A STATISTICAL STUDY OF THE ALKALI NUMBERS
OF VARIOUS STARCHES

by

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INTRODUCTION

The alkali number, subsequently defined in this thesis as
the quantity of base consumed per hour per unit weight of starch,
has been used for many years in both industry and research. In
industry, alkali number has been used for product quality con-
trol, and, in research, to measure the effects of pre-treatment
on starch behavior. The values obtained have been correlated
with other starch characteristics such as pasting properties,
including rate of gelatinization and gel strength. In these re-
spects this determination has been of considerable value.

The reaction of starch with alkali has been studied by
numerous investigators. There likewise has been more than one
interpretation of the results obtained. Most of these interpre-
tations have led to confusion, because further experiments have
given results which are not consistent with the theories evolved.
Previous work in this laboratory and elsewhere has shown that the
accepted theories fail to explain many of the observed phenomena.

Recent work in this laboratory involving a statistical study
of the alkali numbers of different starches showed that they
varied from determination to determination. It was found also
that this variability was not the same for all starches, but dif-
fered in a regular manner according to the source of the starch
used.

This work suggested a more thorough study of this reaction
with starches selected to cover the range of pasting behavior.

In this study, it was planned to conduct the experiments so that the results would be adequate for statistical analysis, and to use the results for a further interpretation of the nature and behavior of different starches. The present experimental work was outlined and undertaken with these objectives in mind.

LITERATURE SURVEY

Taylor and his co-workers (11) made early studies of the factors influencing the relative amounts of alkali-labile and alkali-stable material present in or formed from the starch granule. They learned that the initial reducing value of a starch was very small, but that if the starch was treated with hot alkali solution, then neutralized, the reducing value could be magnified. Further, only a portion of the starch was found to be stable toward hot alkali. The increased reducing value of the starch was explained by assuming that the alkali begins its action at the aldehydic end group of the molecule.

Taylor and Keresztesy (12) found that the alkali lability values vary with the starch source and previous history. According to their views the alkali lability, which is a measure of the reducing value, can be increased either through the dissociation of coordinately linked chains, to uncover available aldehyde groups, or through hydrolytic scission of glucosidic linkages, giving shorter chains and thus an increased number of aldehyde or potential aldehyde groups.

The procedure developed by Taylor for the determination of

alkali lability values is difficult to follow accurately, and
gives results that can be reproduced by only a very experienced
operator. This method involves the treatment of the starch sam-
ple with hot aqueous alkali, neutralization, and the subsequent
measurement of reducing value by addition of standard iodine
solution, and back titration with standard sodium thiosulfate
solution.

Difficulty in carrying out this determination, and the un-
reliable results obtained, led to the simplified Schoch pro-
cedure. Schoch and Jensen (10) defined the alkali number as the
rate of starch-alkali interaction expressed as the number of
cubic centimeters of 0.1 N sodium hydroxide consumed by one gram
of starch during digestion in alkali for one hour at 100° C. This
is an empirical method for determining an index of hydrolytic or
other forms of degradation. The authors suggested that enoliza-
tion of the free terminal aldehyde group resulted in decompo-
sition of the starch into simple acidic substances.

These workers also found that the alkali number is a func-
tion of the pre-treatment of the starch, and that it varies in
the same manner as the alkali-labile value of Taylor. Cornstarch
treated with hot alkali, neutralized, and precipitated with
alcohol, was found to have a lower alkali number than the origi-
nal starch. However, when this reaction is continued until 80
to 90 per cent of the starch is affected, the alkali number of
the residue does not drop below four. They interpreted this as
meaning that no portion of the original starch is entirely stable

to alkali. However, recent work in this laboratory has shown
that starches with alkali numbers less than one can be prepared,
in contradiction to the previous theory.

Barham et al. (3) found that the alkali number closely paral-
lels the ratio of cold peak viscosity to hot peak viscosity,
W_2/W_1, for a large number of different starches.

In work concerned with the effects of adsorption and de-
sorption of palmitic acid on the behavior of a sorghum grain
starch, Barham and Campbell (1) noted that the alkali consumption
depends upon the manner of distribution of the palmitic acid
within the granule. They also reported a quantitative inverse
relationship between the reactivity of starch toward water and
that toward alkali. Loss in pasting capacity, brought about by
solvent extraction, ageing, and drying, results in an increase
in the alkali number. Elements of granular structure which re-
strict the availability of water during gelatinization also in-
crease the susceptibility of starch to alkaline decomposition.
These authors found changes in alkali consumption without de-
gradation of the granular starch. They suggested that Levene's
concept of activated glucose (6), a free radical, might provide
an explanation for changes in alkali number of starch in the
absence of hydrolytic degradation. They considered strain to be
of major importance in the formation of active glucosidic units,
and stated that if an occasional glucose molecule in a glucose
solution can be activated by strain into a free radical, it is
even more probable that similar free radicals could be formed in

greater numbers from the glucose residues of the rigid, meta-
stable organization of the starch granule or in starch substance
where organization persists.

