WEATHERING EFFECTS ON YIELD AND COMPOSITION OF PYROLYTIC COAL TARS

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INTRODUCTION

Over the past few years the main thrust of our fossil fuels research program at the University of Utah Biomaterials Profiling Center has been to investigate the oxidation ("weathering") behavior of coals and coal liquids. Specific objectives of this program are: elucidation of relevant structure/reactivity relationships and of regressive reaction mechanisms; determination of the influence of weathering on technological properties (e.g., caking, calorific value, flotability and extractibility as well as liquefaction and gasification behavior); and development of novel, reliable methods for measuring the "weathering index" of coal samples from a given seam or field.

Our experimental approach has been primarily based on a combination of conventional coal pyrolysis and characterization methods and more advanced instrumental techniques, such as pyrolysis mass spectrometry (Py-MS), thermogravimetry (TG) and liquid chromatography (LC), with sophisticated numerical analysis methods, such as factor and discriminant analysis (1,2,3).

In previous reports we have discussed our findings with regard to weathering effects on structure/reactivity relationships (1), free swelling index (1,2), calorific value (1,2), extractability (1,4) and tubing bomb reactor (TBR) conversion yields (1). In many instances, interpretation of our findings appeared to benefit from - and thus lend additional support to - a "binary" coal structure model, recently proposed by Given (5). According to this model, most coals contain a sizeable fraction of "mobile phase" components, many of which are physically trapped in clathrate-like structures formed by the "network phase". From our weathering studies on HVB Hiawatha coal we concluded that the main weathering effect could be explained as a loss of mobile phase components through "grafting" onto the network phase (1).

In this paper, we present the results of a study on the effects of weathering on pyrolytic tars produced by a vacuum micropyrolysis technique (Curie-point Py-MS) which can be used as a model system for short contact time pyrolysis processes in bench scale, as well as pilot plant scale reactors.

EXPERIMENTAL

Coal samples were obtained from fresh channel cuts in the Hiawatha and Adaville #6 (Kemmerer field, Wyoming) seams as well as from a recent, carefully preserved, drill core of the Anderson seam (Powder River basin, Wyoming). All samples were milled to <60 mesh in nitrogen atmosphere. Sample storage took place under nitrogen in hermetically closed glass bottles at -20°C in the dark. A fresh Blind Canyon seam (Wasatch Plateau field, Utah) coal tar sample was obtained from a pilot plant scale Wellman-Galusha gasifier run (3) and stored in tough fluorocarbon plastic containers immersed in liquid nitrogen.

In the laboratory weathering experiments, 15-20 g aliquots of coals were exposed to air at different temperatures using a specially constructed bench scale weathering equipment described elsewhere (6). Weathering temperatures and times of the coals

studied are listed in Table I. Weathering of the coal tar took place in oxygen heating 150-300 mg samples in sealed glass vials at 80°C for 64 hours. Control coal and tar samples were exposed to nitrogen atmosphere under similar conditions as the air and oxygen weathered samples.

Pyrolysis experiments were performed using an Extranuclear 5000-1 Curie-point Py-MS system (7). Twenty five μg coal samples were coated on ferromagnetic wires from methanol or toluene suspensions. Pyrolysis and mass spectrometry conditions were as follows: heating rate approx. 100°C/s, end temperature 610°C, total heating time 10 s, electron energy 12 eV, mass range scanned m/z 20-260. Tar evaporation/-pyrolysis spectra were obtained under the same conditions by coating 10 μg samples on the wires from dichloromethane solutions. Time-resolved spectra of fresh and weathered Hiawatha coals were obtained by scanning 3-8 mass peaks during each pyrolysis experiment and recording the envelopes of the ion intensities.

Computerized data analyses were performed on the Py-MS data sets of fresh, N_2 exposed and air/oxygen weathered coal and tar samples. Weathering-induced differences were analyzed using factor and discriminant analysis methods (8,9).

RESULTS AND DISCUSSION

A systematic investigation of the effects of coal weathering on the yield and composition of pyrolytic tars requires the availability of suitable model systems for controlled weathering and pyrolysis of well defined coal samples. Bench scale equipment for weathering coal samples in controlled atmospheric environments has been described in previous reports (6,10). Moreover, tubing bomb reactor (TBR) equipment has been used widely to study coal pyrolysis behavior and is reported to provide a valid model for pilot plant scale coal conversion processes (11).

