

SIMULTANEOUS THERMOGRAVIMETRIC AND MASS SPECTROMETRIC OBSERVATIONS ON VACUUM PYROLYSIS OF ARGONNE PCSP COALS

Yongseung Yun and Henk L.C. Meuzelaar
Center for Micro Analysis & Reaction Chemistry, University of Utah
Salt Lake City, Utah 84112

ABSTRACT

The most serious limitations of many coal gasification and liquefaction models are due to the lack of reliable char and total volatiles yield data, of accurate kinetic parameters, and of reliable data on the composition of the total volatiles in the initial devolatilization step. Consequently, a vacuum thermogravimetry/mass spectrometry (TG/MS) system consisting of a Mettler TA1 Thermoanalyzer and a Finnigan MAT 3200 quadrupole mass filter was built to obtain accurate quantitative and qualitative data on coal devolatilization processes at heating rates in the 10^{-2} - 10^0 K/s range. Hundreds of mass spectra can be obtained during a single TG run, thereby providing detailed information about the concentration of various devolatilization products as a function of temperature while continuously recording the sample weight loss. Moreover, factor analysis-based methods enable deconvolution of overlapping trends and numerical extraction of chemical component spectra. TG/MS results on four Argonne PCSP coals are discussed.

INTRODUCTION

Previous mass spectrometric studies of coal devolatilization phenomena in our laboratory [1, 2, 3] have focussed on the use of Curie-point pyrolysis mass spectrometry (Py-MS) techniques using heating rates in the 10^2 - 10^4 K/s range. This enabled Chakravarty *et al.* [1] to identify at least four structural components with distinct kinetic profiles in an ANL-PCSP Pittsburgh #8 coal: (1) a relatively minor vacuum distillate fraction consisting primarily of alkylsubstituted one- and two-ring aromatic hydrocarbons; (2) a sporinite-like fraction consisting of branched and/or alicyclic hydrocarbon components; (3) a cutinite- or alginite-like polymethylenic component; and (4) a vitrinite-like component consisting primarily of alkylsubstituted hydroxyaromatic and aromatic moieties. Attention was drawn to the fact that only the two aliphatic components appeared to exhibit a simple depolymerization behavior consistent with the idea of a first-order unimolecular decomposition reaction. The vacuum distillate component was thought to be more appropriately described by a reaction order between 0 and 1, whereas the vitrinite-like component appeared to behave like a char-forming thermoset, and thus, should be described by a reaction order considerably greater than 1. Attempts to obtain more accurate kinetic parameters, however, were only partially successful due to the very short reaction times involved (approx. 8 s) and the significant broadening of the product evolution profiles by diffusion processes between the pyrolysis zone and the ionization region.

In order to overcome this problem we decided to build a vacuum thermogravimetry/mass spectrometry (TG/MS) system capable of precisely controlling heating rates in the 10^{-2} - 10^0 K/s range while providing accurate temperature and weight loss information and simultaneously recording the evolution profiles of gas and tar products.

Vacuum TG/MS experiments with coals have been reported previously by Ohrback *et al.* [4, 5]. However, in the experiments reported here we were especially interested in using the set of eight standard coals available from the Argonne National Laboratory Premium Coal Sample Program (ANL-PCSP) in order to enable direct comparison with TG/FTIR experiments performed by Serio *et al.* [6], as well as to enable reproduction of our experiments by other researchers. Moreover, since most of our extensive Py-MS data on U.S. coals [7, 8, 9] has been obtained under low voltage (approx. 12-14 eV) electron ionization conditions, we wanted to perform the TG/MS analyses under comparable ionization conditions.

Finally, an important goal of the experiments reported here was to use sophisticated multivariate analysis techniques, as developed by Windig *et al.* [10], in order to deconvolute overlapping trends in the TG/MS data and to identify the underlying chemical components.

At the time of writing, only 4 of the 8 ANL-PCSP coals have been analyzed and a full report of the results on all 8 coals will be published elsewhere.