Youmans (13) found differences in the standard deviations of
the alkali numbers of different starches. He interpreted these
differences as indicating differences in the probability that the
reaction follows a given path. He found that the nonglutinous
starches have higher alkali numbers, but lower standard deviations
than the glutinous starches. He found also that solvent extracted
starches have lower standard deviations, but higher alkali numbers
than do the natural starches. He interpreted this as being due
to increased uniformity of the granular structure. It was noted
that probably the alkali-labile structures, not functional groups
in the usual sense, are formed for the most part during the gela-
tinization process which occurs as a part of the alkali number
determination.

METHOD OF STATISTICAL TREATMENT OF DATA

Since the purpose of this study is to evaluate certain
parameters of the alkali number for various starches, it would be
most desirable to evaluate the true parameters of the population.
However, in the case of data of this nature, this ideal cannot
be reached, and samples must be relied upon to give estimates of
the true population parameters. If large enough samples are
taken, the estimates yielded by the samples approach the true
parameters to an extent governed by sampling errors and the de-
gree to which the samples are representative of the true popula-
tions. Very large samples were used in this case in order to

limit the degree of uncertainty as much as possible.

It is assumed in this study that the experimental data follow a normal frequency distribution. This assumption is reasonable since there is nothing apparent in the determination which would tend to cause a bias. Such a normal distribution would be symmetrical, with the average value for all determinations having the greatest frequency of occurrence.

The normal distribution is defined in terms of the variance, σ^2, and the mean, μ. The mean is the expected value, or first moment of the variate, $\underline{x}$, and is defined by

$$\mu = E(x) = \int_{-\infty}^{+\infty} x \cdot f(x) \, dx \quad .$$

The variance is the second moment about the mean, and is defined by

$$\sigma^2 = E(x - \mu)^2 = \int_{-\infty}^{+\infty} (x - \mu)^2 \cdot f(x) \, dx \quad .$$

The variance is a measure of the dispersion of the population about the mean. If most of the area under the curve lies near the mean the variance will be small, while if the area is spread out over a considerable range, the variance will be large.

When the values for μ and σ^2 for a normal population are unknown, as is the case with analytical data, sampling must be relied upon to estimate these quantities. They are best estimated by the following equations:

$$\hat{\mu} = \bar{x} = 1/n \sum_{i=1}^{n} x_i$$

n = number of data in the sample

$\bar{x}$ = sample mean

$$\hat{\sigma}^2 = s^2 = 1/n - 1 \sum_{i=1}^{n} (x_i - \bar{x})^2$$

x_i = individual datum

s^2 = sample variance

These quantities, $\bar{x}$ and s^2 , are the unbiased estimators of μ and σ^2 respectively.

The positive square root of the variance is often used in statistics, and has been given the name standard deviation, σ. Correspondingly the square root of the sample variance is the sample standard deviation, s.

For a normal population the quantity $\frac{x_i - \mu}{\sigma}$ is normally distributed. However, when the standard deviation is unknown, a corresponding ratio, called t is not normally distributed.

$$t = \frac{\bar{x} - \mu}{s_{\bar{x}}} \qquad \text{where } s_{\bar{x}} = s/\sqrt{n}.$$

In order for estimates of parameters to have significance, it is necessary to be able to show the limits of reliability of the estimates. A confidence interval on the mean may be shown by determining an interval such that there is a definite probability that the interval includes the true mean. An interval may be calculated by means of the above ratio which has the t distribution with n - 1 degrees of freedom. For a definite probability of 0.99 it is possible to write the inequality

$$P\left[-t_{.01} < \frac{\bar{x} - \mu}{s_{\bar{x}}} < t_{.01}\right] = 0.99 \ ,$$

which becomes

$$P\left[-t_{.01} < \frac{\bar{x} - \mu}{\sqrt{\frac{\sum(x_1 - \bar{x})^2}{n(n-1)}}} < t_{.01}\right] = 0.99 \ .$$

This rearranges to

$$P\left[\bar{x} - t_{.01}\sqrt{\frac{\sum(x_1 - \bar{x})^2}{n(n-1)}} < \mu < \bar{x} + t_{.01}\sqrt{\frac{\sum(x_1 - \bar{x})^2}{n(n-1)}}\right] = 0.99.$$

The values of $\bar{x}$ and x_1 are obtained from sample data, and the values for $t_{.01}$ are obtained from statistical tables (7).

It is possible also to calculate a confidence interval for the variance of a normal distribution. For samples of size n from a normal population, the quantity

$$\chi^2 = \frac{\sum(x_1 - \bar{x})^2}{\sigma^2}$$

has the chi-square distribution with $n-1$ degrees of freedom. A confidence interval can be set up in a similar manner to the above, to obtain

$$P\left[\frac{\sum(x_1 - \bar{x})^2}{\chi^2_{0.995}} < \sigma^2 < \frac{\sum(x_1 - \bar{x})^2}{\chi^2_{0.005}}\right] = 0.99 \ .$$

The values of x_1 and $\bar{x}$ are obtained from sample data, and the values of χ^2 are obtained from statistical tables (7).

PREPARATION AND SELECTION OF STARCHES

A group of different starches was selected and prepared
which would cover as wide a variety of starch types as possible,
in order to study statistically the variations in alkali number
over a wide range.

