

INFRARED STUDIES  
OF CELORINATED STARCH

by

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## INTRODUCTION

Infrared spectroscopy is widely used as a technique for the analysis of chemical compounds, being especially useful for the analysis of organic materials. The technique is based on the ability of many atomic configurations to absorb radiation of characteristic frequencies, these frequencies usually occurring in the infrared range. Some of these configurations and the frequencies they absorb are listed by Randall et al (1). The infrared spectrum of a compound containing any of these absorbing groups will show absorption bands at the characteristic frequencies. For some of the less complex molecules the characteristic frequencies can be calculated mathematically according to methods described by Herzberg (2), but in general they are determined experimentally. The frequency at which a particular atomic group absorbs is often influenced by the relationship of that group to the remainder of the molecule and may also depend somewhat on the physical state of the material. Because of the former effect the spectrum often yields information pertaining to the structure of the molecule which is not obtainable by other means. Thus the infrared spectrum of a compound may be considered one of its physical characteristics and will serve for identification purposes just as do other fundamental characteristics.

## STATEMENT OF THE PROBLEM

A process for the chlorination of starch in liquid chlorine (3) was developed by the Starch Laboratory at Kansas State College

under the direction of Dr. H. N. Barham. Subsequently, a kinetic study was undertaken by E. S. Stickley as partial requirement for the Ph. D. degree (4). During the course of this work, a series of products was prepared which, according to the chemical analyses, contained certain functional groups in variable amounts. Since the nature and course of the reaction of liquid chlorine with starch is related to the functional groups in question and to their development, it seemed highly desirable to check the results of chemical analyses with those obtained by some physical means. The most likely approach which suggested itself for this purpose was the use of infrared analysis.

The purpose of the present work was to perform the infrared analysis of the chlorinated starch products. The analysis required the development of techniques for obtaining infrared spectra of the products. When obtained, the spectra were to be evaluated qualitatively and quantitatively if possible.

The starch products used in the work, and some of their chemically determined characteristics are listed in Table 1.

Table 1. Chlorinated starch products and their characteristics as determined by chemical analyses. Information from reference (4).

Product	Reaction time	$M_n$	C=O	$Cl_G$	Secondary OH
SC-1E	0 hours	162.14	0.0	0.0	2.00
SS-16	36.5 "	168.40	.19	.193	1.81
SS-17	38 "	169.56	.21	.228	1.78
SS-18	40 "	170.00	.20	.240	1.80
SS-19	42 "	188.73	.53	.803	1.45
SS-20	44 "	217.36	1.45	1.688	.50
SS-21	48 "	207.38	1.60	1.407	.38
SS-22	72 "	219.85	1.60	1.769	.37

$M_n$  is the equivalent weight of the glucose unit,  
C=O is the number of C=O groups per glucose unit,

$Cl_2$  is the number of chlorine atoms per glucose unit, Secondary OH is the number of secondary OH groups per glucose unit.

All the samples listed are presumed to consist of varying amounts of the three structures shown in Fig. 1.

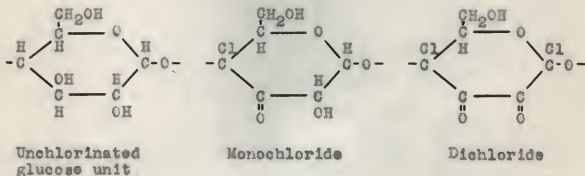


Fig. 1. Structures occurring in chlorinated starch samples (3).

#### EXPERIMENTAL METHOD

All the spectra used and referred to in this work were obtained using an oil mull technique. This technique is used for samples in the solid state and consists of suspending the particles of the powdered sample in a suitable oil. The oils used in this work were Perfluorolube Oil PGX-512 for the spectral region from 2 to 7 microns, and a mixture of Nujol and Vaseline, hereafter referred to as Nu-Va, for the spectral region from 8 to 24 microns. The products as obtained were in the powdered form. These were mixed with the oil in the desired proportion by weight, which was in most cases either five percent or ten percent. The mixture, which shall now be referred to as the mull, was then ground with a motor driven mortar and pestle to reduce the

particle size if possible and to insure a homogeneous mull. The sample prepared in such a fashion was then placed in the conventional rock salt cell, consisting of two rock salt plates separated by an aluminum spacer. The spectrometer used was a Perkin Elmer Model 12C Infrared Spectrometer with a Leeds and Northrup Speedomax Recorder. For the spectral region from 2 to 12 microns the NaCl prism was used, while the KBr prism was utilized for the region from 12 to 24 microns. Curves recorded by the Speedomax Recorder gave the intensity of radiation transmitted by the cell containing the mull and also that transmitted by the cell containing only the oil. The former is called the transmitted intensity  $I$ , and the latter is considered the incident intensity  $I_0$ . From the curves of  $I$  and  $I_0$ , the optical density, defined as  $D = \log I_0/I$ , was computed.

