CHANGES IN THE PECTINOUS MATERIALS IN DEHYDRATION OF ONIONS

by

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CHAPTER I

INTRODUCTION

Recent advances in Food Industry have been toward the manufacture of better quality products. Research technique is employed to find a probable cause or even a remote correlation between the changes occurring apparently or invisibly and their effects on the product. With that view in mind, the work undertaken may prove its real value.

Fruit and vegetable dehydration has grown in importance; though compared to other food processing industries it may not present a favorable picture. Temperature and other reactions are somewhat different during dehydration from the moist heat applied in canning and cooking. The subject of pectic changes has been partially investigated under condition of cooking and canning.

Plant physiologists have not yet come to the final conclusion regarding the specific role of pectin, but they all agree that it forms one of the important constituents of the cell wall. The structural framework of tissue is based on the rigidity of the cell wall, which, if not fully, at least partly is dependent on the pectic substances. Any changes occurring in the nature of pectic
substances or their complete or partial disappearance may affect the plant tissue and eventually the product. Pectic substances are attacked by enzymes, heat, acid, alkali and other factors. They could be gradually hydrolyzed to simpler substances under favorable conditions. An attempt is made here to investigate the changes in pectic substances.

There are no available data on the changes in pectic substances during the process of dehydration. Also it is a laboratory practice to dry any kind of plant material for later analyses. The information may become useful if the preserved samples have any relation to pectic substances. Even if the results could not be correlated with quality, texture, rehydration ability or as an objective measurement of the processing, there is at least an academic interest in understanding the changes.

The American Chemical Society (1) has revised the nomenclature of pectic substances as follows:

Pectic substances is a group designation for those complex colloidal carbohydrate derivatives which occur in or are prepared from plants and contain large amounts of anhydrogalacturonic acid units which are thought to exist in a chainlike combination. The carboxyl groups of polygalacturonic acids may be partly or completely neutralized by one or more bases.
Protopectin is applied to a water insoluble parent pectic substance which occurs in plants and which upon restricted hydrolysis yields pectin or pectinic acids.

Pectinic acid is used for colloidal polygalacturonic acids containing more than a negligible proportion of methyl ester groups. Pectinic acid under suitable conditions is capable of forming gels with sugar and acid or if suitably low in methoxyl content with certain metallic ions. The salts of pectinic acid are either normal or acid pectinates.

Pectin is the general term designating those water soluble pectinic acids of varying methoxyl content and degree of neutralization. It is capable of forming gels with sugar and acid under suitable conditions.

Pectic acid is applied to pectic substances composed mostly of colloidal polygalacturonic acids and essentially free from methyl ester groups. The salts of pectic acids are either normal or acid pectates.

Pectin degradation objectives in dehydration work are to determine any changes in pectin fractions and total pectin as between fresh and dehydrated samples and as between samples dehydrated in different conditions. Such studies may show changes in pectin fractions as between high quality and poor quality of finished product and between poor rehydrating material and that which rehydrates.
well.

Pectin changes in maturing of fruits and vegetables in storage and in cooking could be compared with changes occurring during the process of dehydration. The difficulties in dehydrating some products may be explained through the study of such changes which affect the structural framework of tissue. The final comparison between the dehydrated cooked product and fresh cooked product may reveal the same degree of degradation of pectic substances.
CHAPTER II

REVIEW OF LITERATURE

Historical reviews of literature on pectin have been presented often throughout the literature. It is not the objective of this paper to present all the pros and cons on the subject at large but at the same time no effort has been made to limit the information. The subject of pectin has remained vague and as yet no marked degree of agreement is found between different workers except those who belong to the same school of thought. Even the nomenclature adopted by the American Chemical Society (1) does not give satisfactory classification of the pectin fractions. Most of the work before 1929 must be reinterpreted in the light of present knowledge of the subject.

Different pectin fractions have varied properties. The ratio of one fraction to the other remains more or less constant in the growing stage. Protopectin and pectin are usually the only fractions recognized in plant tissue, while pectic acid and pectates have been seldom reported to be present. Nevertheless protopectin, pectin, pectic acid, and pectates have an established recognition. Comparison of only total pectic substances will give an idea of retention or disappearance of the material en masse, but, as said before, the different constituents exhibit
specific properties and have definite roles in the cell. Whether or not the ratio of the constituents remains the same is a more accurate indication of pectic changes in plant material. Only from the study of each constituent will it be feasible to explain the relationship with many other factors. Even if the total pectin remains the same after processing the constituents might have undergone moderate or severe change from one form to another, which exhibit different properties regarding solubility, colloidal characters, viscosity (in solution), structural rigidity, reconstitution and the degree of degradation. Such study should provide data for the optimum conditions for controlling pectic changes.

Each constituent has been histologically studied. Protopectin and soluble pectin are found in cell walls or incrusting substances (cell wall thickening). The middle lamella is generally assumed to be either calcium pectate or protopectin. Some pectin with traces of pectic acid may be found in the cell sap. Very little precise information (15) exists as to the state and condition of the pectic constituents in situ in the plant. Most of the conclusions have been reached on the particular means of extraction used in a particular work. Such assumptions are rather dangerous to make and to that degree there is a limitation in the solubility fractionation study of
pectic constituents. Total pectin could be extracted to indicate the quality of pectin expressed as viscosity or other means and such work has been undertaken. It may perhaps throw significant light on the same objectives and may prove to be an easier method of expression of empirical correlation. Nevertheless the bases of such studies will only expand with more detailed information of the constituents of total pectin.

