THE EXTRUSION PROPERTIES OF POTATO GRANULES

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by

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Summary

Potato granules from different sources were found, on extrusion, to produce potato snacks of variable quality. In some instances strip formation was unsatisfactory, in other instances blistering of the snack occurred on frying. In total, about 20-25 batches of potato granules were examined and classified in relation to these two phenomena.

The amylose/amylopectin ratios of these samples of potato granules were determined by the semi-micro potentiometric iodine titration technique, but it was found that there was no significant differences in the amylose/amylopectin ratio in relation to the extrusion behaviour of the granules.

The determination of the amount of free starch present outside the potato granules also did not show any clear differences between the satisfactory and unsatisfactory potato granules, though the extract from the unsatisfactory potato granules tended to indicate that they contained more lipid than the satisfactory ones.

The unsatisfactory potato granules yielded a higher amount of total extractable soluble starch than their satisfactory counterpart, for the same variety of potato granules. The amount of soluble starch increased on extrusion and it was also found to be related to the breaking strength of the extrudate and their blistering behaviour. A stronger strip which gave a higher amount of soluble starch possessed a greater tendency to blister. Addition of PSA additives to potato granules prior to extrusion increased the soluble starch content, but the degree of blistering was suppressed.

Gel permeation chromatography experiments showed that the starches extracted from inside the potato granules consisted of mostly high molecular weight macromolecules (very similar to that of amylopectin) and a smaller quantity of low molecular weight macromolecules similar to amylose. The soluble starch extracted from the outside of potato granules also

consisted of a greater amount of high molecular weight macromolecules whereas, after extrusion, a greater quantity of smaller molecular weight macromolecules was found to be present which presumably had been expressed from the granules and was assisting in forming the network, binding the potato granules together to form a coherent strip.

Determination of the total phosphate and glucose-6-phosphate contents of both potato granules and extracted starches did not show any correlation between the satisfactory and unsatisfactory potato granules. The quantities of phosphate present were small (<0.8%).

Studies were conducted to elucidate the differences in the cell wall material between satisfactory and unsatisfactory potato granules. Results showed only minimal differences in both the amount of cell wall material and the composition of neutral sugars in the cell wall extract of different potato granule samples.

Investigations of the macromolecular order in the granules were pursued along several lines. By x-ray diffraction it was found that the manufacture of potato granules by the add-back process produced changes in the molecular order of the starch component transforming the B-type x-ray pattern of native potato starch to, in the potato granules, the A-type typically found in cereal starches. The differences in molecular order of the starch component between the satisfactory and unsatisfactory potato granules were also investigated using infra-red spectroscopy and differential scanning calorimetry besides x-ray diffractometry. However, there was no simple correlation with either the crystal type or relative crystallinity of potato granules and their extrusion behaviour. Infra-red studies also did not reveal any differences in the spectra nor the absorbance values at wavelengths of 935, 855 and 760 cm^{-1}.

D.S.C. and x-ray results, followed subsequently by lipid analysis, established that the unsatisfactory behaviour of certain batches of

potato granules was due to the presence of excess GMS (>0.3%), which prevented the formation of a coherent strip, whereas satisfactory granules had a normal amount of GMS (<0.3%) which was not detected by either D.S.C. or x-ray techniques. The excess GMS of unsatisfactory granules when monitored as the unassociated material (by the M_L peak), was found to decrease with storage time.

Extrusion of satisfactory potato granules, when examined by D.S.C. was accompanied by an increase in the amylose-lipid complex (V-amylose) as indicated by the M_{A-L} peak and this was further enhanced on the addition of PSA additives. However, the formation of the V-amylose complex was not very evident in the x-ray patterns. X-ray crystallinity studies indicated that the extrudates exhibited a lower order and it was presumed that there was less x-ray order in the V- than in the A-form. The crystallinity of potato granule samples were found to be affected by their moisture content, the highest crystallinity was achieved with samples having approximately 38% moisture.

NMR experiments in conjunction with heating experiments which had been designed to ascertain the amount of bound water before and after heating the granules to 90°C, indicated that although the bound water content before heating did not show any clear differences between satisfactory and unsatisfactory samples, there was a tendency for the unsatisfactory granules to show a slight decrease in bound water after heating. Experiments using varying amounts of water revealed that the spin-spin relaxation time (T_2) increased with the water content of both satisfactory and unsatisfactory granules. The increase was greater for the satisfactory granules at 65% and 55% moisture content and lower for 45% and 35% moisture content, compared to the unsatisfactory granules.

A mathematical model has been constructed which assumed that blistering was the consequence of an over-strong intergranular network which had a low permeability for water vapour. The experimental physical

constraints of time, temperature and water content when introduced into the model showed that the blistering phenomenon could readily be explained.

It was finally concluded that unsatisfactory strip formation was a consequence of the presence of excess GMS while blistering occurred when extrusion yielded a higher intergranular polysaccharide network (as evidenced by the amount of the total soluble starch).

INTRODUCTION

1. Introduction

Dehydrated potato granules are an important product of the potato processing industry and are widely used as a convenience food both at home, in restaurants and other group feeding establishments. In recent years the use of potato granules as raw materials has extended to the snack food industry where they are used for producing extruded French fries, fabricated potato chips, potato puffs and many other products.

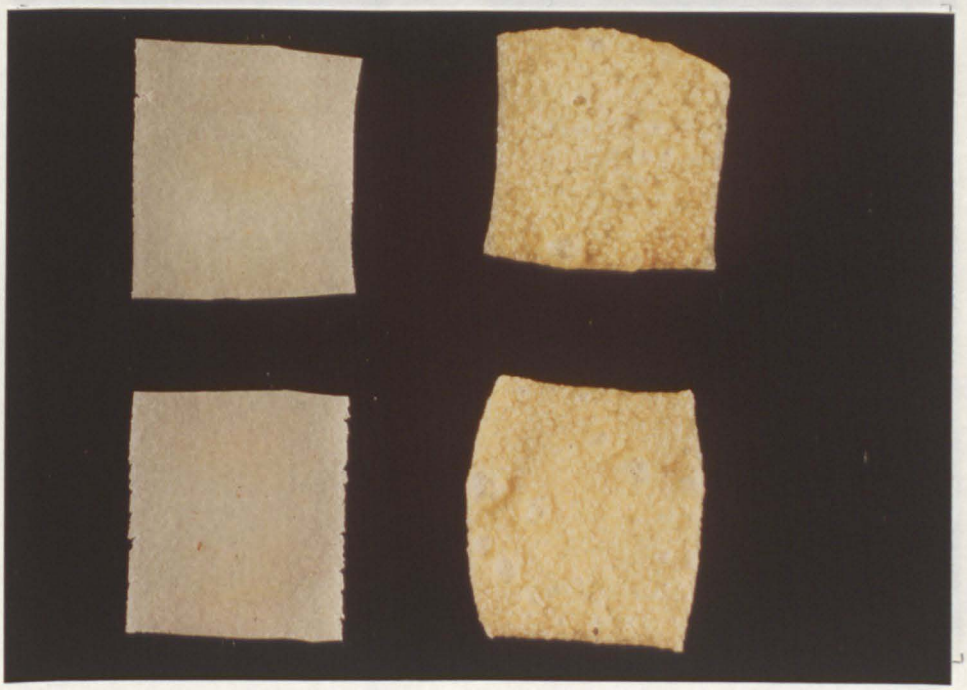
In the 1970's, a new product was developed for the United Kingdom market, with potato granules as the major constituent. The texture and flavour of this product have been both attractive and well accepted by the consumer. However, considerable technical problems have been encountered which severely affected the efficiency of the process and resulted, for reasons described below, in high wastage.

The potato snack is produced by extruding a preconditioned dough, consisting of potato granules, water and potato snack additives (PSA), yielding a ribbon-shaped extrudate which is cut into pieces and fried in deep fat at 180°C, as shown in Figure 1. During production two major problems have been encountered:

(a) Under certain conditions it is impossible to produce a coherent strip of extrudate, as shown in Figure 2.

(b) In other circumstances, the desired modest and even expansion is replaced by irregular blistering which may, in extreme cases, occupy as much as 1/4 to 1/2 of the snack surface (Figure 3). Not only are these unsightly, but also extremely vulnerable to disintergration on

Figure 1. Extrusion of the SATISFACTORY potato granules yielding a ribbon -shaped extrudate.

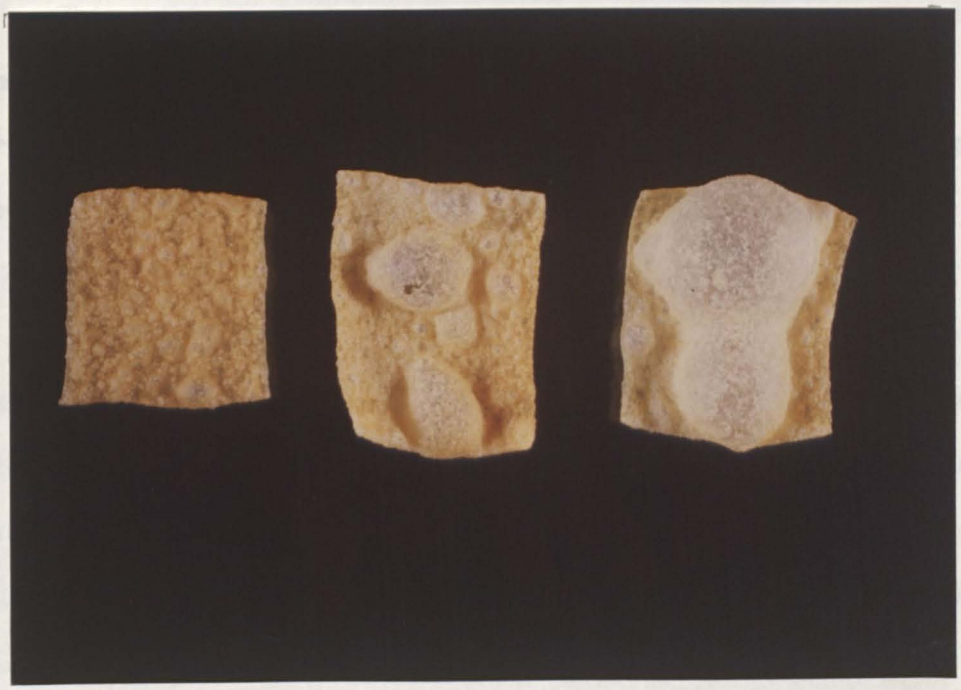


Unfried extrudate. Fried potato snacks - a satisfactory product with no blisters.