## DISCUSSION AND RESULTS

### Effects of Grinding

Before proceeding to the analysis of the spectra it seems expedient to take note of the changes in the spectrum of a given sample with changes in the amount of grinding the sample received. The grinding, as previously noted, was done with a motor driven mortar and pestle which made long periods of grinding possible. It was also felt that more uniformity in amount of grinding was possible with this arrangement than if the grinding had been done manually. Plates I and II illustrate the type of changes which occurred in the spectrum of a particular



sample with changes in amount of grinding. Plate I, Fig. 1, is a plot of optical density versus wave length from 2 to 7 microns for a mull of sample SS-19 (10 percent by weight) in FCX-512 for various grinding times. Only the curves for grinding times of 0, 2, and 18 hours are shown, the others ranging between the extremes of 0 and 18 hours. Plate I, Fig. 2, is a plot of optical density versus grinding time for specific choices of wave length. The wave lengths chosen for representation were those at which characteristic absorptions occurred, that is the wave lengths at which maxima occurred in Plate I, Fig. 1. For purposes of comparison, one wave length was chosen at which no characteristic absorption occurred. Plate II, Figs. 1 and 2, show similar curves for wave lengths from 7.5 to 13 microns for a mull of sample SC-1E (10 percent by weight) in Nu-Va. The amount of grinding in this instance was recorded in total number of strokes of the pestle, rather than in time of grinding. This was felt to be a more reliable measure of the amount of grinding received by the sample. Both Plate II, Fig. 2, and Plate I, Fig. 2, indicate a tendency for optical density to increase with grinding at wave lengths of characteristic absorption, whereas at wave lengths of no characteristic absorption, the optical density shows a tendency to decrease with grinding. It was assumed that the only effect of grinding on the sample was to decrease the particle size, and accordingly the spectral changes in regions of no characteristic absorption were taken to be due to a decrease in the radiation scattered by the particles. A

EXPLANATION OF PLATE I

Fig. 1. Spectrum of 10 percent SS-19 in FCX-512 for various grinding times.

(————) 0 hours grinding;  
(-----) 2 hours grinding;  
(.....) 18 hours grinding.

Fig. 2. Plot of D versus grinding time at various wave lengths for mull of Fig. 1.

(———○———) 2.90 microns;  
(———□———) 3.31 microns;  
(———△———) 5.64 microns;  
(.....×.....) 6.65 microns.