**Soluble Pectin**

Further limitations of fractionation are more evident as the literature is reviewed. Fractionation is based on the solubilities. Water has been used as a solvent for soluble pectin by practically all workers, though they differ in the method of extraction, time, temperature, and repetition. Time of extraction varies from short extractions of two minutes to 24 hours. Cold water as well as a temperature of 85° C has been employed. One to eighty extractions have been made.

Carre' and Haynes (6) in their first trials for extraction of soluble pectin minced apples finely, assertedly "killed the enzymes" by freezing and after warming, the pulp was pressed through cloth. The residue was ground with fine sand and repeatedly washed with cold water and pressed. After the first few extractions further
extractions yielded very dilute solutions, but it has been found that a large portion of pectin (50%) comes out in later extractions. Sixty to eighty extractions are usually required and the bulk of the extract is quite large. Carre' (7) in another place remarks that it is not possible to reach a stage where no further soluble pectin is removed. However, when the fractions contain negligible quantities, the extraction is assumed to be complete.

Manji and Norman (14) contradicted the cold water extraction of Carre' and Eymes (6). Cold water extract would in probability remove little more than the pectin in solution in the cell sap. Repeated extractions (60-80) may make an insoluble colloidal substance disperse and pass into apparent solution. The difficulty is purely structural and not chemical, i.e. the inability of the extraction agent to penetrate properly into all the cells of tissue. The optimum time and temperature had to be found for the extraction to be complete, yet not so prolonged that hydrolysis might take place beyond the pectic acid stage. Actual boiling was avoided. Heating at 85° C for 24 hours was needed to yield complete extraction. To inactivate the enzymes, fresh material was placed in a hot steam oven, moisture determinations were made, and the material was dried, ground and reground. The figures reported for fresh and dried leaves are 0.9 and 3.7 grams
of calcium pectate respectively. Heat degradation is very evident while the enzymic inactivation may not be complete. The fraction obtained was named as free pectin but from our present knowledge the temperature has been known to affect the degradation of protopectin and pectin itself.

Appleman and Conrad (3) extracted soluble pectin by grinding the pulp with water in a large mortar and straining it through double layers of cheesecloth. They made four extractions, each for two minutes.

Elwell and Dehn (8) did not recognize the definition of pectin fractions. They contended that a single treatment with water did not remove any definite pectic compound but yielded part of the series of pectic substances from the layers of cell wall and middle lamella. Continued hydrolysis progressively dissolved the entire protopectin. They obtained the first extract by heating the material in water at 90° C for one hour. Freeman and Ritchie (10) followed more or less the same line of reasoning though they recognized pectic acid as a separate fraction. Cold water extracted only traces of soluble pectin and was found to be unreliable. While two additional extractions of 24 hours each at 37° C yielded half of the total pectin and the further extraction at 85° C yielded all the pectin in cooked potatoes and in every case as much as did an acid extract.
Simpson and Halliday (16) extracted soluble pectin in five successive extractions of 50 ml each in 25 minutes of boiling water. Heinze and Appleman (12), unlike other workers, assigned the name soluble pectin to the fraction extracted with 0.2% ammonium citrate after shaking for one hour.

Pectic Acid and Pectates

Ammonium salts have long been employed as solvents of pectic acid and pectates. Ammonium oxalate and ammonium citrate have been used by most of the workers. Different concentrations of ammonium salts have been used but the results do not vary significantly. Conrad (7) who has made a biochemical study of insoluble pectic substances presents three insoluble substances, protopectin, pectic acid and pectates. He extracted pectic acid and pectates by ammonium salts but did not make any attempt to distinguish between the two. Two extractions with 1% ammonium oxalate or citrate were enough to extract pectic acid and pectates. He has raised certain objections to ammonium oxalate because he claimed that pectic acid has to be precipitated with 1% HCl, which may affect the pectic acid. The washing necessary to remove oxalate ions dissolves a certain amount of pectic acid, while ammonium citrate is as good a solvent and does not need any washing.
Manji and Norman (14) made separate (not sequential) extractions as follows:

A  Solvent: Water 85°C  - Free pectin
B  Solvent: 0.5% oxalic acid  - Free pectin and protopectin
C  Solvent: 0.5% ammonium oxalate  - Free pectin, protopectin, and pectic acid

Each fraction was then determined as:

A  Pectin
B-A  Protopectin
C-B  Pectic acid

This method of differentiation is widely followed.

They made three separate determinations on the sample while Carre' and Haynes (6) removed the soluble pectin and ran further extractions on the same material. Manji and Norman have argued that any incompleteness in the initial extractions would render the later results unreliable. But, on the contrary, if the extractions have been proved to be sufficient, the determinations run on the same sample will furnish the data exclusively of sampling error. The variation in different samples is bound to occur, even if the sampling is done carefully. Separate determinations may save time by running all the fractions simultaneously.

Appleman and Conrad (3) stored the material after water extraction in alcohol which is removed by filtration.
on hard filter using suction. The moist pulp is then re-
moved and extracted twice with 50 ml of 1% ammonium cit-
rate for two minutes. Two additional extractions were
made, evidently to wash free of ammonium citrate before
extraction for protopectin.

