

## An Infrared Absorption Study of Coal-Metal Salt Catalyst Interactions

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### Introduction

A thorough study of the infrared absorption patterns produced by coal samples conducted by Friedel, et. al., (1) resulted in the assignment of absorption bands to specific structures or components of coal. Those assignments of importance to this study are listed in Table I.

Although some uncertainty exists with respect to these assignments the 3030  $\text{cm}^{-1}$  band is considered to represent the aromatic C-H and the 2920  $\text{cm}^{-1}$  and 2850  $\text{cm}^{-1}$  bands represent aliphatic C-H.  $\text{CH}_3$ ,  $\text{CH}_2$ , and CH (aliphatic) configurations all contribute to these absorption bands but the dominant effect is that from  $\text{CH}_2$  because of its relative abundance. However, the IR differentiation does not discriminate between aliphatic C-H bonds in aliphatic side chains, in hydroaromatic structures, in cycloparaffins or in aliphatic connecting bridges. The 1610  $\text{cm}^{-1}$  band is assigned to double bond carbon and/or carbon only bonds. In coal this is taken to be aromatic carbon (2,3). The 1450  $\text{cm}^{-1}$  band is assigned to aliphatic H bending and/or aromatic carbon stretching. The 1260  $\text{cm}^{-1}$  band is assigned to phenoxy and ether structures. Figure 1 shows these band assignments as derived by Friedel (1) and applied to the IR pattern of a thin section of vitranite.

Temperature effects on functional groups in coal have been studied by several authors (1,3,4,5,6). These reports indicate that the IR band assigned to the OH structures in bituminous coals disappears near 500°C. The band attributable to phenoxy structures (1260  $\text{cm}^{-1}$ ) decreases in intensity at 300°C but does not completely disappear even at 550°C. The C-H stretching band intensities decrease and the aromatic C-C and C-O band (1610  $\text{cm}^{-1}$ ) is unchanged at temperatures approaching 600°C. Oelert (4) has published an extensive interpretation of thermally induced structural changes in coal as a result of IR measurements.

The present study is an attempt to use the IR absorption procedure to measure change in coal structure under nitrogen and hydrogen (one atmosphere pressure) and in the presence of metal salt catalysts.

### Experimental

A Beckman IR-20 Infrared Spectrophotometer was used to measure infrared spectra of KBr pellets containing finely dispersed coal and char samples. Kapaiowitz, Utah coal sized to 44-53 microns (-270 +325 mesh) was used. Proximate and ultimate analyses of this coal are given in Table II.

Coal samples were impregnated with metal salt catalysts ( $\text{ZnCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) by mixing the coal with a water

solution of the salt and drying the slurry under vacuum at 110°C. The catalyst application rate was 0.112 moles of catalyst per 100 grams of MAF coal. The prepared sample (50 mg) was heated to various temperatures (250, 350 or 450°C) for 30 minutes in the presence of either H<sub>2</sub> or N<sub>2</sub> gas (99.98 % purity). Figure 2 shows a schematic drawing of the equipment used for heat treatment.

Following reaction, the chars were weighed to permit a correction for loss of volatile matter and KBr pellets were prepared. Twenty mg of each sample were ground in a Wig-L-Bug vibrator for 1 hour. Then, 0.5 to 2.0 mg of the coal or char were mixed with 250 mg of IR grade KBr for 10 minutes in the same device. Two hundred mg of the mixture were briquetted in a hot die (110 C) after evacuation. The result was a clear pellet 13 mm in diameter and 0.6 mm thick. Each sample was measured 4 times, not as duplicates, but at 0.2, 0.4, 0.6, and 0.8 weight percent of the KBr disc.

### Results and Discussion

Figure 3 shows the IR pattern to be expected from different amounts of coal dispersed through a KBr pellet. Because the grinding and mixing were done in polystyrene vials there is an obvious contamination of this polymer in the sample as measured by the spectrometer. In fact, because the polystyrene contains similar bonding to that found in coal, the spectra of KBr with no coal present (but with polystyrene contamination) is very similar to the pattern obtained when coal is present. The effect of this contamination becomes constant at 10 minutes grinding or mixing time and hence is a constant which can be subtracted from the KBr plus polystyrene plus coal pattern.