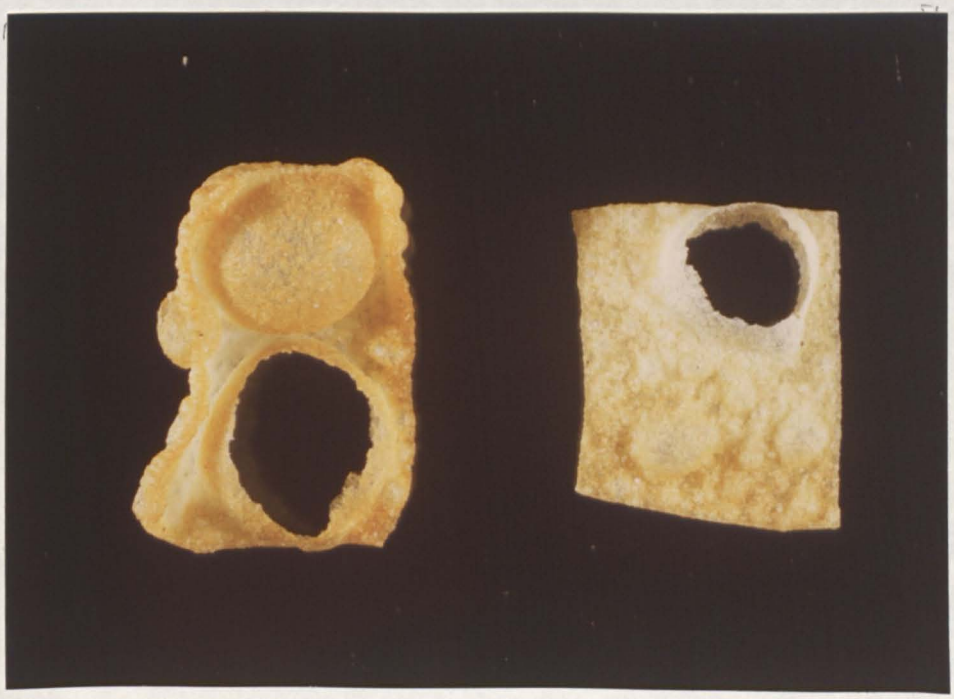
Figure 2. Extrusion of the UNSATISFACTORY potato granules, yielding a 'flaky' extrudate.

Unfried UNSATISFACTORY extrudate

Figure 3. Fried potato snacks showing different degrees of blistering.



'Ideal' snack 'Slight' blistering 'Severe' blistering



Blisters broken - 'Polo' snacks

packaging; in some instances the result may be a 'polo' snack!

This project was initiated with a view to gaining an understanding of the process at large and an insight into the reasons for the occurrence of both unsatisfactory strip formation and blistering and to determine whether they were related or separate problems and to seek possible solutions.

The general approach in this project has been to conceive of the potato granule as a micro-organised system of gelatinised starch enclosed within the cell wall. Further, it was assumed that the formation of a satisfactory ribbon depended on the expression of some of the contents of the potato granules. This starch would provide a cohesive matrix linking the potato granules together.

On further consideration a number of questions seemed worthy of detailed examination. They were:

(i) Are there significant differences in the molecular order between satisfactory and unsatisfactory granules? The starch granules in the native potato have a characteristic birefringence and x-ray crystallinity. Is this lost on precooking and/or during cooking in the potato granule production process and if so, is there a variable recovery of order on granulation?

(ii) Are there significant differences in the composition and structure of the cell walls between satisfactory and unsatisfactory granules? If granules respond differently to extrusion it is possible that the cell walls are acting

as a sieve releasing the polysaccharides of the granule interior with different degrees of efficiency for different samples. Such differences in cell wall behaviour could be the consequence of their having a different composition, or(what would be more difficult to determine) a different structure.

(iii) Are there significant differences in the composition, structure and overall quantity of polysaccharide either inside the granule or outside after expression from the granules by extrusion? It is possible that differences in cohesion of the network may be a consequence of variations in polysaccharide composition or through the effects of interactions of additives with either the polysaccharides within the granule, on the cell wall or extragranular material after extrusion.

(iv) What role does the lipid material (glyceryl monostearate -GMS) play? Its crucial importance in potato granule production is well known; its general importance in snacks is also recognised, but its significance in this system is less clear.

(v) What role does water play in the production of satisfactory versus unsatisfactory product? Water is vapourised during the frying process. It is possible that blistering is a consequence of some particular spectrum of free and bound water which may vary between different samples.

(vi) Can differences in potato granule behaviour observed on extrusion under apparently constant conditions which then lead to satisfactory or unsatisfactory product be overcome by appropriately modifying extrusion conditions?

With these questions in mind, various investigations have been carried out to answer as far as possible the points at issue. Within the confines of a three year project it was not feasible to consider all possible avenues of investigation, but those which have been pursued are listed briefly below. They have been designed:

(a) To characterise the starch components in potato granules by finding,

(i) the amylose and amylopectin contents using a potentiometric titration method,

(ii) the free starch present in potato granules using the 'Blue Value' method,

(iii) the total soluble starch content of potato granules and extrudates,

(iv) the molecular size distribution of the extracted starches using gel permeation chromatography and

(v) the phosphorus content in the starch.

(b) To investigate the role of cell wall and to find:

(i) the amount of cell wall material in potato granules and

(ii) the composition of neutral sugars in the cell wall material.

(c) To study the changes in molecular order of the starch in potato granules,

(i) during the production of potato granules,

(ii) during extrusion, with and without the addition of additives, and

(iii) to assess the effect of GMS.

These studies were carried out using techniques like infra-red spectroscopy, differential scanning calorimetry and x-ray diffraction.

(d) To investigate the physical state of water in potato granules, measured using pulse NMR.

(e) To conduct extrusion trials to establish the optimum operating conditions (mainly temperature and moisture) and to characterise the extrusion behaviour of different potato granules.

It is perhaps valuable to comment at this juncture, on three points which have been a feature of this project. In so doing, it will permit the reader to understand certain aspects of the research which is described in the body of the thesis.

(i) Samples

In contrast to the idealised situation where uniform samples should be prepared to a given level of performance and composition which would not thereafter vary with time, the actual behaviour of potato granules is very different. The granules even immediately after production mirror variations in the raw materials of the process

(the potatoes themselves) and reflect seasonal changes which are a consequence of the physiology of the potato tuber, as well as vagaries in production schedules and techniques. Even after production, there is evidence that their functionality may vary with time of storage.

(ii) Lipid content

As was reasonable from a scientific point of view, early efforts were directed at trying to discover techniques which would at the laboratory level show differences and which might both give some understanding of the process of granulation and strip formation and also provide a basis for quality control and raw material specifications. Four samples were supplied and selected which seemed particularly promising since they covered the range from "excellent" (Eba) to "impossible" (Ajax) in terms of strip formation. Such samples had, we understood been prepared according to standard routines and subjected to the necessary quality control procedures. The differences in their extrusion behaviour, must, it was concluded, lie in their composition or structure. The use of a number of techniques viz. pulsed NMR , x-ray diffraction and analysis for amylose/amylopectin ratios showed differences which appeared to offer the basis for a concise solution to the problem. However, on extending the sample range, the original indications were not confirmed and the whole situation became most confused. (This is the reason for the proliferation of samples which were examined by the above and certain other techniques). In due course, towards the end of

the project, a further series of samples were prepared according to standard procedures, all of which were again impossible to extrude satisfactorily like the original Ajax sample. At this point it proved possible through the experience that had accrued to pinpoint by a physical technique (D.S.C.) that those unsatisfactory samples almost certainly had an excess GMS content, though we presumed they also had already been subjected to quality control. In the event, it was shown that the GMS content was wildly in excess (five times more) of that anticipated and a similar picture emerged on retrospective analysis of the first Ajax sample. These human omissions and errors did therefore in the long run lead to an understanding of the crucial role of GMS in strip formation even though in the first instance their properties led us along a false trail.

(iii) "Fine Tuning" of Product Quality

One of the exciting and challenging features of this project has been that the research has been directed at solving problems and gaining understanding of a process which teetered on the edge of technological feasibility. Throughout the project both supplier (Dornay) and user (Smith's) have worked hard to improve the quality of the raw material and the efficiency of the production. There were considerable commercial advantages for both companies in being successful in their aims. Of necessity therefore what was 'satisfactory' and 'unsatisfactory' (Eba and Ajax samples) at the commencement of the project had been refined to a much narrower band of acceptability

which resulted in less significant differences to investigate. This "fine-tuning", with the wrong directions that had been adopted from preliminary studies, led to much, largely fruitless endeavour. But of such is research and experience thus hard won is not to be despised!

LITERATURE REVIEW

2. Literature Review

2.1. The Potato Granule and its Production

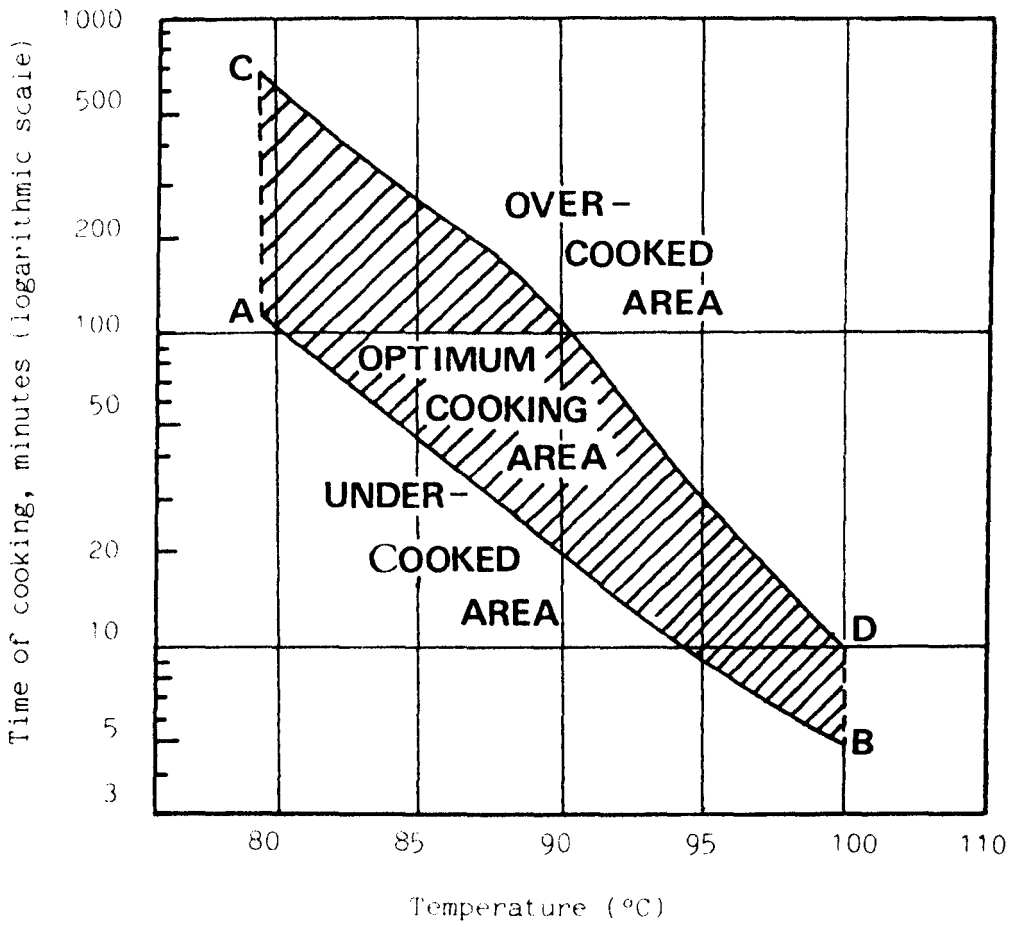
A number of processes have been developed for the production of potato granules of which the 'add-back' and 'freeze-thaw' processes are particularly well known. The 'add-back' process is probably the only process used commercially for large scale production of dehydrated potato granules.

2.1.1. 'Add-back' process

The 'add-back' process was first developed by Bunimovitch and Foutelowitz in 1936. Since then many modifications and improvements have been made to the processing conditions and these have been reviewed by Olson and Harrington (1955 A, B), Kueneman (1957), Cording and Willard (1957) and Feustal et al. (1964).