A glutinous sorghum starch, Cody starch, was selected to
represent a starch with very low alkali number. The starch was
extracted from the grain in this laboratory in May, 1950, and
viscosity records showed it to be a good, representative gluti-
nous starch. This starch was taken from a laboratory sample
designated No. 119.

An Idaho potato starch having a low alkali number was also
chosen. This starch was milled at the Idaho Potato Starch Company
plant in Blackfoot, Idaho, and was received at this laboratory on
August 20, 1951. The starch was termed by a representative of
the firm as being representative of the starch they produce. It
had been flash dried. On the basis of its viscosity record, this
starch was glutinous, and possessed a relatively low alkali num-
ber.

Pink kafir starch was selected to show the properties of a
starch which is about mid-way on the glutinous-nonglutinous
scale. The starch chosen was a mixture of two samples, Nos. 208
and 291, milled in this laboratory.

To indicate the properties of a nonglutinous starch, a sam-
ple of cornstarch was chosen. This starch was part of a shipment

of industrially produced starch and designated as CS-11.

A portion of CS-11 was solvent extracted according to the Schoch procedure in order to show the effects of solvent extraction on the alkali number values. This sample was designated CS-11-E.

Wheat starch was chosen to represent starch of even more nonglutinous character than that obtained from corn. The starch used was part of a quantity of industrially produced starch received June 8, 1951.

In order to obtain a starch of even higher alkali number than any of these native starches, a sample of CS-11 was treated further as follows. A 300-gram sample was brought to equilibrium with moist air at 25° C. and 90 per cent relative humidity in a Tenney constant humidity chamber. The starch was then removed from the humidity chamber and placed in an oven, equipped with a blower. The temperature was set at 100 ± 0.5° C, and the starch allowed to remain over night (15 hours). At the end of this time the starch was placed in the humidity chamber to re-equilibrate at the original conditions for nine hours. It was again placed in the oven at the above conditions. This cycle was carried out 15 times. The starch then was brought to equilibrium with room conditions, screened through a 60-mesh sieve, and bottled. The sample showed no change in color or granular form, but was almost completely inhibited with respect to pasting capacity. This sample was designated 77100.

It should be emphasized that there are three starches in the

group which are related. These are CS-11, CS-11-E, and 77100, the latter two being derived from the first. This permits a comparison of starches with respect to history.

EXPERIMENTAL PROCEDURE

The procedure used was a modification of the method of Schoch and Jensen (10). The titration of the excess alkali was followed with a Beckman model H-2 pH meter. In an effort to limit the number of variables, control measures were taken to make each determination as much like every other one as possible. The procedure was as follows.

Samples of 0.5000 g dry weight of powdered starch were transferred to eight-ounce Pyrex nursing bottles. The total number of eight determinations, seven starches and one blank, were made in each run. Twenty ml of water was added to a bottle and the sample swirled gently to wet the starch and suspend it in the water. The alkali, 25.00 ml of 0.4 N NaOH, then was added. The sample was swirled during the addition of alkali to assure a uniform gelatinization. If a sample did not paste uniformly the entire run was stopped, and all the values discarded.

After gelatinization, 55 ml of boiling water was added to the sample and the bottle was capped with a rubber stopper pierced with a small hole to provide an exit for steam. The bottle was then placed in a vigorously boiling water bath. At the time one bottle was placed in the water bath, another, containing only water was removed and placed in a second bath at

the same temperature. When a sample bottle was removed from the
first bath for titration, another containing water was returned
from the second water bath to take its place. This procedure
was followed in order to keep the same number of bottles in the
cooker at all times, and thus keep the conditions constant.

After exactly 60 minutes in the boiling water bath, the
sample was removed and placed in a water bath which was maintain-
ed at approximately 18° C. The stopper was removed, the lip of
the bottle was rinsed with a few ml of water, and 65 ml of water
at room temperature was added. The bottle was allowed to stand
in this bath for eight minutes. At the end of this time it had
reached room temperature. The sample was then transferred to a
titrating container using three 15 ml portions of water to rinse
the bottle. The sample was titrated to a pH of 7.0 within five
to six minutes using 0.2 N sulfuric acid.

The time for titration was maintained constant in order to
keep the absorption of CO_2 from the air constant for any given
run of eight determinations. The samples were run at intervals
of ten minutes. Only recently boiled distilled water was used
throughout the determinations. During the determinations, the
bottles containing alkali were kept covered at all times in order
to minimize the sorption of CO_2.

After every run, the bottles were filled with 0.1 per cent
hydrochloric acid and heated for one hour in the boiling water
bath. The bottles then were cooled, thoroughly rinsed with
water, and placed on a rack to dry.

The relative order in which the starches were run was kept the same, but the samples were rotated, so that the starch which was run last during one series was run first during the next series of determinations. In this way no variability in results was introduced by virtue of the relative time at which a determination was made on a given starch.

In order to assure good estimation of the mean and variance of the alkali numbers, 100 determinations were made on each starch. Enough extra runs were made to make up for those discarded because of errors.

The alkali number is given by

$$\text{Alk. No.} = \frac{\left(\begin{array}{c}\text{ml acid to}\\\text{titrate blank}\end{array} - \begin{array}{c}\text{ml acid to}\\\text{titrate sample}\end{array}\right)\left(\begin{array}{c}\text{normality}\\\text{of acid}\end{array}\right)\left(10\right)}{\text{weight of sample}}$$

APPARATUS

The titration apparatus was basically the one suggested by Rockland and Dunn (9). A few changes were made to adapt it to the alkali number determination.