Beer's law for absorption states that:

$$A = km/S + A_0 = k M/100S + A_0 = Kc + A_0$$

where A = sample absorbance at a specific absorption band

A<sub>0</sub> = constant absorbance due to the polystyrene

k = specific extinction coefficient (cm<sup>2</sup>/mg)

m = weight of coal in the disc (mg)

S = area of disc (cm<sup>2</sup>)

M = weight of the disc (mg)

c = weight percent of coal in the disc

K = slope of the line A vs c

The values of k, K and A<sub>0</sub> as measured for this study are shown in Table III for the 2920 cm<sup>-1</sup> absorption peak. Some literature values of k are included for comparison. Because the data obtained using the conventional base line (3120-2780 cm<sup>-1</sup>) did not yield a straight line of A vs c for either the 2920 or 3030 cm<sup>-1</sup> bands, a second base line (3740-2200 cm<sup>-1</sup>) was used. This base line provided the desired straight line function and also gave larger values of k and K without significantly changing A<sub>0</sub>. Slopes were calculated for each of the A vs c lines (K values in the Beer law relationship). Correlation coefficients (r<sup>2</sup>) were calculated for

all the lines and data points generated. Statistically, all data points gave  $r^2$  values in excess of the 90 percent confidence level and most cases were in excess of the 95 percent level.

Subsequent calculations have included data for  $N_2$  and  $H_2$  atmosphere, 350 and 450°C and no catalyst, plus the metal salts listed above. The data obtained on samples treated at 250°C were not included because of overlap of lines caused by water absorption with lines used in the calculations. For statistical purposes, the data provide two levels of atmosphere, two levels of temperature and two levels of catalyst application for each of the 5 metal salts used. The total data (K values) accumulated are included in Table IV. Changes in K values from one condition to another indicate an increase or a decrease in the type of bonding that gives rise to that particular absorption band. Therefore, changes in K values can be related to changes in aromatic hydrogen, aliphatic hydrogen, aliphatic carbon, etc., in the coal or char structure.

The infrared absorbance data were analyzed by means of a multivariable linear regression analysis procedure to discover which absorbances were statistically related. The percent volatile matter from each trial was included as the dependent variable in the computation. The correlation coefficients shown in Table V are the result of this calculation. The following comments can be made with respect to these correlation values.

1. The  $3030\text{ cm}^{-1}$  absorbance peak (aromatic hydrogen) has a negative correlation with all other peaks, but a positive correlation with volatile matter. Although the correlation is not high in any case it means that the concentration of aromatic bonding in the char increases with increase in volatile matter production. This supports the concept that aromatic bonds are produced in the char as more volatile matter is produced.

2. All the absorbance bands, except  $3030\text{ cm}^{-1}$ , have a negative correlation with respect to volatile matter. This indicates that the bonds represented by the absorbance bands, aliphatic or naphthenic hydrogen, aromatic carbon, carbonyl, carboxylates, phenoxy structures, etc., are destroyed or removed to produce volatile material.

3. A very good correlation coefficient (+0.785) is found for the 2920 and  $2850\text{ cm}^{-1}$  bands. This supports the concept that these two bands measure the same thing, in this case aliphatic or naphthenic hydrogen.

4. Good positive correlation coefficients between 1610, (aromatic C and/or C=O), 1450 ( $CH_2$ ,  $CH_3$ , C-C) and 1260 (C=O in phenoxy structures) indicate that they are also a measure of the same thing, or at least that the bonds they measure are affected simultaneously by the various sample treatment procedures.

5. The fairly good inverse correlation between the 2920 and  $2850\text{ cm}^{-1}$  absorbance bands and the percent volatile matter is in agreement with published ideas on the origin of volatile components. The changes found in aliphatic hydrogen bonding indicate a decrease with increased volatile matter. This can be explained as abstraction of hydrogen from hydroaromatic structures by thermally produced free radicals, a second order reaction, (8,9) or by a first order pyrolytic breaking of aliphatic bonds (10,11).

6. The positive, but low, correlation between 2920 and  $2850\text{ cm}^{-1}$  with 1610, 1450 and  $1260\text{ cm}^{-1}$  indicates that the bonds responsible for these

absorbances are again treated similarly by the various sample treatment procedures. Although the bonds involved may not be the same, the various peaks do increase or decrease together.

The significance of the numerical (K) data of Table V was tested with the conventional F ratio, using three variables, each at two levels. The results of this study are shown in Table VI. In this table, the significance is noted by a number which is the statistical probability of error. The number 0.20 indicates a 1 in 5 probability that the statement is in error, 0.05 indicates a 1 in 20 probability that the statement is in error, 0.01 indicates a 1 in 100 and 0.001 indicates a probability of 1 in 1000 that the statement is in error.

