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CHARGE-TRANSFER COMPLEXES IN KRAFT LIGNIN.

PART 1: OCCURRENCE

G. S. FURMAN AND W. F. W. LONSKY

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Dedicated to Prof. Dr. Karl Kratzl on the Occasion of his 70th Birthday

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PART 1: OCCURRENCE

G. S. Furman[*] and W. F. W. Lonsky
The Institute of Paper Chemistry
Appleton, Wisconsin 54912

ABSTRACT

Charge-transfer complexes were found to occur between kraft lignin
and an added model quinone, 3,5-di-tert-butyl-1,2-benzoquinone.
The occurrence of charge-transfer interactions was also apparent
in an oxidized kraft lignin with an increased quinone content. In
these systems, free phenolic groups within the lignin were con-
sidered the donor moieties and ortho-quinones the complementary
acceptor moieties. Carbon-14 labeling revealed that the quinone
content of the investigated kraft lignin averaged 3%. These
quinones were determined to have a molar absorptivity of 528
L/mol-cm. Upon sodium borohydride reduction of this lignin, only
one-third of the absorbance decrease could be accounted for by
this number of quinones. The remaining two-thirds of the decrease
in absorbance was assigned to the disruption of charge-transfer
complexes. The quinones, therefore, played a dual role as a chro-
mophore by participating as acceptor species in these complexes.

INTRODUCTION

A major drawback to the kraft pulping process is the dark-
colored pulps which are obtained. This dark color requires the
pulps to be extensively bleached for many end uses. As is well
known, the dark color of kraft pulps originates with residual
lignin not removed during the pulping process. In the area of

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[*]G. S. Furman's present address is: Kimberly-Clark Corporation,
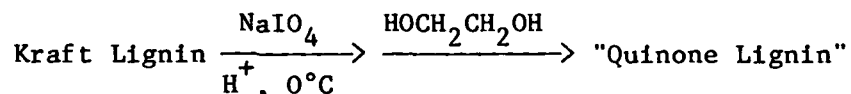Neenah, WI 54956·

absorption. Also, a relationship was observed between the absorbance at the CT maximum and the concentration of the quinone which was added to the lignin. As is shown by Fig. 3, the absorbance linearly increased at low quinone concentrations before leveling off at higher concentrations. In Fig. 3, the quinone concentration is plotted as a ratio according to the phenolic content of the lignin. Both this relationship and the effect of acetylation pointed to the fact that free phenolic groups in the kraft lignin were acting as donating moieties in this CTC.

[Fig. 3 here]

Substitution of a model phenol in place of the kraft lignin in the above system substantiated the results that were found. Again, a CT absorption was observed, this time between 2-methoxy-4-methylphenol and 3,5-di-tert-butyl-1,2-benzoquinone. This complex had a maximum absorption at 428 nm in n-hexane, with a molar absorptivity of 131 L/mol-cm (assuming complete complexation of the quinone). The CT absorption band between the model phenol and quinone was substantially reduced in intensity (79 L/mol-cm) and slightly shifted to shorter wavelengths (424 nm) when the phenol was acetylated.

CTC's in Oxidized Kraft Lignin

In another line of investigation, ortho-quinone structures were incorporated into kraft lignin by a periodate oxidation method. These structures were retained in the kraft lignin when the periodate oxidation was quenched by the addition of ethylene glycol:

$$\text{Kraft Lignin} \xrightarrow[\text{H}^+, \ 0°C]{\text{NaIO}_4} \xrightarrow{\text{HOCH}_2\text{CH}_2\text{OH}} \text{"Quinone Lignin"}$$

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The presence of ortho-quinones in the lignin was verified by visible, FTIR, and ^{13}C NMR spectroscopy. The oxidized lignins were much darker in appearance than the original lignins. Visible spectra revealed the increase in absorbance was centered near 430 nm. The $\pi-\pi^*$ absorption band of ortho-quinones occurs in this region of the spectrum.[15] FTIR spectra of the oxidized lignins (see Fig. 4) showed a strong new absorption band at 1663 cm^{-1}. Otting and Staiger[16] found the carbonyl stretching band of ten ortho-benzoquinones occurred from 1667 to 1656 cm^{-1}. ^{13}C NMR spectra of reductively acetylated, periodate oxidized lignins revealed an upfield shift in the phenolic acetate carbonyl peak (Fig. 5), resulting from steric crowding in the newly formed ortho-diacetate structures. The steric crowding effect was confirmed in model compounds.

[Fig. 4 and 5 here]

The dark color of the periodate oxidized kraft lignin is evidenced by the visible spectra in Fig. 6 and by the difference spectrum, between the oxidized and original lignins, in Fig. 7. The rationale behind the incorporation of quinones within kraft lignin was to enhance the likelihood of CT interactions. The skewed shape of the difference band in Fig. 7 led to speculation that this band was composed of two separate components; the quinone band and a CT band.

[Fig. 6 and 7 here]

That there was indeed a CT component present in this lignin was demonstrated by the effects of solvent, pressure, and derivatization on the oxidized lignin's spectrum. Charge-transfer complexes in solution are influenced by the polarity of the solvent surrounding them. For the weak $\pi-\pi$ CT interactions considered here, increases in solvent polarity result in slight red

shifts and decreases in intensity of the CT absorbance band.[17]
Difference spectra between the periodate oxidized, or "quinone
lignin," and the original kraft lignin in the solvents 2-methoxy-
ethanol and DMF are shown in Fig. 8. In terms of physical
constants DMF is the more polar solvent, having both a dielectric
constant and a dipole moment which are approximately twice as
large as those for 2-methoxyethanol.[18] As shown in Fig. 8, the
absorption maximum was slightly red-shifted in DMF, occurring at
434 nm, compared to 430 nm in 2-methoxyethanol. At the maximum,
the absorbance was 25% more intense in 2-methoxyethanol than in
DMF. The solvent behavior of the difference band, therefore,
indicated the presence of a CTC in the quinone lignin.

[Fig. 8 here]

Changes in ambient pressures also have relatively strong
influences on weak CTC's. Offen[19] has summarized these effects.
In short, CT absorption maxima shift red and increase in intensity
with increasing external pressures. In this study, solutions of
the quinone and original kraft lignins were subjected to pressures
up to 360 MPa. Their resultant spectra were then examined for
indications of CT behavior. The difference band between the
quinone lignins and original lignins in 2-methoxyethanol, see Fig.
9, increased in intensity and showed a general red shift at high
pressures. Since difference spectra are compared in Fig. 9, in-
creases in the lignin's absorbances due to the increased concentra-
tions of the lignin solutions at these high pressures canceled
out. The pressure behavior of the quinone lignin in 2-methoxy-
ethanol again indicated the presence of CTC's.

[Fig. 9 here]

Finally, derivatization of the quinone lignin provided quali-
tative evidence of the presence of CTC's in this lignin. The
derivatizations included acetylation and reductive acetylation of

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the quinone lignin. The results of these acetylations are shown
by the visible spectra given in Fig. 10. Both derivatizations
significantly reduced the visible absorbance of the quinone lignin.

[Fig. 10]

In the case of acetylation, free phenolic groups in the
lignin were derivatized to the corresponding acetates. Since free
phenolic groups are involved as donating moieties in the proposed
CTC, this would necessarily disturb these complexes. When model
acceptors were added to acetylated kraft lignin, the observed
CTC's were completely eliminated. The effect of acetylation was
similar for the quinone lignin; the decrease in absorbance was
caused by the disruption of CTC's. In the case of reductive ace-
tylation, besides the removal of CTC's due to the acetylation of
phenolics, quinones were reduced to catechols and then also acety-
lated. Consequently, two chromophore types were removed from the
lignin, and, as shown in Fig. 10, reductive acetylation had the
greater effect in reducing the lignin's absorbance.

