

IN SITU ACETYLATION STUDY OF A SUBBITUMINOUS COAL BY DIFFUSE REFLECTANCE
INFRARED FOURIER TRANSFORM (DRIFT) SPECTROSCOPY

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ABSTRACT

Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy has been utilized to monitor the in situ acetylation of a powdered subbituminous coal at the Oak Ridge Y-12 Plant. The acetylation reaction was carried out by the adsorption of acetic anhydride onto the powdered coal from the gas phase with subsequent heating above 100°C required to initiate the reaction. This technique can be used to gain insight into the hydroxyl (O-H) content of the specific coal sample under study by simultaneously observing the disappearance of infrared absorptions due to various types of O-H functional groups and the appearance of absorptions due to carbonyl functional groups resulting from reaction with the anhydride. This entire study can be carried out on a single sample without any intervening sample handling or the introduction of extraneous parameters that could alter the results.

INTRODUCTION

The determination of hydroxyl functional groups in coal by infrared (IR) and Fourier transform infrared (FTIR) methods has been previously attempted. One of these approaches (1-3) involves direct measurement of the intensity of the broad O-H band in the spectrum of coal centered at ~ 3400 cm^{-1} , while a second technique relies on the measurement of band intensities due to products derived from chemical reaction with the various O-H groups, such as by acetylation (4-6). Both methods utilized standard transmission techniques using potassium bromide (KBr) pellets. Although the direct-measurement approach has been used with some apparent success, this method suffers potential interference from moisture (whether it be in a latent form within the coal or from KBr or other sources in the pellet-preparation step). The acetylation approach has also been used with a certain degree of success but can suffer potential problems related to uncertainty in the extent and completeness of reaction and in the handling and pellet-preparation steps subsequent to the chemical-reaction step. This appeared to be an area where in situ diffuse reflectance (DR) measurements could incorporate the best aspects of both methods and have the potential of yielding more accurate and more detailed information without introducing unknown factors due to sample manipulations.

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The first work to demonstrate the analytical significance of the infrared DR technique as applied to coal was a report by Fuller et al., (7) and subsequent studies (8-10) in our laboratory have further proven the value of this technique. The DR method, however, has really not received widespread use and acceptance in relation to coal work, probably because the quantitative correlation of band intensities with concentration is not as straightforward as it is with transmission spectroscopy. There is one property of coal that makes it ideally suited for DR measurements, which is not a well-known fact. Coal forms its own dispersion medium and can be directly examined in the neat form without dilution in another dispersion matrix.

Perhaps the single strongest point associated with the DR sampling method is the ability to perform in situ reaction studies. This ability, when coupled with the aforementioned property of coal, makes the DR method a very powerful technique for the study of coal. We have previously demonstrated the usefulness of DR in situ measurements in the study of coal oxidation (8-10) and other heterogeneous reactions involving inorganic materials (10-12). In this particular report, we present some preliminary results of in situ acetylation studies of a subbituminous coal by DR.

EXPERIMENTAL

A 30-mg sample of a powdered subbituminous coal from the Wyodak Mine in Wyodak, Wyoming, was placed on a gold-plated, 304 stainless sample pedestal within the DR cell [thoroughly described in a previous report (11)]. This cell can be used in applications involving ultra-high-vacuum and/or flowing-gas conditions at varying temperatures (-77° to 800°C). The cell is used in conjunction with a Harrick Model DRA-SID DR accessory designed for adaptation to a Digilab Model FTS-15 side-focus FTIR spectrometer.

The coal sample used in this study was obtained directly from a freshly opened mine face and stored under argon to minimize oxidation until the experimental work was initiated. A similar technique has been described in a recent article (13) for maintaining coal samples from various sections of the country as known quality reference standards.