Unfortunately, even TBR runs require time-consuming equipment preparation and product work-up steps. One of the largest TBR studies reported in the literature, involving 104 U.S. coals, was carried out by Given and co-workers (12) over a one year period. The size of the study was dictated by the need to perform a thorough statistical analysis of the relationships between coal characteristics and coal yield. In contrast, a vacuum micropyrolysis study of 102 U.S. coals by means of Curie-point Py-MS, as reported by Meuzelaar *et al.* (13), was carried out in only two weeks while including quadruplicate runs of each sample to further enhance statistical analysis possibilities.

Moreover, several other studies have provided strong indications that Curie-point Py-MS can be used as a valid model for short contact time pyrolysis processes in TBR systems. For instance, the composition of pyrolytic tars obtained by means of a rapid heating TBR system has been shown to be comparable to that of coal pyrolyzates obtained by direct Py-MS (1). Moreover, pyrolysis tar from a pilot plant scale Wellman Galusha fixed bed reactor (Figure 1a) can be seen to be quite similar to a Curie-point pyrolyzate (Figure 1b) when allowing for the loss of gaseous products during collection of the Wellman-Galusha tar. More recently, a systematic Py-MS study of 47 U.S. coals, carried out by Voorhees and co-workers (14), has further demonstrated the validity of Curie-point Py-MS as a coal pyrolysis model capable of predicting tar yields in TBR experiments as well as in larger scale pyrolysis retorts.

Examples of the use of the Curie-point Py-MS technique to study the composition of pyrolytic coal tars from three Western coals, a Hiawatha high volatile A bituminous coal, an Adaville #6 subbituminous coal and an Anderson seam lignite, are shown in Figure 2. As expected, rank related differences between the three coals, e.g. reflected by an increase in dihydroxybenzenes and phenols and a relative decrease in naphthalenes and short chain aliphatic hydrocarbons (13) are dominant in the spectra.

Nevertheless, weathering-induced changes (marked by arrows on the spectra of fresh coals in Figure 2), e.g., involving an increase in aliphatic carboxylic acids and ketones accompanied by decreased yields of phenols and dihydroxybenzenes in the lignite and subbituminous coal samples as well as a strong reduction in naphthalenic peak intensities in the hvb coal, are also easily recognizable. Earlier studies on weathered Hiawatha coal samples showed that conversion yields obtained by short contact time pyrolysis in a tubing bomb reactor (25 s at 420°C) decreased by 50% (1), whereas micropyrolysis (Curie-point Py-MS at 610°C for 5 s) yields decreased by an estimated 20% (4). Preliminary results from Py-MS experiments on all three Western coals discussed here indicate that vacuum micropyrolysis conversion yields decrease by an estimated 10-30% upon weathering.

Comparison of the ion intensities as a function of pyrolysis time (time profile curves) reveals that the evolution shape of several ion intensity curves is different between fresh and air weathered coals as shown for Hiawatha coal in Figure 3. Increased solvent (methanol; m/z 32) retention indicates increased polarity in the weathered coal. The fact that carbon dioxide (m/z 44) as well as benzene (m/z 78) curves both show an increasing, early component may indicate aromatic carboxylic acid formation during weathering. Moreover, aliphatic carboxylic acid ions show increased early components as well (e.g., CH_3COOH^+ in Figure 3f). On the other hand alkylnaphthalenes (e.g., the C_2-alkylnaphthalene in Figure 3c) show a strong decrease at lower temperatures in the weathered coal.

The discriminant analysis results shown in Table I and Figure 4 reveal characteristic changes in the composition of the pyrolytic tars obtained from coals weathered in air, whereas little or no change is observed in the control samples exposed to N_2 atmospheres. Although a quantitative comparison of weathering-induced changes in the different coals is not possible because of variations in the total duration of the three experiments as well as in the weathering temperatures, qualitative analysis of the three discriminant spectra in Figure 4 reveals marked differences. For example, the pyrolytic tar obtained from weathered Anderson lignite shows a decreased contribution of dihydroxybenzenes, whereas the spectrum of the subbituminous Adaville #6 tar exhibits a more pronounced decrease in phenolic compounds as well. Moreover, slight increases in the relative contributions of aromatic hydrocarbons (benzenes + naphthalenes) can be noted in the latter. Furthermore, the pyrolyzate of weathered hvb Hiawatha coal tar shows a pronounced loss of naphthalenic compounds.