According to the above analysis, proper subtraction of the
lignin spectra in Fig. 10 will yield the individual absorption
bands of the quinone and CTC chromophores. These difference
spectra are presented in Fig. 11. The spectrum (A-C) is a measure
of both the quinone and CTC chromophores, the spectrum (A-B) is a
measure for the CTC's in the quinone lignin, and the spectrum
(B-C) a measure for the quinones in this lignin. The derivatiza-
tions, therefore, were successful in separating the difference
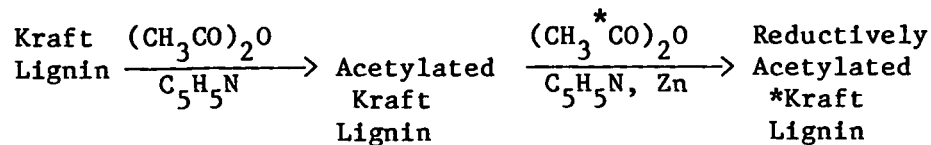band into its two component absorptions.

[Fig. 11 here]

CTC's in Kraft Lignin

The observance of CTC's when quinonoid model compounds were
added to kraft lignin and within oxidized kraft lignin pointed out
the CT capabilities of kraft lignin. The occurrence of CTC's in

unaltered kraft lignin should also be expected. However, since the quinone content in the original kraft lignin was much smaller than in the oxidized lignin, evidence for the occurrence of CTC's was more difficult to obtain. In order to ascertain if CTC's were present in the original lignin, the following approach was taken. First the actual number of quinones present in this lignin was determined. Next an absorbance was assigned to this number of quinones, based on their calculated molar absorptivity. Finally, additional absorbance present in the quinone region of the spectrum that could not be directly assigned to the quinones was assigned to charge transfer interactions.

The concentration of quinones in the original kraft lignin was determined by a carbon-14 labeling technique. In this technique, outlined below, quinones were labeled as radioactive acetates. The activity of the lignin was, therefore, directly related to the concentration of the quinones present in it.

$$\text{Kraft Lignin} \xrightarrow[\text{C}_5\text{H}_5\text{N}]{(\text{CH}_3\text{CO})_2\text{O}} \text{Acetylated Kraft Lignin} \xrightarrow[\text{C}_5\text{H}_5\text{N, Zn}]{(\text{CH}_3{}^*\text{CO})_2\text{O}} \text{Reductively Acetylated *Kraft Lignin}$$

The activities from several sets of lignins are given in Table 1. The control lignins were exposed to the radioactive acetic anhydride but not under reducing conditions. They served to establish the background radiation introduced to the lignins from acetate exchange and impurities. The raw data, in counts per minute (cpm), were converted to disintegrations per minute (dpm) from the determined efficiencies of the samples. The "Net DPM" values were obtained by subtracting the control dpm values from the corresponding sample dpm values after normalizing the samples to an activity per mg basis. The "Actual DPM" values are dpm values for the samples on a total weight basis. From these values and the specific activity of the radioactive acetic anhydride $(1.62 \times 10^4$ Bq/mmol), the number of millimoles of labeled acetic anhydride incorporated within the lignin samples was calculated.

This value was equal to the millimolar quantity of quinones in the sample, since each acetic anhydride molecule contained two radioactive carbons, and since there were two sites for acetylation in each quinone. Finally, the quinone concentration for each sample was calculated by dividing the molar quantity of quinones by the molar quantity of acetylated lignin in that sample. For the original kraft lignin, the quinone concentration averaged 3.05%. Other quinone concentrations in Table 1 follow the expected trends.

[Table 1 here]

A molar absorptivity was calculated for the quinones in the original kraft lignin from their concentration and a corresponding absorbance. The absorbance was obtained from the difference spectrum between the acetylated and reductively acetylated original kraft lignins. This spectrum revealed the quinone maximum occurred at 431 nm, with an intensity of 0.026 AU (2-methoxy-ethanol as solvent.) Substituting the values of concentration and absorbance into Beer's Law, a molar absorptivity of 528 L/mol-cm for the quinones in the original kraft lignin was calculated. This value was similar to the molar absorptivities found by Imsgard and coworkers[2] for the ortho-quinones of acetoguaiacone and isoeugenol (600 and 741 L/mol-cm, respectively).

Once the molar absorptivity and the concentration of the quinones in the original kraft lignin were known, the percentage of absorbance at the quinone maximum actually due to quinones, and the percentage of absorbance due to their participation in CTC's, was calculated. Spectra resulting from the sodium borohydride reduction of the lignin, which removed quinones and consequently CTC's, were used to calculate the total absorbance due to these two chromophores. Difference spectra between the original and sodium borohydride reduced kraft lignins revealed a drop in absorbance averaging 0.01 AU (at 431 nm). The proportion of this

Table 1. Activities and quinone concentrations of kraft lignins.

Lignin Type	Sample No.	CPM[a]	% Efficiency	DPM	DPM/ mg	Net DPM/ mg[b]	Actual DPM	mmol of *Ac$_2$O[c]	Quinone Conc., %
Control	1	882	5.91	14,924	350.3	--	--	--	--
	2	942	5.90	15,966	366.2	--	--	--	--
Original kraft lignin	3	3466	16.28	21,290	481.7	123.45	5,456	5.61	3.13
	4	3937	18.20	21,632	475.4	117.15	5,330	5.48	2.97
NaBH$_4$ reduced	5	6147	37.85	16,240	384.8	26.55	1,120	1.15	0.67
	6	6113	35.12	17,406	381.7	23.45	1,069	1.10	0.60
Quinone lignin[d]	7	1212	3.53	34,334	725.9	367.65	17,390	17.9	10.61
	8	1807	13.76	13,132	795.9	437.65	7,221	7.42	12.61
	9	2307	6.70	34,433	812.1	453.85	19,243	19.8	13.09

[a]At least three separate determinations each; at 95% confidence level, values within 1% of the mean.

[b]Net DPM = (sample DPM) - (average control DPM).

[c]Values multiplied by 1000.

[d]Lignin was previously treated with sodium borohydride, diimide, and EDTA, then periodate oxidized 40 seconds.

absorbance decrease actually due to the removal of the quinone absorbance from the sample was calculated to be 0.0284 AU or 31.2% of the total.

The remainder of the decrease in absorbance caused by sodium borohydride reduction was assigned to CTC's in which the quinones were participating as acceptor species. This meant the major portion (68.8%) of the absorbance decrease at 431 nm was due to the removal of CTC's. If every quinone is assumed to be participating in CT complexation, a molar absorptivity for the complex of 1163 L/mol-cm may be calculated. This assumption is reasonable, considering the high phenol to quinone ratio in the original kraft lignin. This molar absorptivity is typical of the values found for other phenol-quinone CTC's.[12,13]

Nature of CTC's in Kraft Lignin

From the observations made on CT interactions in systems involving kraft lignin, charge-transfer complexes in kraft lignin may be generally described as follows. Interactions are predominantly between free phenolic and ortho-quinone structures in lignin, acting as the donating and accepting halves of the complex, respectively. CT interactions are expected to be primarily intramolecular due to the steric constraints present between large lignin molecules. In addition, hydrogen bonding may play an important role in attracting the two halves of the complex into close proximity, thereby allowing CT interactions to occur.

EXPERIMENTAL

Lignin Isolation and Analysis

Loblolly pine chips were cooked to a kappa number of 39 employing the following conditions: effective alkali, 16%; sulfidity, 27.5%; final temperature, 173°C; cooking time, 3 h (90 min to

final temp.). The kraft lignin was isolated by acid precipitation
(pH 2-3 with H_2SO_4) of the resultant black liquor. H_2S was
removed from the acidified black liquor using a rotary evaporator,
and the precipitated lignin was then collected by centrifugation.
The lignin was washed to a neutral pH with distilled water, dried
thoroughly, and ground to a uniform powder.