EXPERIMENTAL

Four ANL ampule samples (Pittsburgh #8 (-100 mesh), Illinois #6 (-100 mesh), Wyodak (-20 mesh), Beulah-Zap (-100 mesh)) were employed in vacuum TG/MS runs and the ultimate analysis data of the samples were described elsewhere [11]. The TG/MS system (Figure 1) consists of a Mettler TA1 Thermoanalyzer directly interfaced to a small Finnigan MAT 3200 quadupole mass filter. Pyrolysis was performed directly in front of the ion source of the mass spectrometer in order to prevent recombination reactions and/or secondary decomposition of reactive compounds as well as to minimize the loss of polar compounds through condensation. A turbomolecular pump (Balzers TPU 050) was used for evacuating the MS chamber up to 4×10^{-7} torr in 7-8 minutes. In addition, two diffusion pumps were employed to maintain a pressure of less than 1×10^{-4} torr in the TG balance chamber. Moreover, the LN₂ cold trap in Figure 1 was used to guarantee a low background signal level in the mass spectra. A detailed description of time-resolved Curie-point pyrolysis MS (TR Py-MS) can be found elsewhere [2].

Sample aliquots of approximately 4-5 mg were heated under vacuum ($3-6 \times 10^{-7}$ torr) while the temperature was increased from ambient to 700°C at 25°C/min. MS conditions were as follows: electron impact energy 14 eV, mass range scanned m/z 33 to 193 (m/z 48-193 for Pittsburgh #8 seam coal), total number of scans 80, and total scan time 27 minutes. Each spectrum scanned was stored separately in the memory of an IBM 9000 computer.

Factor analysis was employed to deconvolute overlapping time trends and to numerically extract the chemical component spectra. In order to give all the variables an equal contribution, factor analysis was done on the correlation around the origin matrix. Deconvolution was performed by using a combination of pure mass [12, 13] and variance diagram (VARDIA) [10, 14] techniques.

RESULTS AND DISCUSSION

The time-integrated low voltage mass spectra of Pittsburgh coal obtained by TG/MS and by TR Py-MS are highly similar with regard to type and relative abundance of the pyrolysis products (as shown in Figure 2) in spite of a

factor 3×10^2 difference in heating rate and a factor 2×10^2 difference in sample size, as well as differences in pyrolysis technique, ion source, quadrupole, etc. In fact, since Curie-point Py-MS patterns obtained at heating rates of 6×10^4 K/s and 1×10^2 K/s are highly similar too (not shown here), we can conclude that the mechanisms of primary coal devolatilization reactions appear to be independent of heating rate over at least five orders of magnitude (10^{-1} - 10^4 K/s range).

The main differences between the TG/MS and TR Py-MS data on Pittsburgh #8 coal in Figure 1 appear to be the much larger SO_2^+ and HSSH^+ signals (due to the higher end temperature of the TG/MS system; similar SO_2 increases can be seen when using higher temperature Curie-point wires), and the somewhat increased dihydroxybenzene. The dihydroxybenzene intensities in the TR Py-MS spectrum can be increased by preheating the pyrolysis chamber. Hydroaromatics (e.g. tetralins) tend to form relatively late during the devolatilization process, therefore the higher end temperatures explain their increased abundance in the TG/MS spectrum.

The sharp evolution profile and the constant evolution temperature of SO_2 , as illustrated in Figure 3, offer exciting possibilities for controlling the final distribution of sulfur between the char and the gas phase (e.g., in low temperature gasification and/or liquefaction processes). However, we do not see the very early SO_2 components shown by Serio *et al.* [6] in TG/FTIR. Possibly, the FTIR signal shows interference from a different compound.