Analysis of Table VI tells us that little difference is realized by virtue of hydrogen pressure at one atmosphere.  $\text{FeSO}_4$  affects both the 3030 and the 2850  $\text{cm}^{-1}$  absorption bands when hydrogen is present. Since both are increased, the Ar/Al ratio as represented by 3030/2920 is not affected.  $\text{ZnCl}_2$  depresses volatile matter evolution at low temperature but increases it at high temperatures when hydrogen is present.  $\text{CdCl}_2$  does act to increase volatile matter evolution when hydrogen is present. The 1610  $\text{cm}^{-1}$  band is not affected by hydrogen presence with any of the metal salts.

Temperature acts to increase volatile matter evolution with all of the salts present. However, this volatile matter is obtained at the expense of different bonds in the presence of different salts.  $\text{SnCl}_2$  and  $\text{CdCl}_2$  act to increase aromatic hydrogen while  $\text{FeSO}_4$  acts to decrease the aliphatic hydrogen at higher temperatures.  $\text{CdCl}_2$  is the only salt of the five tested which does not decrease the aromatic carbon at the higher temperature.

The catalytic effect, as opposed to hydrogen or temperature, is shown in the final section of Table VI.  $\text{ZnCl}_2$  acts to decrease the absolute amount of aromatic hydrogen in the char while  $\text{SnCl}_2$  acts to cause an increase. This would appear to be an anomaly but can be explained if we assume that these salts influence different bonds.  $\text{ZnCl}_2$  may influence hydrogen release from aromatic structures with consequent polymerization of the residual groups.  $\text{SnCl}_2$  may influence hydrogen abstraction from hydroaromatic structures yielding aromatic structures in the residue which are less condensed than with  $\text{ZnCl}_2$ .  $\text{ZnCl}_2$  increases the aliphatic hydrogen as does  $\text{FeSO}_4$ . For  $\text{ZnCl}_2$  this indicates a transfer of hydrogen from some aromatic to form some aliphatic structures.  $\text{ZnCl}_2$ ,  $\text{CdCl}_2$  and  $\text{CoCl}_2$  decrease the ratio of aromatic hydrogen to aliphatic hydrogen while  $\text{SnCl}_2$  increases it.  $\text{SnCl}_2$ ,  $\text{CdCl}_2$  and  $\text{FeSO}_4$  decrease the absolute content of aromatic carbon.  $\text{SnCl}_2$  acts to increase volatile matter evolution while  $\text{FeSO}_4$  has a slight tendency to repress the evolution. Other salts seem to have no effect on the final quantity of volatile matter evolved.

As a summary we can say that infrared absorption technique is capable of differentiating some types of bonds affected by coal pyrolysis in the presence of metal salts. Further, these salts do not act uniformly with respect to specific bonds. This is especially apparent in the cases of  $\text{ZnCl}_2$  and  $\text{SnCl}_2$ , both of which are effective as coal hydro-generation-liquefaction catalysts.  $\text{ZnCl}_2$  acts to decrease the absolute content of aromatic hydrogen bonding while  $\text{SnCl}_2$  acts to increase the absolute quantity of aromatic hydrogen in the char.