Excess carbohydrate material was removed from the lignin based
on the carbohydrates insolubility in 2-methoxyethanol. In this
procedure, the lignin was dissolved in an excess of 2-methoxy-
ethanol (Mallinckrodt AR), and the insoluble carbohydrate material
filtered off. The lignin in solution was recollected by removal
of the 2-methoxyethanol on a rotary evaporator. The oily residue
was dried over P_2O_5 in a vacuum desiccator, treated with distilled
water, and collected by filtration. It was redried and ground to
a uniform powder.

Ash contents, elemental compositions, and methoxyl contents
were determined at the Microanalytical Laboratory of the Univer-
sity of Vienna, Waehringestrasse 38, A-1090 Vienna, Austria.
These contents were as follows: 63.46% C, 5.87% H, 26.49% O,
3.53% S, 14.74% OMe, and 0.66% ash. Carbohyrate analyses were
determined by the alditol acetate method.[20] The lignin contained
1.3% carbohydrates after the 2-methoxyethanol treatment, predomi-
nantly of the xylose variety. The phenolic hydroxyl content of
the kraft lignin (58 per 100 C_9 units) was determined according to
the aminolysis method given by Månsson.[14]

Instrumental Methods

Electronic absorption spectra were recorded on a Perkin-Elmer
320 Spectrophotometer. High pressure electronic spectra were
obtained on a modified Cary Model 14 spectrophotometer at the
University of California at Santa Barbara. The high pressure
optical cell, window assembly, and sample capsule have been
described by Dawson and Offen.[21] Data storage and manipulation

were accomplished with Apple III computers interfaced to the spectrophotometers. Solution spectra of lignin samples were obtained in either spectroscopic grade DMF (Baker), or 2-methoxyethanol (Burdick and Jackson).

Infrared spectra of lignin samples were recorded as KBr pellets on a Nicolet 7199C Fourier Transform Infrared Spectrometer.

Carbon-13 NMR spectra were recorded on a Joel FX100 Fourier Transform NMR Spectrometer using TMS as a reference. Spectra of the reductively acetylated lignins, shown in Fig. 5, were obtained in $CDCL_3$ solution (200-300 mg/0.5-0.6 mL) using a 5 mm tube. For these samples, 60,000 to 65,000 transients were accumulated using 70° pulses, one second apart. The spectra were recorded at a temperature of 52°C.

Lignin Preparations

Lignin samples were acetylated in pyridine/acetic anhydride (2:1 by volume). After standing overnight at room temperature, the reaction mixtures were hydrolyzed over crushed ice. The acetylated lignin precipitate was collected by suction filtration. The lignin was then washed with cold distilled H_2O followed by cold 0.01N HCl and cold distilled H_2O again. It was then dried over P_2O_5 and KOH.

Reductive acetylation of lignin samples was also carried out in pyridine/acetic anhydride (2:1). Zinc dust (20-30% by weight of lignin) was used as the reducing agent. The reaction flask, equipped with a $CaCl_2$ tube, was placed in a 100°C glycerol bath for one hour. The mixture was continuously stirred during this time. After cooling to room temperature, any excess Zn dust was removed by filtration and washed with several mL of a 1:1 mixture of acetic acid and pyridine. The combined filtrates were hdyrolyzed over crushed ice and the reductively acetylated lignin collected as above.

Periodate oxidation of kraft lignin was conducted in a manner similar to that given by Marton and Adler.[22] However, the oxidation

was halted by the addition of a large excess of ethylene glycol instead of SO_2. Following addition of the ethylene glycol, the reaction solution was stirred for a few minutes and then poured into a large volume of cold distilled water. The precipitated, oxidized lignin was concentrated by centrifugation and collected by filtration. It was washed with cold distilled water and dried over P_2O_5 and KOH in a vacuum desiccator.

Sodium borohydride reduction of kraft lignin was conducted similarly to the procedure given by Marton.[23]

Labeling Techniques

Quinone groups in kraft lignin were tagged as carbon-13 or carbon-14 acetates using the reductive acetylation procedure outlined above. The reductive acetylations were performed on kraft lignin which had been twice previously acetylated, and by using the appropriately labeled acetic anhydride. Carbon-13 enriched $(CH_3*CO)_2O$ (90%) was obtained from Stohler Isotope Chemicals, Waltham, MA. Carbon-14 labeled $(CH_3*CO)_2O$ (liquid under vacuum; specific activity 20 mCi/mmol) was purchased from Amersham Corp., Arlington Heights, IL.

Activities of radioactive lignin samples were determined on a Beckman LS 380 Liquid Scintillation System. The samples (40–50 mg) were dissolved in 10 mL of dioxane cocktail [naphthalene (100 g) and 2,5-diphenyloxazole (5 g) in 1 liter of dioxane] and placed in glass vials for counting. The efficiencies of these samples were determined by the internal standard method.[24]

Compounds

The compounds 2-methoxy-4-methylphenol and 3,5-di-tert-butyl-1,2-benzoquinone were purchased from Eastman Kodak Company and Aldrich Chemical Company, respectively. 1-Acetoxy-2-methoxy-4-methylbenzene was synthesized from the corresponding phenol using a method similar to that given by Ludwig and coworkers.[25]