Four factors were employed to deconvolute overlapping trends in total ion count profiles from TG/MS. The eigenvalues and variances explained by the first six factors are illustrated in Table 1, showing that the first four factors can explain approx. 98% of total variance for each coal. Our deconvoluted data provide a strong indication for the presence of two kinetically distinct pyrolysis regimes (under our TG conditions at approx. 370-380°C and at 420-440°C, respectively). Whereas each of these regimes may indeed be relatively independent of rank as suggested by Serio *et al.* [6], the "vitrinitic component" (m/z 124/138) appears to shift from the lower to the higher temperature regime with increasing rank. The aliphatic hydrocarbon component always pyrolyzes in the higher regime. The following hypothesis for these observations would be possible: the two temperature regimes represent ether bridges (or other weak bonds) and methylenic bridges, respectively. In liptinites such as alginites or cutinites methylenic bridges are present from the beginning (and thus already in low rank coals). In vitrinitic macerals derived from lignin-like structures the initial bridges are primarily ether type. With increasing rank these are "replaced" by methylenic bridges (or perhaps lost through CO elimination with consequent formation of new methylenic cross-links).

The rank dependent shift in the ratio of aromatic vs. terpenoid (isoprenoid) structure reported by Blazso *et al.* [15] was also confirmed by our findings (disappearance of m/z 191 component, appearance of m/z 156 component).

The rank dependent appearance of the "oil formation" window in high volatile A and B bituminous coal [1] is evident in Pittsburgh #8 coal. Perhaps this could be called "geothermal pyrolysis". However, the relatively aromatic oil formed does not appear to contain many polymethylenic moieties (contrary to the suggestion by Serio *et al.* [6]). Also the term "guest molecules" is an obvious misnomer. These are not "guests" but "offspring" (sons or

daughters). The TG/DTG curves (only shown DTG curve in this preprint) show only very small quantities of these vacuum distillable components. This can be explained as follows: assume that the total amount is only a few percent of dry coal weight and that the total tar yield is approx. 20%, then (e.g., 30% gas, 40% char, 10% ash) the vacuum distillable "bitumen" could still be as much as approx. 10% of the tar.

Although SO₂ evolution appears to coincide with the end of the main tar formation phase (and/or onset of the char formation process) neither the origin nor the mechanistic significance of the SO₂ evolution are entirely clear at present.

It should be pointed out here that the charring stage is strongly underrepresented in our study due to the limited lower mass range ($\geq m/z$ 34) and the low voltage EI conditions (low MW pyrolysis products tend to have higher ionization potentials). Further TG/MS runs are planned to investigate low MW pyrolysis products.

ACKNOWLEDGEMENTS

This work was sponsored by the Advanced Combustion Engineering Research Center. Funds for this Center are received from the National Science Foundation, the State of Utah, 23 participants and the U.S. Department of Energy.

REFERENCES

1. Chakravarty, T., H.L.C. Meuzelaar, W. Windig and G.R. Hill, ACS Preprints (Div. of Fuel Chem.), 32(3) 1988, 211-216.
2. Jakab, E., W. Windig, and H.L.C. Meuzelaar, Energy and Fuels, 1(2), 1987, 161-167.
3. Jakab, R., B. Hoesterey, W. Windig, G.R. Hill and H.L.C. Meuzelaar, Fuel, 67, 1988, 73-79.
4. Ohrback, K.H. and A. Kettrup, ACS Preprints (Div. of Fuel Chem.), 29(2), 1984, 12-19.
5. Ohrback, K.H., A. Kettrup and G. Radhoff, J. of Analytical and Applied Pyrolysis, 8, 1985, 195-199.
6. Serio, M.A., P.R. Solomon and R.M. Carangelo, ACS Preprints (Div. of Fuel Chem.), 33(2), 1988, 295-309.
7. Meuzelaar, H.L.C., A.M. Harper, G.R. Hill and P.H. Given, Fuel, 63, 1984, 640-652.
8. Harper, A.M., H.L.C. Meuzelaar and P.H. Given, Fuel, 63, 1984, 793-802.
9. Metcalf, G.S., W. Windig, G.R. Hill and H.L.C. Meuzelaar, Int. J. of Coal Geology, 7, 1987, 245-268.
10. Windig, W. and H.L.C. Meuzelaar, Anal. Chem., 56, 1984, 2297-2303.
11. Vorres, K.S., ACS Preprints (Div. of Fuel Chem.), 32(4), 1987, 221-226.
12. Knorr, F.J. and J.H. Futrell, Anal. Chem., 51, 1979, 1236-1241.
13. Malinowski, E.R. and D.G. Howery, Factor Analysis in Chemistry, John Wiley & Sons, 1980, New York.
14. Windig, W., E. Jakab, J.M. Richards, and H.L.C. Meuzelaar, Anal. Chem., 59, 1987, 317-323.
15. Balzso, M., T. Szekely, F. Till, G. Varhegyi, E. Jakab and P. Szabo, J. of Analytical & Applied Pyrolysis, 8, 1985, 255-269.