The DR sample cell was first evacuated to ~20 mtorr for 40 h. Previous studies for this particular sample (8,9) have shown that these conditions are adequate for removing the most loosely bound "bed moisture" associated with this coal sample. The sample was then exposed under dynamic flowing conditions to argon/acetic anhydride vapors by bubbling dry argon through a reservoir of the anhydride at room temperature (RT). The temperature of the sample was then raised from RT to 450°C in roughly 100-degree intervals. A final deuteration experiment using D₂O was carried out on the sample, which contained some residual O-H groups that could not be forced to react or that were inaccessible to the anhydride. Spectra were scanned periodically throughout this sequence of events.

All spectra were obtained on a Digilab Model FTS-15C FTIR spectrometer at a resolution of 2 cm⁻¹ using a triglycine sulfate (TGS) pyroelectric bolometer detector. The merits for use of the TGS detector versus a mercury cadmium telluride (MCT) are discussed in Ref. 10 for the DR reaction studies of coal and other materials at elevated temperatures. The benefit of greater sensitivity derived by using an MCT detector can largely be over-

ridden by its nonlinear response and the saturation effects encountered as the temperature of the sample is increased. For most of the experiment, 100 scans proved adequate to produce spectra with a satisfactory signal-to-noise (S/N) ratio and yet short enough in duration to kinetically follow the reaction. Some scans of longer duration were also obtained for production of high-quality spectra for use as subtraction standards. All reflectance spectra recorded in this paper are plotted in the absorption format $[-\log(R_s/R_o)]$. (See the appendix in Ref. 11 for a discussion of the merits of various plotting formats.)

RESULTS, DISCUSSIONS, AND CONCLUSIONS

Figure 1 represents the DR spectra of the sample of Wyodak powdered coal in the C-H and O-H stretching regions before and after evacuation to 23 mtorr at 25°C. Refer to Table 1 for correlation of the spectrum numbers appearing in Fig. 1 and with those appearing in subsequent figures to the corresponding experimental conditions. These spectra show that the loosely bound "bed moisture" can essentially be totally removed under these evacuation conditions. Comparison of Curves 7 and 3 reveals some distinct features in the O-H stretching region at 3625, 3540, 3390, and 3290 cm^{-1} that were not observable prior to evacuation. Previous work involving this sample (8,9) has shown that further heat treatment under vacuum causes little or no change in the spectrum depicted by Curve 7. This spectrum was chosen as a vacuum reference state to which all subsequent spectra will be compared.

Curve 15 in Fig. 2 represents the spectrum of an equilibration state resulting from exposure of the coal sample to a flowing argon/acetic anhydride mixture at 25°C for 2.25 h. The difference spectrum (Curve 15 - Curve 7) very clearly shows bands that are present in the exposed state that are not present in the reference vacuum state.

For simplification of the subsequent discussion, all difference spectra using Curve 7 as the reference state for the subtraction are referred to merely by the corresponding spectral or sequence number. All difference spectra are also direct 1:1 subtractions with no scaling. Curve 15 was presumed to represent an equilibration state because very little if any change could be noted from the two previous spectra (see Fig. 3).

Bands are observed to grow at 900, 1000, 1130, 1375, 1760, and 1825 cm^{-1} in Fig. 3 and maximize in intensity in Curve 15. These bands can be attributed to acetic anhydride physically adsorbed onto the powdered coal surface. A band at 1730 cm^{-1} also appears immediately, as noted on Curve 10, that remains at a near-constant intensity through Curve 15. This band may possibly be due to some residual adsorbed acetic acid. A quantity of moisture is also adsorbed in this sequence, as noted by the growth of a broad feature in the O-H stretching region.