Elwell and Dehn (8) followed a different pattern and
reported two fractions of protopectin as easily and diffi-
cultly hydrolyzable material but did not mention pectic
acid or pectate extraction. Freeman and Ritchie (10),
though following a similar pattern, gave the fraction sol-
uble in ammonium citrate but insoluble in hot water. This
fraction consisted of pectic acid and insoluble salts of
the acid.

Simpson and Halliday (16) followed the same schedule
of fractionation of Nanji and Norman (14). They suggested
refluxing with dilute ammonium oxalate for the extraction
of pectic acid and pectates.

Heinze and Appleman (12), as said before, used ammo-
nium citrate for estimation of soluble pectin. They in-
cluded pectic acid and pectates with soluble pectinie
acid.

 Protopectin

Protopectin, the insoluble fraction, has to be
hydrolzyed to yield to extraction. Carre' (5) found that
after extraction of soluble pectin if the material was subjected to very mild hydrolysis by very dilute acid, quite a large amount of pectinous material was extracted. She used N/75 HCl for hydrolysis under reflux condenser for three hours. Boiling for more than three hours might lead to decomposition. Tutin (17) doubted the existence of protopectin as being an insoluble pectin material. He believed that due to incomplete disintegration of the material all the pectinous material was not extracted, but as soon as such conditions are favored the extraction is made possible. Nanji and Norman (14) have supported this view partially, though Carre' (5) has conclusively proved the presence of insoluble pectinous material. Elwell and Dehn (8) seem to have carried the idea of Tutin and extracted protopectin in two fractions, one by adding 0.155 ml H₂SO₄ in 500 ml water (pH 1.5) and extracting as easily hydrolysable protopectin and the second with the same amount of acid, extracting as difficultly hydrolysable protopectin. Fredrick Hardy (11) who studied different extraction media for estimation of total pectin has proved that extractions appeared to vary directly with H ion concentration if carried out at temperatures below the boiling point. Under similar conditions extractions made with water were much less than those made with dilute acid.

Conrad (7) investigating the best method for the
acid hydrolysis of protopectin in vegetables gave experimental evidence that the optimum concentration was N/30 or N/40 HCl, boiling at atmospheric pressure for one hour. A longer period may destroy part of the pectin liberated. Additional pectic acid was extracted by ammonium oxalate after the protopectin hydrolysis, although before refluxing with acid ammonium oxalate did not yield any further pectic acid. He believed that pectic acid was held from the earlier extraction by impermeable walls composed partly of cellulose and partly of protopectin or it may have been chemically united in some way and was only liberated by the treatment for protopectin. It seems more reasonable to believe that during hydrolysis the protopectin has been hydrolyzed to pectic acid and is not extracted with soluble pectinic acid or pectin. Conrad determined the total insoluble pectic substances by refluxing with N/30 HCl and 1% ammonium oxalate for one hour. Refluxing with N/30 HCl yielded only protopectin.

Appleman and Conrad (3) after extracting pectic acid and pectates covered the residue with alcohol. The residue was first boiled for 30 minutes in water and again 30 minutes in N/30 HCl. The pectin and pectic acid were determined as protopectin.

Freeman and Ritchie (10) did not find any difference in cooked potatoes between the hot acid extract and water
extract under the same conditions. They contended that not acid extract did not define the protopectin fraction, because water extracted as much if not more pectin.

Simpson and Halliday (16) as a separate determination refluxed the material in N/30 HCl for one hour. Soluble pectin was subtracted from this value. While Heinze and Appleman (12) determined total pectin on the sample previously boiled in 95% alcohol, washed with alcohol and ether, and dried, by combining the extracts from gently boiling with 0.5% ammonium citrate for 30 minutes followed by N/30 HCl reflux for 30 minutes. They used 0.2% ammonium citrate for extracting soluble pectin, thereby getting pectic acid and pectates in both cases. Here too total pectin minus the soluble pectin gave the protopectin fraction.

Comparing the work of these few workers in pectin fractionation methods, it is rather difficult to select the method followed by one worker. By a few trials and coordination of different points from different workers a satisfactory method has been evolved for the purpose of this research. In the beginning more attention had to be paid to the method of estimation and as such the extraction technique was more or less the same, but as the work progressed a better and quicker method had been established. The method is not claimed to be perfect but with
minor changes could be applied to other substances.

Conversion of Pectinous Fractions to Calcium Pectate

Pectin due to its colloidal properties is readily precipitated as a solid gel by the addition of a little dehydrating agent such as alcohol. All negative bio-colloids do not behave similarly, e.g. gum arabic, although many do. According to Sommer (4) pectin consists of very small gel particles which under normal conditions are not quite able to coalesce to a uniform gel; however, this is possible if the hydration of these particles is reduced to a small extent.

The negative charge of pectin is mostly due to carboxyl groups. Pectinous materials have been generally classified according to the methoxyl content as follows:

Protopectin and pectin: Completely methylated, no free COOH

Pectinic acid: Partly methylated, some free COOH

Pectic acid: Not methylated, all free COOH

It is because of this very high negative charge that pectic acid is so readily precipitated by electrolytes. Pectinic acid has a low negative charge and as such is less readily precipitated by electrolytes. If one adds a salt with a polyvalent cation (CaCl₂) to a sol of pectic acid, one should expect an increase of "effective
electrometric attraction between the chains and if this attraction becomes large enough, there will be a precipitate. Both these methods, viz alcohol precipitation and calcium precipitation, have been reported in the literature, though one which combines the advantages of both precipitations has been found the most suited and reliable.