The process involves the following steps: potatoes are peeled, sliced and precooked, followed by steam cooking (the optimum conditions in relation to time and temperature are shown in Figure 4) and mashing. The mashed potatoes are mixed with sufficient dried potato granules (known as add-back) from a previous batch. The composite material is conditioned before dehydration to produce the dried granules. An outline of the process and the rationale for the sequence of steps is shown in Figure 5.

Figure 4. Optimum cooking conditions for potatoes during the 'add-back' process.



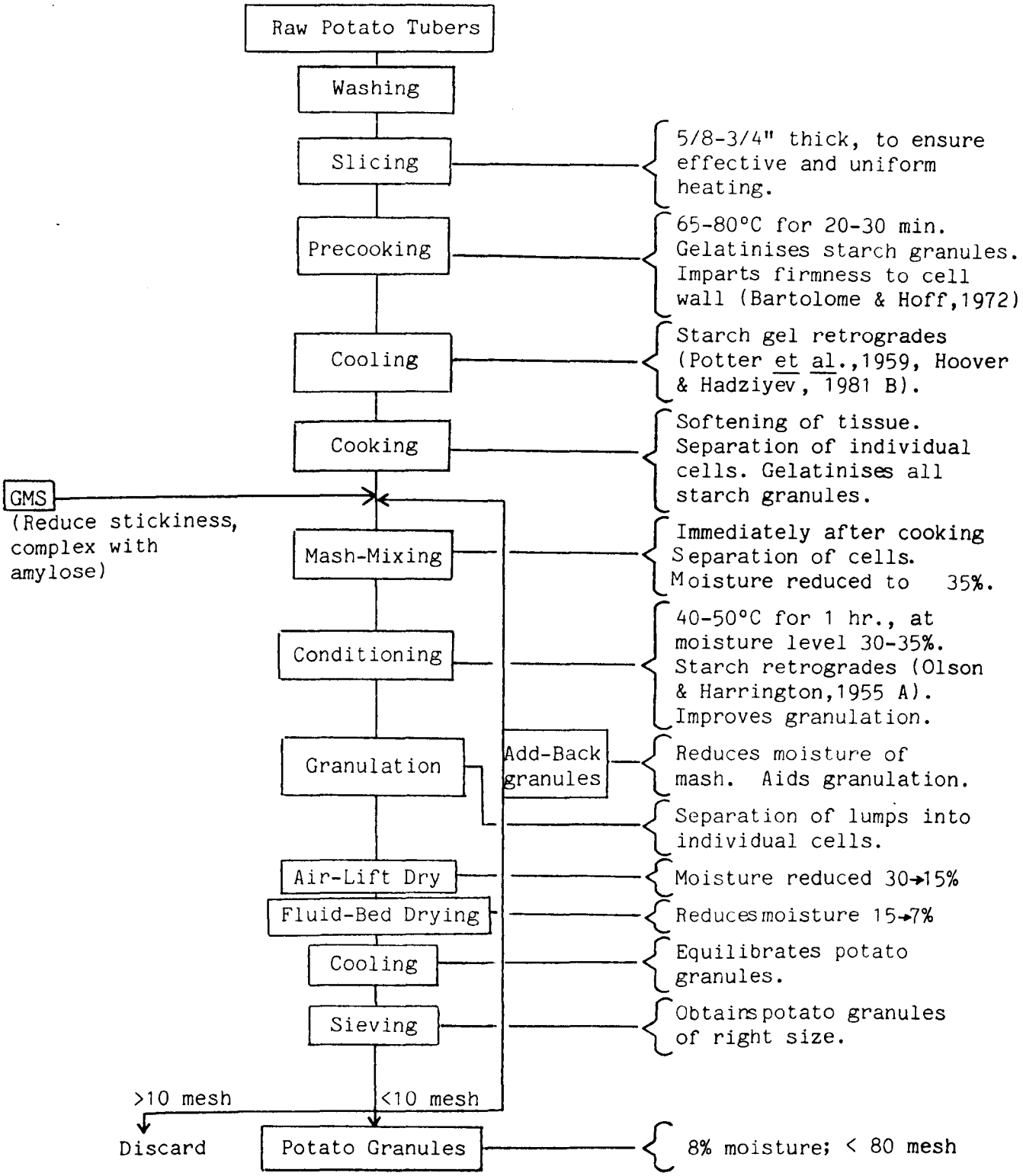


Figure 5 Schematic Outline of the 'Add-Back' Process.

2.1.2. 'Freeze-thaw' process

This process was recently developed by Ooraikul (1977). It is similar to the process described by Shub and Bogdanova (1977), which includes slicing the tubers, followed by steam-cooking, mashing, freezing the moist-mash, thawing, predrying, granulation and finally drying and sieving of the granules. An outline of the process is given in Figure 6.

2.1.3. Differences between the 'freeze-thaw' and 'add-back' process and the potato granules produced

The difference between the 'add-back' and 'freeze-thaw' process lies essentially in the method of granulation. The 'add-back' process requires about 85-90% of dry granules to aid in cell separation and reduction of moisture content, whereas the 'freeze-thaw' process is a straight through process that requires minimal (<10%) recycling of the dry granules.

Because of the different processing conditions used, the potato granules produced have different properties. The freezing and thawing in the 'freeze-thaw' process induce drastic changes to the cells, resulting in granules having angular shape with considerable shrinkage, a lower bulk density and a faster rehydration rate. In contrast, the 'add-back' potato granules are largely round and more compact with a relatively smooth surface and the water reabsorption capacity tends to vary with the dry matter content of the raw potatoes (Ooraikul, 1978).

All the potato granules used in the research are prepared using the 'add-back' process.

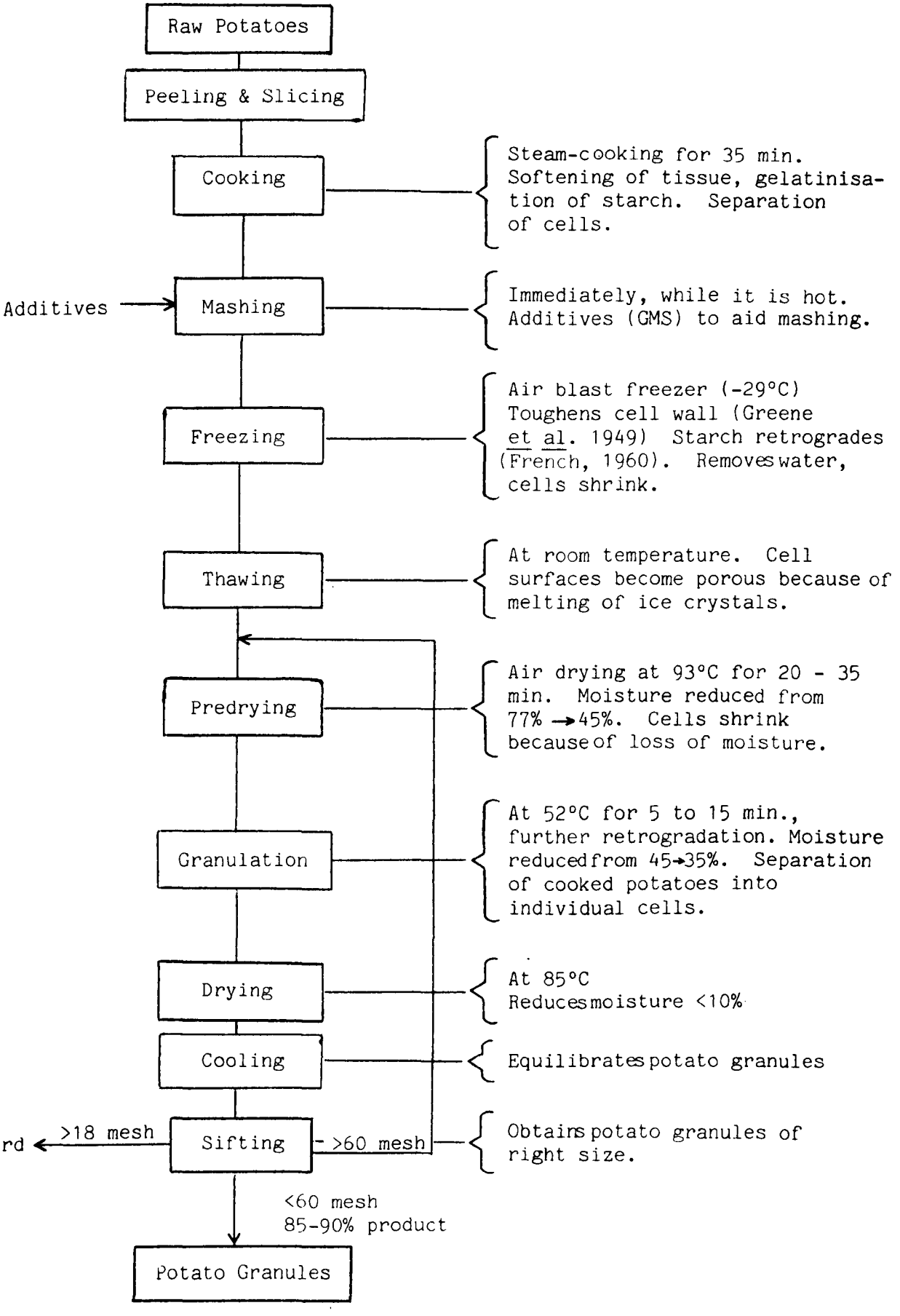


Figure 6 Schematic Outline of the 'Freeze-Thaw' Process

2.2 The Composition of Potato Granules

The potato granule can be described as a mass of gelatinised starch enclosed within a layer of cell wall. The important constituents present are the gelatinised starch (>90%), cell wall (2-3%) and minor quantities of lipids and protein.

2.2.1. Lipids

The amount of lipids present in potato tissue (0.65% - Pun et al., 1979) is very low compared to the lipid content in wheat flour (1.91% - Chung et al., 1982) and corn grits and flour (4.6% - Bhuiyan and Blanshard, 1982). It would therefore not be unreasonable to assume that natural lipids play only a very minimal role in determining the characteristic properties of products made from potatoes, except that they may cause off-flavours and rancidity problems (Burton, 1949; Buttery et al., 1961).

Detailed studies of potato lipids have been provided by Lepage (1968) and Galliard and co-workers (Galliard, 1970, 1973; Galliard et al., 1975; Berkeley and Galliard, 1974 A, B). They showed that the total lipid, about 0.5% on a dry weight basis, was similar for all varieties. The relative amounts of each lipid class also showed no varietal difference. Fatty acid analysis established that at least 90% of the total acids were a saturated acid (palmitic acid) and 2 polyunsaturated acids (linoleic and linolenic acids). The percentages of the individual acids vary only slightly among varieties and the polyunsaturated acids account for 70 to 76% of the total acids for all varieties (Table 1).

Table 1.

Total fatty acid content and composition of lipids in tubers from different varieties of potatoes[a].

Potato	Total fatty acid content (mg/100g fresh wt.)	Fatty Acid Composition (% of total fatty acid)						
		Palmitic	Palmitoleic	Stearic	Oleic	Linoleic	Linolenic	Linoleic and Linolenic
Desirée	54.6	18.2	0.7	4.9	2.0	59.6	14.5	74.1
Maris Piper	49.6	19.4	1.8	5.2	1.3	56.2	16.2	72.4
Pentland Crown	46.3	18.5	1.2	5.3	2.2	54.8	18.2	72.9
Record	54.5	16.3	0.8	5.3	1.1	52.7	24.0	76.6
King Edward	53.9	17.8	1.3	5.9	1.9	59.9	13.4	73.3
Majestic	53.7	18.2	0.9	5.3	1.6	57.9	16.2	74.0
Red Skin	53.7	17.5	1.2	6.1	1.0	52.0	22.2	74.2
Potato granule[b]	-	17.4	Trace	5.4	0.5	53.3	22.6	75.9

[a] Galliard, 1973

[b] Buttery et al., 1961

2.2.1.1. Effects during processing

Except for the reports by Mondy and Mueller (1977) on the effect of householdcooking methods on lipid composition and Schwartz et al. (1968) on fatty acid contents in dehydrated potato dices and flakes, relatively little has been published on the effects of processing on the lipids of potatoes.

