

## NUMERICAL EXTRACTION OF CHEMICAL COMPONENT PATTERNS FROM PYROLYSIS MASS SPECTRA OF U.S. LIGNITES

Henk L.C. Meuzelaar, Willem Windig and G. Steven Metcalf

Biomaterials Profiling Center, University of Utah  
391 South Chipeta Way, Suite F  
Salt Lake City, Utah 84108

### INTRODUCTION

Structural characterization of lignites presents a major challenge because of the extreme complexity and heterogeneity of these low rank coals. Whereas most peats still contain macroscopically and microscopically identifiable plant remains, morphological analysis of lignites is much less straightforward. Moreover, routine coal characterization tests such as Free Swelling Index or Vitrinite Reflectance, are less readily applicable to lignites whereas sophisticated spectroscopic techniques such as IR, NMR or MS tend to give highly complex spectra due to the presence of multiple, overlapping chemical components. Although combined analytical methods such as MS/MS, GC/MS or GC/FTIR are capable of resolving and identifying many of these overlapping components, such "hyphenated" techniques tend to be costly and require time-consuming data evaluation and interpretation steps thus making it impractical to apply these methods to large sample series.

A novel approach capable of resolving overlapping signals in spectra of complex mixtures involves numerical extraction of component patterns by means of factor and discriminant analysis (1). Thus far, this numerical extraction approach has been applied especially to pyrolysis mass spectrometry (Py-MS) patterns of coals and other fossil fuels, because of the relative ease of numerical conversion of mass spectra (compared to the continuous curves obtained by IR, NMR or chromatographic techniques).

The main advantages of combining single stage analytical techniques with numerical extraction methods rather than using "hyphenated" physicochemical techniques are: high speed and relatively low cost. Moreover, numerical extraction methods are especially powerful when relatively large series of samples need to be studied. Meuzelaar *et al.* (2) demonstrated the applicability of the combined Py-MS/numerical extraction approach to a series of over 100 coal samples from the Rocky Mountain Coal Province obtained from the Penn State Coal Sample Bank. Other, smaller Py-MS studies of coals have been published by Van Graas *et al.* (3), De Leeuw *et al.* (4) and Larter (5). As listed in Table I, the Py-MS study reported here involves a selection of samples representing both U.S. coal provinces with major lignite reserves, namely the Northern Plains Province (6 samples) and the Gulf Province (16 samples).

### EXPERIMENTAL

Lignite samples were obtained from the Penn State Coal sample bank in hermetically sealed metal cans containing 500 g, 20 mesh aliquots under Argon. All further grinding and splitting operations were performed under N<sub>2</sub>, finally resulting in 10 mg, 300 mesh aliquots which were subsequently suspended in 2 1/2 ml of Spectrograde methanol. Two 5  $\mu$ l drops of these suspensions were applied to ferromagnetic wires (Curie-point temperature 610°C) and air-dried at room temperature under continuous rotation, resulting in a sample size of approx. 40  $\mu$ g. Within one hour after preparation, all coated wires were analyzed by Curie-point pyrolysis mass spectrometry using an Extranuclear 5000-1 quadrupole MS system described elsewhere (6). Py-MS conditions were as follows: temp. rise time 5 s, equilibrium temp. 610°C, total heating time 10 s, electron energy setting 11 eV, mass range scanned m/z 20-

260, scanning rate 2000 amu/s, total scanning time 20 s. Each lignite sample was analyzed in triplicate and the resulting 66 spectra were normalized using the NORMA program (7). Subsequent multivariate analysis was carried out with the SPSS program package (8) and consisted of factor analysis followed by discriminant analysis using the 11 most significant factors (eigenvalue >1), according to a procedure described previously by Windig *et al.* (9). It should be noted that each set of three duplicate analysis was assigned a separate category number in the discriminant analysis procedure, thus avoiding the creation of artificial clusters and divisions in the data set. Finally, the five most significant discriminant functions were analyzed with the aid of the variance diagram (VARDIA) procedure developed by Windig *et al.* (10). This resulted in the localization of at least six individual component axis which were then evaluated further by means of discriminant loading and spectrum plot procedures, as described by Windig *et al.* (9).