Carre' and Haynes (6) and again Emmet and Carre' (9) have repeatedly objected to alcohol precipitation. It has been found to be inaccurate and inconvenient, and is difficult in dilute solution. The precipitates are of variable composition, as they tend to carry down the impurities which cannot be washed off. Elwell and Dehn (8) have reported figures of pectin estimation as alcohol precipitate. The results are indeed high and are strongly criticized by Kertez (13). Elwell and Dehn did run some parallel analyses by other methods.

**Calcium Pectate Method**

Carre' and Haynes (6) presented the calcium pectate method which in short consisted of direct precipitation of pectin as calcium pectate by CaCl₂, after hydrolyzing with NaOH and acidifying with acetic acid. The difficulty of alcohol precipitation is avoided for calcium pectate can be made to flocculate from solution of very low concentration. A product of definite composition is obtained.
Since calcium pectate is a colloid its state of aggregation varies greatly with the conditions under which it is precipitated. If a sticky condition occurs the precipitate can only be filtered and washed only with great difficulty. This has been found to be the result of precipitation in alkaline solution in which case Ca(OH)$_2$ is absorbed by the gel. If the period of hydrolysis is too prolonged or the alkali is too concentrated, there is a similar result. Too small an excess of alkali is unsatisfactory. Best results were obtained by leaving the solution overnight. Pectin in alkaline solution is unsatisfactory, so to remove Ca(OH)$_2$ and any CaCO$_3$, excess of acetic acid is added. This also removes any occluded impurities. Tutin (17) contended that any acid yielding a calcium salt insoluble in acetic acid would be weighed as pectin. Nanji and Norman (14) made it obvious that the method could not be employed when using oxalic acid and oxalates as the extracting agents.

One molar strength of CaCl$_2$ is used for precipitation. Calcium pectate precipitate is washed with boiling water until free of Cl$_2$. The precipitate is washed back into a beaker, boiled and filtered again. This also was tested for Cl$_2$. Then it is filtered into a small fluted filter from which it can be transferred to a dish and finally to a Gooch crucible which has been dried previously at 100°C.
Calcium pectate is dried at 100° C for 12 hours. Carre' reported the composition of calcium pectate as C_{17}H_{22}O_{16}Ca. When there is excess of ash it may be due to colloidal mineral matter, possibly associated with protopectin.

Nanji and Norman (15) filtered calcium pectate precipitate as hot as possible and washed free of Cl. Goethe crucibles were found to be too slow. In the case of ammonium oxalate extract the precipitate was washed with dilute NH_{4}OH.

Appleman and Conrad (3) have modified the final phase of Carre' and Haynes method. To find the true weight of calcium pectate, the beaker containing calcium pectate and impurities was weighed and 50 ml of 2% ammonium citrate was added. The gel was loosened and transferred to a flask, with 50 ml of water, and boiled for 45 minutes to dissolve calcium pectate. The residue obtained after filtration and through washing was transferred to a tarred beaker and dried to a constant weight. This weight was subtracted from the first which gave calcium pectate.

Elwell and Dehn (8), Freeman and Ritchie (10), and Simpson and Halliday (16) have followed the calcium pectate method for final precipitation. Heinze and Appleman (12) determined nitrogen and deducted protein from the value obtained for calcium pectate.
Modification of Calcium Pectate Method

In view of the fact that pectin solutions containing oxalates could not be directly estimated by direct precipitation with CaCl₂, Emmet and Carre¹ (9) suggested a modification of the calcium pectate method. Manji and Norman (14) independently suggested the same modification. In short the method adopted consisted of precipitation by acidified alcohol, resolution of the precipitate and subsequent hydrolysis and precipitation as calcium pectate.

Acidification of the alcohol leads to more complete precipitation and also increases the rate of filtration of alcohol precipitate. The activity of the H ions causes the precipitation of oppositely charged colloids. Emmet and Carre¹ (9) tried different concentrations of HCl and found N/10 concentration to be satisfactory. When weaker acid was used the precipitation was not as quantitative as in the case of HCl. It is probable that the large increase in H ion concentration in the case of alcohol acidified with HCl was responsible for the quantitative precipitation. Manji and Norman (14) have proved that the concentration of acid is not very important as long as the alcohol is made acidic. They acidified the alcohol with 5-6 drops of concentrated HCl.

Manji and Norman (14) concentrated the extract by gently boiling it on a hot plate. The object of
concentration is merely to reduce the quantity of alcohol. It may help the precipitation as the solution becomes more concentrated. The temperature is not mentioned but it is probable that it could be effective enough, if too high, to cause heat degradation of pectin beyond the stage of pectic acid. The concentration could be done under vacuum at lower temperature.

Final concentration to 70% alcohol had been advocated. The pectinous material is allowed to precipitate for several hours but preferably for 24 hours. The precipitate is dissolved in hot water. In the case of ammonium oxalate (Manji and Norman) this is washed with dilute ammonium because if any salts of pectic acid are present they will have been converted to free pectic acid due to acid alcohol treatment. Pectic acid is insoluble in water but soluble in dilute NH₄·OH.