Recently, Pun and Hadziyev.(1978), completed a study on lipid changes during production of dehydrated potato granules by the freeze-thaw process (Oooraikul, 1978). They found that steam-cooking followed by hot mashing caused a 12.9% loss of the total lipid with the greatest loss in the neutral and phospholipid fractions and least in galactolipids. The decrease in triglyceride content and the loss of other lipids were not accompanied by an increase in the content of free fatty acid. During the entire process the lipid composition of dehydrated potato granules showed a 14.7% loss of total lipids when compared to raw potatoes as shown in Table 2. The fatty acid composition was very much the same as that of the tuber (Buttery et al., 1961).

Table 2. Composition of lipids in raw and processed potatoes (wt. in mg. per 100g dry wt.).

Lipid	Raw potato	Steam cooked mashed potato	Dehydrated potato granules
Total phospholipid	335	299	282
Total galactolipid	128.6	127	125
Total stearoylipid	101	80	82
Free Fatty Acid	15	11.3	11.5
Triglycerides	33	24	25
Other neutral lipid	34	20	27
Total lipid	645	563	551.7

2.2.2. Cell Wall

Cell wall material constitutes only a minor portion of the total solids present in the potato tuber, but it has a profound effect on the textural properties of processed potato tissue (Potter and McComb, 1957; Linehan and Hughes, 1969; Bartolome and Hoff, 1972).

The cell wall lies outside the plasma membrane, which defines the boundary of the cell itself. The wall is freely permeable to virtually all molecules, whereas the membrane is only selectively permeable; this helps to maintain the integrity of the cell.

Cell wall material consists almost entirely of polysaccharides ($\approx$ 90%) and a small quantity of protein ($\sim$ 10%). The organisation of the cell wall can be envisaged as layers of cellulose microfibrils embedded in a matrix of xyloglucan arabinogalactan, rhamnogalacturonan and pectic galacturonan (Talmadge et al., 1973; Bauer et al., 1973; Keegstra et al., 1973). A model of the structure of the cell wall has been proposed by Keegstra et al. (1973) and is given in Figure 7. Although it was based on suspension-cultured sycamore cell wall, it provides us with a basis for reasonable speculation on the overall performance of the cell wall.

A comparison of the cell wall composition obtained by Le Tourneau (1956), Emiliani and Retamar (1968) and Hoff and Castro (1969) is given in Table 3.

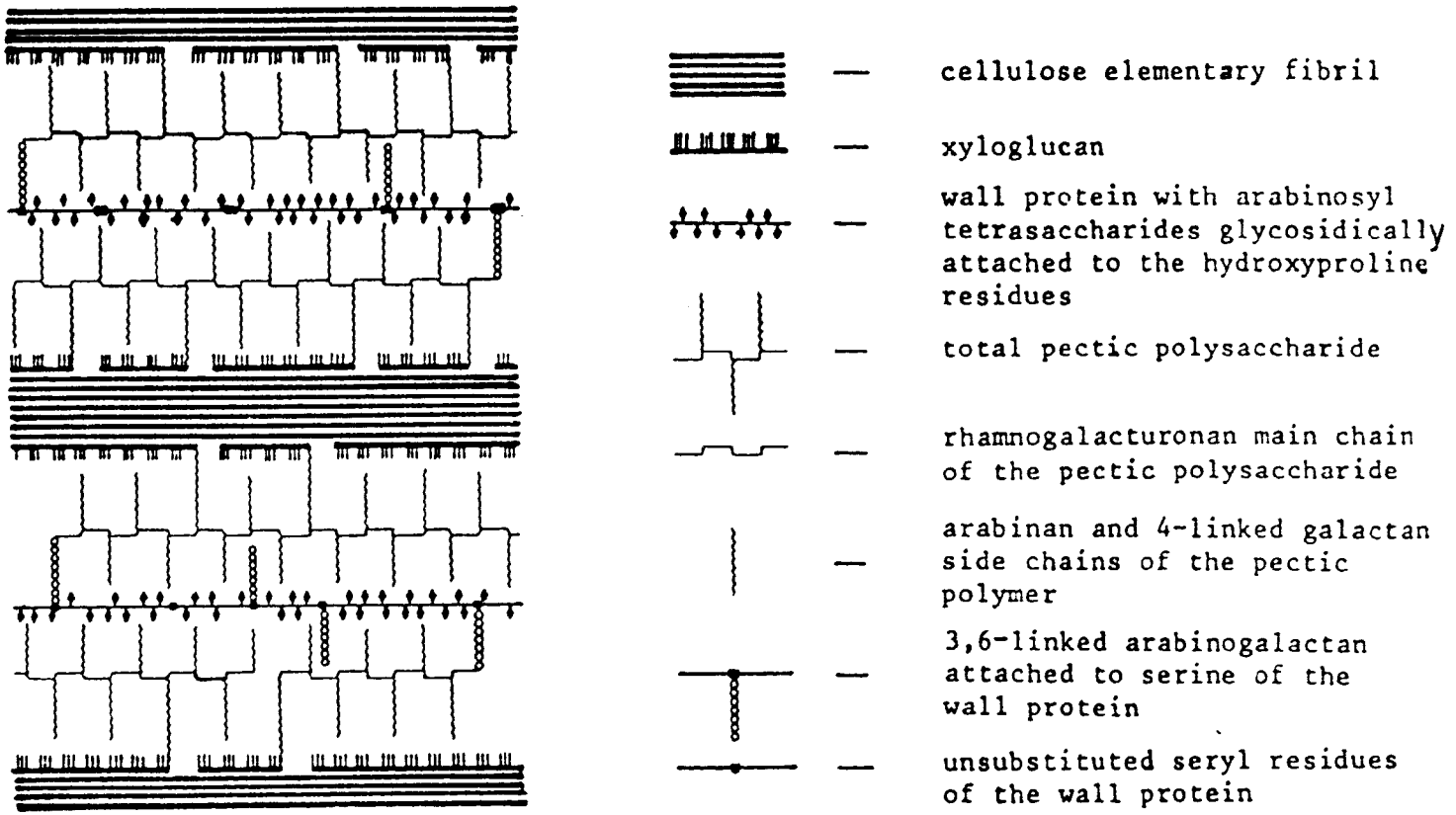


Figure 7. Tentative structure of cell walls of suspension-cultured sycamore cells (Keegstra et al., 1973).

Table 3. A comparison of the potato cell wall composition.

(fractions as % of dry matter)

Components	Le Tourneau (1956)	Emiliani & Retamar (1968)	Hoff & Castro (1969)
Pectic substances[a]	60	64-66	55
Hemicellulose[b]	10	8-10	7
Cellulose	15	24-26	28
Glycoprotein[c]	15	1	10
Cell wall material[d]	-	-	5.6

a Rhamnogalacturonan, araban, galactan

b Includes sugars like glucose, xylose and mannose

c Protein with tetraarabinosides and some galactan or arabinogalactan

d Percentage dry weight of tubers

The differences in the cell wall composition obtained by the three workers are probably due to the difference in extraction and analytical procedures.

William (1963) and Sterling and Bettelheim (1955) reported that the proportions of different cell wall components show little change among varieties and that the cell wall content was also relatively constant within a given variety.

2.2.2.1. Changes during processing

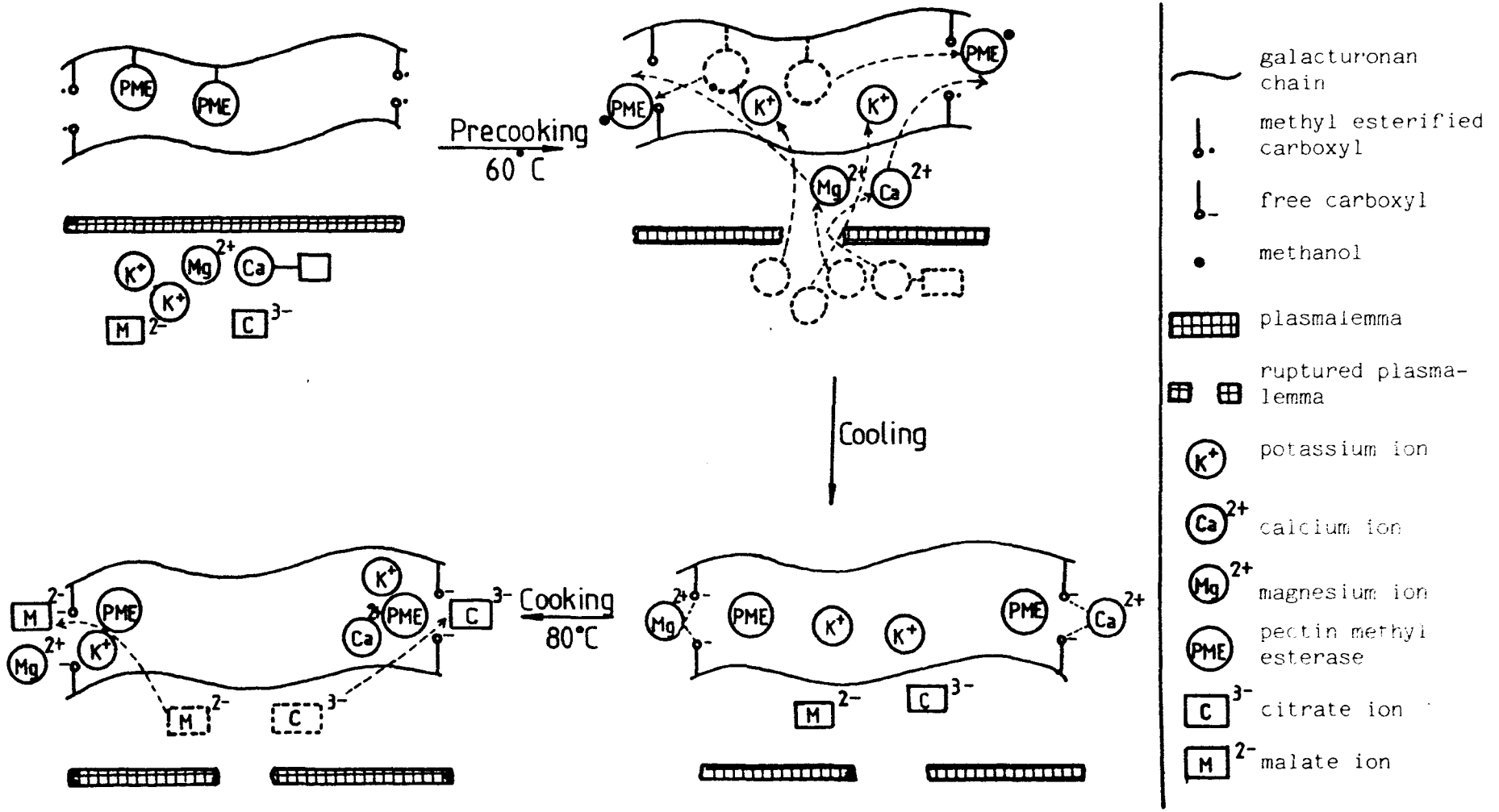
The most important function of the 'add-back' process is the separation of potato cells without causing too much rupture. This is achieved by precooking the potatoes at about 60°C, followed by cooking at 80°C.