The titration cup was a 15 mm pyrex funnel with a six mm stopcock sealed to the funnel stem. By means of a rubber tube the cup could be drained to a sink.

A 50 mm burette was held by a burette clamp in such a way that it drained to a point about half-way between the center and one side of the funnel.

A cone-drive electric stirrer was clamped to the ring stand, and a glass stirring rod was fastened directly in the chuck of

the stirrer.

The pH meter electrodes were held by an electrode clamp which was supported by the pH meter. The electrodes were placed in the funnel in a position roughly opposite to both the stirrer and the point to which the burette drained. The principal parts of the apparatus are shown in Plate I.

EXPERIMENTAL RESULTS

Alkali Numbers of the Various Starches

The average alkali numbers, their standard deviations, and confidence intervals for a probability level of 0.99 are shown in Table 1.
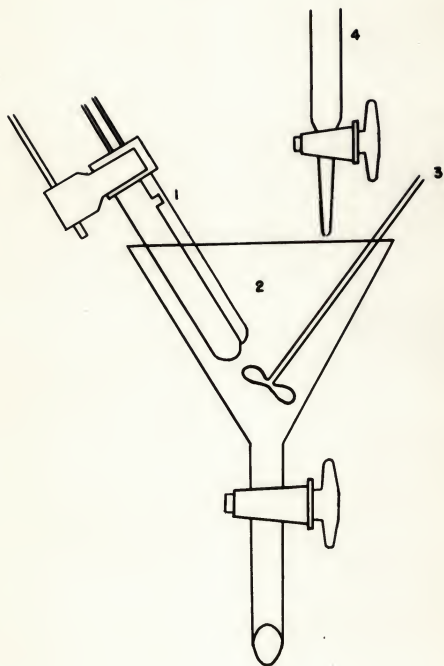
Table 1. Alkali number data for various starches.

Starch	Average alkali number	Standard deviation	Confidence interval on mean of alkali number
Cody	1.02	0.26	± 0.07
330 Potato	1.67	0.36	± 0.10
Pink kafir	5.13	0.39	± 0.10
CS-11	7.63	0.54	± 0.14
CS-11-E	8.31	0.50	± 0.13
Wheat	8.61	0.46	± 0.12
77100	11.51	0.41	± 0.11

EXPLANATION OF PLATE I

1 - pH meter electrodes

2 - Titration funnel

3 - Stirrer

4 - Burette

PLATE I

An attempt was made to calculate confidence intervals for the standard deviation values, but since there were so many data, the intervals were reduced to such values that they became essentially single points.

Average Data for Titration Curves

The data necessary for plotting the titration curves are shown in Table 2. The pH reading at the point at which 20.0 ml of acid had been added is an average of 76 readings. All the rest of the points are averages of 100 readings. The titration curves utilizing these data are plotted in Figs. 1 through 7.

Comparison of Initial Points on Titration Curves

Confidence intervals for a probability level of 0.99 were calculated for the mean of the initial pH for each starch. In no case did the interval for a starch sample overlap that of the blank. This indicates that the differences observed are significant to a level of 0.99. These data are shown in Table 3.

The calculated intervals are actually smaller than the accuracy of the pH meter for a single sample. The limits of accuracy of the meter are $\pm$ 0.02. However, the data would be expected to be normally distributed about the true value, so that when a large number of samples are taken, as in this work, the accuracy of the mean value would be greater than that for an individual datum. For this reason the calculated limits should have significance.

Table 2. Average pH data for the titration of various starches and the blank.