The pectin content of the solution is determined by the calcium pectate method formerly adopted. Among the workers mentioned before, only Simpson and Halliday (16) have followed the modification of Carre' and Haynes method.

The results have been reported in various ways. Carre' and Haynes (6) have determined the calcium content of the calcium pectate. Manji and Norman (14) have reported the results as amount of calcium pectate per 100 grams of dry matter. They called this the calcium pectate
number. This is a more logical and a more widely accepted method. Freeman and Ritchie (10) reported the results as milligram of calcium pectate per gram or as per cent of total pectin.

In the beginning of this work, direct precipitation of pectin by CaCl₂ was used for the estimation. On smaller samples the results seem to be reliable but as soon as large samples were run difficulties were encountered. In some cases the reagents themselves produced precipitates. Finally the acid alcohol method followed by calcium pectate precipitation was adopted. This has been found reliable though tedious and prolonged.
CHAPTER III

EXPERIMENTAL

Selection of Vegetables

The primary aim of this research was to study pectic changes in vegetables due to dehydration. Because of the difficulties involved in the quantitative estimation of pectin, a careful selection of vegetables for the study would simplify the procedure. Starchless vegetables would cause less interference with the analytical work, as it is known starch would be dragged down with the precipitate. Four vegetables were selected, namely, onions, spinach, kale, and rutabagas. Dehydrated samples were obtained from previous workers, except for one large commercial sample, for the purpose of preliminary trials. Spinach, kale and rutabaga samples were more than two years old and of poor quality. The quality of dehydrated onions was good.

Preparation and Dehydration of Onions

Preliminary trials on all the four vegetables showed that spinach and kale did not give satisfactory results, probably due to the presence of oxalates. The onions responded well in the experimental work and more data were collected on onion samples. To concentrate the study on
one product as well as to reduce the number of experimental difficulties, it was decided to work with onions only.

White Spanish variety of onions was specially obtained. The onions were skinned by hand and sliced by a shredder to a uniform thickness of one-fourth inch. Each batch of onions weighed three to four pounds. The sliced onions were spread evenly on stainless steel trays, half a pound or less per square foot. The linear velocity of the air in the dehydrator was 725 to 750 feet per minute.

Details of the dehydration work are presented in Table I. The object was to produce varying qualities of end product due to differences in temperature of dehydration. A greater resemblance to commercial multistage dehydration would be desirable. Weather conditions of 60 to 70 grains of humidity per pound of dry air were above the optimum for finishing to 4% moisture content within a short time to prevent some discoloration concomitant with lowering of quality. The temperatures used in batches 6 to 12 are those recommended by U.S.D.A. Miscellaneous Publication 540 (18). Without exception all the first six batches tasted bitter and had very poor appearance because of brown color. The presence of the bitter principle could not be explained. It was thought the variety of onion was not suited for the purpose of dehydration.
### TABLE I

**DEHYDRATION OF WHITE SPANISH AND WHITE GLOBE ONIONS**

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* Batches analyzed.

* D.B. is dry bulb °F.; W.B. is wet bulb °F.
White Globe variety, which is commercially well-known and valued highly, was obtained. A batch was dehydrated at the temperature previously yielding the best results. The bitterness and browning occurred even in this batch. It was obvious that the variety was not the cause of the trouble. The preparation procedure was checked to investigate any step which may lead to bitterness and excessive browning. The shredder was suspected as the cause of metallic contamination. The bearing and some screws were made of brass and might have caused copper contamination. Another source could have been the trays. A series of experiments (8-11) were conducted by eliminating both the probable causes. The onions were sliced with a stainless steel knife and dehydrated on the same trays. Another batch was sliced with the shredder and dehydrated on a wooden tray. The results were significant and gave a product of sweet taste and white color in the case of the batch sliced with the stainless steel knife. The other batch was bitter and though dried at the same time and under the same conditions had a little brown color. The cause of the browning could not be solely by the metallic contamination but it is probable that it is enhanced by the presence of metal. Both varieties, the White Spanish and White Globe, did not turn bitter when sliced with the stainless steel knife.
Due to weather conditions in the month of October the humidity was 60 to 70 grains of moisture per pound of dry air. For better finish, quicker and efficient dehydration the recommended humidity is not more than 50 grains of moisture. Therefore it was not possible to produce a series of dehydrated samples with fine variation of quality. Nevertheless, enough samples have been obtained which have a marked degree of difference in quality.

Measurement of Quality

There are no known methods and standards to measure the quality of such samples objectively. Some rehydration tests were conducted by the method recommended by Western Regional Research Laboratory (U.S.D.A., 18). The ratios were not significantly different or were not consistent. Likewise no valid objective tests for texture of the rehydrated material are known. In judging the samples, observations on the general qualities and appearance were employed as an index of the quality. For the purpose of this work, this has been adequate.

Preliminary Trials

The first few experiments involved small samples (1 gram). The samples were powdered and weighed. Consecutive pectin extractions were made on the same sample as follows:
Soluble pectin  Water extract (a)
Pectic acid and pectates Ammonium citrate extract (b)
Protopectin Reflux with N/30 HCl one hour (c)

Ammonium citrate extract (d)

Some extractions were made by shaking the material in a mechanical shaker. Disintegration with a Waring Blender (five minutes) gave better extraction because it was more vigorous and gave finer particles. The time of extraction (standing) varied from 12 to 16 hours, for water as well as ammonium citrate extractions. On an aliquot of the extract the pectin content was determined by direct precipitation with CaCl₂ after hydrolyzing with NaOH, and acidifying with acetic acid.