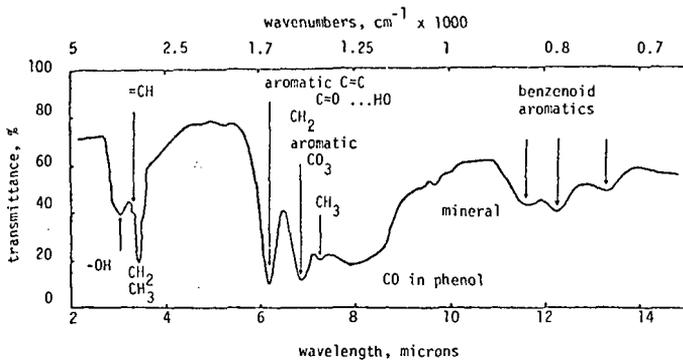


Figure 1. Infrared Spectrum of Vitrain Thin Section

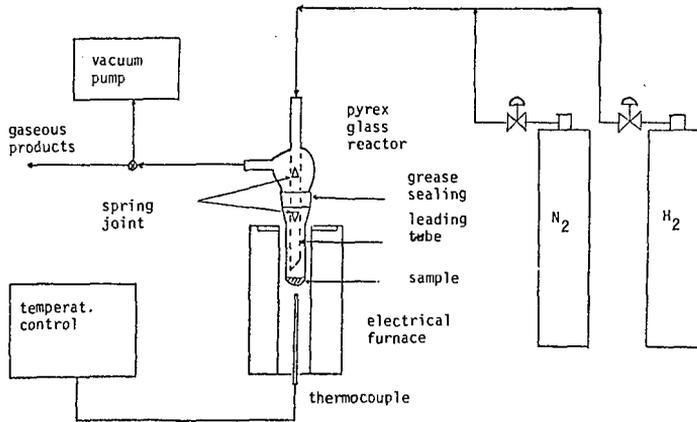


Figure 2. Flow Scheme of Reactions with  $\text{N}_2$  and  $\text{H}_2$

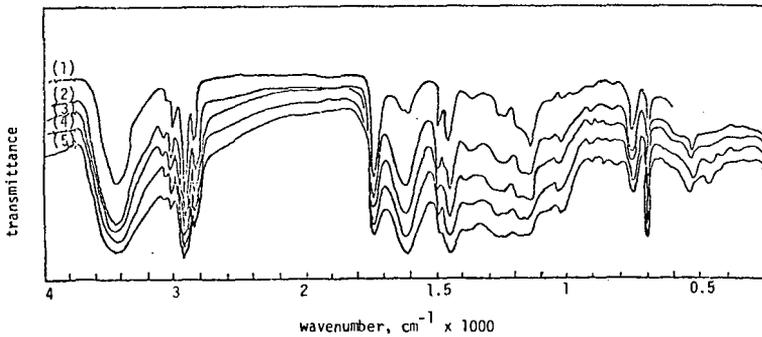


Figure 3. Spectra by Varying the Hiawatha Coal Concentration in the KBr Pellet; (1) KBr alone, (2) 0.218%, (3) 0.420%, (4) 0.600%, (5) 0.807%

TABLE I  
Selected Infrared Absorption  
Absorption Assignments in the Coal Structure (1)

Absorption Band, $\text{cm}^{-1}$	Assignment
2920	Naphthenic and/or aliphatic C-H
3030	Unsaturated CH, probably aromatic
1610	Aromatic C-C and/or C-O...HO-; carboxilates
2850	Naphthenic and/or aliphatic C-H
1450	$\text{CH}_2$ and $\text{CH}_3$ ; aromatic C-C or ionic carbonates
1260	C=O in phenoxy structures

TABLE II  
Proximate and Ultimate Analysis  
of Kaiparowitz, Utah Coal

Dry Basis		MAF Basis				
% Ash	% V.M.	% C	% H	% N	% S	% O
10.8	51.4	73.4	6.17	1.91	0.55	18.00

TABLE III  
Constants Obtained From Beer's Law,  $2920 \text{ cm}^{-1}$

Coal Sample	k	K	$A_0$
This work 3120-2780 base	0.27	0.401	0.245
3740-2200 base	0.40	0.599	0.264
Freidel (1) 3120-2780 base vitrain (84% C)	0.17		
Fujii (7) 3210-2780 base vitrain (83.4% C) vitrain (84% C)	0.38 0.42		