## RESULTS AND DISCUSSION

The pyrolysis mass spectra of three of the twenty two lignite samples are shown in Figure 1, demonstrating marked differences in the bulk composition of the pyrolyzates, e.g., with regard to hydroxyaromatic compound series, aliphatic hydrocarbon series and sulfur signals. Moreover, arrows in Figure 1 point to minor "biomarker" peaks at  $m/z$  234 (retene) and  $m/z$  194 (unknown biomarker) which were found to be quite characteristic for lignite samples from the Northern Plains and Gulf provinces respectively.

Before describing a more detailed chemical interpretation of the Py-MS findings, it should be pointed out that chemical labels assigned to peak series or individual peaks in Figure 1 (as well as throughout this paper) are tentative only. Generally these interpretations are based on literature data although some of the chemical identities are backed up by Py-GC/MS studies on the same lignites (11). Another factor to consider when interpreting Py-MS data on coals is the incomplete pyrolytic conversion. Under the experimental conditions employed in our study, estimated tar yields for high volatile bituminous coals are in the 50-60% range (12) whereas lignite conversion yields are basically unknown but may well fall in the same range. Moreover, not all the tar products will be detected by our mass spectrometric procedures. Ultimately, perhaps only 20-30% of the (dry) bulk of the original lignite sample contributes directly to the mass spectrum.

In view of the large number of spectra obtained and the hundreds of mass peaks in each spectrum, the use of sophisticated data reduction and correlation methods is indispensable. As described under "Experimental", factor analysis followed by discriminant analysis was applied to the Py-MS data set. This resulted in seven "significant" discriminant functions (see Table II). The scores of the first two functions are plotted in Figure 2, revealing a relatively good separation between lignites from the two different coal provinces (on DI) as well as a definite separation between lignites from different seams, fields or regions (on DII).

The nature of the underlying chemical components responsible for the clustering behavior in Figure 2 was examined by means of a novel, interactive method known as the Variance Diagram (VARDIA) technique (10), which enables us to determine the optimal location of each major chemical component in discriminant space. The VARDIA method has proven to be capable of extracting numerical components from mass spectra of complex mixtures, including fossil fuel pyrolyzates (10).

Two VARDIA plots, representing discriminant functions I and II as well as III and IV respectively, are shown in Figure 3, revealing the presence of at least six major component axes (labeled A-F) in the space spanned by these four functions. The mass spectral patterns associated with these component axes are shown in Figures 4 and 5. Component axes A and B (Figure 4a, b) obviously represent

the two bulk components seen in the lignite spectra, namely hydroxyaromatic compounds and aliphatic hydrocarbon moieties.

The nature and origin of the hydroxyaromatic compound series becomes clear when comparing the spectral pattern of component axis A (Figure 4a) with that of a softwood lignin model compound (Figure 4c). Although obvious quantitative differences exist between the two spectral patterns, the qualitative similarities strongly suggest a direct chemical relationship. That lignin-like patterns can be preserved in pyrolysis mass spectra of fossil organic matter  $10^7$  to  $10^8$  years old has also been reported in several other studies (4,6,13).

The chemical nature and origin of the aliphatic hydrocarbon pattern in Figure 4b presents a more difficult problem. Nevertheless, an intriguing qualitative match was obtained with the Py-MS pattern of Apiezon L, a high MW petroleum distillate consisting of 67% aliphatic, 28% naphthenic and 5% aromatic hydrocarbons (14). Since the petrographic analysis data available from the Penn State Coal data bank did not reveal major contributions of liptinite macerals (see Table I), it may be assumed that the hydrocarbon moieties observed by Py-MS represent maceral types easily overlooked by routine petrographic analysis, e.g., from exsudatinite or bituminite (15). An interesting speculation is that we may be dealing with hydrocarbons derived from algal precursors although major contributions from bacterial lipids (16) cannot be ruled out either.

The spectral patterns of the component axes shown in Figure 5a-c are interpreted to represent terpenoid resins (Figure 4a; e.g. retene signal at  $m/z$  234), unknown biomarker compounds (Figure 5b; e.g., signals at  $m/z$  194, 179 and 168) and sulfur moieties as well as related marine-influenced peak series (Figure 5c), respectively.

