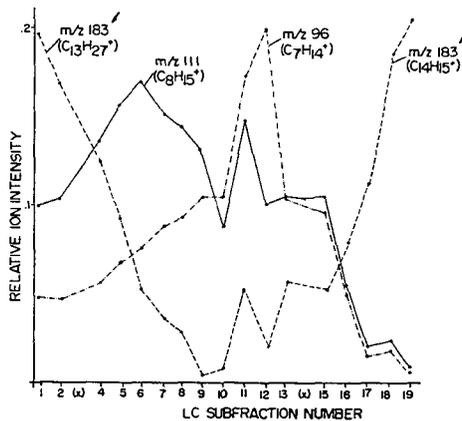


Figure 4. Relative ion intensities of selected fragment ions representing general compound classes present in the subfractions.

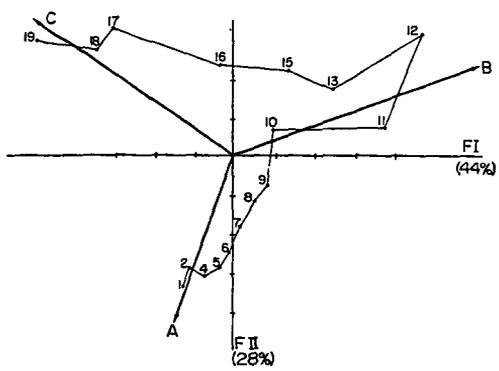


Figure 5. Score plot of subfractions on factors 1 and 2 with component axes indicated. Note resemblance to a ternary mixture diagram.

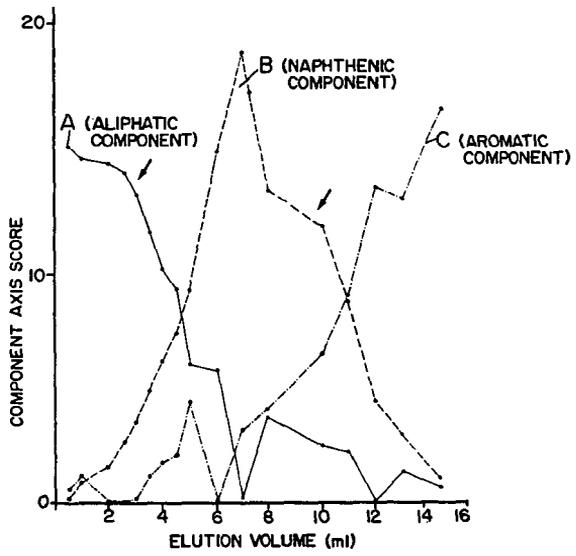


Figure 6. Relative scores of subfractions on components A, B, and C versus elution volume (calculated from factor score plot in Figure 5).