Curves 16 and 21 represent the first spectra obtained after the sample had been heated to 100° and 200°C, respectively. Each step up in temperature was taken only after the reaction had reached a state of equilibration, with no further reaction appearing to occur at the given lower temperature. The bands due to the adsorbed anhydride and moisture diminish until they are barely observable in Curve 21. Also, a band starts to grow at 1770 cm^{-1} in Curve 16 that is hard to distinguish from the 1760 cm^{-1} band of the

Table 1. Diffuse reflectance spectra sequence: Wyodak coal acetylation

Spectrum number	Sample conditions	Temp. (°C)	Time conditions changed	Time spectral collection complete	Day
1	Air (1 atm)	25	-	3:00 p.m.	0
2	Ar purge	25	-	3:10 p.m.	0
3	Ar purge	25	-	3:20 p.m.	0
4	Ar purge	25	-	3:35 p.m.	0
5	Vacuum (30 mtorr)	25	-	3:55 p.m.	0
6	Vacuum (23 mtorr)	25	-	4:50 p.m.	0
7 ^a	Vacuum (23 mtorr)	25	-	8:00 a.m.	1
8	Ar purge	25	-	9:25 a.m.	1
9	Ar/acetic anhydride	25	9:45 a.m.	9:53 a.m.	1
10	Ar/acetic anhydride	25	-	10:10 a.m.	1
11	Ar/acetic anhydride	25	-	10:25 a.m.	1
12	Ar/acetic anhydride	25	-	10:45 a.m.	1
13	Ar/acetic anhydride	25	-	11:20 a.m.	1
14	Ar/acetic anhydride	25	-	11:30 a.m.	1
15	Ar/acetic anhydride	25	-	12:00 a.m.	1
16	Ar/acetic anhydride	100	12:08 p.m.	12:15 p.m.	1
17	Ar/acetic anhydride	100	-	12:30 p.m.	1
18	Ar/acetic anhydride	100	-	12:45 p.m.	1
19	Ar/acetic anhydride	100	-	12:55 p.m.	1
20	Ar/acetic anhydride	200	1:00 p.m.	1:05 p.m.	1
21	Ar/acetic anhydride	200	-	1:25 p.m.	1
22	Ar/acetic anhydride	200	-	1:50 p.m.	1
23	Ar/acetic anhydride	300	2:10 p.m.	2:20 p.m.	1
24	Ar/acetic anhydride	300	-	3:15 p.m.	1
25	Ar/acetic anhydride	300	-	3:55 p.m.	1
26	Ar/acetic anhydride	300	-	4:30 p.m.	1
27	Ar/acetic anhydride	300	-	5:05 p.m.	1
28	Ar/acetic anhydride	300	-	9:35 p.m.	1
29	Ar/acetic anhydride	428	9:40 p.m.	9:45 p.m.	1
30 ^b	Ar/acetic anhydride	428	-	10:05 p.m.	1
31 ^b	Ar purge	300	10:07 p.m.	7:30 a.m.	2
32	Ar purge	300	-	7:45 a.m.	2
33	Ar/acetic anhydride	450	8:00 a.m.	10:20 a.m.	2
34	Ar purge	100	10:25 a.m.	11:00 a.m.	2
35	Deuterium oxide flow	100	11:20 a.m.	11:25 a.m.	2
36	Deuterium oxide flow	100	-	11:33 a.m.	2
37	Deuterium oxide flow	100	-	11:40 a.m.	2
38	Deuterium oxide flow	100	-	11:55 a.m.	2
39	Deuterium oxide flow	100	-	12:23 p.m.	2
40	Deuterium oxide flow	100	-	1:00 p.m.	2
41	Deuterium oxide flow	80	1:02 p.m.	1:10 p.m.	2
42	Deuterium oxide flow	65	-	1:25 p.m.	2
43	Deuterium oxide flow	50	-	1:40 p.m.	2
44	Deuterium oxide flow	34	-	1:55 p.m.	2
45	Vacuum (30 mtorr)	30	1:57 p.m.	2:10 p.m.	2
46	Vacuum (23 mtorr)	28	-	2:30 p.m.	2