Plate I

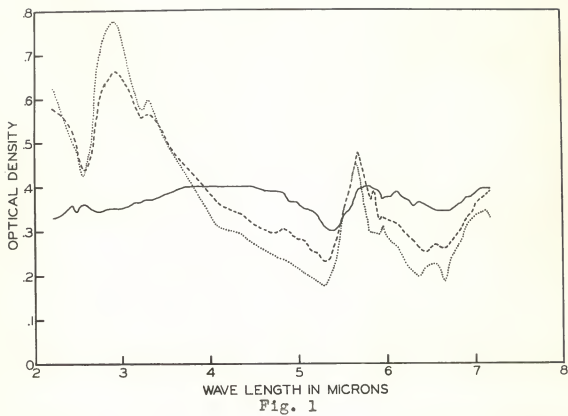


Fig. 1

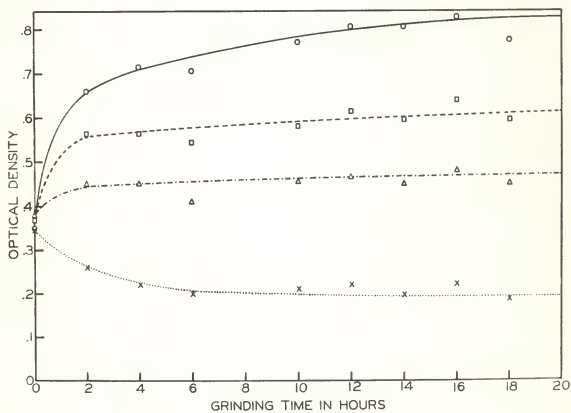


Fig. 2

# EXPLANATION OF PLATE II

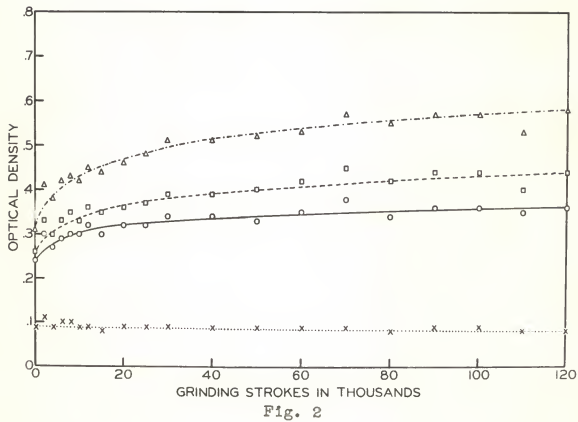
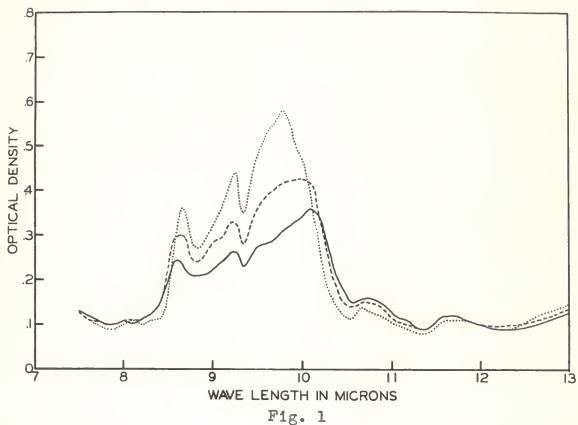
Fig. 1. Spectrum of 10 percent SC-1E in Nu-Va for various amounts of grinding.

( ————— ) 0 strokes;  
( - - - - - ) 10,000 strokes;  
( ..... ) 120,000 strokes.

Fig. 2. Plot of D versus amount of grinding at various wave lengths for mull of Fig. 1.

( ———○——— ) 8.65 microns;  
( ---□--- ) 9.25 microns;  
( ---△--- ) 9.77 microns;  
( .....×..... ) 11.30 microns.

## Plate II



number of workers, among them Gamble and Barnett (5) and Henry (6), have investigated the effects of changes in particle size on scattering. The results indicated in Plates I and II for regions of no characteristic absorption are in qualitative agreement with the results of these workers. The primary concern in this work, however, was with the spectral changes at wave lengths of characteristic absorption. As the particle size is decreased, there appears to be a distinct increase in optical density at these wave lengths. This increase may be partly accounted for by supposing that in a sample composed of large particles, many of the atomic groups which would contribute to the optical density at a particular wave length are inaccessible, due to their location in the interior of a large particle. However, this does not account for the total absence of an absorption peak at 2.9 microns in the unground sample, as shown in Plate I, Fig. 1. Another noticeable characteristic is the shift of the absorption maxima as particle size decreases. This effect has been noted by Kortüm (7), who suggests that it is possibly connected with the influence of particle size on anion and lattice vibrations. This shift in wave length toward lower values and also the increased optical density may possibly be due to a decrease in the amount of hydrogen bonding as the particles are broken up.

No further explanation for the effects described in the previous paragraph can be suggested without additional study. At this time it is desirable to take note of their existence and to indicate that they must either be eliminated or be taken into

account when data including them is to be used quantitatively. In obtaining the spectra referred to in the remainder of this work, the samples to be compared were given the same amount of grinding and the assumption was made that the particle size and size distribution was the same in all samples.

### Qualitative Discussion of the Spectra

Plate III, Figs 1, 2, and 3, are reproductions of the spectra of three of the samples. The complete spectral region from 2.2 to 24 microns was covered, except for the region between 7.3 and 7.5 microns which was inaccessible due to strong absorptions by the oil vehicles. For the portion from 2.2 to 7.3 microns the mulls were five percent by weight of sample in FCX-512, ground 50,000 strokes. For the portion of the spectrum from 7.5 to 24 microns the mulls were five percent by weight of sample in Nu-Va, ground 25,000 strokes. The spectra from 2.2 to 12.5 microns were obtained with the NaCl prism, and from 12 to 24 microns with the KBr prism. The sample cell thickness in all cases was approximately .05 millimeter.