TABLE 1
 VARIANCE EXPLAINED BY THE FIRST SIX FACTORS OBTAINED BY PRINCIPAL COMPONENT
 ANALYSIS OF THE CORRELATION AROUND-THE-ORIGIN MATRIX FOR EACH TG/MS DATA SET

Factor Number	Pittsburgh #8		Illinois #6		Wyodak		Beulah-Zap	
	Eigen-value	% variance	Eigen-value	% variance	Eigen-value	% variance	Eigen-value	% variance
1	119.99	87.27	138.07	88.29	135.92	87.39	129.53	84.32
2	7.02	5.11	8.33	5.33	8.92	5.74	12.46	8.11
3	5.07	3.68	4.43	2.83	5.29	3.40	6.66	4.33
4	2.43	1.77	3.47	2.22	2.99	1.90	2.83	1.85
5	1.74	1.27	1.38	0.88	1.48	0.95	1.31	0.85
6	1.23	0.90	0.71	0.46	0.92	0.59	0.83	0.54

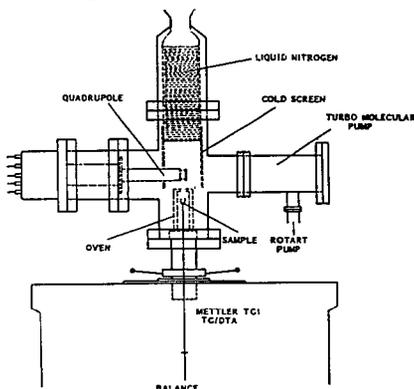


Figure 1. Schematic diagram of vacuum TG/MS system, based on the combination of a Mettler TA1 TG/DTA system and a Finnigan MAT 3200 mass spectrometer with specifically designed vacuum housing.

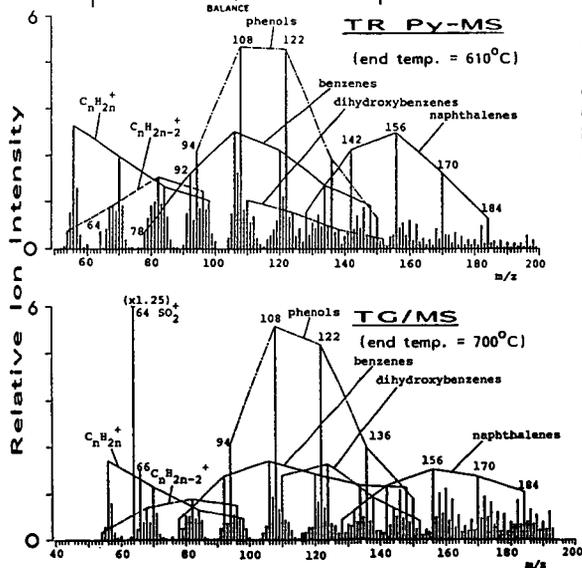


Figure 2. Time-integrated spectrum obtained by summing all 41 (TR Py-MS), 80 (TG/MS) spectra scanned on Pittsburgh #8.