^a20,000 scans; ^b10,000 scans

anhydride at the expansion shown in the figure. This band stands out essentially by itself in Curve 21 and really appears at 1770 cm^{-1} , as denoted in Fig. 4. The temperature of the sample was raised again to 300°C , with Curve 23 being the first spectrum to be collected after this step. This spectrum was also the first to be corrected for window background due to condensation of a volatile acetylation product that was discovered on the cell windows after the experiment had been completed. The spectrum due to the window background appears in the upper curve of Fig. 5, along with the difference spectra before and after correction for Curve 31 presented as a typical example. The proper amount of scaling for this correction was determined by nulling out the intensity of the C-H stretching bands in the difference spectrum as depicted in the lower curve in Fig. 5. The C-H stretching bands could be utilized in this way since the acetylation reaction is expected to alter this portion of the spectrum little if any. All spectra including and subsequent to Curve 23 have been similarly corrected for this background, since the higher temperatures readily facilitated volatilization of the product onto the zinc selenide windows.

The 1770 and 1200 cm^{-1} bands, along with some weaker features, are observed to continually grow in Fig. 4 until Curve 28 where the temperature was again raised to 428°C . These bands can be attributed to acetylated esters of the various O-H functional groups in the coal. In this same sequence of spectra, a broad negative band can also be observed to grow in the 3600 to 3000 cm^{-1} region, which can be attributed to the corresponding loss of O-H groups. A weak band appears at 2150 cm^{-1} (starting with Curve 24) that is apparently due to formation of gas-phase carbon monoxide. This band appears only when the temperature is 300°C or above and when the anhydride reactant mixture is present. A good explanation for the observation of this species has not presently been formulated. The sample had essentially reached the final state of acetylation, as noted in Curve 30. At this point exposure to acetic anhydride was terminated and the sample temperature was reduced to 300°C . The difference spectrum representing the final acetylated state is shown in Curve 31. A raw spectrum of this state appears in Curve 33 of Fig. 6, which shows that some residual O-H bands at 3550 and 3440 cm^{-1} remain--indicating either a lack of reactivity for these remaining O-H groups or, more likely, an inaccessibility due to steric effects. The position and relative sharpness of these O-H bands indicate that hydrogen bonding effects have been reduced considerably for these residual O-H groups, which supports the latter contention that the groups are isolated and difficult to access by the relatively large acetic anhydride molecule.

In an effort to gain more information about the residual O-H groups, the hydrogen atoms on these groups were then allowed the opportunity to exchange with deuterium by exposure to flowing D_2O as the sample was cooled from 100°C to near RT. Curve 46 in Fig. 6 represents the raw spectrum of the final deuterated state of the acetylated Wyodak powdered coal sample. Essentially all of the remaining O-H groups experience exchange, with the exception of those due to the inherent mineral bands--as noted by the loss of intensity in the O-H stretching region and the appearance of a band in the 2600 cm^{-1} region due to O-D stretching. The difference spectra for the deuteration sequence, again referenced to Curve 7, are displayed in Fig. 7. Deuteration was essentially complete by the time Curve 40 was collected, as noted by a lack of further increase in the intensity of the positive 2620

cm^{-1} O-D band or that of the negative O-H feature. An interesting observation that can be noted from Fig. 7 is the reappearance of adsorbed acetic anhydride on the powdered coal surface, as indicated by the growth of bands at 1825 and 1130 cm^{-1} with a decrease in temperature. This readsorption must result from residual acetic anhydride in the vacuum system and is easily removed by evacuation, as indicated in Curve 46.