The regions of interest in Plate III are reproduced on a larger scale in Plate IV and five of the eight samples are represented. The assignments of the bands are tabulated in Table 2.

### EXPLANATION OF PLATE III

Fig. 1. Spectra of several chlorinated starch products from 2.2 to 7.3 microns. Concentration five percent by weight in FOX-512. NaCl prism.

( ————— ) SC-1E;  
( ..... ) SS-18;  
( ----- ) SS-22.

Fig. 2. Spectra of several chlorinated starch products from 7.5 to 12.5 microns. Concentration five percent by weight in Nu-Va. NaCl prism.

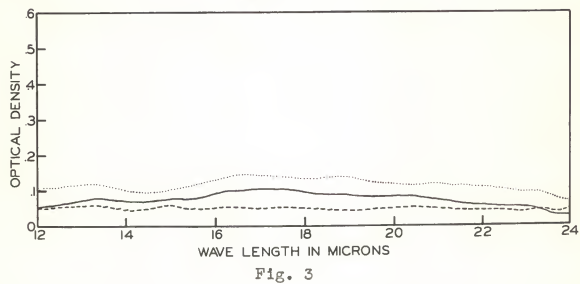
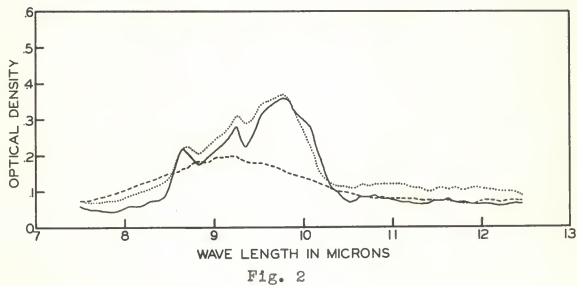
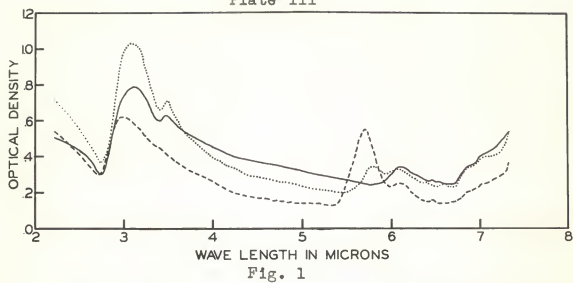
( ————— ) SC-1E;  
( ..... ) SS-18;  
( ----- ) SS-22.

Fig. 3. Spectra of several chlorinated starch products from 12 to 24 microns. Concentration five percent by weight in Nu-Va. KBr prism.

( ————— ) SC-1E;  
( ..... ) SS-18;  
( ----- ) SS-22.



## Plate III



# EXPLANATION OF PLATE IV

Figs. 1 to 3. Portions of the spectra of Plate III plotted on an expanded scale.

( ————— )	SC-1E;
( - - - - - )	SS-17;
( - - - - - )	SS-19;
( ..... )	SS-21;
( - - - - - )	SS-22.