These two steps cause changes to the pectic substances which are the predominant component in the cell wall and middle lamella (Albersheim, 1965; Rees, 1969 and Northcote, 1972).

During precooking at about 60°C, the permeability of the plasma-membrane changes (Personius and Sharp, 1973), allowing diffusion of cell solutes (predominantly K^+) into the cell wall region (Bartolome and Hoff, 1972) which then desorb and activate the pectin methyl esterase (PME). The enzyme decreases the degree of esterification (DE) of pectin galacturonan by a β-elimination process. Ca^{2+} and Mg^{2+} which are released from the starch during gelatinisation, diffuse through the destroyed plasmamembrane and form bridges with the pectin free carboxyl groups. Cooling reduces the solubility of the calcium pectate, which cause the firming of the pectin gel in the cell wall and middle lamella (Bartolome and Hoff, 1972; Keijbets, 1974). The firming effect renders the cells more resistant to breakdown during cooking. A proposed mechanism is given in Figure 8.

During cooking, the high temperature ($\sim$80°C) rapidly inactivates the pectin methyl esterase. The pectic material solubilises, probably due to the interaction of anions and cations (potassium, calcium, magnesium, citrate and malate ions) with pectic galacturonan (Keijbets, 1974), resulting in cell separation. Keijbets and Pilnik (1974) found that citrate and malate ions help the solubilisation of the galacturonan by chelating with Ca^{2+} as well as facilitating β-eliminative degradation of the galacturonan. A proposed mechanism by Keijbets (1974) is shown in Figure 8.

Figure 8. Proposed mechanism to account for the firming effect during precooking and solubilisation of pectic substances during cooking (Keijbets, 1974).



2.2.3. Starch

Each potato cell has about 18-20 starch granules (Fedec et al., 1977) and in each starch granule about 70% of the total solid is starch. In the native state the starch granule is considered as a semi-crystalline entity and is comprised of crystalline and amorphous regions. The exact nature of these two regions is a matter of speculation. However, a lot of evidence (Hizukuri and Nikuni, 1957; Montgomery and Senti, 1958; Doi and Doi, 1969; French and Kikumoto, 1973 and Robin et al. 1974), indicate that the crystalline component consists mainly of amylopectin while amylose is concentrated more in the amorphous regions.

2.2.3.1. Changes during processing

2.2.3.1.1. Gelatinisation of starch

During the precooking and subsequent cooking steps, the starch granules become hydrated, swollen and gelatinised. These three phenomena are described diagrammatically in Figure 9. Potato starch gelation is accompanied by an extensive release of solubilised starch, mainly amylose, from the starch granules (Reeve, 1963; Miller et al., 1973; Hoover and Hadziyev, 1981A). The amount of amylose released is a function of temperature. After gelatinisation the hydrated starch gel occupied nearly the entire cell volume (Fedec et al., 1977). Some cells may rupture resulting in extensive release of gelled starch (Mullins et al., 1955; Potter et al., 1959). The amount of starch released will determine the quality of the potato granules.

The changes in the starch granules during gelatinisation are reflected in their x-ray diffraction pattern (Katz, 1928). He found that heating the wheat starch in excess water led to a change of the A-pattern of the native starch into the less crystalline V-pattern while on further heating he obtained an amorphous pattern, suggesting

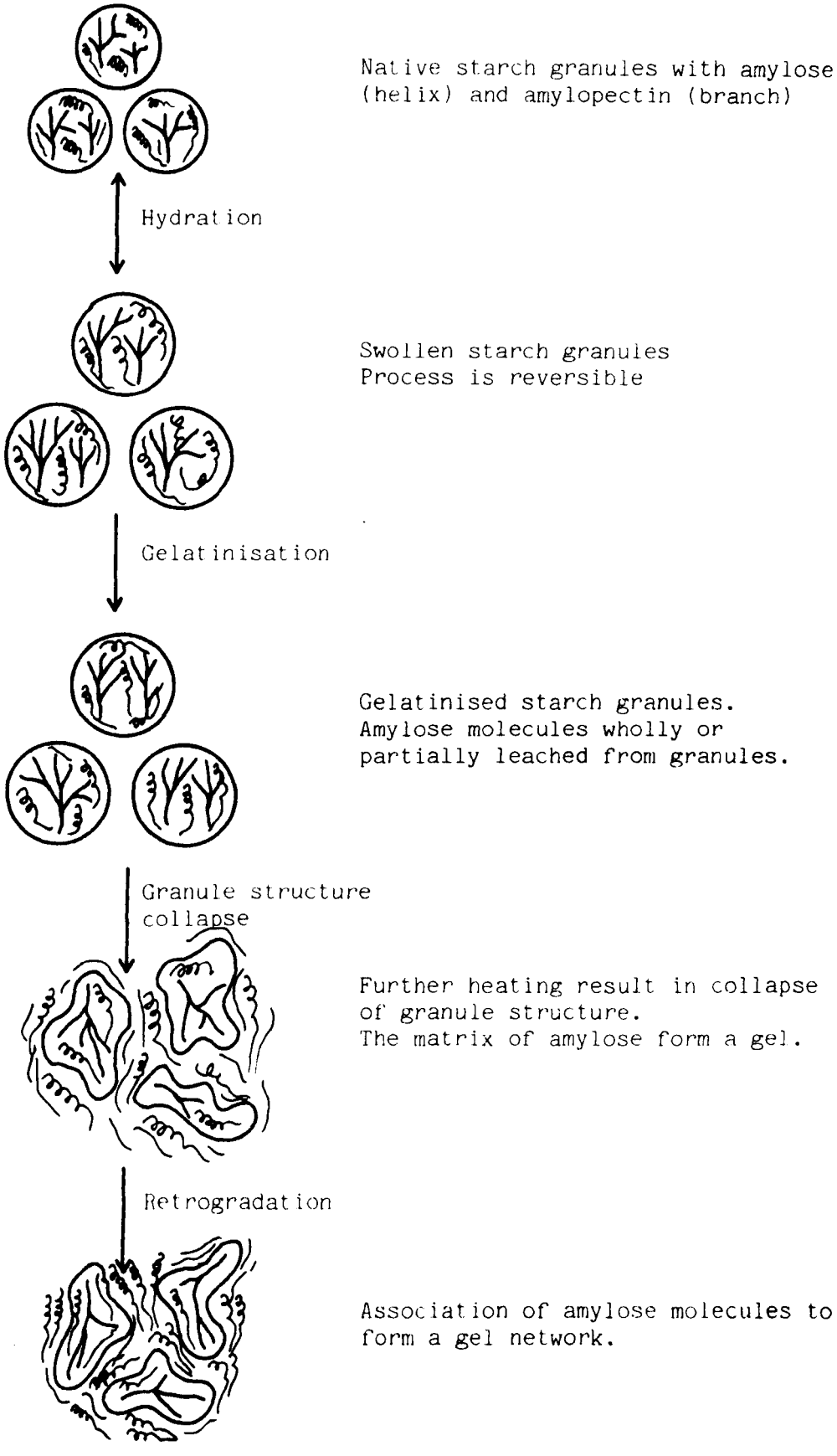


Figure 8. Mechanism for starch gelatinisation and retrogradation.

a complete breakdown of the granule structure.

When potato starches are heated at restricted moisture levels, Sair (1964, 1967) observed that the x-ray patterns were dramatically altered from type B to an A+C pattern, quite similar to that of cereal starches. The physicochemical properties of the gelatinised starch such as gelatinisation temperature range, swelling behaviour and paste translucency were also changed, in a way simlar to that of wheat starch (Kulp and Lorenz, 1981). They concluded that the heat treatment had altered the molecular organisation of the starch.

2.2.3.1.2. Retrogradation of starch during cooling and conditioning

The cooling and conditioning steps cause the cooked starch to retrograde which then becomes less sticky and less soluble. Retrogradation also results in some hardening of the starch which facilitates separation of cells and results in less cell damage (Reeve, 1954; Olson and Harrington, 1955; Harrington et al., 1960 and Potter et al., 1959).

The conditions during these two steps (i.e. 40-50°C at 30-35% moisture for 1 h), is most favourable for retrogradation to occur (Potter, 1954; Olson et al., 1953). As shown in Figure 10, at high moisture content only a slight retrogradation is noticeable. The rate increases rapidly with decreasing moisture content and reaches a maximum at 30% moisture content. Retrogradation hardly takes place at a low moisture content of 15%. Figure 11 shows that the solubility of starch diminishes more rapidly on cooling the mix.

During retrogradation, the molecular reorganisation is believed to be associated with the linear fraction forming junction zones, the energy for association being provided by hydrogen-bonding between parallel carbohydrate chains (Bear and French, 1941; Kim and Robinson, 1979). Hydrogen bond formation has been detected by shifts in hydroxyl absorbing frequency in the infra-red spectrum (Samec, 1957). Amylopectin is far

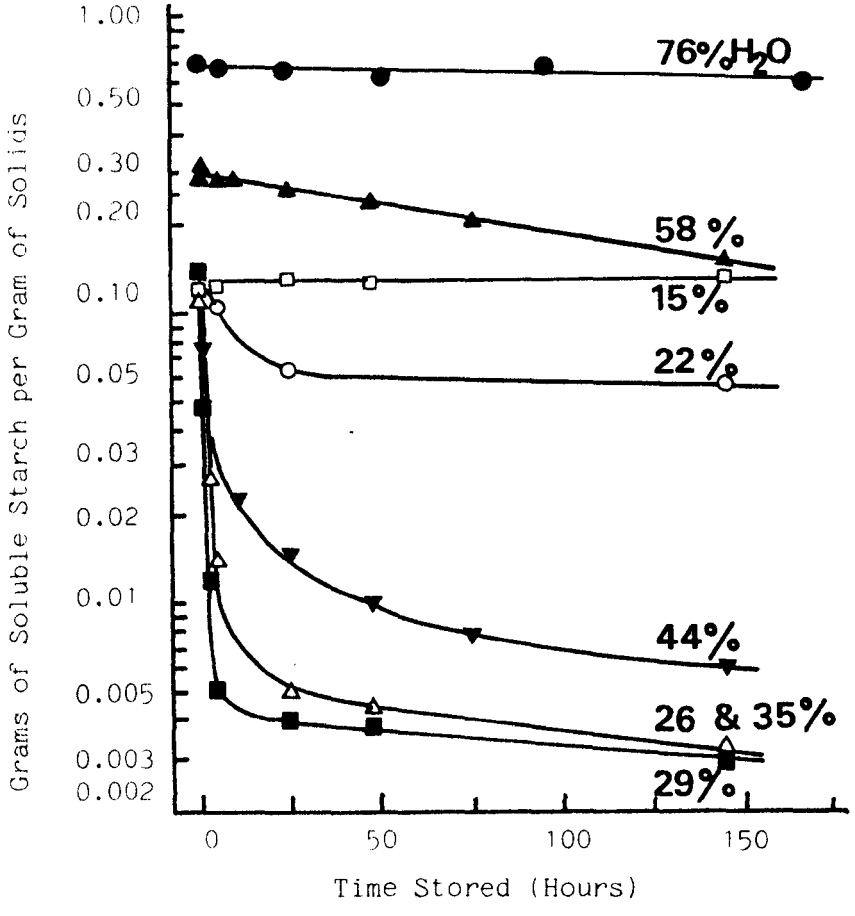


Figure 10. Effect of moisture content of moist-mix on retrogradation of starch (Potter, 1954).