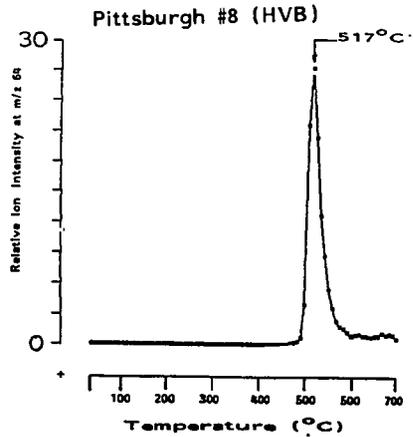
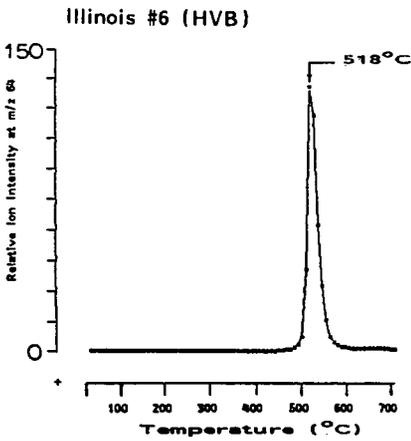
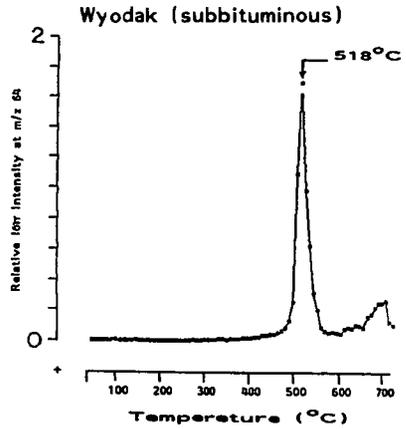
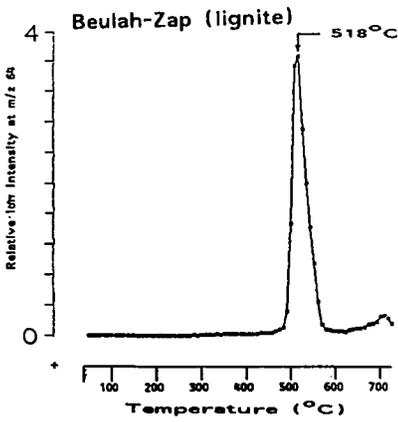


Figure 3. Evolution profiles of m/z 64 (SO_2^+) for four ANL-PCSP coals. Note the similar evolution profile and maximum evolution temperature independent of rank.