## Plate IV

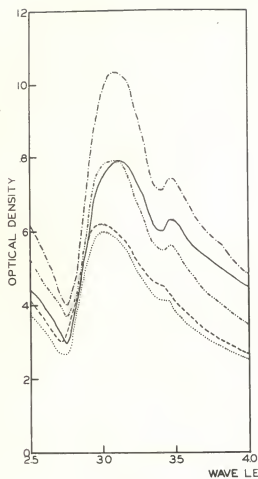


Fig. 1

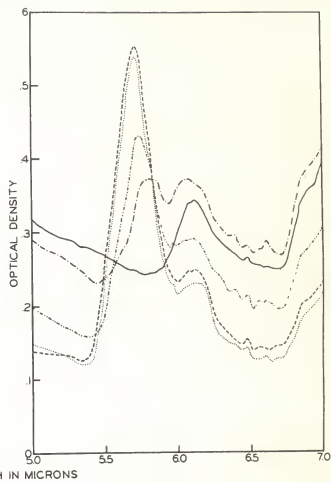


Fig. 2

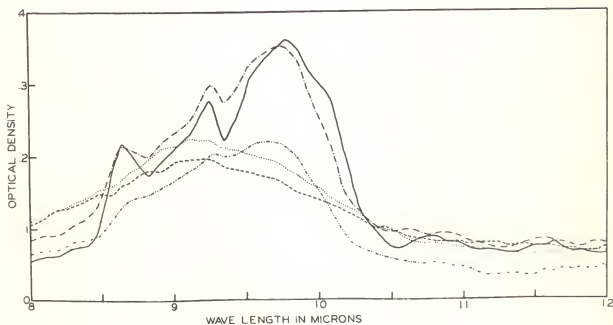


Fig. 3

Table 2. Tentative assignments of absorption bands in chlorinated starch products.

Wave length	:	Tentative assignment
3.01 microns		CH and OH stretching
3.49 "		CH and/or OH stretching
5.71 "		C=O stretching
6.11 "		gross structure
8.65 "		C-OH stretching
9.19 "		C-OH stretching
9.77 "		C-OH stretching

The assignments listed in Table 2 are tentative and are therefore subject to change should further investigation warrant it. The assignments were made on the basis of information given by Randall et al (1). The wave lengths in Table 2 which represent the absorption bands may in some cases appear to be ill-chosen. The tabulated wave lengths were believed, however, to be the most logical choices after consideration was given to the shift of apparent maxima due to nearby overlapping bands. It seemed justifiable to assign three different bands to C-OH stretching considering the existence of three distinct C-OH configurations in the glucose unit. The unchlorinated starch contains one primary hydroxyl group per glucose unit and two secondary hydroxyl groups, one of which is sterically hindered. In Table 2 there will be noted the obvious omission of the bands characteristic of the CH and OH bending vibrations which would be expected between 6 and 8 microns and also those of the C-Cl stretching vibrations which should appear somewhere between 8 and 24 microns. It will be noticed in Plate III that there is a short section of the spectrum between 7.3 and 7.5 microns

which could not be covered adequately because of the absorption characteristics of the particular oils used for the mulls. It is expected that the bands characteristic of CH and OH bending occur in this region. The absence of C-Cl absorption bands may be due to low optical activity or they may occur at wave lengths greater than 24 microns, which are beyond the range of the spectrometer.

### Quantitative Discussion of the Spectra

In the attempt to extract some quantitative information from the spectra, a modified form of Beer's Law was assumed to hold. This form may be written symbolically

$$D = \sum_i c_i k_i t + c_s k_s t + A' \quad (1)$$

where

$D$  = optical density; depends on sample and wave length,  
 $c_i$  = concentration of the  $i$ th atomic group,  
 $k_i$  = absorption coefficient for the  $i$ th atomic group;  
       depends only on wave length,  
 $t$  = thickness of mull; assumed constant,  
 $c_s$  = concentration of scattering particles,  
 $k_s$  = scattering coefficient of same nature as  $k_i$ ,  
 $A'$  = a constant characteristic of a particular sample.

The concentration  $c_i$ , which appears in equation (1) represents the total number of the  $i$ th atomic groups in the beam of radiation. This concentration is proportional to the number of  $i$ th atomic groups per gram of mull. Thus  $c_i$  was factored into

$$c_i = x_i N_r$$

where

- $x_1$  = number of  $i$ th atomic groups per glucose unit; depends on sample,  
 $N$  = number of glucose units per gram of sample; inversely proportional to the equivalent weight per glucose unit ( $M_n$ ); depends on sample,  
 $r$  = number of grams of sample per gram of mull; assumed constant for all samples.

The concentration  $c_s$ , however, represents the total number of particles in the beam of radiation which is proportional to the number of glucose units per gram of mull. Therefore,  $c_s$  was factored into

$$c_s = Nr$$

where  $N$  and  $r$  are identical with those above.

Making these substitutions in equation (1), it becomes

$$D = \sum_i x_i N r k_{1t} + N r k_{st} + A'$$

which, when divided by  $N$ , yields

$$\frac{D}{N} = \sum_i x_i r k_{1t} + r k_{st} + A \quad (2)$$

where  $A = A'/N$ .