TABLE IV  
K Values Obtained from IR Spectra

A	T	C	3030	2850	2920	1610	1450	1260	V.M.%
N <sub>2</sub>	350	None	0.184	0.263	0.268	0.835	0.636	0.547	6.9
N <sub>2</sub>	450	"	0.214	0.234	0.207	0.751	0.611	0.537	21.8
H <sub>2</sub>	350	"	0.223	0.307	0.388	0.787	0.648	0.474	6.2
H <sub>2</sub>	450	"	0.258	0.267	0.247	0.789	0.711	0.497	24.7
N <sub>2</sub>	350	ZnCl <sub>2</sub>	0.200	0.245	0.382	0.819	0.587	0.478	7.1
N <sub>2</sub>	450	" <sup>2</sup>	0.159	0.367	0.426	0.654	0.524	0.523	21.4
H <sub>2</sub>	350	"	0.155	0.335	0.466	0.819	0.675	0.548	6.4
H <sub>2</sub>	450	"	0.171	0.286	0.401	0.789	0.692	0.512	25.4
N <sub>2</sub>	350	SnCl <sub>2</sub>	0.227	0.341	0.404	0.734	0.460	0.434	12.5
N <sub>2</sub>	450	" <sup>2</sup>	0.330	0.258	0.118	0.419	0.267	0.387	29.0
H <sub>2</sub>	350	"	0.219	0.197	0.287	0.665	0.470	0.438	17.3
H <sub>2</sub>	450	"	0.290	0.168	0.199	0.464	0.334	0.323	28.8
N <sub>2</sub>	350	CdCl <sub>2</sub>	0.209	0.290	0.383	0.744	0.610	0.469	3.4
N <sub>2</sub>	450	" <sup>2</sup>	0.236	0.323	0.312	0.595	0.581	0.529	19.4
H <sub>2</sub>	350	"	0.171	0.332	0.518	0.676	0.582	0.401	13.4
H <sub>2</sub>	450	"	0.246	0.242	0.372	0.750	0.632	0.464	34.7
N <sub>2</sub>	350	CoCl <sub>2</sub>	0.280	0.407	0.539	0.858	0.708	0.536	2.4
N <sub>2</sub>	450	" <sup>2</sup>	0.240	0.231	0.335	0.773	0.592	0.488	17.5
H <sub>2</sub>	350	"	0.244	0.396	0.525	0.888	0.703	0.591	2.4
H <sub>2</sub>	450	"	0.269	0.324	0.415	0.735	0.630	0.571	26.7
N <sub>2</sub>	350	FeSO <sub>4</sub>	0.228	0.338	0.443	0.693	0.536	0.488	0.0
N <sub>2</sub>	450	"	0.189	0.283	0.462	0.653	0.447	0.404	12.1
H <sub>2</sub>	350	"	0.238	0.331	0.497	0.657	0.512	0.449	0.0
H <sub>2</sub>	450	"	0.258	0.315	0.318	0.664	0.512	0.449	23.9

TABLE V  
Multilinear Regression Analysis Correlation Coefficients

Correlation	Coefficient	Correlation	Coefficient
3030-2920	-0.225	2850-1260	+0.478
3030-2850	-0.098	1610-1450	+0.841
3030-1610	-0.167	1610-1260	+0.709
3030-1450	-0.120	1450-1260	+0.779
3030-1260	-0.129	3030-V.M.	+0.289
2920-2850	+0.785	2920-V.M.	-0.594
2920-1610	+0.327	2850-V.M.	-0.557
2920-1450	+0.234	1650-V.M.	-0.322
2920-1260	+0.182	1450-V.M.	-0.119
2850-1610	+0.353	1260-V.M.	-0.190
2850-1450	+0.371		

TABLE VI  
Statistical Significance of I.R. Absorbance Data

ATMOSPHERE

N <sub>2</sub> or H <sub>2</sub>	3030		2850		3030/2920		1610		% V.M.	
	S	E	S	E	S	E	S	E	S	E
ZnCl <sub>2</sub>	---	---	---	---	---	---	---	---	0.01	I Hi T D Lo T
SnCl <sub>2</sub>	---	---	---	---	---	---	---	---	---	---
CdCl <sub>2</sub>	---	---	---	---	---	---	---	---	0.05	I
CoCl <sub>2</sub>	---	---	---	---	0.20	D	---	---	---	---
FeSO <sub>4</sub>	0.05	I	0.05	I	---	---	---	---	---	---

TEMPERATURE

350 or 450°C

ZnCl <sub>2</sub>	---	---	---	---	0.05	I	0.05	D	0.001	I
SnCl <sub>2</sub>	0.01	I	---	---	---	---	0.001	D	0.001	I
CdCl <sub>2</sub>	0.05	I	---	---	0.01	I	---	---	0.01	I
CoCl <sub>2</sub>	---	---	---	---	0.01	I	0.05	D	0.001	I
FeSO <sub>4</sub>	---	---	0.05	D	---	---	0.05	D	0.01	I

CATALYST EFFECT

ZnCl <sub>2</sub>	0.05	D	0.20	I	0.01	D	---	---	---	---
SnCl <sub>2</sub>	0.05	I	---	---	0.20	I	0.001	D	0.05	I
CdCl <sub>2</sub>	---	---	---	---	0.05	D	0.05	D	---	---
CoCl <sub>2</sub>	---	---	---	---	0.01	D	---	---	---	---
FeSO <sub>4</sub>	---	---	0.01	I	---	---	0.01	D	0.20	D

S = Significance

E = Effect

I = Increase in measured absorbance

D = Decrease in measured absorbance

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