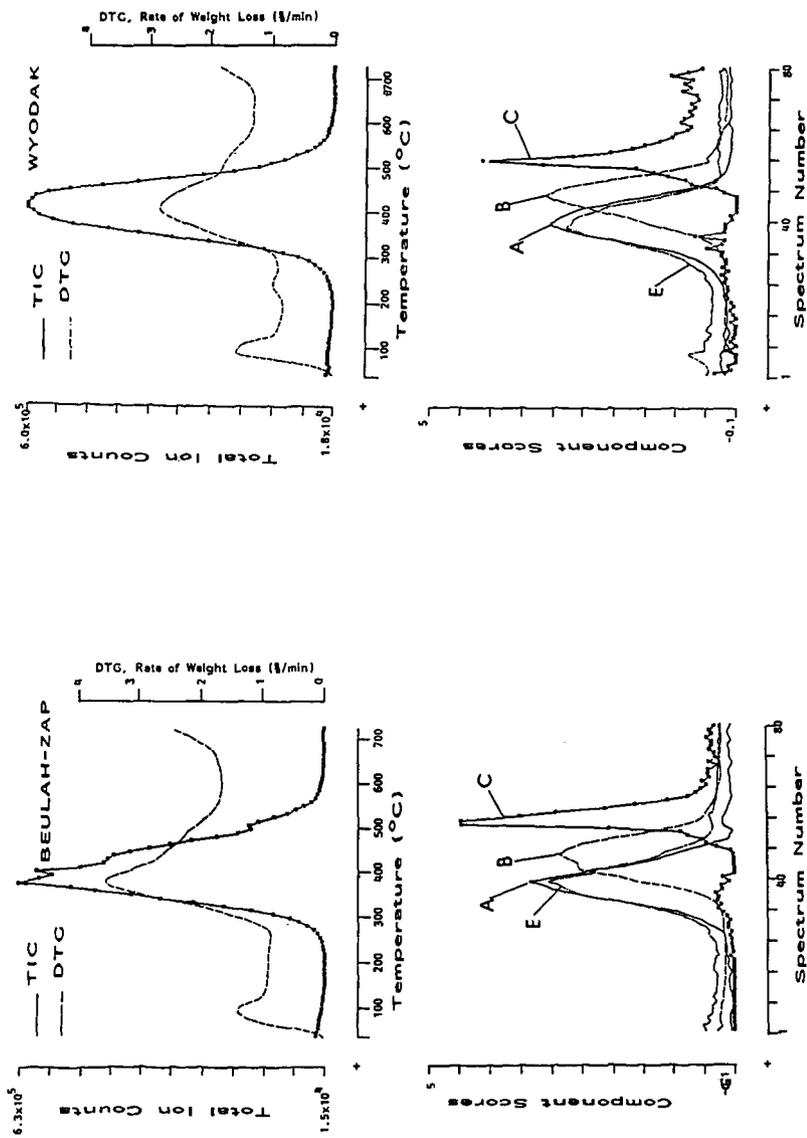


Figure 4. TIC, DTG profiles with temperature and the corresponding deconvoluted components (A,B,C,E) for Wyodak, Beulah-Zap coals. The numerically extracted ("deconvoluted") spectra of each component are shown in Figure 6. Mainly component A consists of dihydroxybenzenes, component B aliphatics + phenols, component C SO₂, component E terpenoid fragments.