Although the detailed mechanism behind these changes are not yet understood the differences between three discriminant spectra in Figure 4 are more or less consistent with the differences observed between the composition of the pyridine extractable fractions of each of the three coals (not shown here). Consequently, our earlier interpretation of the loss of naphthalenic components in the pyrolyzate of Hiawatha coal as due to "grafting" of extractable mobile phase components onto the network phase (1), may well hold true for the two lower rank coals as well. Obviously, further work is required to confirm these findings and interpretations.

Finally, it should be noted that whereas changes in the relative abundance of aromatic compound series appear to be quite specific for each coal, all three coals show increased mass peak intensities at m/z 28 (e.g., $CO^{+\cdot}$), 44 (e.g. $CO_2^{+\cdot}$) and 60 (e.g. $CH_3COOH^{+\cdot}$). Apparently, the formation of polar functional groups, e.g. in short chain aliphatic moieties, is a general characteristic of oxidative changes in Western coals independent of differences in rank.

Whereas our experiments demonstrate that coal weathering influences the composition of pyrolytic tars it is also known that such tars are often quite reactive and prone to regressive reactions which may cause marked changes in the physical and chemical properties of the tar (15). In order to compare the effect of "regressive" reactions on the composition of pyrolytic tars with that of coal weathering processes,

carefully preserved samples of "fresh" tar from the Wellman Galusha gasifier and tar samples exposed to oxygen as well as control samples exposed to N_2 were analyzed by low voltage MS. Minor, but highly characteristic changes in chemical composition were found in the oxygen exposed samples by means of discriminant analysis techniques. The discriminant spectrum in Figure 5 reveals a decrease in the relative abundance of dihydroxybenzene peaks along with several other peak series thought to represent naphthols and phenols (and/or quinones). These observations are in agreement with earlier studies by McMillan *et al.* (15).

The Blind Canyon coal used to produce the Wellman Galusha tar is closely related to the Hiawatha coal and shows similar weathering behavior (10). Therefore it is interesting to note that whereas naphthalene moieties play a prominent role in coal weathering related changes they do not appear to be directly involved in oxidative tar processes. This would seem to indicate that both types of oxidative processes involve quite different reaction mechanisms. Whereas weathering induced loss of aromatic and hydroxyaromatic tar components is thought to be due primarily to "grafting" reactions between the mobile and the network phase, loss of hydroxyaromatic components during tar oxidation is more likely to be caused by simple condensation reactions. Additional evidence for such reactions is found in Figure 5 showing an increased abundance of small mass peaks in the high mass range (possibly representing condensed tar components) upon weathering.

CONCLUSIONS

Weathering-induced decreases in relative yields of pyrolytic tars from Western coals of different rank (lignite to hvb) may range from 20 to 50%, depending on pyrolysis conditions.

Pyrolytic coal tars of remarkably similar composition are obtained from a Wellman Galusha reactor and from a vacuum micropyrolysis experiment in spite of 8-9 orders of magnitude differences in sample size.

Vacuum micropyrolysis experiments on three Western coals of different rank (lignite, subbituminous and hvb-A) which were oxidized ("weathered") under controlled laboratory conditions show marked differences in the behavior of aromatic tar components but an overall similarity in the increase of polar, aliphatic compounds.

In each coal the observed changes in the relative abundance of aromatic compounds appear to be explainable by a loss of mobile phase components through "grafting" reactions with the network phase during coal weathering.

Small but characteristic changes which occur in the composition of a Wellman Galusha reactor coal tar during exposure to oxygen at 80°C point to the occurrence of condensation reactions involving dihydroxybenzenes and other hydroxyaromatic compounds.

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TABLE I

WEATHERING CONDITIONS OF THE COALS STUDIED

Sample Treatment	Hiawatha	Adaville # 6	Anderson
Air weathered	100°C, 96 hr.	100°C, 96 hr.	80°C, 232 hr.
N_2 exposed	80°C, 120 hr.	100°C, 96 hr.	80°C, 232 hr.