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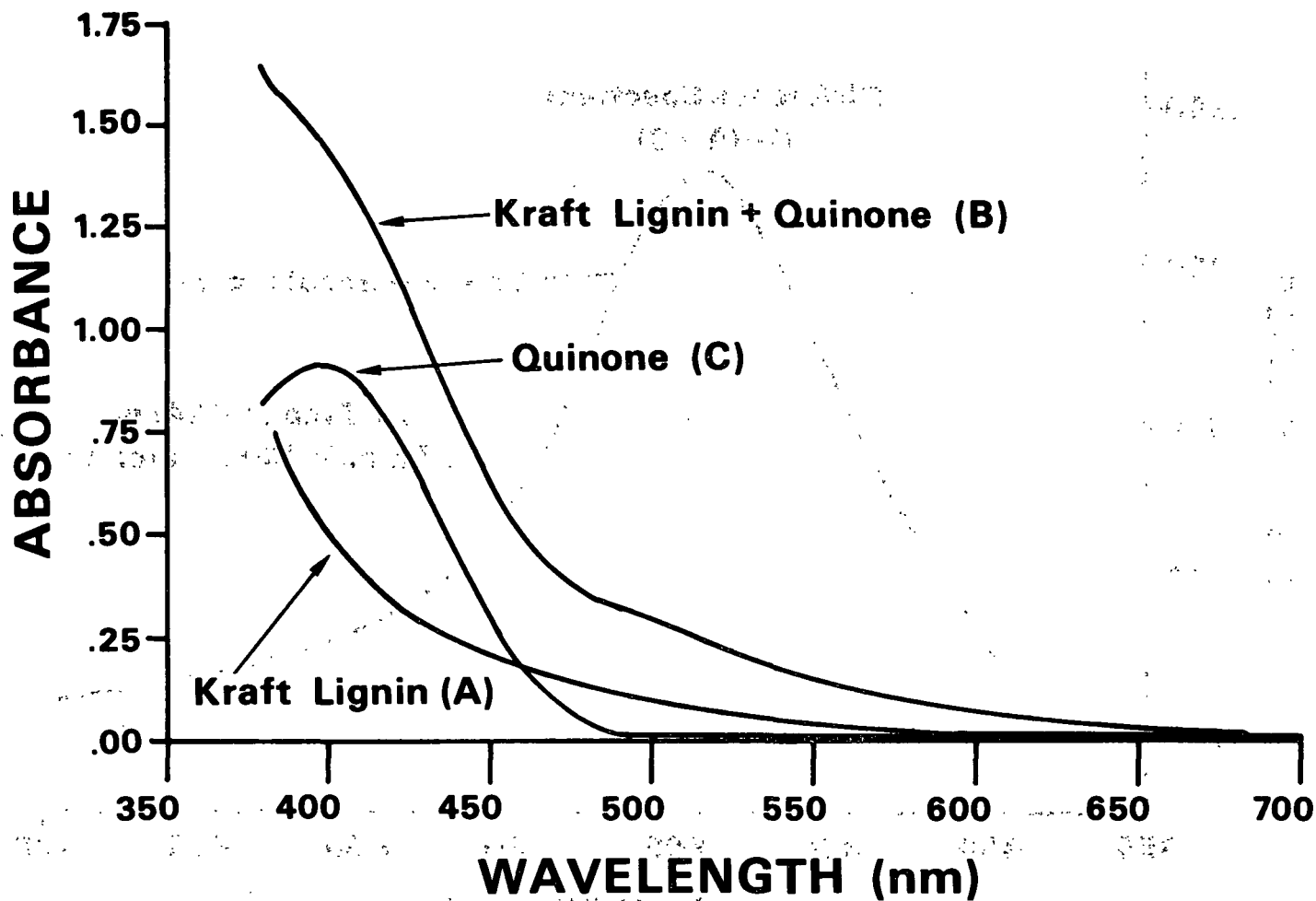
Figure 1. Visible spectra of (A) kraft lignin [1.63 x 10^{-3}M], (C) 3,5-di-tert-butyl-1,2-benzoquinone [5.00 x 10^{-4}M], and (B) kraft lignin plus quinone [same concentrations]; 2-methoxyethanol as solvent.
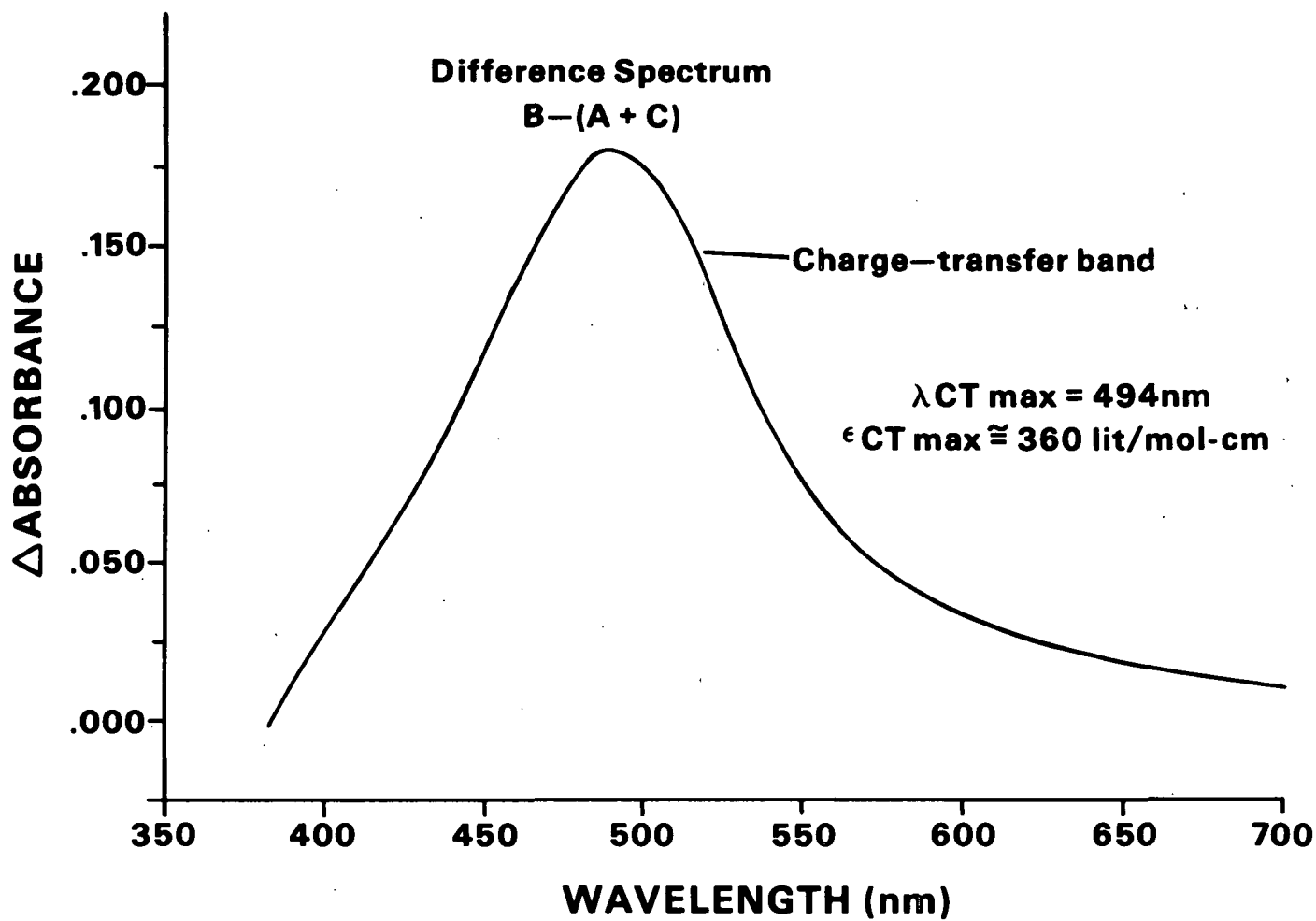
Figure 2. Difference spectrum from Fig. 1.