Although the present acetylation work represents only a preliminary, qualitative study, it reveals an additional, potentially powerful technique for probing the structure of coal with regard to hydroxyl functional groups. This technique appears to provide complimentary information to previous liquid-solid acetylation work (4,5) by permitting O-H groups which are either relatively inaccessible to reaction with acetic anhydride from the gas phase or are less reactive under these conditions to be sorted from the total hydroxyl content. Another area where our results appear to differ somewhat from previous acetylation studies involves the relative amounts of phenolic- versus alkyl-type acetyl esters that are formed in reaction with similar subbituminous coals. Examination of the carbonyl region of the difference spectrum of the final acetylated state (Curve 31 of Fig. 4) shows essentially a single band centered at 1770 cm^{-1} with no apparent asymmetry observed on the low-frequency side that would indicate the presence of other bands. The 1770 cm^{-1} band has been attributed to phenolic acetyl esters, while bands at 1740 and 1670 cm^{-1} have been assigned to alkyl and amide acetyl esters (4). Presuming the assignments are correct, our data can be interpreted in either of two ways, one being that the coal sample we studied contains only phenolic type O-H groups with essentially none of the alkyl type. The other interpretation, which is probably the least plausible, would be that only the phenolic groups reacted in the acetylation--leaving the alkyl O-H groups unreacted. Further work should be done in this area to clarify this discrepancy. The acetylation technique in combination with deuteration appears to be an excellent method for revealing information with regard to hydroxyl-containing mineral matter. Considerably more work needs to be done in determining the quantitative potential of in situ DR technique. It is quite clear, however, that such a technique applied to acetylation, and possibly to other types of derivative reactions, can yield new and potentially enlightening information with regard to the structure of coal.

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VACUUM DEHYDRATION: WYODAK POWDER (D-1)

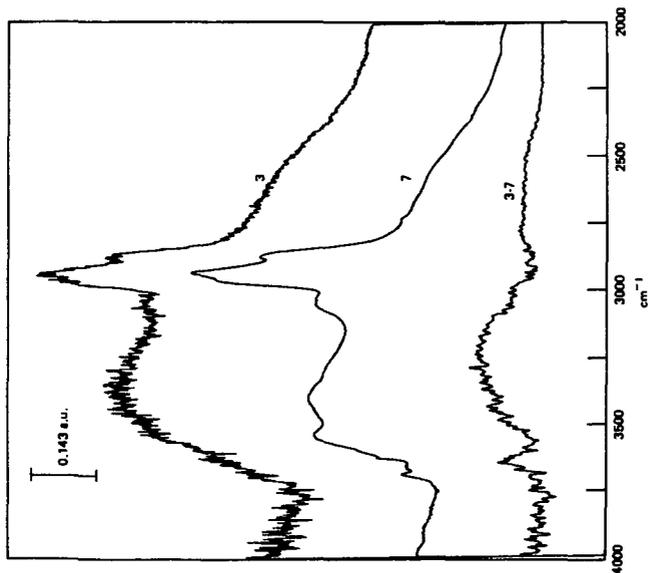


Fig. 1. Diffuse reflectance spectra of Wyodak coal: Curve 3 is the spectrum under argon purge at 25°C for 100 scans, Curve 7 is the spectrum under vacuum at 23 mtorr at 25°C for 10,000 scans, and Curve 3-7 is the difference spectrum.

ACETIC ANHYDRIDE ON WYODAK POWDER (D-1) AT 25°C

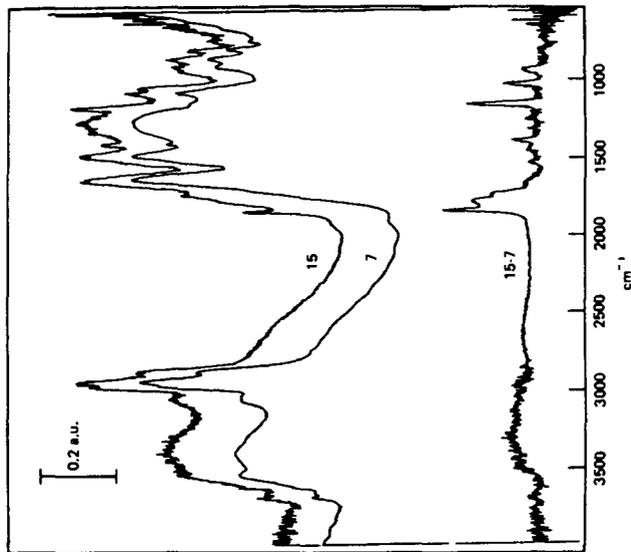


Fig. 2. Diffuse reflectance spectra of Wyodak coal: Curve 15 is the spectrum of Wyodak coal exposed to a flowing argon/acetic anhydride mixture for 2.25 h at 25°C, Curve 7 is reference state spectrum under vacuum at 20 mtorr at 25°C, and Curve 15-7 is the difference spectrum.