Designating the unchlorinated sample by the subscript "o" and any of the chlorinated samples by the subscript "n", equation (2) becomes

$$\frac{D_o}{N_o} = \sum_i x_{i0} r k_{1t} + r k_{st} + A_o \quad (3)$$

$$\frac{D_n}{N_n} = \sum_i x_{in} r k_{1t} + r k_{st} + A_n$$

Only those factors which are characteristic of a particular sample carry the subscripts "o" or "n".

Consider now a wave length at which no characteristic



absorption occurs. At such a point  $k_1 = 0$ , and equations (3) become

$$\begin{aligned}\frac{(D_o)}{N_o} &= r(k_s)t + A_o \\ \frac{(D_n)}{N_n} &= r(k_s)t + A_n\end{aligned}\quad (4)$$

The parentheses around  $D$  and  $k_s$  in these expressions indicate that those quantities are for a different wave length than are the corresponding quantities in equations (3).

Subtracting the first of equations (4) from the first of equations (3), and the second of equations (4) from the second of equations (3), the following expressions are obtained:

$$\begin{aligned}\frac{D_o - (D_o)}{N_o} &= \sum_1 x_{1o} r k_1 t + r t [k_s - (k_s)] \\ \frac{D_n - (D_n)}{N_n} &= \sum_1 x_{1n} r k_1 t + r t [k_s - (k_s)]\end{aligned}\quad (5)$$

Subtract the first of equations (5) from the second to obtain

$$\begin{aligned}\frac{D_n - (D_n)}{N_n} - \frac{D_o - (D_o)}{N_o} &= \sum_1 (x_{1n} - x_{1o}) r k_1 t \\ &= \sum_1 (x_{1n} - x_{1o}) K_1\end{aligned}\quad (6)$$

where  $K_1 = r k_1 t$ .

Equation (6) was applied at the wave lengths listed in Table 2. The wave lengths used for the evaluation of  $(D_n)$  and  $(D_o)$ , that is where  $K_1 = 0$ , were chosen to satisfy two requirements. These were that  $K_1$  be zero or very nearly zero and also that the wave length be as close as possible to that of the band

being considered. The latter requirement was made to assure that the quantity  $[k_s - (k_s)]$  in equation (5) be as small as possible. In this way the effect of any variation of  $k_s$  with particle size and wave length would be minimized.

The essentials of the calculations for the C=O band at 5.71 microns are given in Table 3.

Table 3. Evaluation of  $\sum (x_{in} - x_{io})K_i$  for C=O absorption band at 5.71 microns.

Sample	$D_n$ at : 5.71 : microns	$(D_n)$ at : 6.68 : microns	$1/N_n = M_n$	$D_n - (D_n)$ : $\frac{D_n - (D_n)}{N_n}$	$\sum (x_{in} - x_{io})K_i$
SC-1E	.249	.250	162.14	.16	0.0
SS-16	.283	.220	168.40	10.6	10.8
SS-17	.337	.270	169.56	11.4	11.6
SS-18	.300	.227	170.00	12.4	12.6
SS-19	.427	.196	188.73	43.6	43.8
SS-20	.486	.115	217.36	80.6	80.8
SS-21	.538	.123	207.38	86.0	86.2
SS-22	.554	.139	219.85	91.2	91.4

In the case of this particular band only one atomic group is contributing to the absorption, so the sum  $\sum (x_{in} - x_{io})K_i$  contains only one term and may be written  $(x_n - x_o)K$ . It is also known that  $x_o = 0$  since it represents the number of C=O groups per glucose unit of unchlorinated starch. From these considerations it is seen that the last column of Table 3 may be correctly headed  $x_n K$ . By comparison with column four of Table 1 an average value for K was determined and a comparison made of this data with the chemical data. Plate V shows the comparison for a value of  $K = 57.0$ .

The C=O band is the only one which lends itself to this

degree of analysis. For all the other bands listed in Table 2 there seems to be more than one atomic group contributing to the absorption, with the result that the sum  $\sum_i (x_{in} - x_{i0})K_i$  contains more than one term. The simple procedure used above can not be used in such a case until some independent information is obtained about all but one of the atomic groups contributing to the band. Some of this extra needed information may conceivably be obtained from the spectrum itself. For example, the effects of the OH group in the 3.01 micron band may possibly be eliminated with the help of information obtained about the OH group from the bands at 8.65, 9.19, and 9.77 microns. Until the present time this has not been accomplished. Therefore, in lieu of any more refined information,  $\sum_i (x_{in} - x_{i0})K_i$  is plotted versus reaction time in Plate VI, Figs. 1 to 4, for four of the bands listed in Table 2.