The next step was to employ a larger sample to have more quantity of pectin for future use. The quantity of solvent used was increased proportionately and as the size of the sample was 30 grams the solutions became too large to handle successfully. Filtration was too slow and caused fermentation of the solution during the process. Onion samples were run successfully even on a large scale. Spinach and kale gave more trouble in filtration and gave very large and flocculent precipitates, apparently calcium oxalate.

The results were unreliable and not at all comparable
to the small samples, e.g.:

Spinach - soluble pectin 5.6% as calcium pectate on one gram sample
25.7% as calcium pectate on thirty grams sample

This necessitated a change in the method of estimation. The modification offered by Emmet and Carre' (9) and Nanji and Norman (14) was tried and found to be satisfactory. Details of the procedure are given under the caption of Methods of Analyses.

Some parallel samples were run with and without alcohol blanching to inactivate the enzymes. Isopropyl alcohol was used. The results are presented in Table II. The samples were dropped in boiling alcohol and boiled for 10 minutes. Alcohol was removed by filtering through a sintered glass filter with suction. From the results, it is evident that there is degradation of pectinous material during the analytical work unless the samples are alcohol blanched. It must be realized that dehydrated onions are not blanched commercially. The soluble pectin does not seem to have changed while pectic acid and pectates and protopectin fractions have changed considerably. But if the process of hydrolysis is considered progressing from protopectin through soluble pectin to pectic acid, the soluble pectin fraction must have lost and gained equally and due to the balance the weight remained constant.
### TABLE II

**COMPARISON OF PECTIN FRACTIONS OF SAMPLES OF COMMERCIALLY DEHYDRATED ONIONS, WITH AND WITHOUT ALCOHOL BLANCHING**

<table>
<thead>
<tr>
<th>Pectin Fractions</th>
<th>Alcohol Blanched</th>
<th>Not Treated</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Code # 42 42 45 31 32 33 36</td>
<td></td>
</tr>
<tr>
<td>Soluble pectin (a)</td>
<td>Water extract</td>
<td>1.39 1.92 1.76 1.68 0.52 1.42 0.35</td>
</tr>
<tr>
<td>Pectic acid and pectates (b)</td>
<td>Ammonium citrate extract</td>
<td>0.99 1.43 0.88 1.87 2.66 2.68 3.65</td>
</tr>
<tr>
<td>Protopectin (c plus d)</td>
<td>HCl reflux and ammonium citrate extract</td>
<td>3.23 3.78 3.51 2.67 1.82 2.66 4.11</td>
</tr>
<tr>
<td>a and b</td>
<td></td>
<td>2.37 3.45 2.64 3.55 3.19 3.10 4.48</td>
</tr>
<tr>
<td>Total</td>
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<td>5.61 7.13 6.15 6.22 5.01 6.75 8.59</td>
</tr>
</tbody>
</table>

*Grains of calcium pectate per 100 grams of dry matter or calcium pectate number expressed as % of the total*

| Soluble pectin (a) | 24.6 26.8 28.6 27.0 10.4 21.0 10.0 |
| Pectic acid and pectates (b) | 17.8 20.1 14.3 30.0 53.4 39.7 43.0 |
| Protopectin (c & d) | 57.6 53.0 57.2 43.0 36.4 39.6 47.0 |
| Total | 100 100 100 100 100 100 100 |
The average loss of protopectin fraction (c and d) is 1.43 grams of calcium pectate while the average gain of pectic acid and pectate fraction (b) is 1.68 grams of calcium pectate. The degradation does not seem to have gone beyond the pectic acid stage.

Method of Analyses

1. Sampling of fresh onions was done by taking 1/8 radial segments from several onions. Dehydrated onions were first mixed by coarsely grinding in a Waring Blender and then weighed. Five-gram samples of the latter seem to be adequate and easier to work with. An equivalent dry basis sample of the fresh vegetable was used.

2. Samples were immediately dropped in boiling alcohol and were boiled for 10 minutes. After cooling they were filtered through a sintered glass filter with suction and washed into beakers with 100-200 ml of water.

3. Fresh onion samples were then put in a Waring Blender and run for 5 minutes. Dehydrated samples were allowed to rehydrate for three to four hours at room temperature and then Waring Blend for five minutes. This resulted in a very finely divided state of material.
4. A Buchner funnel was prepared with rapid filter paper. Suction was drawn before pouring the solution. Suction was released when fast filtration stopped and only dripping was seen. This helped to keep the residue wet on the filter paper.

5. The residue was removed from the filter paper by washing it with a jet of solvent from the wash bottle. The removal of the residue was more efficient when it was wet. The Buchner funnel was kept in a slanting position. The residue was collected with 100-200 ml of water in a beaker. The extraction was done by stirring with a mechanical stirrer for five minutes and again filtered through the same filter paper.

6. Three extractions with water were sufficient to yield all the soluble pectin. The fourth extraction gave negligible precipitate with acid alcohol (paragraph 11) after concentration of the solution. Total extract was 400-500 ml.