ACETIC ANHYDRIDE ON WYODAK POWDER (D-1) 100°C AND 200°C

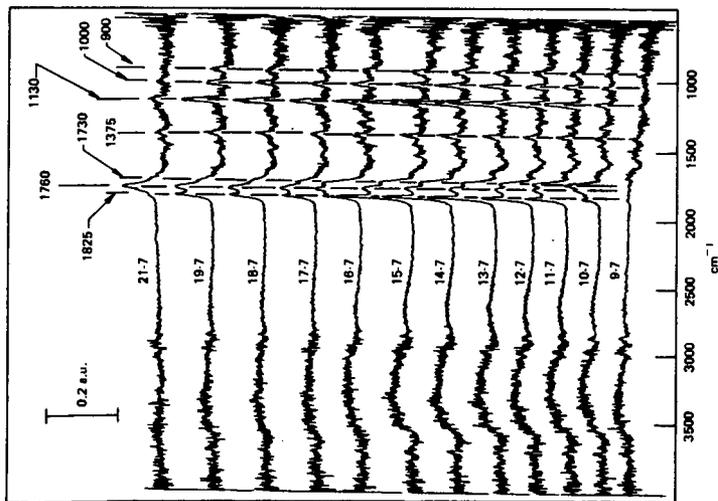


Fig. 3. Difference spectra for acetic anhydride reaction with Wyodak coal at 25°, 100°, and 200°C. (See Table 1 for correlation of spectral numbers.)

ACETIC ANHYDRIDE ON WYODAK POWDER (D-1) AT 200, 300, 428 AND 450°C

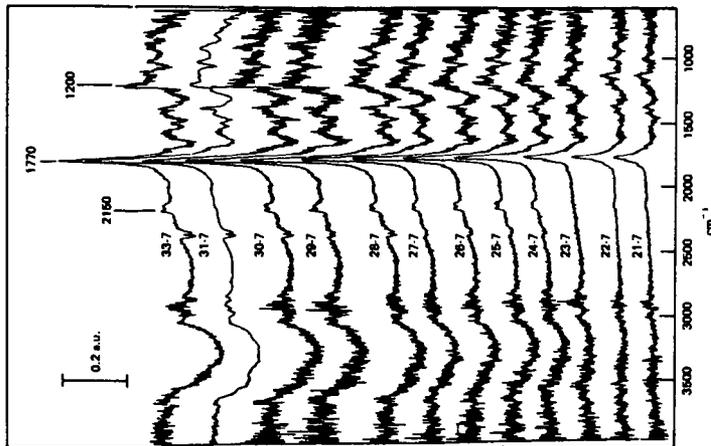


Fig. 4. Difference spectra for acetic anhydride reaction with Wyodak coal at 200°, 300°, 428°, and 450°C. (See Table 1 for correlation of spectral numbers. All spectra starting with no. 23 have been corrected for window background. See Fig. 5 for details concerning this correction.)

D₂O EXCHANGE WYODAK POWDER (D-1)