In Plate VI, Figs. 1 and 3, the curves exhibit a sharp increase for reaction times up to 36.5 hours. This rapid increase in  $\sum_i (x_{in} - x_{i0})K_i$  would normally be attributed to an increase in the number of atomic groups per glucose unit,  $x_1$ . If the assignments of these absorption bands are correct, however, there is no such increase in  $x_1$ , since chemical data does not show it. A possible explanation for the increase of  $\sum_i (x_{in} - x_{i0})K_i$  is that  $K_i$  increases. This amounts to an increase in the optical activity of the atomic group. If, during the early stages of the chlorination reaction the hydrogen bonding in the starch granule is disrupted, which has been suggested by Barham and Thomson (3), some atomic groups may suffer an increase in dipole

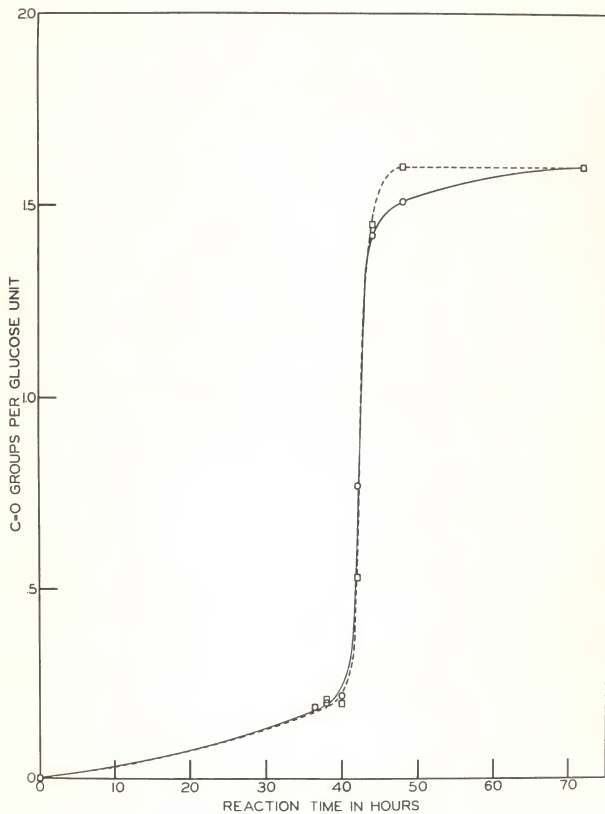
# EXPLANATION OF PLATE V

Comparison of chemical and infrared determinations  
of number of C=O groups per glucose unit as a  
function of reaction time.

( ---□--- ) chemical data;

( ---○--- ) infrared data.

Plate V



EXPLANATION OF PLATE VI

$\sum_i (x_{in} - x_{i0})K_i$  for absorption bands at various wave lengths as a function of reaction time.

Fig. 1. At 3.01 microns.

Fig. 2. At 8.65 microns.

Fig. 3. At 9.19 microns.

Fig. 4. At 9.77 microns.