TABLE II

SCORES OF THE FIRST DISCRIMINANT FUNCTIONS OBTAINED FOR PYROLYSIS MS DATA ON FRESH, N_2 EXPOSED AND AIR WEATHERED SAMPLES

Sample* Treatment	Discriminant Scores (DI)		
	Hiawatha	Adaville #6**	Anderson
Fresh	1.61 ± 0.34	0.88 ± 0.07	1.68 ± 0.34
N_2 exposed	1.20 ± 0.27	0.88 ± 0.44	1.09 ± 0.10
Air weathered	-1.13 ± 0.31	-0.98 ± 0.33	-0.85 ± 0.43

* Weathering conditions are shown in Table I.

** Discriminant function rotated for maximum discrimination.

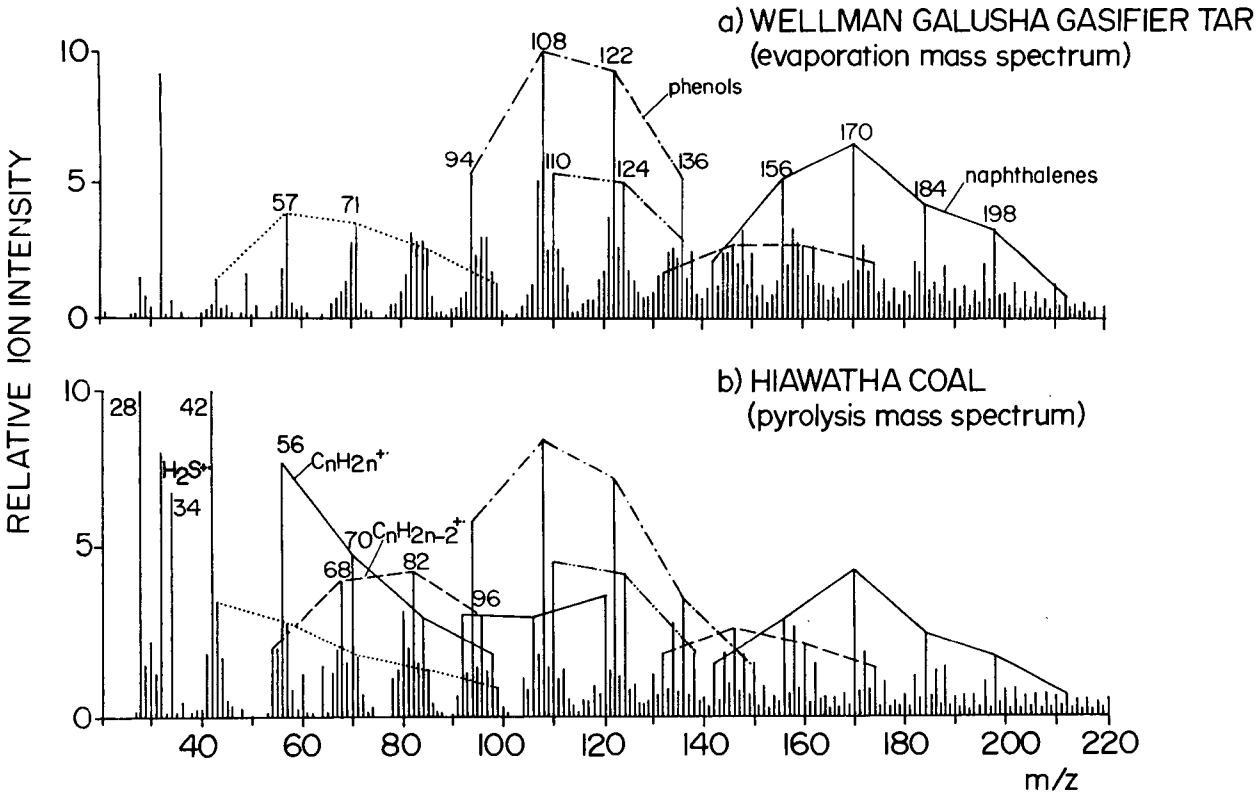

Figure 1. Comparison of low voltage mass spectra of (a) Wellman-Galusha gasifier tar (Blind Canyon seam) and (b) Curie-point pyrolyzate of a coal from a related Wasatch Plateau seam (Hiawatha seam). Note marked correspondence in high mass range.