| Starch	ml of 0.2 N H_2SO_4 added											
	0.0	20.0	30.0	35.0	38.0	40.0	42.0	43.0	44.0	45.0	46.0	End-pt
Cody	12.39	12.17	11.90	11.72	11.56	11.43	11.19	11.01	10.73	10.26	9.30	46.58
330 Potato	12.43	12.18	11.92	11.74	11.58	11.43	11.20	11.01	10.75	10.23	9.04	46.42
Pink kafir	12.41	12.17	11.90	11.68	11.51	11.34	11.01	10.72	10.21	9.25		45.59
CS-11	12.43	12.17	11.90	11.68	11.48	11.29	10.92	10.56	9.84			44.99
CS-11-B	12.43	12.17	11.90	11.66	11.48	11.28	10.88	10.51	9.71			44.85
Wheat	12.42	12.15	11.87	11.64	11.42	11.19	10.70	10.20	9.35			44.77
77100	12.42	12.14	11.84	11.61	11.38	11.10	10.48	9.77				44.08
Blank	12.47	12.21	11.97	11.78	11.61	11.47	11.24	11.05	10.75	10.26	9.42	46.82
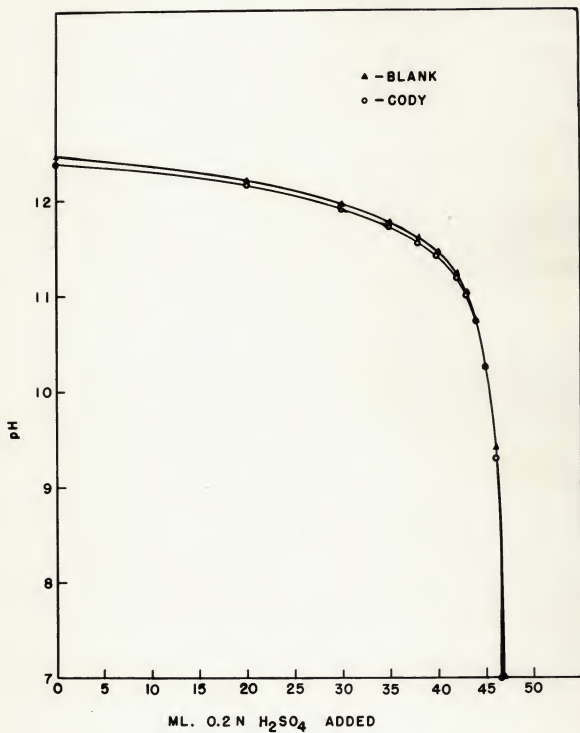
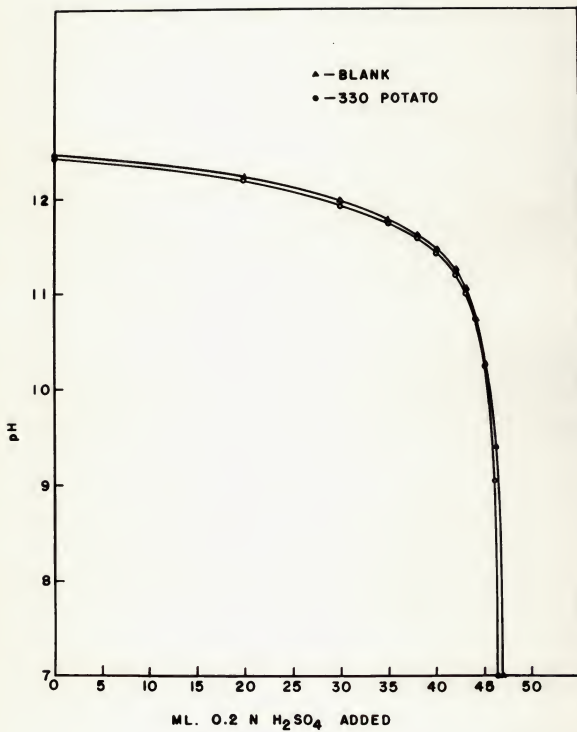Fig. 1. Electrometric titration curve for Cody starch.

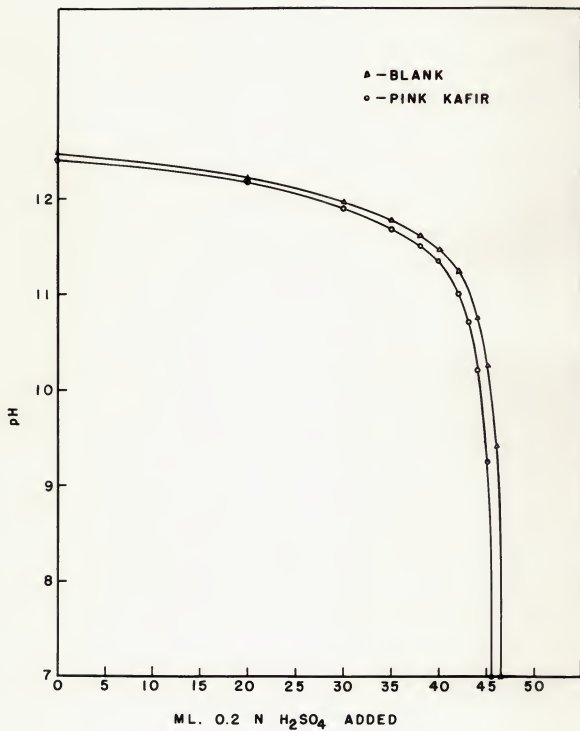Fig. 2. Electrometric titration curve for potato starch.

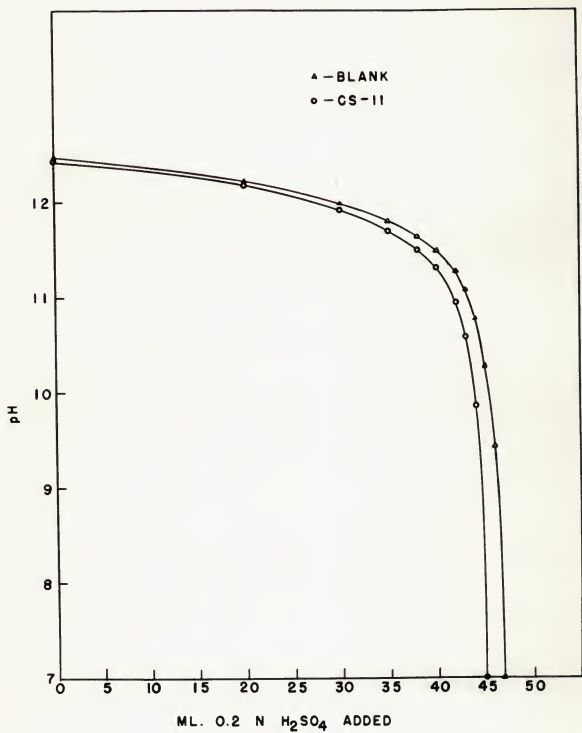Fig. 3. Electrometric titration curve for Pink kafir starch.