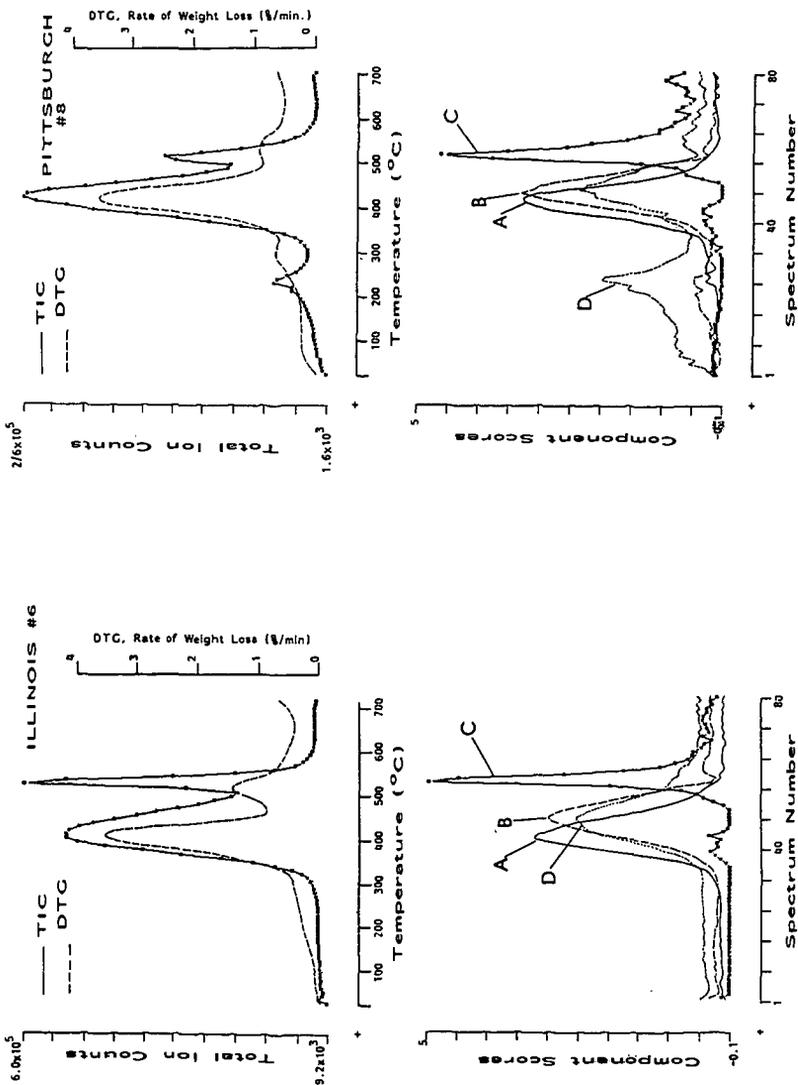


Figure 5. TIC, DTC profiles with temperature and the corresponding deconvoluted components (A, B, C, D) for Illinois #6, Pittsburgh #8 coals. The numerically extracted ("deconvoluted") spectra of each component are shown in Figure 7. Mainly component A consists of dihydroxybenzenes, component B aliphatics + phenols, component C SO_2 , component D bitumen (benzenes + naphthalenes).