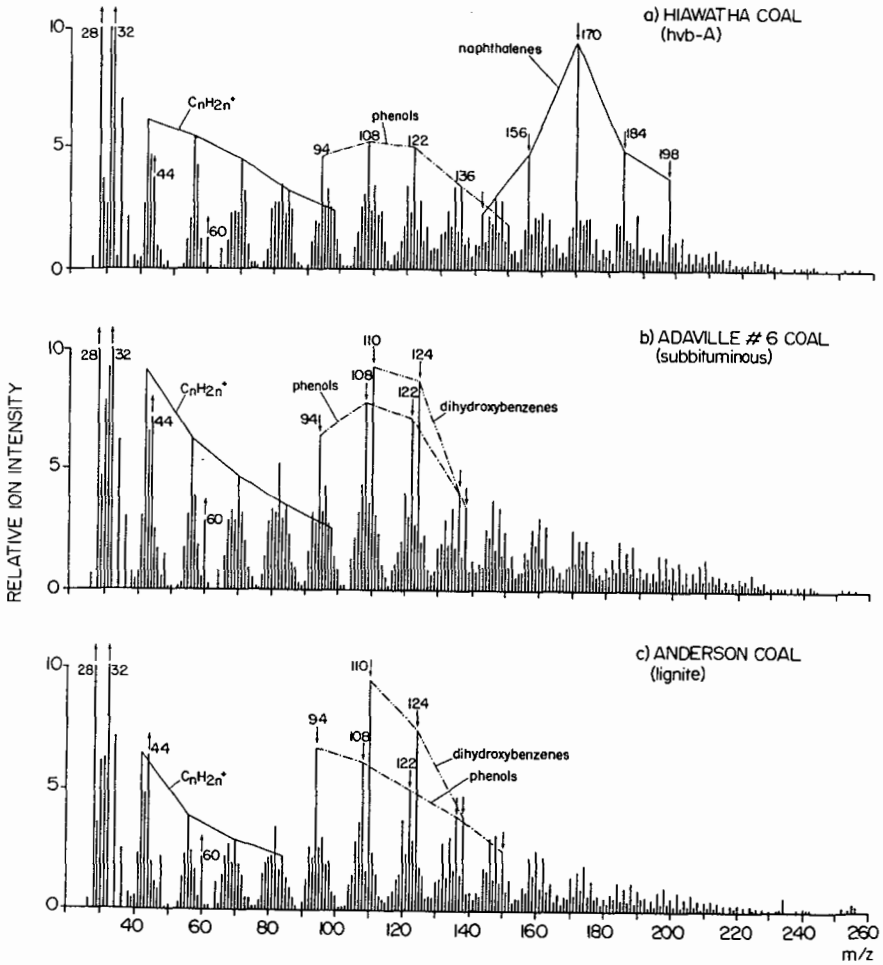

Figure 2. Low voltage pyrolysis mass spectra of fresh coal samples from (a) Hiawatha seam (b) Adaville #6 seam and (c) Anderson seam. Arrows indicate changes in mass peak intensities in the air weathered coals. Note that mass spectrometry conditions were different from that in Figure 1 resulting in increased sensitivity in high mass range.