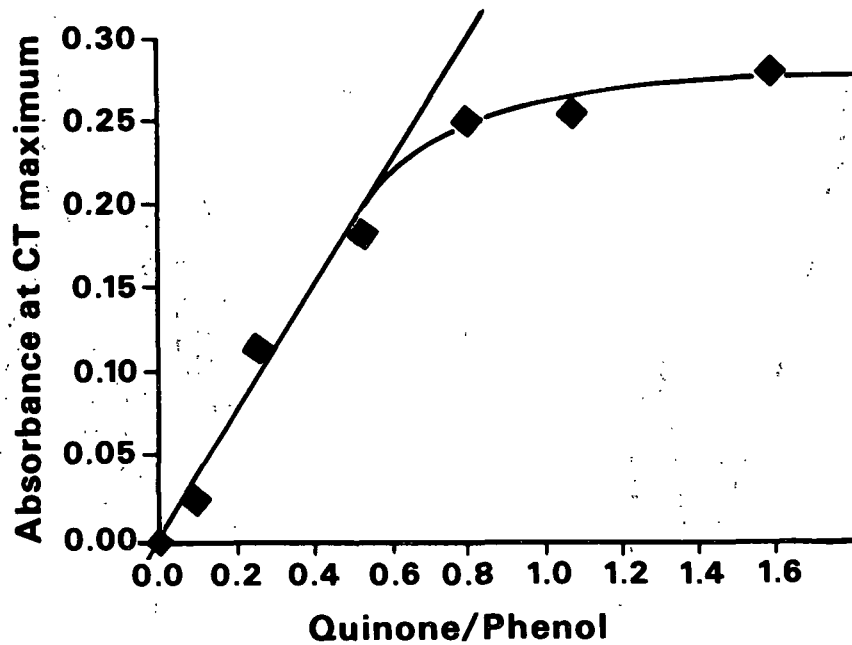
Figure 3. Effect of quinone/phenol ratio on absorbance of CTC between kraft lignin and 3,5-di-tert-butyl-1,2-benzoquinone.
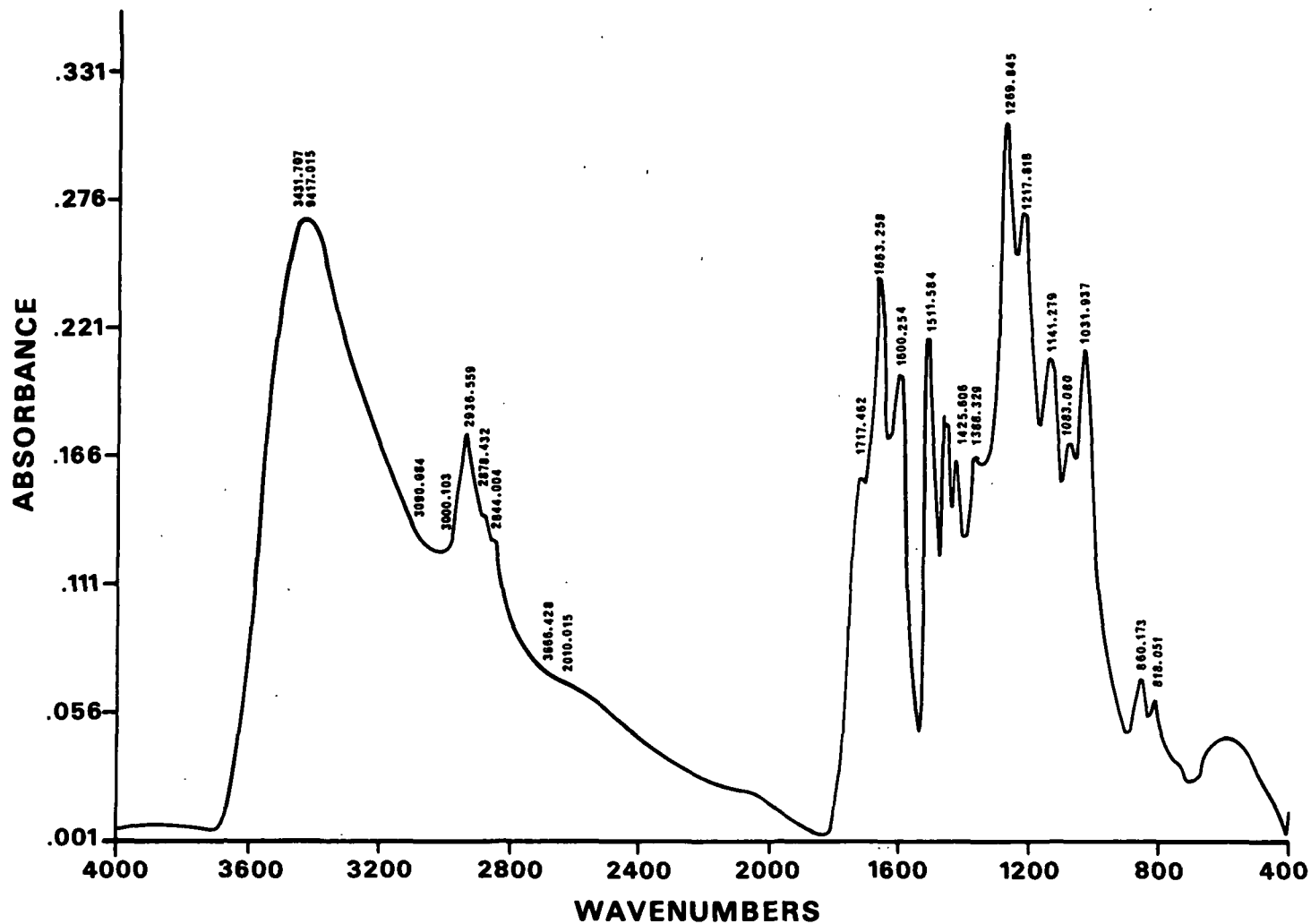
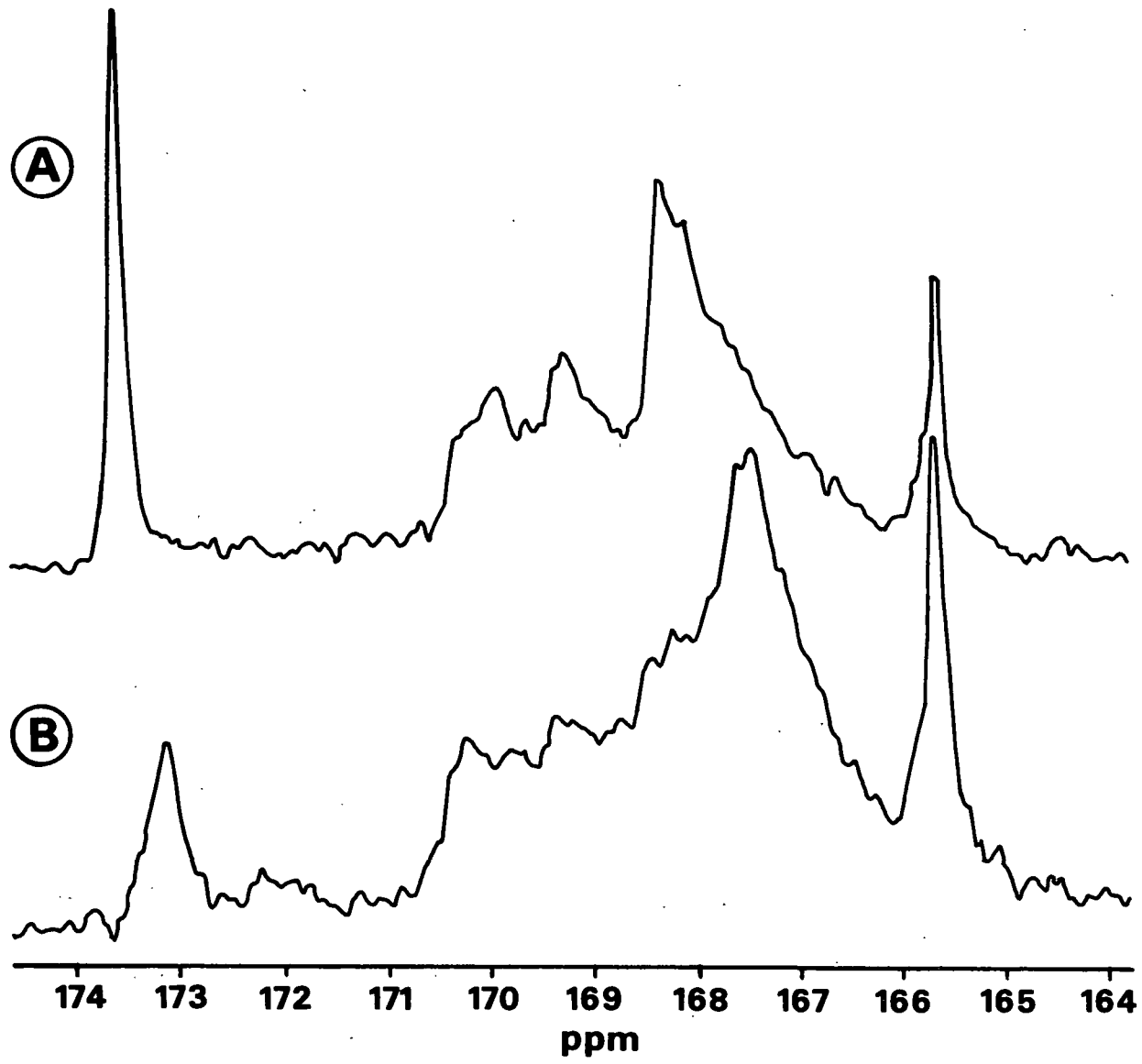Figure 4. FTIR spectrum of periodate oxidized (two minutes) kraft lignin; ethylene glycol added to halt oxidation.