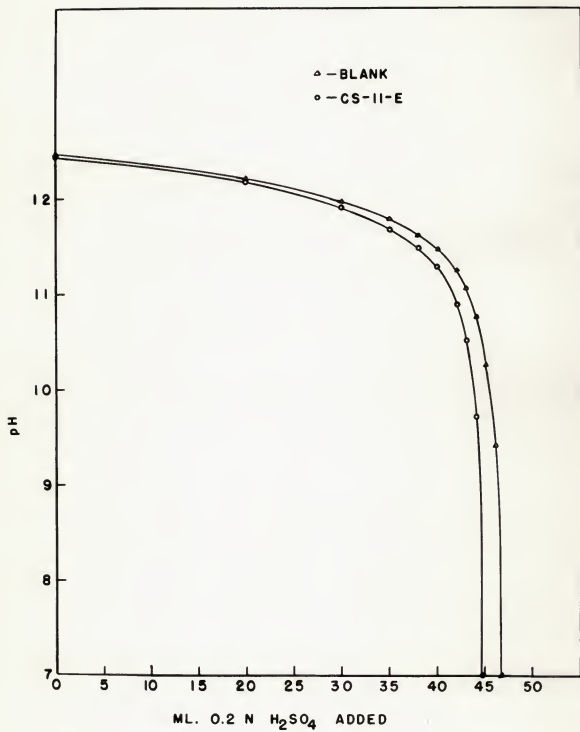Fig. 4. Electrometric titration curve for CS-11.

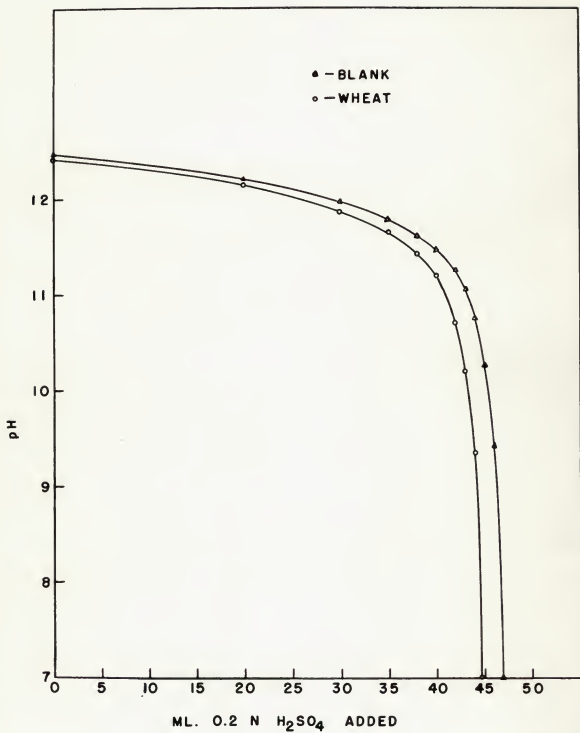Fig. 5. Electrometric titration curve for CS-11-E.

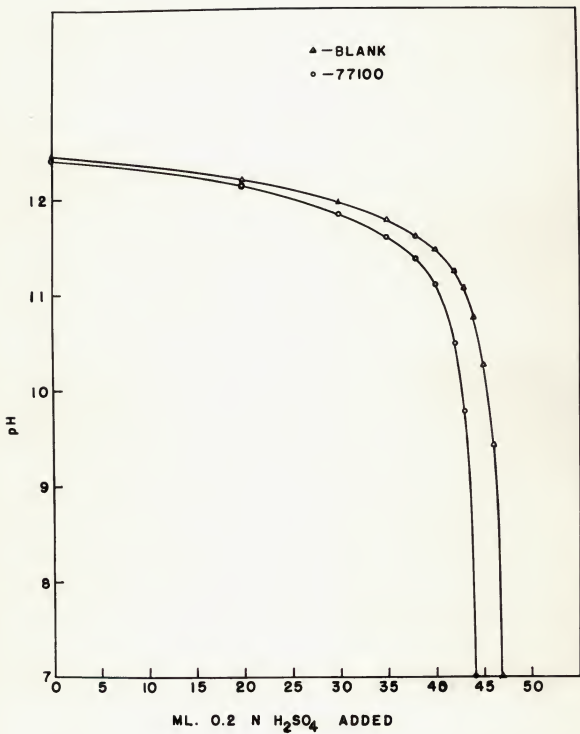Fig. 6. Electrometric titration curve for wheat starch.

Fig. 7.   Electrometric titration curve for 77100.

Table 3. Comparison of initial pH values.