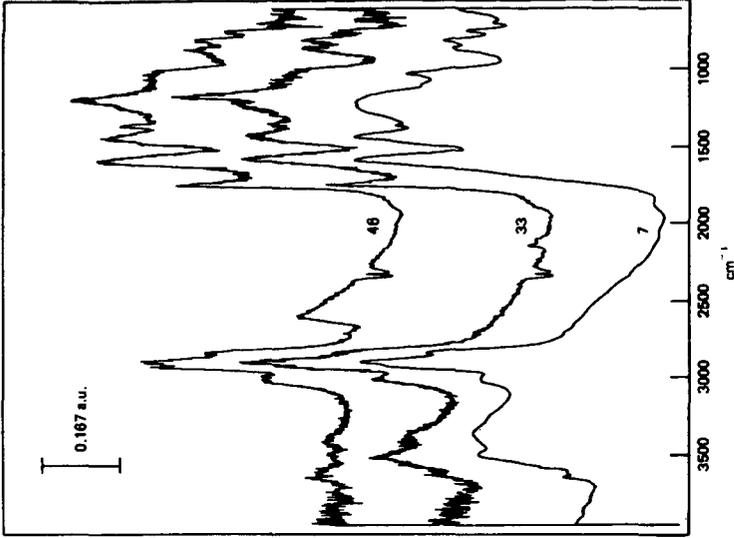


Fig. 6. Diffuse reflectance spectra of Wyodak coal: Curve 46 is the spectrum following deuterium oxide exchange of final acetylated state at 23 mtorr at 28°C, Curve 33 is the spectrum of the final acetylated state, and Curve 7 is the spectrum of the vacuum reference state.

CONDENSATE CORRECTION WYODAK POWDER (D-1)

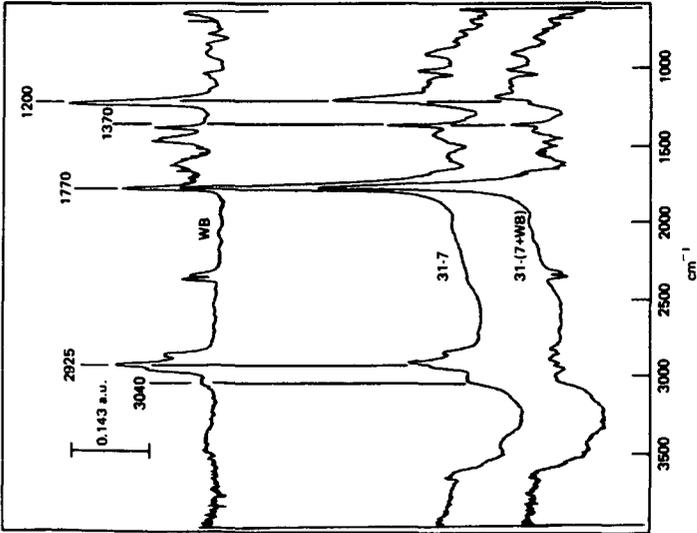


Fig. 5. Window background correction: "WB" is window background of DR cell after completion of the acetylation and deuterium oxide exchange reactions, Curve 31-7 is the difference spectrum of the acetylation reaction at 428°C for 25 min and the vacuum reference state, and Curve 31-(7+WB) is difference spectrum with window background removed.

PROGRESSIVE D₂O EXCHANGE: WYODAK POWDER (D-1)

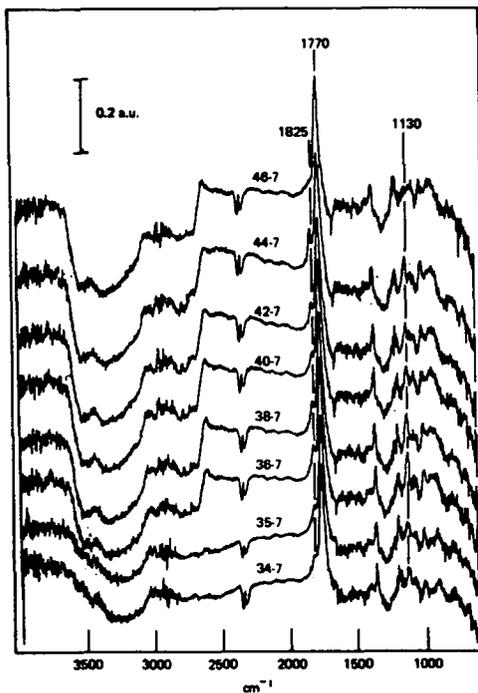


Fig. 7. Difference spectra for the deuterium oxide exchange reaction of Wyodak coal after acetylation. (See Table 1 for correlation of spectral numbers. All spectra have been corrected for window background.)