7. The residue after the water extract was similarly extracted with 0.6% ammonium citrate to extract pectic acid and pectates. Here, too, three extractions were sufficient, while the fourth one did not give any acid alcohol precipitate after concentration of the solution. Total extract was 400-500 ml.
8. Further extraction could only be made by hydrolysis of protopectin. The residue was collected with 200-250 ml of N/30 HCl and refluxed for one hour. After cooling, it was filtered through the original filter paper. The residue was washed with water and stirred for five minutes, filtered and the washings were added to the previous acid extract. A second washing with water did not give any acid alcohol precipitate after concentration of the solution.

9. A second ammonium citrate extraction was similar to the one made before. This extraction was made to recover the pectic acid and pectates formed during the process of hydrolysis of protopectin. Three washings and stirring yielded complete extraction. The fourth one gave no acid alcohol precipitate after concentration. These constituted the fraction (d).

10. Each extract was concentrated under vacuum, boiled at 110° F to 120° F. The volume of the concentrated extract was 80-100 ml from the original volume of 400-500 ml in each case.

11. Acid alcohol precipitation was brought about by adding 96% isopropyl alcohol, 3-4 times the volume of the extract. The alcohol was acidified by 5-6 drops of concentrated HCl. The solutions were allowed to stand for 24 hours.
12. The acid alcohol precipitate was filtered through sintered glass. The precipitate was dissolved in water, 100-150 ml.

13. Fifty ml of N/10 NaOH was added to hydrolyze the pectin. This was allowed to stand overnight.

14. Twenty-five ml of N acetic acid was added. It was checked to make certain that the solution was acidic.

15. Twenty-five ml of N/1 CaCl₂ was added after allowing the solution to stand for five minutes. The precipitation occurred quickly.

16. To insure complete precipitation the solution was allowed to stand for 3-4 hours. The solution was boiled for five minutes and filtered hot. The precipitate was washed free of chloride. Three or four washings with hot water were enough.

17. Glass filters were dried to a constant weight at 70°C and 25 inches vacuum for 24 hours. The results are reported as grams of calcium pectate per 100 grams of dry matter and percentage of total pectin.

**Moisture Determination**

Determination of moisture in fresh onion was done by toluene distillation method. It required 40 minutes to run the moisture test. This was also checked against a
set of determinations made in Brabender moisture tester. The results were close. In the case of White Globe variety the moisture test was run according to the method adopted for the dehydrated onions.

A tentative method of A.O.A.C. (2) for determination of moisture in a dried product was used for the dehydrated samples. Finely ground samples were dried in 28 inches vacuum at 70° C, admitting a slow current of air in the oven.

**Analytical Results**

The analytical results of two varieties of onions, White Spanish and White Globe, are presented in tables III and IV and graphs I and II respectively. Fresh onion analyses can be compared with different batches of dehydrated onions in the case of White Spanish. The results on the first batch are rather high which could not be explained. An average of four analyses on the samples taken from the same batch is presented in each case. Only two dehydrated batches of White Globe variety have been analyzed and here the results are an average of two each, though in the case of fresh onion analyses the average is of four analyses. For a comparative study, analyses of a commercial dehydrated sample are presented. The variety of the commercial sample is not definite but probably it
is White Globe.

Three fractions of pectic substances are presented, namely soluble pectin, pectic acid with pectates, and protopectin. The protopectin fraction is composed of two fractions (c) and (d). The second ammonium citrate extract yields pectic acid and pectates which are formed during the process of hydrolysis. Therefore neither (c) nor (d) constitute the protopectin fraction, only their sum. Justification for the use of the line (a and b) in the tables is as follows. It is apparent that any degradation would have to follow the sequence; protopectin (c and d), to soluble pectin (a), to pectic acid and pectates (b). Therefore any losses of soluble pectin (a) if they show up at all in the pectin fractions will appear as pectic acid and pectates (b). Any increases of (b) fraction above the original material are not alone significant, since they may have come from the degraded soluble pectin (a) fraction. Changes in the sum of fractions (a) and (b) may be more significant and have been included for comparison.
### TABLE III

**COMPARISON OF PECTIN FRACTIONS OF FRESH AND DEHYDRATED ONIONS (WHITE SPANISH)**

<table>
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<tr>
<th>Pectin Fractions</th>
<th>Fresh Onions</th>
<th>Dehydrated Onion Batches #</th>
<th>Quality Rank</th>
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<tbody>
<tr>
<td>Soluble pectin (a) Water extract</td>
<td>3.17</td>
<td>1.9</td>
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<td>1.46</td>
<td>1.56</td>
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<tr>
<td>Pectic acid and pectates (b)</td>
<td>1.67</td>
<td>2.27</td>
<td>0.97</td>
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<td>Ammonium citrate extract</td>
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<td>6.28</td>
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<td>4.24</td>
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<tr>
<td>Protopectin (c and d) KCl reflux</td>
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<td>73.3</td>
<td>73.3</td>
<td>89.6</td>
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<td>Ammonium citrate extract</td>
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<td></td>
</tr>
<tr>
<td>a and b</td>
<td>4.54</td>
<td>4.17</td>
<td>2.24</td>
<td>2.46</td>
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<td>Total</td>
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<td>10.45</td>
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<td>6.84</td>
<td>7.51</td>
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* Grams of calcium pectate per 100 grams of dry matter or calcium pectate number.