Sample	Initial pH	Confidence interval	Initial pH of blank — initial pH of sample
Cody	12.39	± 0.01	0.08
330 Potato	12.43	± 0.01	0.04
Pink kafir	12.41	± 0.01	0.06
CS-11	12.43	± 0.01	0.04
CS-11-E	12.43	± 0.01	0.04
Wheat	12.42	± 0.01	0.05
77100	12.42	± 0.01	0.05
Blank	12.47	± 0.01	--

Viscosity records, showing the paste forming characteristics of the various starches, are shown in Fig. 8.

DISCUSSION

From the titration curves and data for comparison of initial pH values of the various starches it will be noted that in every case there is a significant difference between the initial pH of the blank and that of the starch samples. The largest difference was found for the glutinous Cody starch. Yet, this starch consumes practically no alkali. Thus, the difference in initial pH decreases for starches of more nonglutinous character, and then begins to increase again as more alkali is consumed. This indicates that probably two processes are acting, each of which
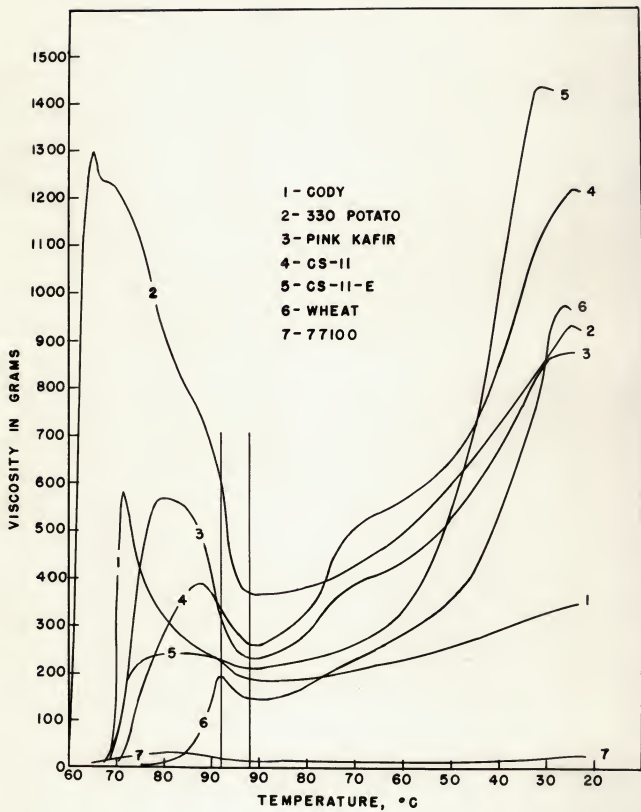
Fig. 8. Viscosity curves for the starches.

causes the pH of the starch sample to be decreased, but by different mechanisms.

In the case of the highly glutinous Cody starch, which consumes practically no alkali, the lowering of pH can be accounted for only by sorption of alkali by the starch. In this case it would be expected that as titration proceeds, and the concentration of free alkali is lowered, there would be a driving force, due to this removal of free alkali, tending to allow any sorbed alkali to be desorbed, and go back into solution. This desorption would be reflected in the titration curve by a later point at which the curve has a rapid decrease of pH with addition of alkali. This character is shown by the titration curve for the Cody starch. At the knee of the curve there are several points at which the curve for the starch coincides with that for the blank. The two curves then separate slightly near the end-point. This same effect is shown by the potato starch, which also consumes very little alkali.

At the other extreme are the highly nonglutinous starches such as the wheat starch and inhibited cornstarch, 77100. In these cases the difference between the initial pH of the alkali treated starch and that of the blank can be accounted for as being largely due to removal of alkali from solution by reaction. Calculations show that a lowering of pH of the order of magnitude of the observed value would be brought about by removal of the amount of alkali actually consumed by the starch. Undoubtedly there is a small amount of sorption in these cases, but it is not

the dominant action.

The intermediate starches are both less able to sorb the alkali than the glutinous starches and less able than the very nonglutinous starches to react with it. For these reasons there is a lesser difference between the pH of the blank and that of the alkali-treated starch.

From the data showing standard deviations for the alkali numbers of the various starches, significant differences can be observed. These standard deviations vary from 0.26 for the Cody starch to 0.54 for the cornstarch. The standard deviation can be interpreted as being a measure of the probability that the reaction follows a definite path. If in every case the reaction followed some definite path, the standard deviation would be governed by titration errors. These errors would be the same for each starch, thus removing the possibility of differences between the standard deviations of starches of different origin and pretreatment.

On the other hand, if each starch has associated with it some probability that a given reaction path will be followed, this probability would be reflected in the value of the standard deviation. Different starches could thus show different standard deviations. These different probabilities could be associated only with differences in structure of the various starches.

The association of probability and starch structure suggests the application of entropy considerations to starch. Planck (8) makes the following statement. "The entropy of a physical system

in a definite state depends solely on the probability of this state." This has been the basis of all further work in considering structure from a standpoint of entropy. Entropy is accepted to be a measure of the disorganization of a system, the greater the disorganization, the higher the entropy.

Referring to the observed sequestration of alkali by the glutinous starch, it would be most likely to occur where there was a minimum of order in the relation of starch chains in the granule. Where regularity of inter-micellar hydrogen bonding is least, the alkali ions could be sorbed and held in the unorganized maze of chains. On the other hand, there would be less sequestration of the alkali in cases where the degree of organization is greater, for there would be more avenues by which the ions could return to solution.