Figure 5. ^{13}C NMR spectra of: (A) the acetylated kraft lignin and of (B) the reductively acetylated periodate oxidized kraft lignin.
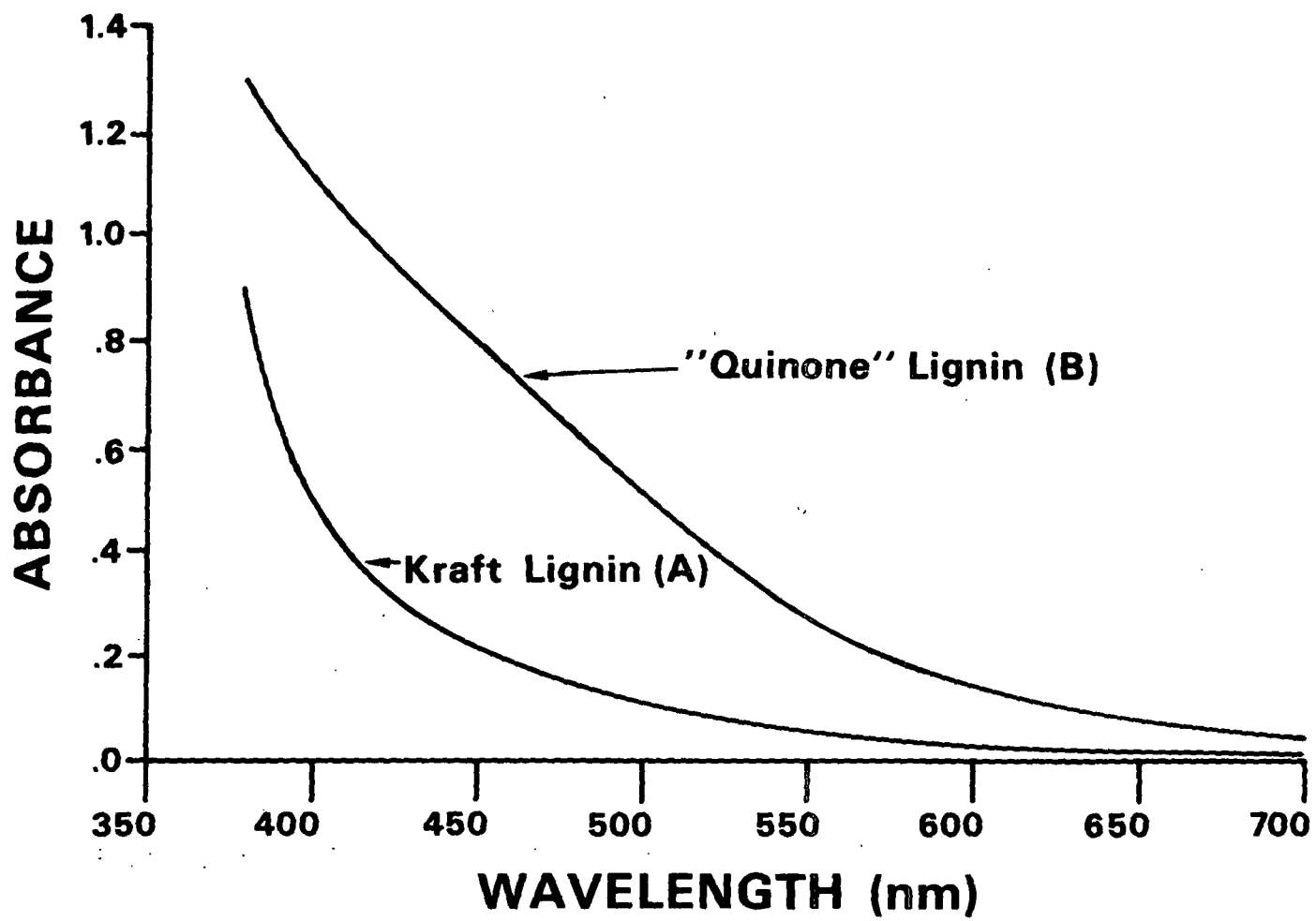