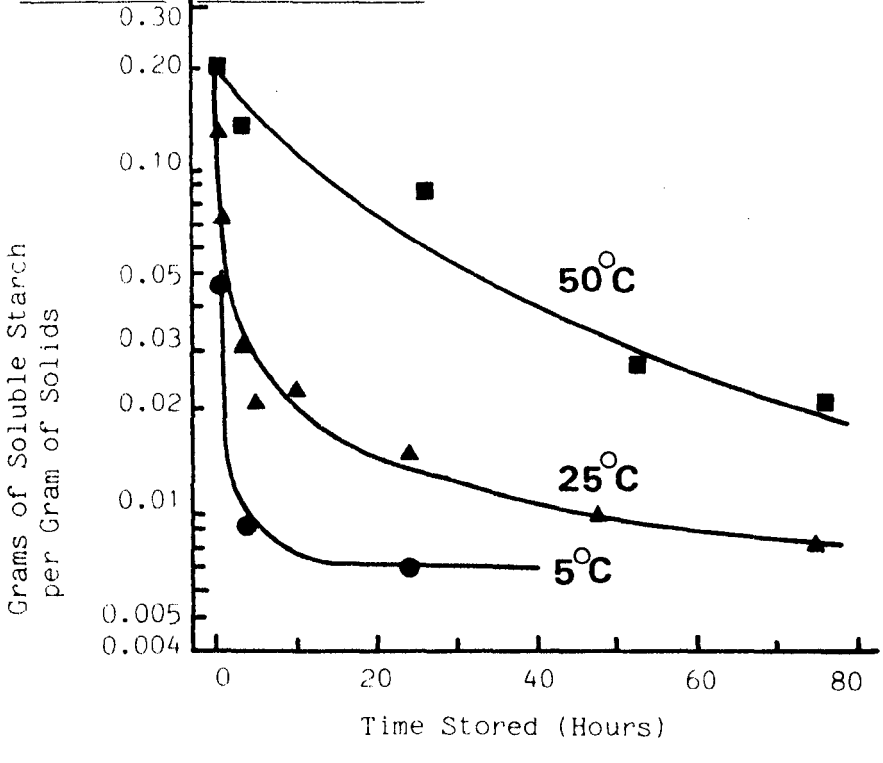


Figure 11. Effect of storage temperature on retrogradation of starch in a moist-mix (Potter, 1954).

less able to form such junction zones (Kim and Robinson, 1979). However, Schoch and French, 1947, working on bread staling believed that staling (retrogradation) may be a spontaneous aggregation of amylose molecule with the outer branches of amylopectin fraction which are suitably orientated for hydrogen bond formation.

These changes in molecular organisation during retrogradation can also be detected by changes in the x-ray diffraction pattern (Katz, 1928, 1930, 1934). He indicated that gels from all starches gave a B-pattern on retrogradation, irrespective of whether the original starch gave an A- or B- pattern. The B- pattern does not form a blue complex with iodine and its configuration is believed to be in an extended form (Rundle et al., 1944). However, Hellman et al., (1954) found that the change in diffraction pattern on retrogradation depends on the moisture content of the gel. Wheat gels containing over 43% water will lose their A- pattern on heating and progressively develop a B - pattern on ageing. Gels containing between 29 and 43% water will give a C-pattern on ageing whereas if the water content is less that 29%, no visible change in x-ray pattern was observed.

These results indicated that during retrogradation there are changes in molecular organisation of the starch and this is critically dependent on the moisture content of the starch gel. These changes are reflected in the properties of the gelatinised starch. Retrogradation, in fact, increases the resistance of starch to hydrolysis by digestive enzymes(Hellendoorn et al., 1970) and decreases its swelling power (Collison, 1968).

2.2.3.2. Role of GMS

The ability of starch to form a complex with fatty acid was first reported by Schoch and Williams, 1944. The complex closely resembles the starch-iodine complex, but the fatty acid chain which is located within

the amylose helix is not readily replaced by iodine (Senti and Erlander, 1964). The complex showed a 'V'-pattern, suggesting that the amylose is in a helical conformation with the lipid occupying the core of the helix (Rundle and French, 1943 A, B; Rundle, 1947; Mikus et al., 1946 and Zobel, 1964).

The use of monoglycerides as emulsifiers in the production of dehydrated potato granules has been reviewed by Gutterson, 1971. Normally, small quantities of approximately 0.25% are added to complex the soluble starch thereby decreasing the glueyness and improving the texture of the product (Severson et al., 1955; Harrington et al., 1960). Apparently, some of the monoglyceride diffuses into the starch granules and insolubilises the amylose, preventing it from leaching out of the granules during gelatinisation (Hoover and Hadziyev, 1981 B). This observation strongly supports a similar conclusion by Schoch (1965) and van Lonkhuysen and Blankestijn, (1974), who found that monoglycerides form a water insoluble complex with amylose. However, in the case of potato granules, Hoover and Hadziyev (1981 B) found that the cell wall is not fully permeable to monoglycerides and they suggested that the monoglycerides form a complex mainly with the released amylose and to a lesser extent with amylose retained within the potato granules. From model studies, it was found that when amylopectin was treated with GMS, no precipitate was formed nor any change in viscosity was observed, which would seem to strongly negate any suggestion that amylopectin will form a complex with lipid (Krog, 1971; Hoover and Hadziyev, 1981A).

In addition to controlling the amount of free starch (amylose), monoglycerides also affect the properties of potato granules such as the water binding capacity (WBC), the swelling power (SP) and the rate of rehydration (Hoover and Hadziyev, 1982) as shown in Figure 12. This set of parameters has been reported to affect the extrusion properties of the dough during the manufacture of French fries (Jadhav et al.,

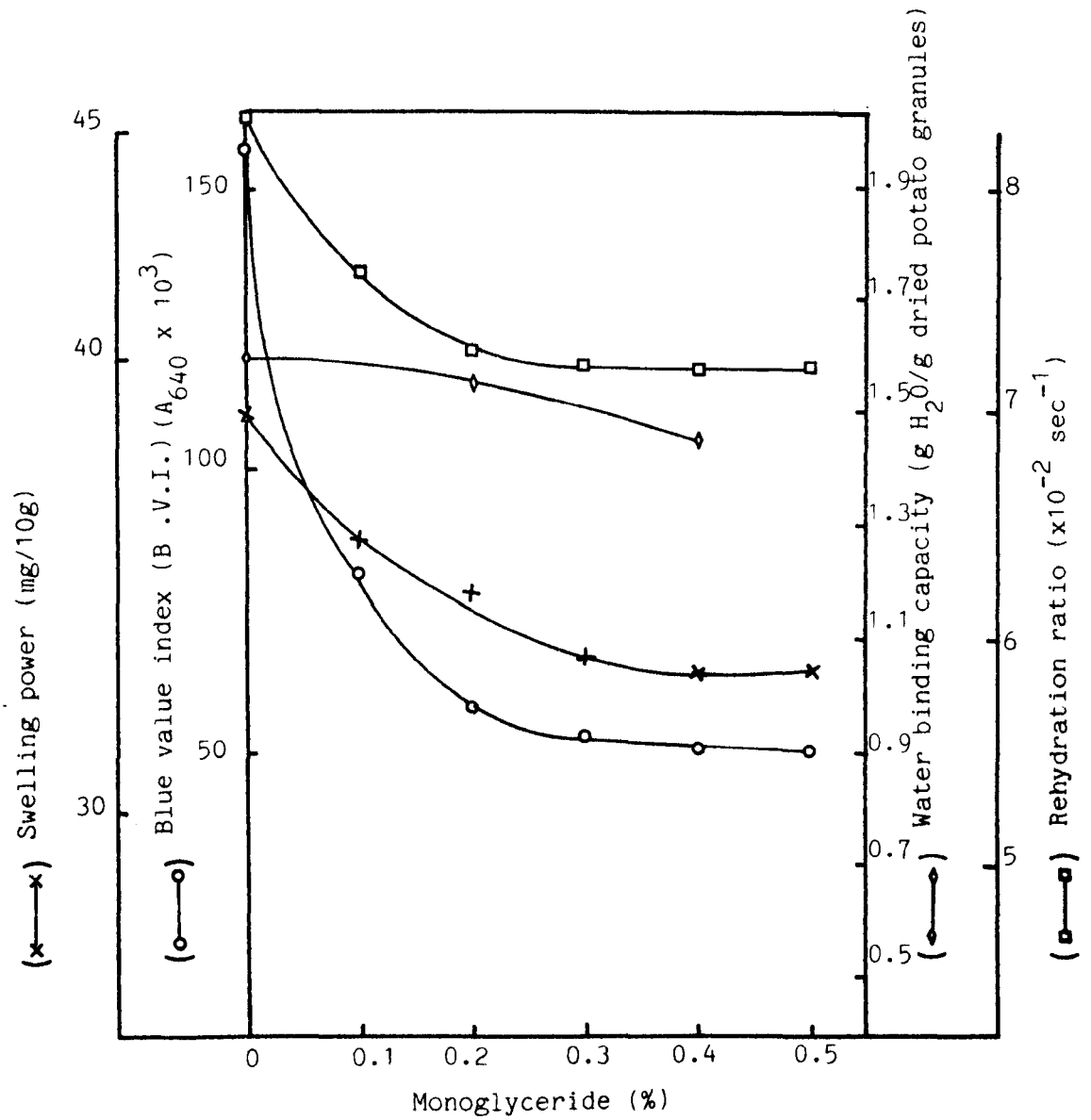


Figure 12. Effect of monoglyceride concentration on swelling power, blue value index, water binding capacity and rehydration rate of potato granules.

1976) and some other granule-based snack foods.

The most pronounced change in properties occurs in the range of 0-0.3% of added GMS. This level has been recommended for use in the production of potato granules (Hoover and Hadziyev, 1982). Higher levels induce negligible change in the properties.

2.2.4. Amylose

Amylose is essentially a linear polymer of α-D-glucose units linked together by α-(1→4) linkages. Some evidence indicates the existence of a very limited amount of branching in the molecule (Peat et al., 1949; Greenwood, 1960). The branch-points appear to be α-(1→6) linkages and they occur to the extent of only one per several thousand glucose units.

In aqueous solution the amylose molecule forms a random coil which consists of linear segments of helical structure. The helical segments are built of 2-20 helical turns, each of them containing 6-8 anhydroglucose units (Erland et al., 1965; Jordan et al., 1978; Ferracini et al., 1982). The helical structure of amylose enables it to form a complex with iodine and lipid. A partial sequence of the amylose molecule is shown in Figure 13.

The amylose content of potato starch granules varies, depending on the size, maturity and variety. Usually the amount present is between 18-22% (Chung, 1979). The percentage of amylose in potato granules has never been reported.

2.2.5. Amylopectin

In contrast, the amylopectin molecule is a highly branched polymer of α-D-glucose containing some 4-5% of α-(1→6) branch points which correspond to an average length of unit-chain of 20-25 glucose units. A partial sequence of an amylopectin molecule is shown in Figure 14.