Comparison of the VARDIA plots in Figure 3 with the discriminant score plot in Figure 2 shows that component axis F (representing reduced sulfur forms such as  $H_2S$  and  $CH_3SH$ ) correlates most strongly with the Wildcat seam lignites from South-Central Texas which are known to have been deposited in marine-influenced, lagoonal environments (17). However, component axis E (representing more oxidized sulfur forms such as  $SO_2$  and  $CS_2$ ) also correlates with the Fort Union Bed lignites of Montana, which lack an obvious marine depositional influence. In these lignites, the oxidized sulfur forms may well represent the relatively high inertinite content since similar correlations were noted in previous Py-MS studies of purified coal macerals (18).

That the two biomarker signals at  $m/z$  234 and  $m/z$  194 are very characteristic, indeed, for the two coal provinces (as also indicated by a comparison of Figures 2 and 3) is confirmed by the bivariate plot in Figure 6. Apparently, the biomarker precursors (conifer resins?) of the Northern Plains province were not present in the ancient depositional environment of the Gulf province; and *vice versa*.

Finally, it should be mentioned that the above discussed interpretations of the Py-MS data were further supported by a systematic correlation with conventional coal characterization data (e.g., petrographic analysis, ultimate analysis, proximate analysis, calorific value and and vitrinite reflectance) obtained from the Penn State Coal Data Bank. The results of these data correlation efforts, e.g., using canonical variate analysis techniques (19), will be reported elsewhere (20).

In conclusion, the data analysis results presented here confirm the feasibility of numerical extraction of chemical components from the low voltage mass spectra of extremely complex lignite pyrolyzates.

#### ACKNOWLEDGEMENTS

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TABLE I  
CONVENTIONAL LIGNITE CHARACTERIZATION DATA

No. 1	PSOC Code 2	Seam Name (State) 3	Maceral Conc. (%)			Ultimate Anal. (%)				% S (tot) 11
			Vit. 4	Inert. 5	Exin. 6	C 7	H 8	N 9	O 10	
1	833	Fort Union Bed (MT)	74.1	23.2	1.4	70.0	4.60	1.29	23.7	0.64
2	838	Fort Union Bed (MT)	81.7	16.9	1.4	71.3	4.74	1.08	22.3	1.34
3	1084	Sawyer (MT)	88.9	10.8	0.3	71.5	4.84	1.01	22.2	0.60
4	1087	Sawyer (MT)	82.5	16.3	1.2	71.0	4.75	1.00	23.0	0.23
5	1090	Sawyer (MT)	89.1	10.2	0.7	71.9	4.66	0.99	22.1	0.35
6	975	Anderson (WY)	79.6	8.0	12.3	73.0	5.18	0.99	20.3	0.48
7	791	A-Pit (TX)	90.7	8.4	0.9	72.3	5.39	1.20	20.2	0.99
8	792	A-Pit (TX)	94.7	4.5	0.8	72.7	5.61	1.18	19.6	0.97
9	414	Darco (TX)	80.6	17.5	1.9	73.0	5.31	1.37	19.3	1.14
10	415	Darco (TX)	83.4	14.1	2.5	73.6	5.66	1.45	18.4	0.89
11	623	Darco (TX)	81.0	17.2	1.8	74.8	5.26	1.32	17.6	1.35
12	625	Darco (TX)	83.3	15.2	1.5	74.1	4.89	1.30	18.1	2.38
13	1037	Unnamed (TX)	86.5	13.1	0.4	73.1	5.31	1.62	18.9	1.16
14	1038	Unnamed (TX)	88.1	10.8	1.1	73.6	5.02	1.65	18.5	1.39
15	427	Unnamed (TX)	90.6	8.1	1.3	72.9	5.37	1.24	19.2	1.61
16	428	Unnamed (TX)	94.5	3.7	1.8	73.3	6.02	1.28	18.0	1.78
17	786	Unnamed (TX)	87.0	12.0	1.0	73.4	5.12	1.34	18.9	1.44
18	788	Unnamed (TX)	91.6	7.9	0.5	73.5	5.46	1.20	18.7	1.15
19	421	Wildcat (TX)	87.7	10.9	1.4	71.6	5.83	1.34	19.4	2.63
20	422	Wildcat (TX)	88.7	10.1	1.2	75.5	5.86	1.39	15.6	2.03
21	424	Wildcat (TX)	90.7	6.1	3.2	73.7	6.05	1.22	17.6	2.08
22	637	Wildcat (TX)	83.8	14.6	1.6	74.8	5.28	1.32	16.6	2.75