EXPRESSED AS % OF TOTAL PECTIN IN FRESH

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<tr>
<th>Pectin Fractions</th>
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<td>Soluble pectin (a) Water extract</td>
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<td>Pectic acid and pectates (b)</td>
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<td>45.0</td>
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<tr>
<td>a and b</td>
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<td>112.5</td>
<td>73.3</td>
<td>73.3</td>
<td>89.6</td>
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### TABLE IV

**COMPARISON OF PECTIN FRACTIONS OF FRESH AND DEHYDRATED ONIONS, COMMERCIAL AND LABORATORY (WHITE GLOBE VARIETY)**

<table>
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<th>Pectin Fractions</th>
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<td>Soluble pectin (a)</td>
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<td>Water extract</td>
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<td>Pectic acid and pectates (b)</td>
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<td>Ammonium citrate extract</td>
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<td>Protopectin (c and d)</td>
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<td>HCl reflux Ammonium citrate extract</td>
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<td>a and b</td>
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*Grams of calcium pectate per 100 grams of dry matter or calcium pectate number

**EXRESSED AS:**

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<th>% OF TOTAL</th>
<th>% OF TOTAL IN FRESH</th>
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<td>Soluble pectin (a)</td>
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<td><strong>Total</strong></td>
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GRAPH I

COMPARISON OF PECTIN FRACTIONS OF FRESH
AND DEHYDRATED ONIONS (WHITE SPANISH)

Grams of calcium pectate.

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</table>

Quality Rank

4 5 6 2

1 t Total.
c & d Protopectin.
a Soluble pectin.
b Pectic acid & pectates.
GRAPH II

COMPARISON OF PECTIN FRACTIONS OF FRESH AND DEHYDRATED
ONIONS-COMMERCIAL AND LABORATORY (WHITE GLOBE)

- t: Total
- c & d: Protopectin
- a: Soluble pectin
- b: Pectic acid & pectates

Grams of calcium pectate:

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</tbody>
</table>

Diagram showing the comparison of pectin fractions.
CHAPTER IV

DISCUSSION OF RESULTS

Comparison of Pectin Content with Quality

White Spanish:

Inspection of the data shows that though there is a loss of soluble pectin, the loss is too erratic to correlate with the quality. The same remains true for the pectic acid and pectate fraction. But when the two fractions, soluble pectin and pectic acid with pectates, are considered together (a plus b), the losses are roughly proportional to the losses in quality. Considering further the total pectin in the dehydrated samples which is only the sum of all the fractions, it can be correlated similarly with quality. The protopectin fraction remains essentially unchanged by the processing.

White Globe:

Here the poorer quality sample shows loss in soluble pectin fraction (a), while in the good sample the soluble pectin fraction remains unchanged. The loss in (a) plus (b) can be assigned to experimental deviation, since the total pectin content remains the same. No other fraction gives indication of losses.
Comparison of White Spanish with White Globe

Since only one lot of fresh onions was used in each variety, it is not certain that the results can be attributed to the varietal difference but the general observation is that each lot is typical of that variety. Total pectin content of White Spanish is higher than in White Globe. The ratios of soluble pectin to pectic acid and pectates in both varieties are about the same (2:1). White Globe has more of its pectin in the form of protopectin (61.5%) than the White Spanish (48.5%). Perhaps the lack of change in pectin fractions and total pectin in the case of White Globe as compared to White Spanish is explained by the stability of the protopectin fraction which undergoes very little change in dehydration. This may be another reason for commercial desirability of White Globe.

Comparison of Fresh and Dehydrated Onions

There is a considerable loss of soluble pectin in the dehydrated samples. This is even true of sample number one which has unexplainably higher results. The pectic acid and pectates fractions are irregular. One arresting observation is that of the protopectin fraction which has remained practically unchanged in all the fractions examined. The excellent commercial sample could be very favorably compared with the fresh onion analyses, although
of unknown derivation.

In conclusion the results show that the soluble pectin fraction undergoes maximum changes during dehydration and for the purpose of any correlations, the soluble pectin content should serve as an index of changes. Since the soluble pectin changes may more conveniently be followed by viscosity studies on the simple extracts, this method should be further investigated for correlating processing and quality with pectin changes.
CHAPTER V

SUMMARY

The pectinous material is here fractionally extracted as (a) soluble pectin, (b) pectic acid and pectates, and (c) protopectin. The extraction is dependent on the specific solvents used, water for the soluble pectin, ammonium citrate for pectic acid and pectates, and acid hydrolysis for protopectin. The extracts containing the pectinous fractions are concentrated, precipitated by acid alcohol, redissolved and reprecipitated by CaCl₂ after being hydrolyzed with alkali and acidified.

An attempt is made to study the changes in the pectinous materials in the dehydration of seven lots of onions. Analyses of fresh as well as dehydrated onions of two varieties are presented. The soluble pectin fraction undergoes maximum losses during dehydration and could serve as an index of changes. The protopectin fraction remains practically unchanged in amount. The pectic acid and pectates fraction is irregular. The assumption is that any degradation would have to follow the sequence: protopectin toward soluble pectin to pectic acid and pectates. Any losses in the soluble pectin, if they show up at all in the pectin fractions, will appear as pectic acid and pectates. When the sum of soluble pectin and
pectic acid and pectates is considered together, it is roughly correlated with the losses in quality. The quality has been judged by the appearance of the material since no objective tests for quality are available and the lots were similar by other subjective estimation. As the soluble pectin changes may more conveniently be followed by viscosity studies on the simple extract, the method should be further investigated.
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