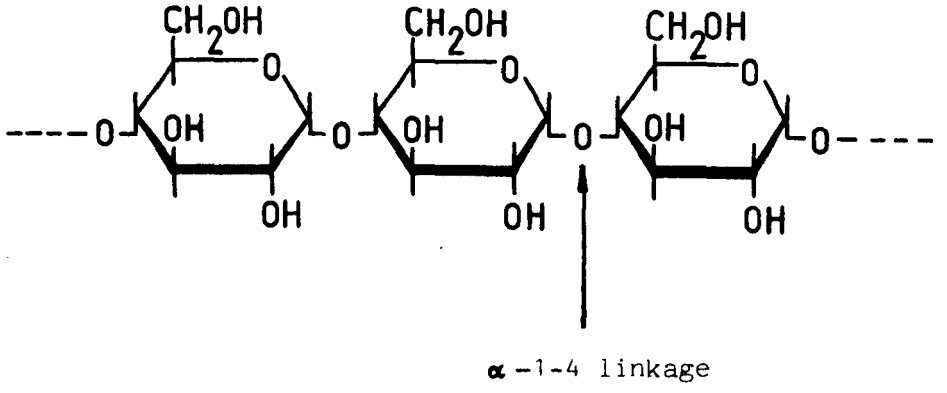


Figure 13. A partial sequence of amylose macromolecule.

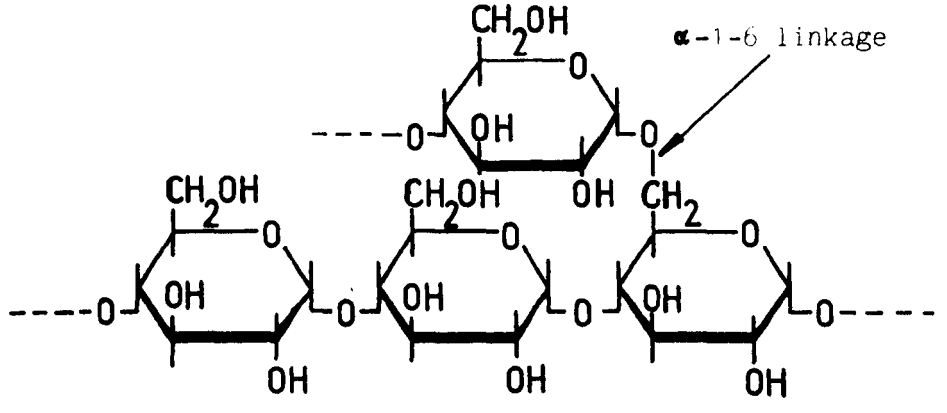


Figure 14. A partial sequence of amylopectin macromolecule.

Table 4 .

A comparison of the properties of amylose and amylopectin.

	Amylose	Amylopectin
Reaction with iodine	Intense blue	Red violet
Absorption maximum (λmax) of iodine complex	About 650 mμ	About 540 mμ
Iodine affinity	19-20%	<1%
Percentage conversion to maltose by		
(1) β-amylase + z-enzyme	95-100	50-60
(2) Crystalline β-amylase	70-96	50-60
Molecular weight	10^5-10^6	10^7-10^8
Chain length (average no. of glucose residues per non-reducing end group)	2000 or more	19-28
Average external chain length	-	12-17
Average internal chain length	-	5-8
Degree of polymerization (glucose residues)	10^2-10^3	10^4-10^5
X-ray analysis	Amorphous	Higher degree of crystallinity
Solubility in water	Variable	Variable
Stability in aqueous solution	Retrogrades	Stable
General structure	Essentially unbranched	Highly branched

Amylopectin is the major component and amounts to 75-85% in most starches. In potato starch, the amylopectin component contains about 0.28% of phosphorus (Sherman and Baker, 1916) and most of this is present in the esterified form (Posternak, 1951), attached to the C-6, C-2 or C-3 positions of the glucose units. The presence of the phosphate ester confers on the amylopectin molecule the properties of a polyelectrolyte. Brantlecht (1953) found that amylopectins of higher phosphate content yielded starch pastes of markedly increased viscosities and electrical conductivities.

A comparison of the properties of amylose and amylopectin is given in Table 4.

2.2.6. Crystalline nature of starch

Using the x-ray diffraction technique, Katz and his collaborators (Katz, 1930, 1937; Katz and Derksen, 1933), distinguished three types of crystalline structure in intact granules, giving diffraction patterns which were designated as:

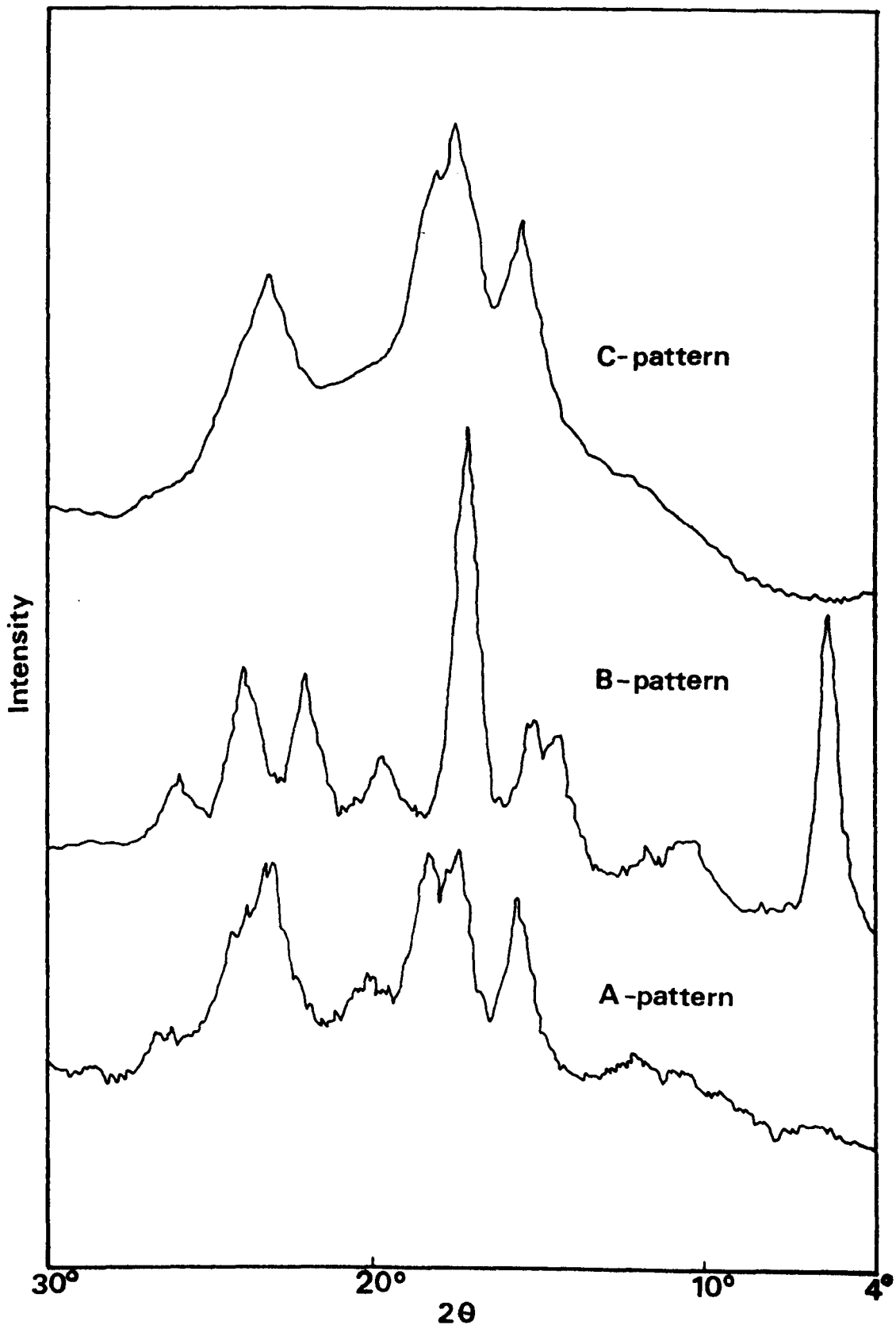
	A-pattern	-	cereal starches
	B-pattern	-	root and tuber starches
	C-pattern	-	bean and manioc starches
and	V-pattern	-	amylose complexing with organic molecule (Mikus et al., 1946).

The A, B and C-patterns are shown in Figure 15.

A detailed analysis of the starch polymorphs has recently been completed by Wu and Sarko, 1978.

The A- and B-polymorphs have been shown to be double stranded helices with both structures nearly identical in molecular configuration and exhibiting hexagonal packing (although for the A-amylose it is slightly distorted). However, they differ considerably with respect to the packing

Figure 15. X-ray diffraction patterns of wheat (A-), potato (B-) and pea (C-) starches.



of the duplex helices in the hexagon and the location of the water molecule.

In the B-structure, a channel of approximately the same diameter as the helix exists in the centre of the hexagon and as much as 30% water can enter this channel (Figure 16). In contrast, in the A-structure, the hexagon is slightly larger and its centre is occupied by another helix and in consequence, not surprisingly, a much smaller amount of water is present which is distributed equally in the interstitial spaces between the helices (Figure 17).

Since there is no 'hole' present in the centre of the duplex, as in the single helix of V-amylose (Rundle and French, 1943), water cannot enter the helices of the A- and B- amyloses. The location of the water molecules in the B-structure, suggest that it is loosely held and are non-crystalline.

It is possible that under certain conditions of high temperature and in the presence of moisture a helix could displace the water in the open channel of the B-structure, thus converting it to the A-form (Sair, 1944). However, by heating potato starch at restricted moisture levels, the x-ray pattern will be altered to an A+C pattern (Sair, 1967). The C-pattern is the result of a mixture of A and B unit cells in the same structure.

The V-pattern was first observed in gelatinised starch by Katz (1937). It can also be produced by precipitation of gelatinised starch with alcohol, iodine and fatty acids, but it does occur naturally in the granules of certain varieties of maize (Zobel et al., 1964). The V-amylose is a left-handed helix with six glucose residues per turn of helix, with the complexing agents found inside the helix channel (Figure 18). The identification of the V-form as a helical inclusion complex resulted from the work of Rundle and his collaborators (Rundle and French, 1943 A, B; Rundle and Edwards, 1943; Rundle, 1947; Mikus et al., 1946).

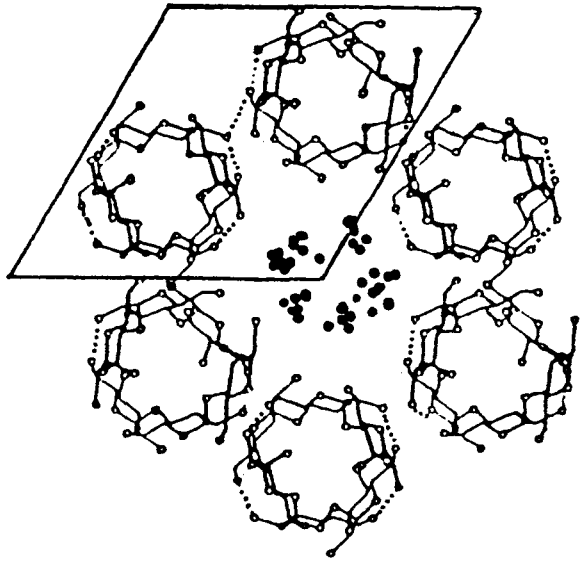


Figure 16. Unit cell and helix packing of B-amylose.