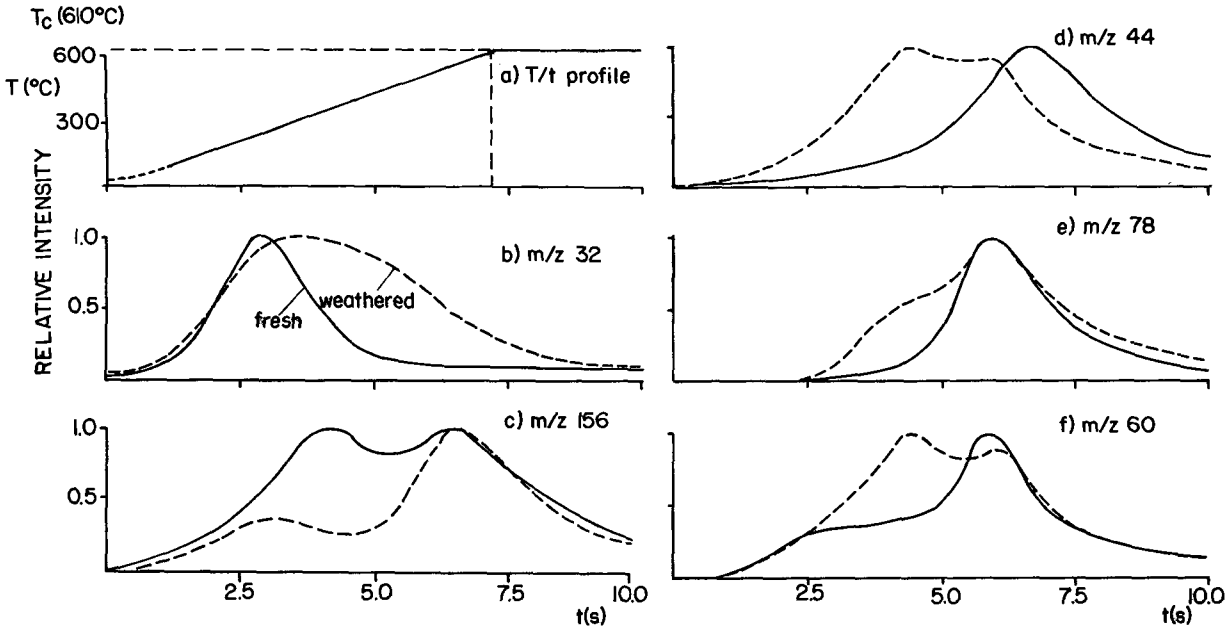

Figure 3. Time-resolved recording of ion signals at: (b) m/z 32 (methanol); (c) 156 (e.g., C_2-alkylnaphthalenes); (d) m/z 44 (mainly carbon dioxide); (e) m/z 78 (e.g., benzene); and (f) m/z 60 (e.g., acetic acid) during Curie-point pyrolysis of fresh (——) and air weathered (---) Hiawatha coal. Estimated temperature/time profile is shown in (a).