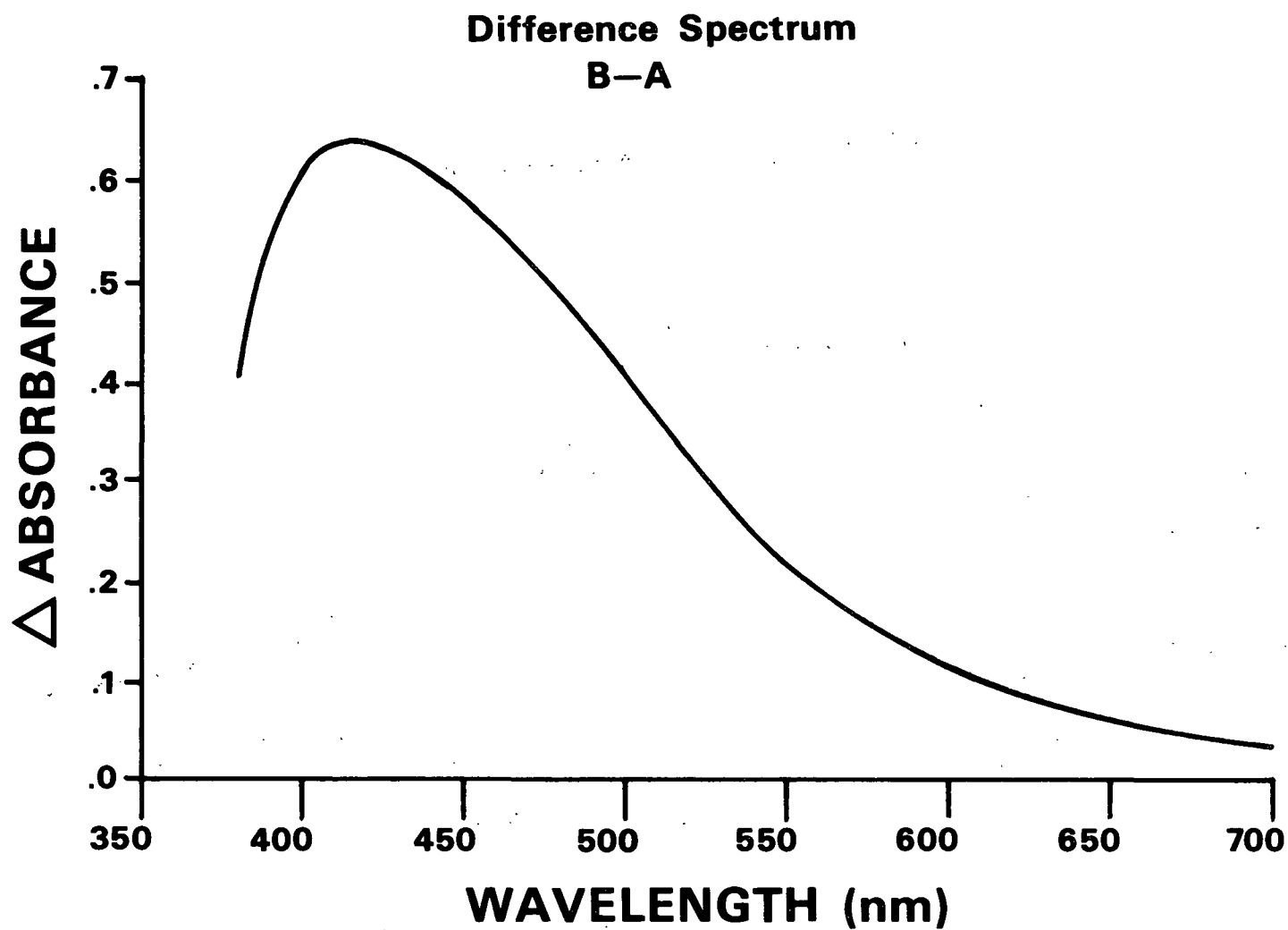
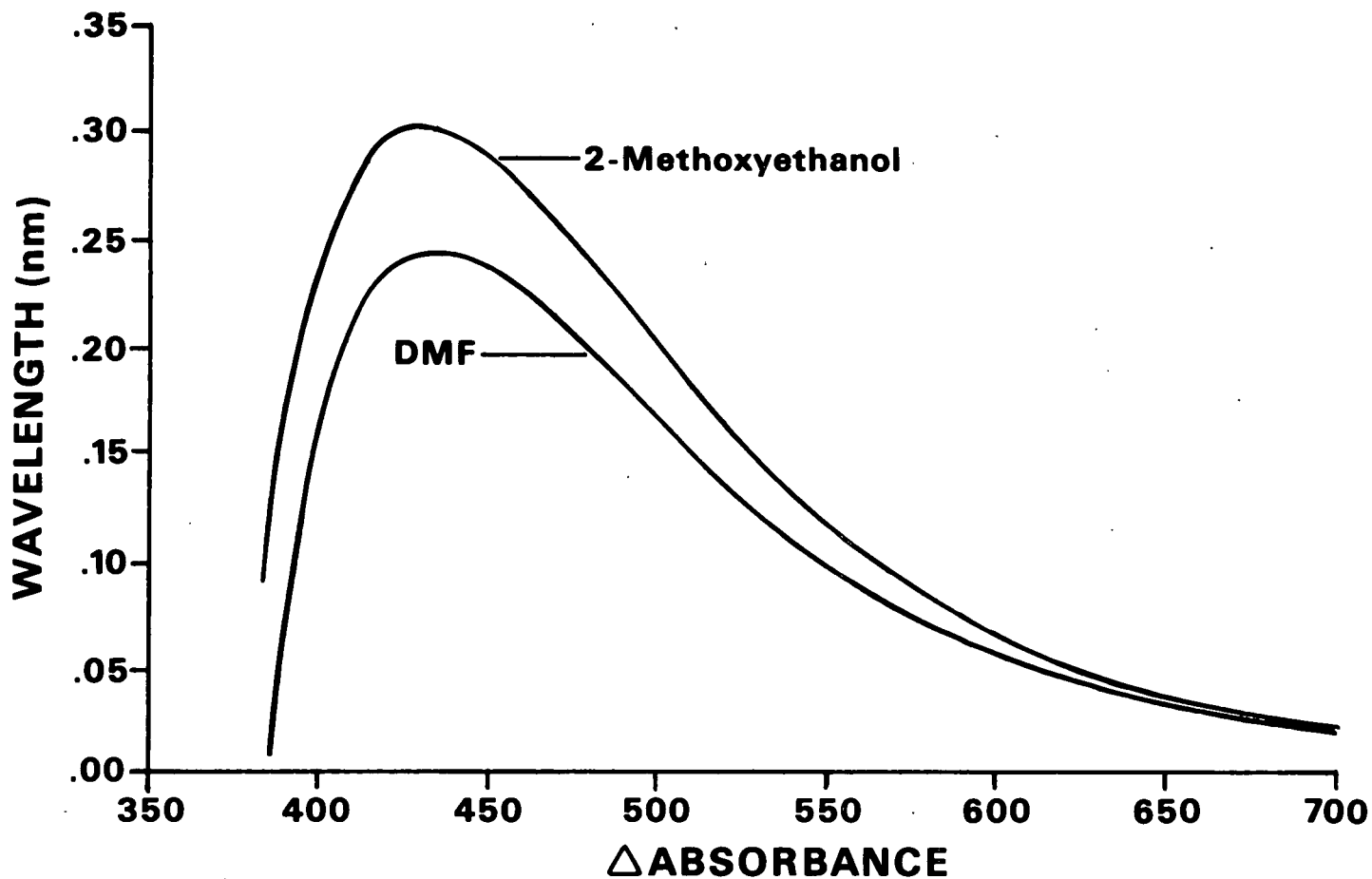Figure 6. Visible spectra of "quinone lignin" and original kraft lignin.