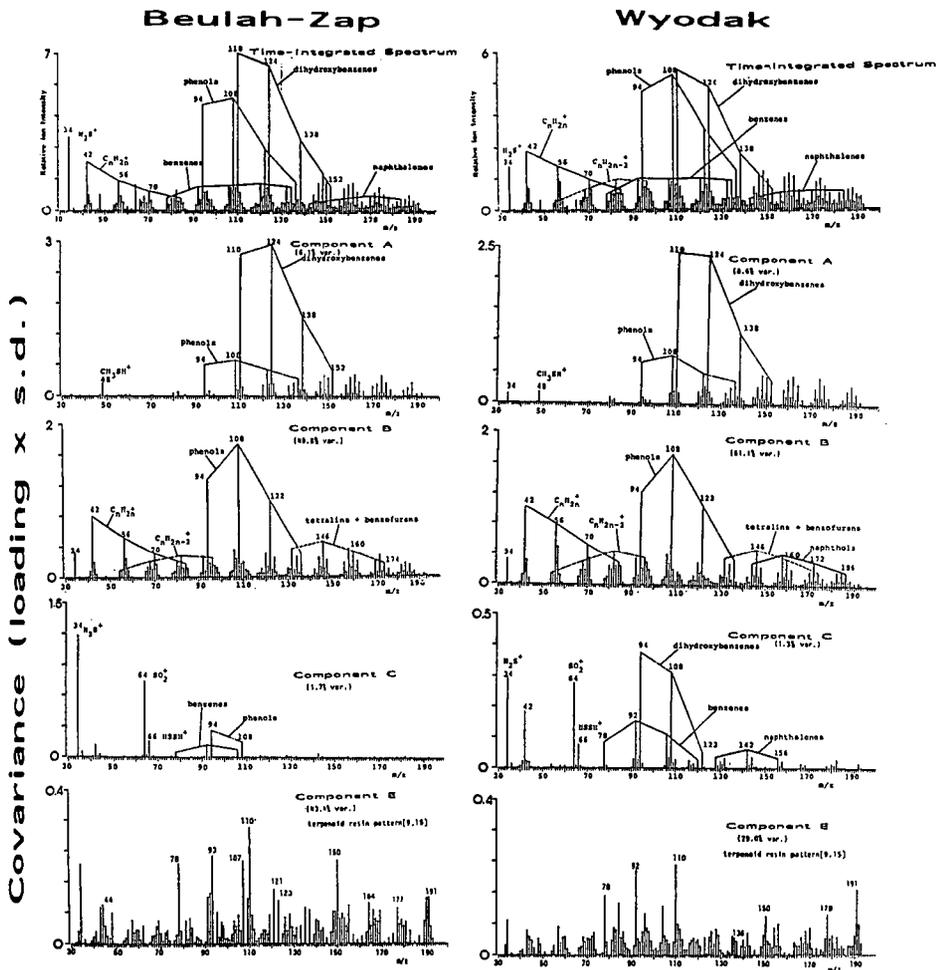


Figure 6. Time-integrated spectra obtained by summing all 80 spectra scanned during TG/MS runs and numerically extracted ("deconvoluted") spectra of the four components shown in Figure 4 for Beulah-Zap and Wyodak coals.

Illinois #6

Pittsburgh #8

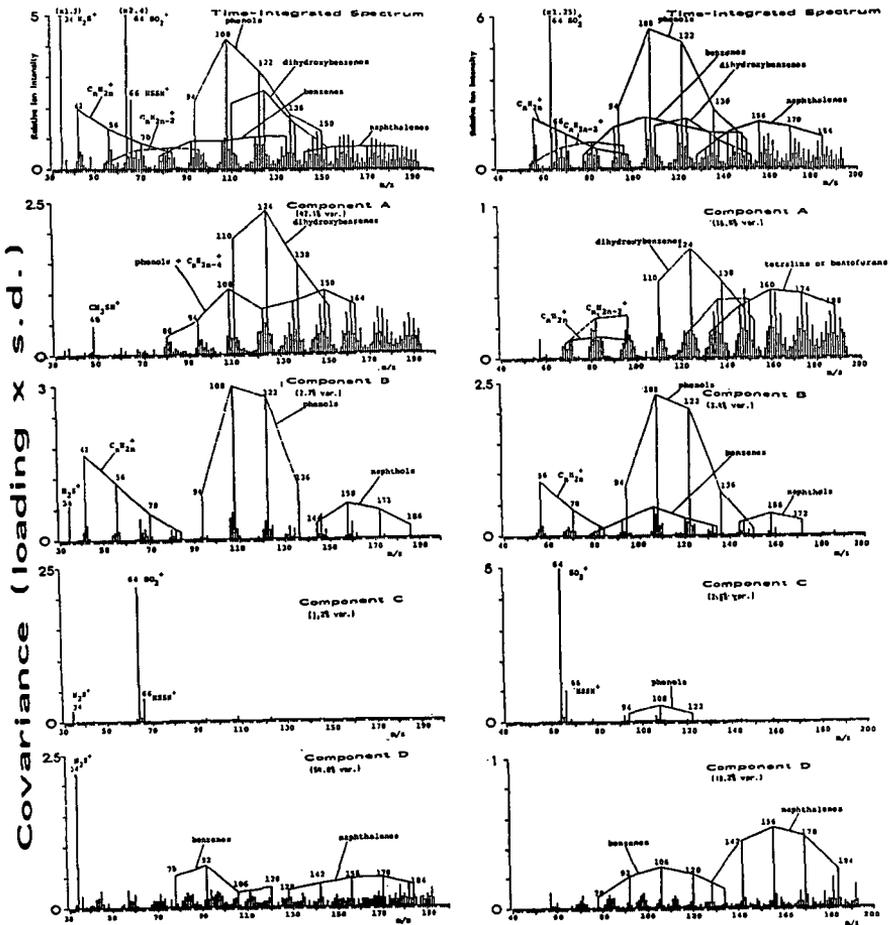


Figure 7. Time-integrated spectra obtained by summing all 80 spectra scanned during TG/MS runs and numerically extracted ("deconvoluted") spectra of the four components shown in Figure 5 for Illinois #6 and Pittsburgh #8 coals.