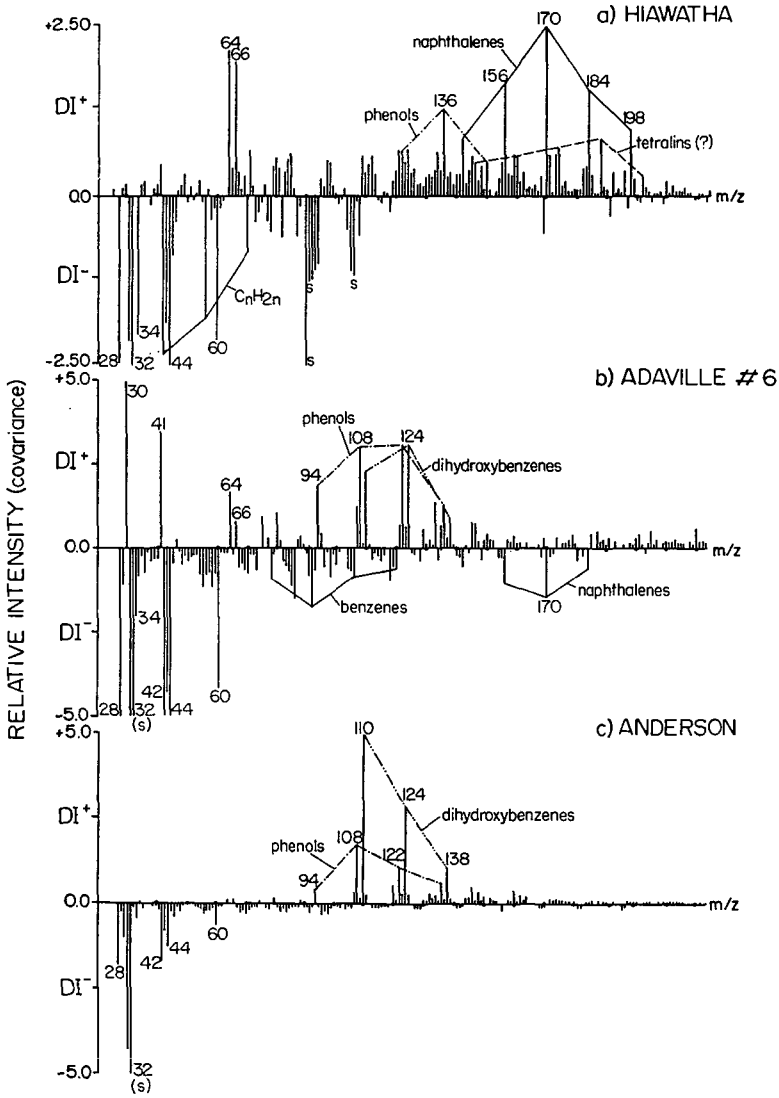

Figure 4. Discriminant spectra obtained on Py-MS data sets of fresh and air weathered coals from: (a) Hiawatha seam; (b) Adaville #6 seam; and (c) Anderson seam. Positive components (DI^+) represent mass peaks decreased in weathered samples. Negative components (DI-) represent compounds increased in weathered samples. (s) denotes peaks originating from solvent(s).

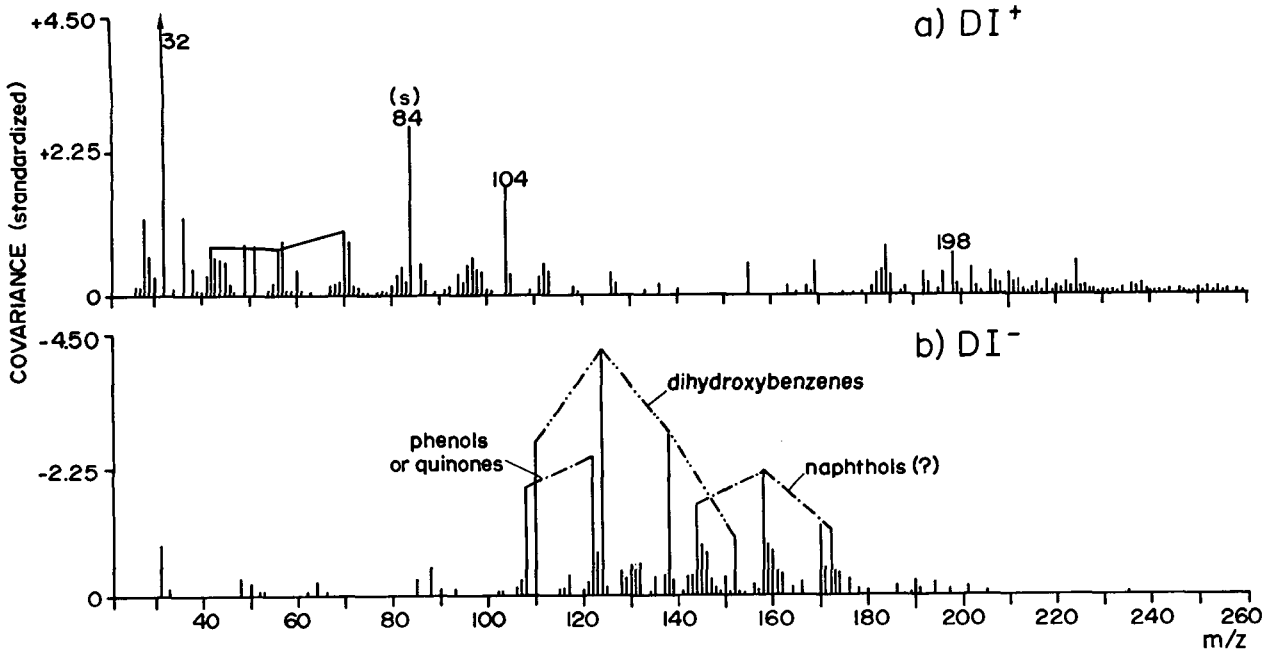

Figure 5. Discriminant spectrum showing the effect of oxygen exposure on the Wellman-Galusha gasifier tar. The negative component (DI^-) represents compounds decreased in oxidized tar. The positive component (DI^+) represents ion signals increased in oxidized tar. (s) indicates dichloromethane solvent peaks.