## Plate VI

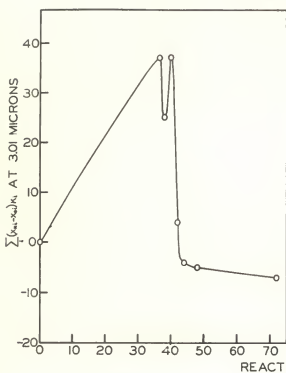


Fig. 1

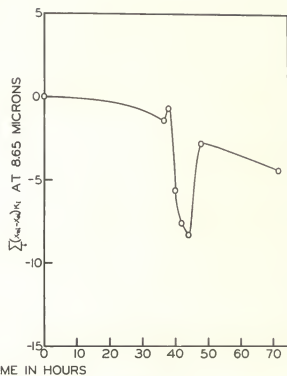


Fig. 2

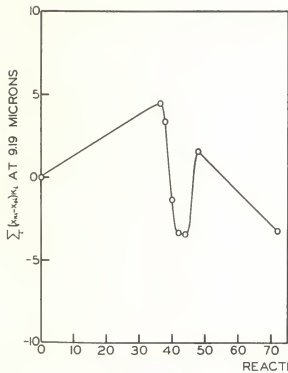


Fig. 3

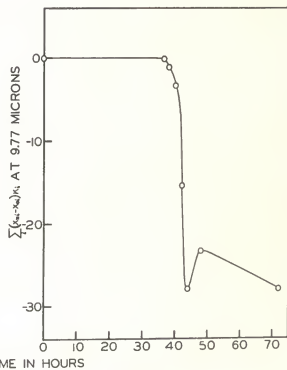


Fig. 4

moment and consequently an increase in  $K_1$ . Another possibility is that the disruption of hydrogen bonding changed the characteristic frequency of some atomic group. Then this group may absorb the frequencies indicated in Plate VI, Figs. 1 and 3, when it occurs in the 36.5 hour sample, but absorbed a different frequency in the unchlorinated starch.

#### SUMMARY

The infrared spectra of starch and chlorinated starch products were obtained using an oil mull technique. The decrease in optical density with grinding in regions of no characteristic absorption was related to particle size, the smaller particles scattering less radiation. It was found that as grinding is continued there is an increase in optical density at wave lengths of characteristic absorption as well as a shift of this absorption toward shorter wave lengths. These changes, due to mechanically breaking up the particles, are probably the result of the disruption of hydrogen bonds between adjacent glucose units. For the quantitative evaluation of the spectra a modified form of Beer's Law was used which states

$$D = \sum_i x_i N r k_i t + N r k_s t + A'$$

where

$D$  = optical density,  
 $x_i$  = number of  $i$ th atomic groups per glucose unit,  
 $N$  = number of glucose units per gram of sample,  
 $r$  = number of grams of sample per gram of mull,  
 $k_i$  = absorption coefficient for the  $i$ th atomic group,  
 $t$  = thickness of mull,  
 $k_s$  = scattering coefficient of same nature as  $k_i$ ,  
 $A'$  = a constant characteristic of a particular sample.

The values of  $\sum_i (x_{in} - x_{io})K_i$  were computed at wave lengths of characteristic absorption. Changes in the number of C=O groups per glucose unit were computed from the increase in D at 5.71 microns and found to be in fair agreement with the chemically determined values. The anomalous behavior of the bands at 3.01 microns and 9.19 microns was considered to be at least partially due to the disruption of hydrogen bonding during the early stages of the chlorination reaction.

## ACKNOWLEDGMENTS

The guidance and assistance given by Dr. Stuart E. Whitcomb throughout this research are gratefully acknowledged. Appreciation is expressed to Dr. H. N. Barham and Dr. E. S. Stickley who initiated this research and contributed generously to a better understanding of the data. The financial assistance of K.I.D.C. and other state funds allocated for sorghum grain research is also gratefully acknowledged.

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INFRARED STUDIES  
OF CHLORINATED STARCH

by

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AN ABSTRACT OF A THESIS

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The methods of infrared spectroscopy were to be applied to the analysis of several chlorinated starch products. These products were the result of a process developed by the Starch Laboratory at Kansas State College for the chlorination of starch in liquid chlorine. The purpose of the infrared analysis was to check the concentrations as determined by chemical methods of certain functional groups in the products. The use of infrared analysis required the development of a technique for obtaining the absorption spectra of the products and subsequently the qualitative and quantitative interpretations of the spectra.

The spectra of the starch products were obtained over a wave length region from 2 to 24 microns using an oil mull technique. The spectra were found to be influenced by the particle size of the sample. Tentative assignments of the characteristic absorption bands were made. For the quantitative evaluation of the spectra a modified form of Beer's Law was used which states

$$D = \sum_i x_i N r k_i t + N r k_s t + A'$$

where

$D$  = optical density,  
 $x_i$  = number of  $i$ th atomic groups per glucose unit,  
 $N$  = number of glucose units per gram of sample,  
 $r$  = number of grams of sample per gram of mull,  
 $k_i$  = absorption coefficient for the  $i$ th atomic group,  
 $t$  = thickness of mull,  
 $k_s$  = scattering coefficient of same nature as  $k_i$ ,  
 $A'$  = a constant characteristic of a particular sample.

The values of  $\sum_i (x_{in} - x_{i0}) K_i$  were computed at wave lengths of characteristic absorption. The above quantity, evaluated at

5.71 microns, yielded the changes in the number of C=O groups per glucose unit, which were found to be in fair agreement with the chemical analysis. This degree of analysis has not been reached for the groups producing the other absorption bands because of the complications introduced by nearby overlapping bands.