<sup>7,8,9,10</sup>-modif. Parr dmmf (<sup>10</sup> calculated by diff.); <sup>11</sup>-daf

TABLE II  
DISCRIMINANT ANALYSIS RESULTS

Discriminant Function	Eigenvalue	Relative Percentage	Canonical* Correlation
I	341.0	61.3	.999
II	124.0	22.3	.996
III	38.2	6.9	.987
IV	23.6	4.3	.979
V	16.1	2.9	.970
VI	8.8	1.6	.948
VII	2.5	0.5	.845

\* with 11 original factors

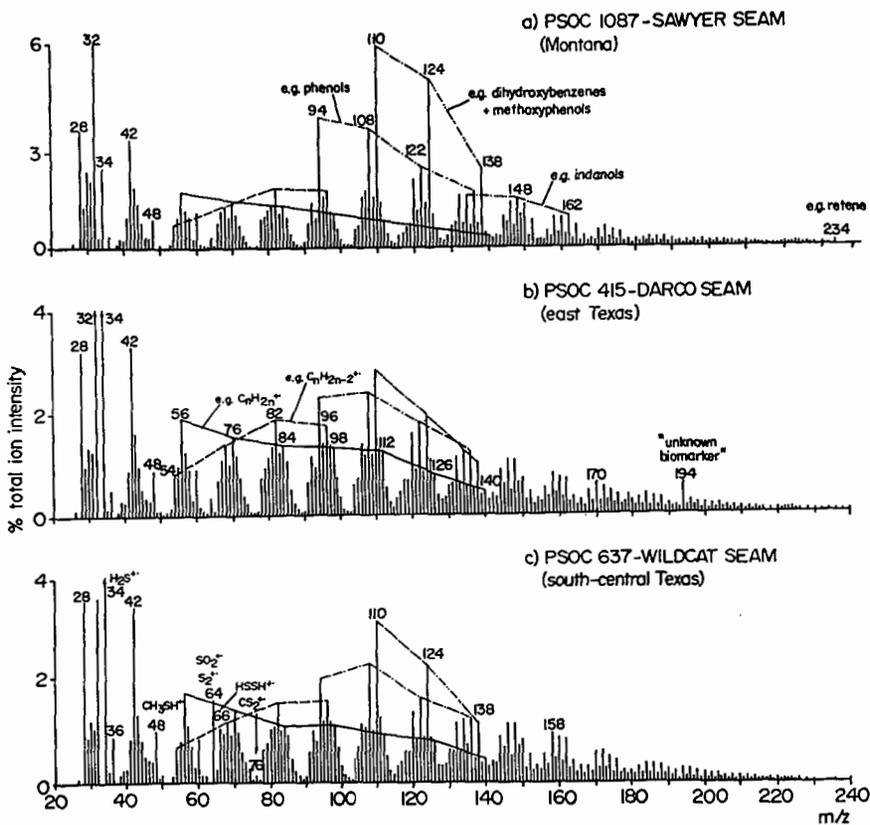


Figure 1. Low voltage pyrolysis mass spectra of three selected lignites representing the Northern Plains province (a) and the Gulf province (b and c). Note the relatively high abundance of hydroxyaromatic series in (a) compared to the more prominent aliphatic hydrocarbon series in (b) and (d). Further note the marked sulfur compounds in (c) and the small biomarker signals (arrows at  $m/z$  234 and 194 in (a) and (b), respectively).