Difference Spectrum
B—A

Figure 7. Difference spectrum from Fig. 6.

Figure 8. Difference spectra between "quinone lignin" and original kraft lignin; concentrations of subtracted lignins were 7.5 mg/25 mL of solvent.
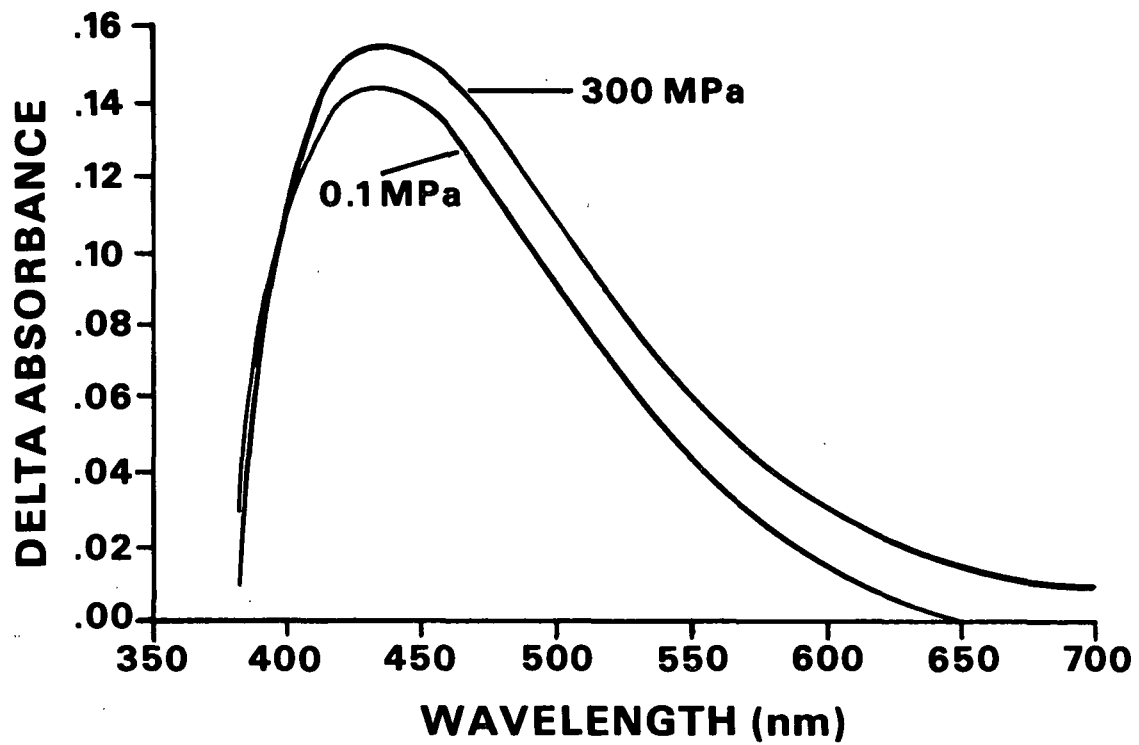
Figure 9. Quinone lignin minus original lignin in 2-methoxy-
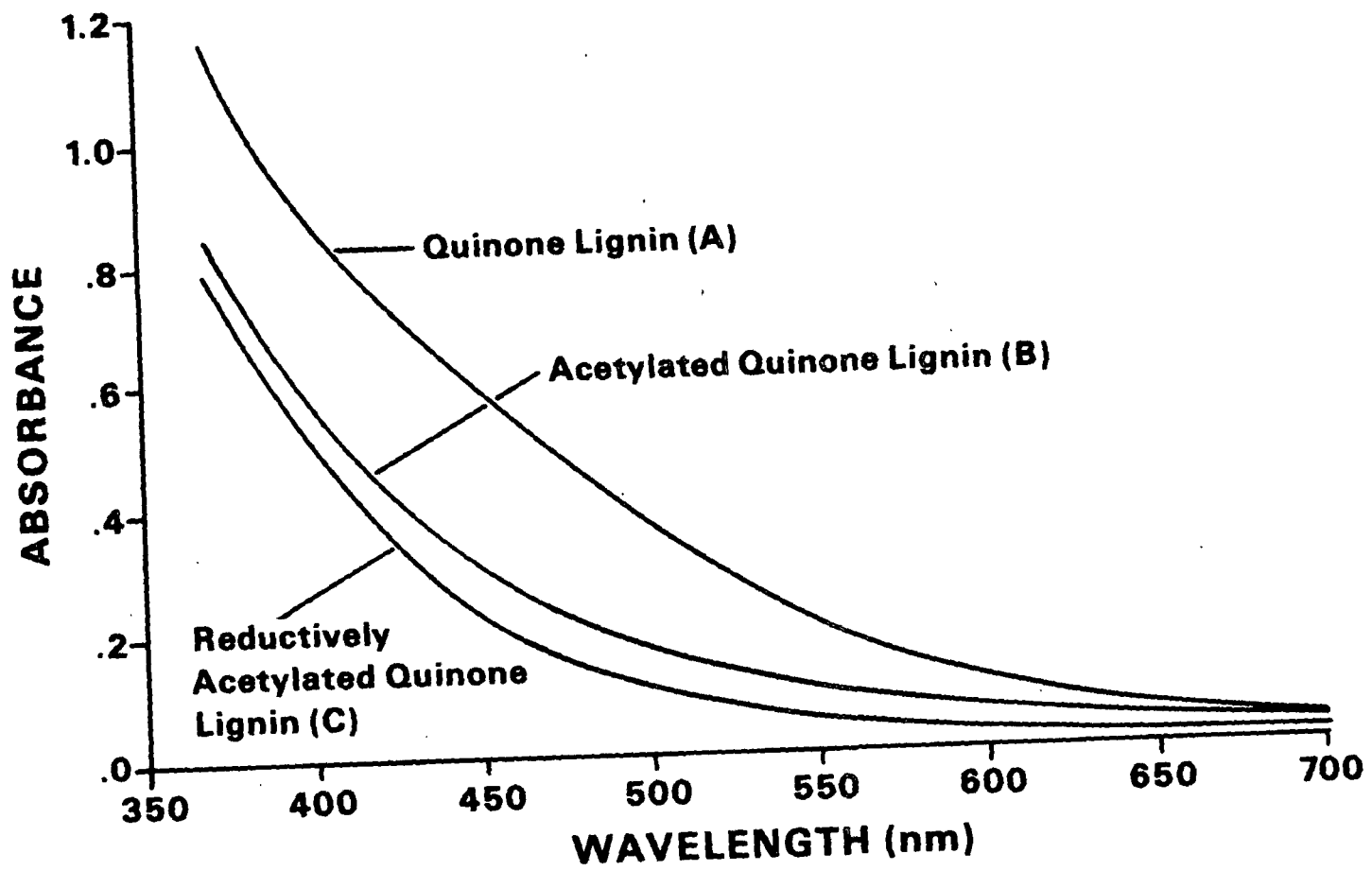ethanol.

Figure 10. Visible absorption spectra of quinone lignin, acetylated quinone lignin, and reductively acetylated quinone lignin; concentration, 7.6 mg/25 mL DMF.
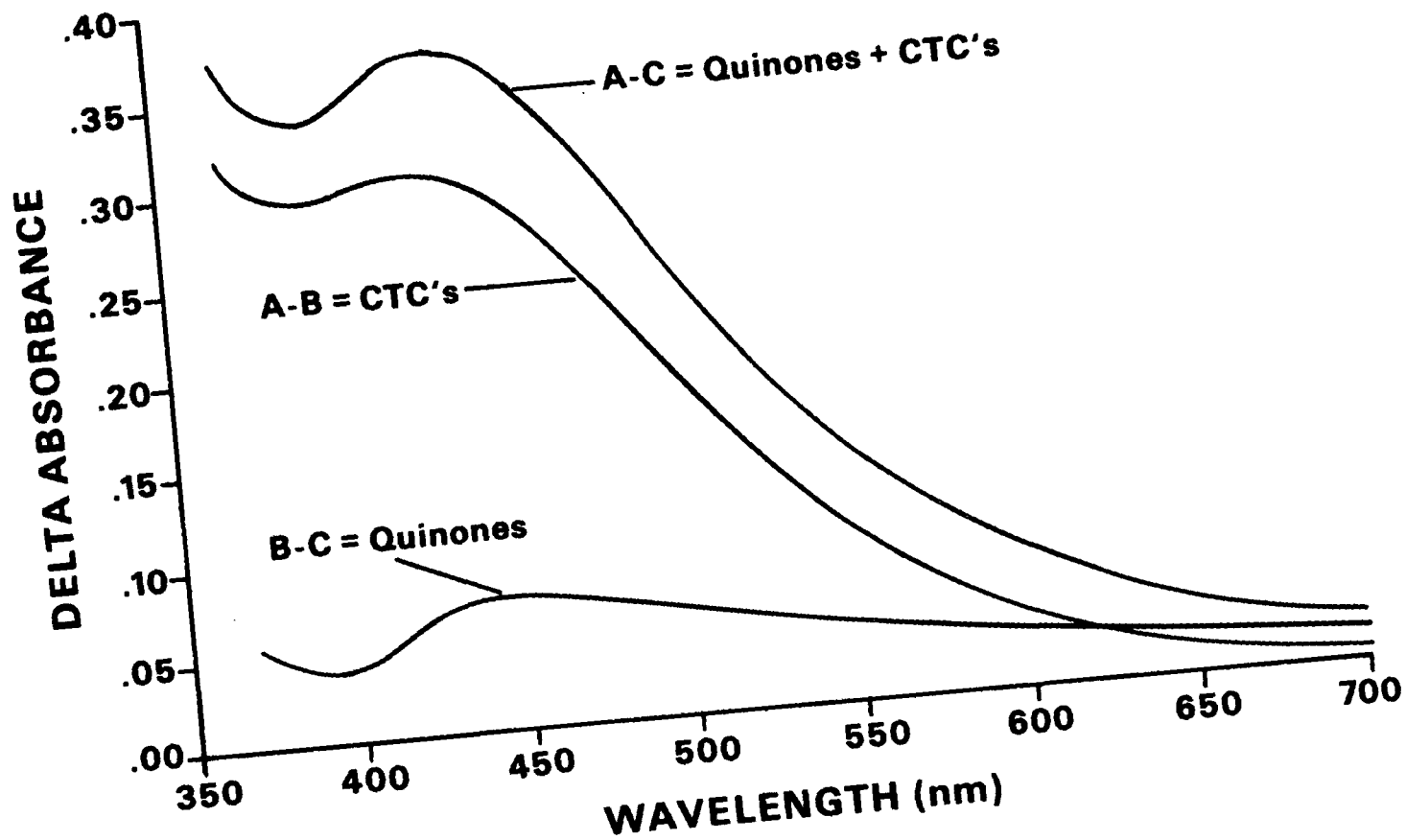
Figure 11.   Difference spectra from Fig. 10.

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AUTHOR-Transfer Complexes in
Charge-Transfer Complexes in

TITLE Kraft Lignin.
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