From this consideration, and from other observed reaction characteristics, the glutinous starches can be considered as having a lower degree of organization than the nonglutinous types. It also is apparent that there is a greater probability that the reaction of the glutinous starches with alkali will follow a definite path, as shown by the lower standard deviation.

It is reasonable, therefore, to consider that the degree of variation of alkali number is a measure of the probability of the reaction following a given path, and is also a measure of the uniformity of structure of the starch.

From the observed behavior of the glutinous starches they can be considered, by virtue of having a higher degree of disor-

ganization, to have a higher probability, and thus a higher entropy than nonglutinous starches. If this is so, then the starches considered in this study can be ranked according to entropy value. Starting with the glutinous starch, there is a steadily decreasing entropy through potato starch, Pink kafir starch, and cornstarch. These are all natural starches whose extraction involved no harsh treatments. The solvent extracted cornstarch shows an increase in entropy, as does the inhibited cornstarch. These increases are expected, since both of the treatments involve the alteration of the granular structure of the starch, as shown by viscosity and liquid phase chlorination studies. If these changes are spontaneous, as expected, they would proceed with an increase of entropy.

This observed decrease of organized structure could be regarded as being at odds with some accepted views of these treatments, but upon further consideration it appears to be otherwise. It is generally accepted that solvent extraction occurs with an increase in structure, whereas this study shows a total decrease. Both of these can be true. The treatment could effect an increase in structure in that part of the granule mainly responsible for paste development but the total result could be an over-all decrease in uniformity of configuration. The same type of behavior was noted by Barham and Thomson (2) when they observed in chlorination studies that one fraction of a hydrogen chloride-treated starch and an ammonia-treated starch had become less and another fraction more available for reaction.

Inspection of the standard deviations shows that the value
for wheat starch is lower than that for cornstarch. This is con-
trary to expectations if both were natural starches. Thus it
appears that the wheat starch was altered when milled. Viscosity
data suggest that this starch was extracted from the grain by the
alkali method, thereby becoming inhibited in its reaction with
water. A spontaneous reaction occurred, with an increase of
entropy.

Although the various treatments result in an increase of
entropy, they do so without an increase in glutinous character
of the starch. In fact, the starch becomes more nonglutinous.
Accordingly, although a trend toward a more glutinous state would
be accompanied by an increase in entropy, an increase also may be
observed when going in the opposite direction. Most of the
natural processes occurring with granular starch proceed with
formation of a product which is more nonglutinous than the origi-
nal. This indicates that possibly some important portion of the
starch tends naturally toward a more highly organized structure,
but that this change is more than balanced by a decrease in
structure in another part. The end result, then, is a total in-
crease in randomness. Granular starch may be considered to be
in a metastable state, tending to change spontaneously both to
increased and decreased structure.

Studies of granular starch by iodine adsorption suggest that
the surface of the granule is restricted by solvent extraction,
as indicated by a decrease in the amount of iodine adsorbed (5).

Data obtained from the liquid phase chlorination of starch suggest that solvent extraction inhibits the surface of the granule with respect to reaction with chlorine (4). The viscosity characteristics of the inhibited cornstarch, 77100, prepared for this study can be interpreted as being the result of granule surface alteration. These results indicate the possibility that the tendency toward an increase of organization occurs in the surface of the granule. The internal portion of the starch granule would tend to undergo a decrease of organization.

These tendencies could explain the difficulties encountered in attempts to increase the glutinous character of a starch. The tendency of the surface of the granule toward increased structure must be inhibited or reversed, and the randomness of the granule uniformly increased.

In view of the complexity of the starch granule, it must be assumed that the above is an overly simplified explanation of observed phenomena. However, the application of entropy to changes involving the starch granule seems to be consistent with the present facts, and may prove to be fruitful in indicating the course of future work.

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A STATISTICAL STUDY OF THE ALKALI NUMBERS
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by

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AN ABSTRACT OF A THESIS

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The consumption of alkali by starch has been studied by numerous investigators. There likewise have been several interpretations of the results obtained. Recent work in this laboratory showed by a statistical study that there was a variability in the amount of alkali consumed, as measured by the alkali number, which seemed to be a function of the history of the starch.

Accordingly, a more thorough study of this reaction was planned, using starches selected to cover the range of pasting behavior. It was decided to use a series of experiments so conducted that the results would be adequate for statistical analysis, and to use such results for a further interpretation of the nature and behavior of different starches.

A series of 100 alkali number determinations was made on each of seven different starches. The mean of the alkali number and its standard deviation, along with confidence intervals, were calculated for each starch. Titration curve data were also taken.

The study showed that glutinous starches, such as Cody starch, are able to sequester alkali, although they react with very little of it. On the other hand, the nonglutinous starches react with a larger amount of alkali and sequester very little of it.

It also was found that the alkali numbers for the glutinous starches had lower standard deviations than the alkali numbers for the nonglutinous starches. The standard deviation was interpreted as being a measure of the probability that the reaction

follows a given path. The standard deviation was also consider-
ed as being related to entropy.

Using this criterion, the nonglutinous starches were shown
to have a lower entropy than the glutinous starches. It was
also shown that the treated starches had higher entropies than
the untreated starches.