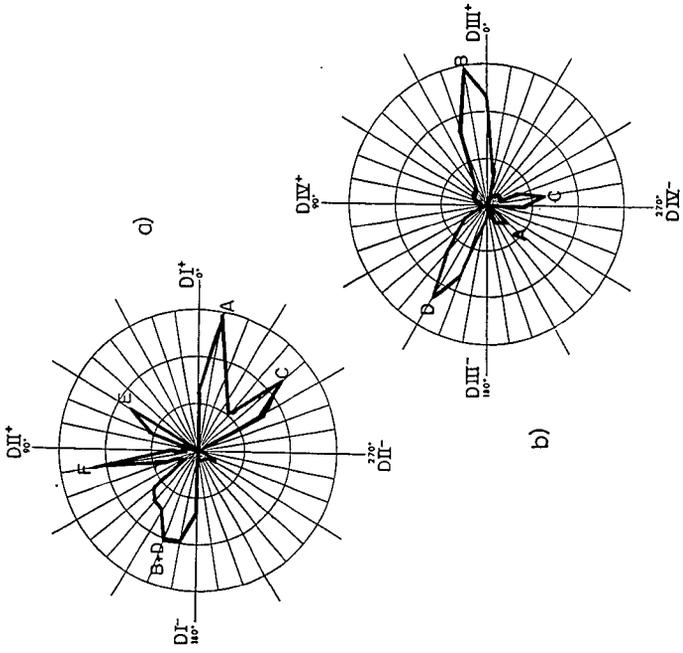


Figure 3. Variance diagrams showing the presence of six major component axes (A-F) in the space spanned by discriminant functions I, II (a) and III, IV (b), respectively.

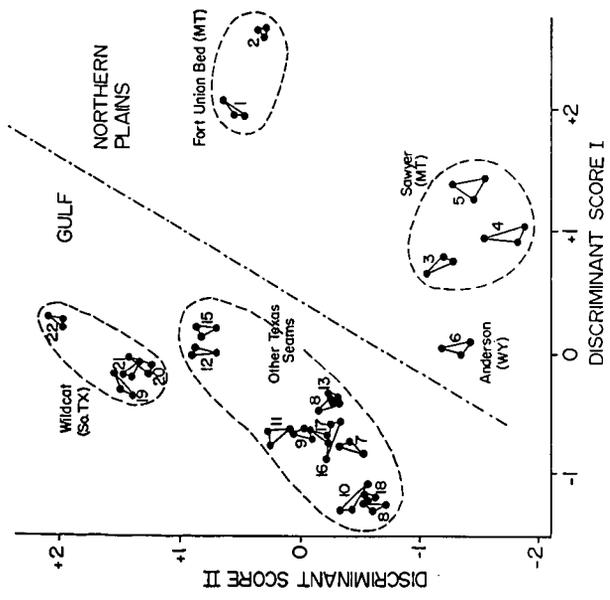


Figure 2. Scatter plot of the scores of the first two discriminant functions showing the clustering behavior of the 22 lignite samples. Triplette analyses of the same sample are connected by solid lines. Dashed lines indicate coal seam or field relationships. For sample codes, see Table 1.

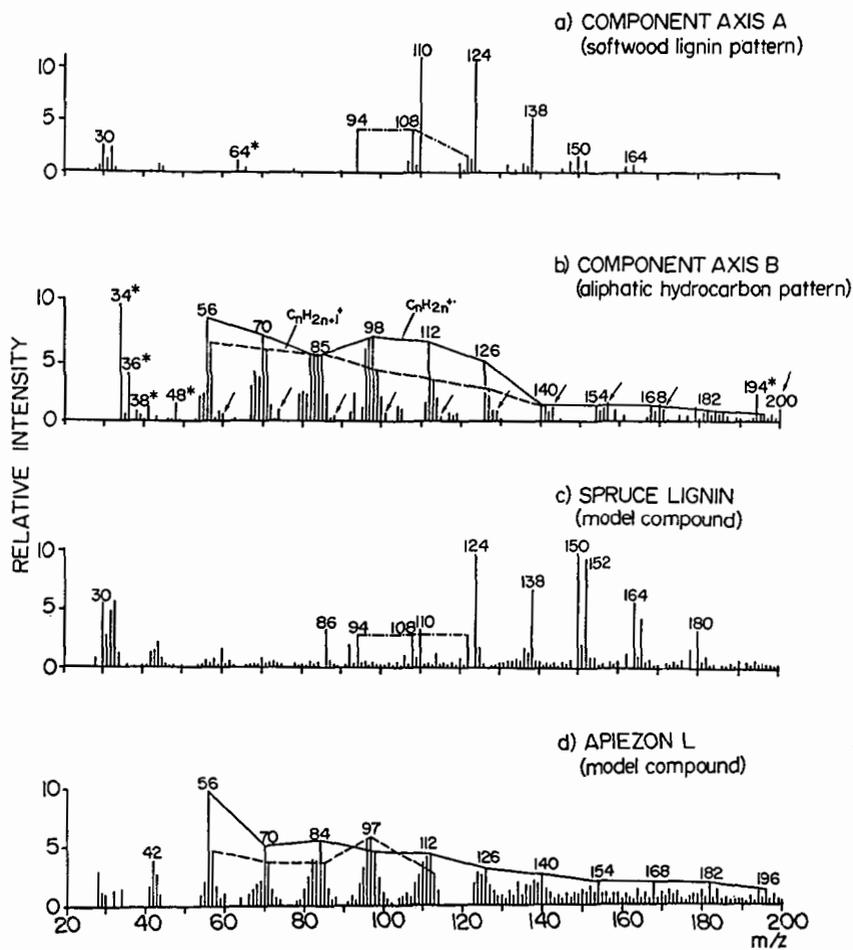


Figure 4. Comparison of the numerically extracted discriminant "spectra" of components A (a) and B (b) with the pyrolysis mass spectra of two model compounds (c and d). Mass peak intensities not optimally represented on the component axes are indicated by asterisks. Arrows point to an aliphatic carboxylic acid series in (b).

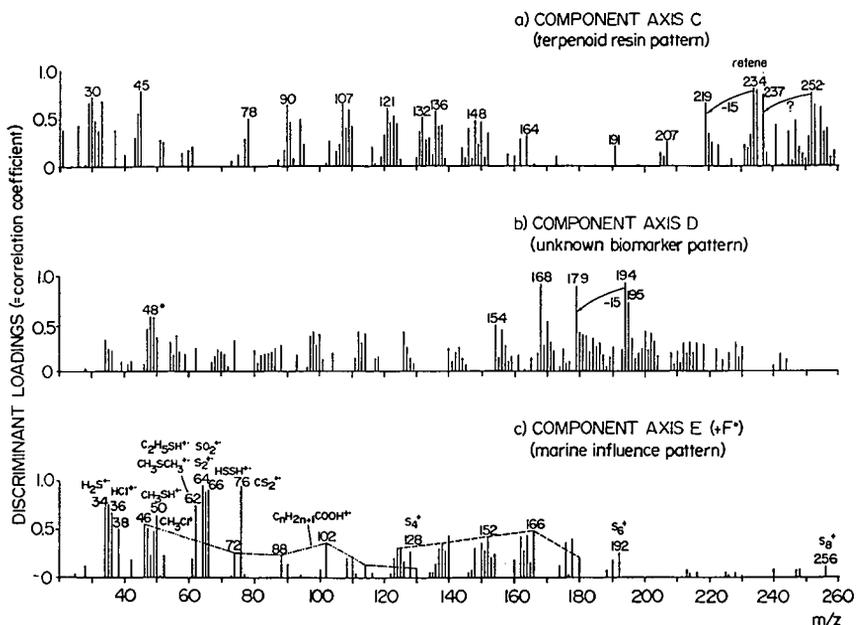


Figure 5. Loading (correlation coefficient) plots representing components C-F in Figure 3. For explanation, see text.

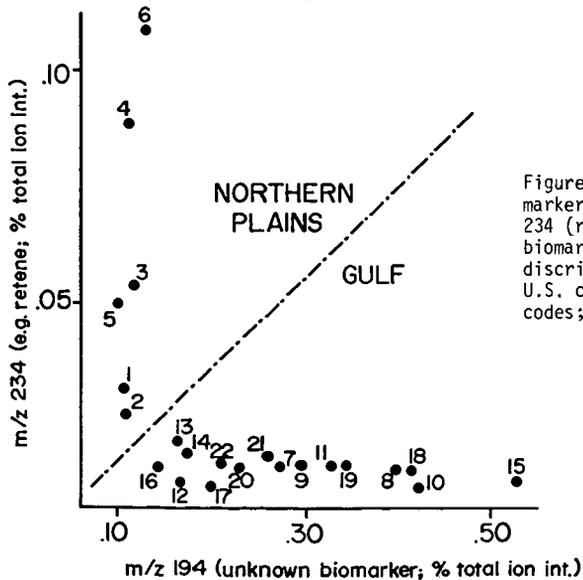


Figure 6. Scatter plot of biomarker peak intensities at m/z 234 (retene) and m/z 194 (unknown biomarker) showing the perfect discrimination between the two U.S. coal provinces. For sample codes; see Table I.