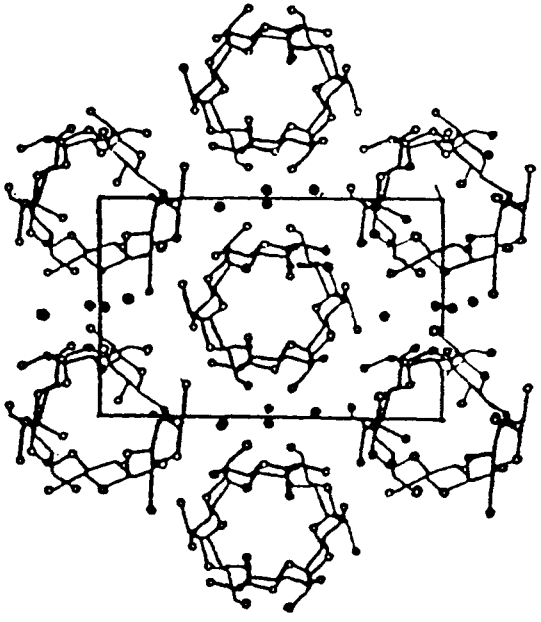
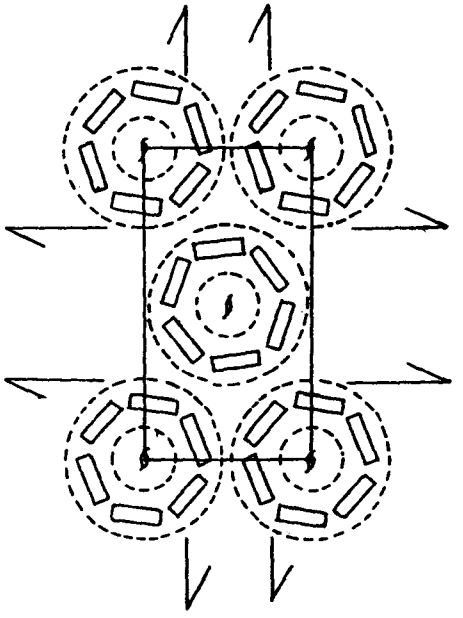
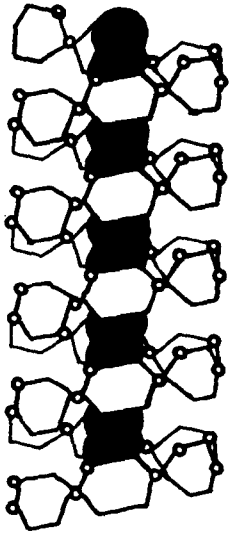


Figure 17. Unit cell and helix packing of A-amylose.

Figure 18. Structure of V-amylose



(a) Basal plane of orthorhombic cell of V crystallite, showing starch helices and crystallographic convections for positions of two-fold screw axes in cell.



(b) Starch helix enclosing iodine molecules.

The V-form is more open than the B-form, with a 'hole' in the centre of helix (Rundle and French, 1943A). As such the hydrated V-complex (V_h-complex) can bind more water on hydrophilic groups (Macchia, 1964), even though the inside of the helix channel is primarily hydrophobic in character. The anhydrous form (Va-amylose) may also possess some water at peripheral sites in the helix (Sarko and Zugenmaier, 1980).

2.2.7 Physicochemical properties of potato granules

The physicochemical properties of potato granules commonly studied, include: swelling power (SP), water holding capacity (WHC), degree of starch retrogradation, amount of soluble starch, moisture change and rate of rehydration. From industrial experience it has been found that some of these properties are readily maintained in a year-round production, while others show a seasonal variation. Changes in physico-chemical properties can also occur during storage, as shown in Figure 19.

These changes in physicochemical properties appeared to be closely interrelated and are believed to be due to the changes in starch during storage. For example, molecular alignment of starch molecules during retrogradation might have caused the release of part of its "bound" water, as detected in the slight increase in moisture content of the granules during storage. The retrograded starch lost its solubility, resulting in a decrease in the swelling power of the granules. The retrogradation of the starch molecules might also have created minute voids in the solid matrix which would trap a quantity of water on reconstitution, contributing to the increase in water holding capacity. The loss of solubility and swelling power of starch will cause a reduction in rehydration rate, allowing the granules to absorb cold water more slowly and uniformly.

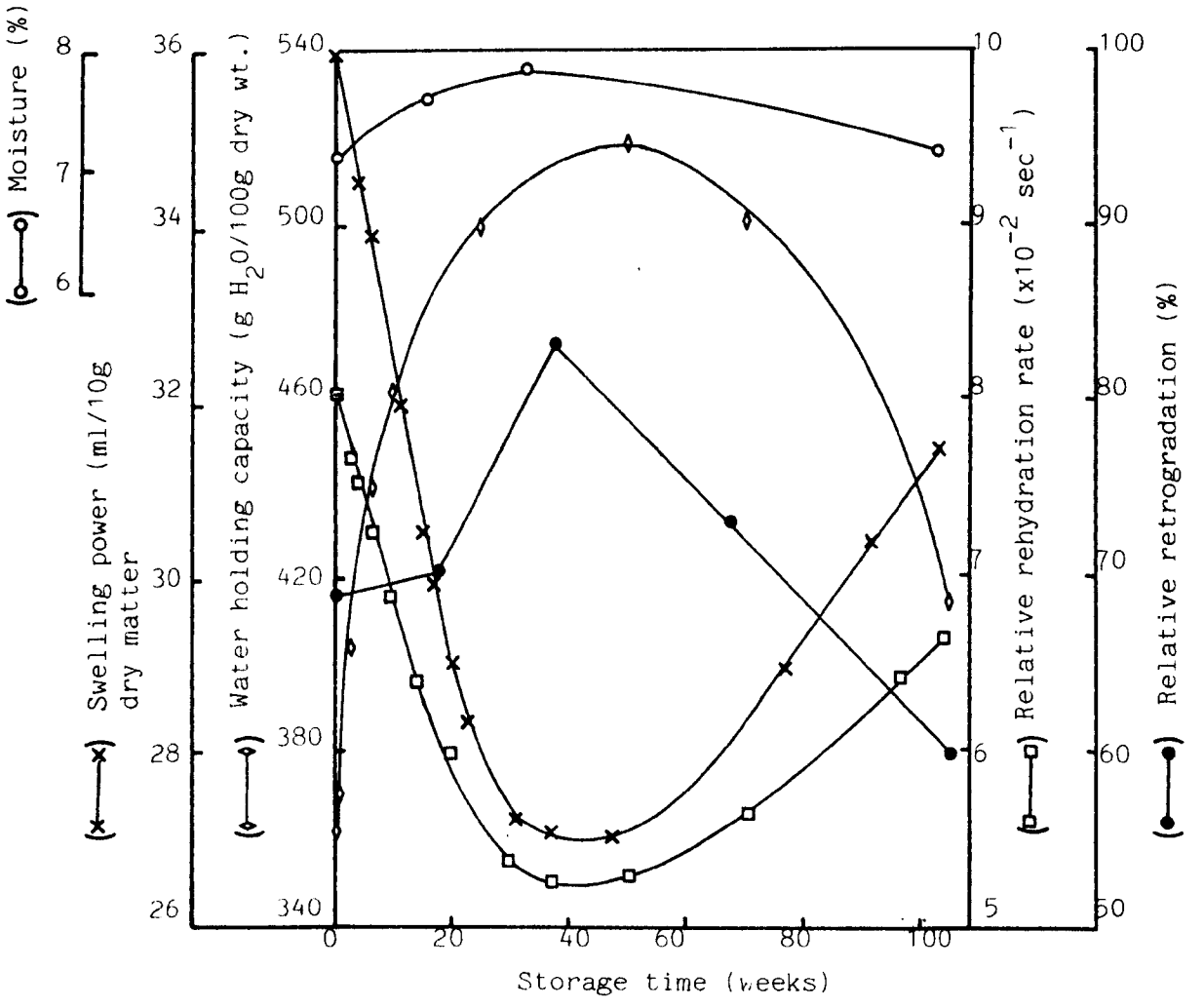


Figure 19. Changes in swelling power, water binding capacity, relative rehydration rate and percentage retrogradation of potato granules during storage at room temperature (Ooraikul and Molidena, 1981).

The physicochemical properties of potato granules can influence their extrusion behaviour. Ooraikul (1977), found that potato granules with high rehydration rate will produce wet and dry spots in the French-fry dough which was detrimental to the shape and appearance of the French fries when extruded, and to the texture and taste when fried. This problem can be overcome by lengthy storage (~40-60 weeks) of the potato granules which is impractical on an industrial scale, or by addition to starch of modifying agents such as Ca^{2+} during processing. When the potato granules with Ca^{2+} added were analysed for their physicochemical properties, it was found that the water holding capacity, rehydration rate and blue value index were comparable to that of 6 months old granules and they form satisfactory dough for the manufacture of extruded French fries.

2.2.8. Evaluating the quality of potato granules

The determination of the quality of potato granules is mostly based on the texture of the reconstituted product. The textural characteristics can be divided into two groups:- (i) desirable characteristics such as mealiness, smoothness and dryness and (ii) undesirable characteristics such as glueyness, sogginess and rubberiness. To evaluate these textural qualities, the industry has all along depended on subjective appraisals. However, due to the high cost and lack of precision of subjective appraisals, objective measurement has been constantly under investigation in an attempt to develop more precise and cheaper methods.

Among the methods developed is the 'Blue Value Index' by Mullins et al. (1955). The Blue Value is a measure, primarily of the quantity of straight-chain amylose and not of the branched amylopectin, which is present in larger quantity than amylose. Perhaps for this reason, this Index has not proved a very reliable method of comparing texture

of potato granules produced by different manufacturers.

A more direct approach, also proposed by Mullins et al. (1957) is the 'drop-test'. They used this method to evaluate consistency and rubberiness of mashed potatoes by measuring the diameter of a mash potato ball falling upon a smooth surface from a certain height. The larger the diameter the more mealy is the potato granules.

Several instrumental methods have been developed and these include the use of Brabender Amylograph for viscosity measurements and determining textural qualities; (Ludwig, 1965; Tape, 1965), the determination of rheological properties using a thermally controlled Adams consistometer (Stadler and Schaller, 1972) and the measurement of flow properties and apparent viscosity with a Rheomat 15 rotational viscometer and Brookfield RVT viscometer, respectively (Schweigruber et al., 1979).

Other workers measured the textural qualities of reconstituted potato flakes using a modified LEE-Kramer shear press (Englar and Kudlich, 1965; Smith and Davis, 1963) and an Instron testing machine to measure torque and energy required to mix reconstituted flakes (Voisey and Dean, 1971).

All the methods mentioned above tried to describe overall texture with one attribute. However, according to Szczesniak (1963) and Sherman (1969), the textural qualities are in fact a complex combination of several characteristics.

When potato granules are used for extrusion, a different set of quality parameters is needed to determine their suitability to produce satisfactory products. Among the parameters currently being used are water binding capacity, rate of rehydration, swelling power and water soluble starch (Hadziyev and Steele, 1978). There is a need for new techniques to assess the quality of potato granules for producing new products.

EXTRUSION

3. Extrusion

During the past decade, production of snack foods has been one of the fastest growing sectors of the food industry. This has been made possible by the introduction of extrusion cooking which is a highly versatile process that is capable of using a wide spectrum of ingredients and formulations and producing a variety of snack foods. In addition, the process is continuous which encourages economy of operation.

3.1. Types of extrusion

A variety of extruders have been developed to produce different types of food products. They can generally be classified under three types:

(i) Cold forming extrusion

(ii) Indirect extrusion (low pressure cooking and forming extrusion)

(iii) Direct extrusion (high pressure cooking extrusion)

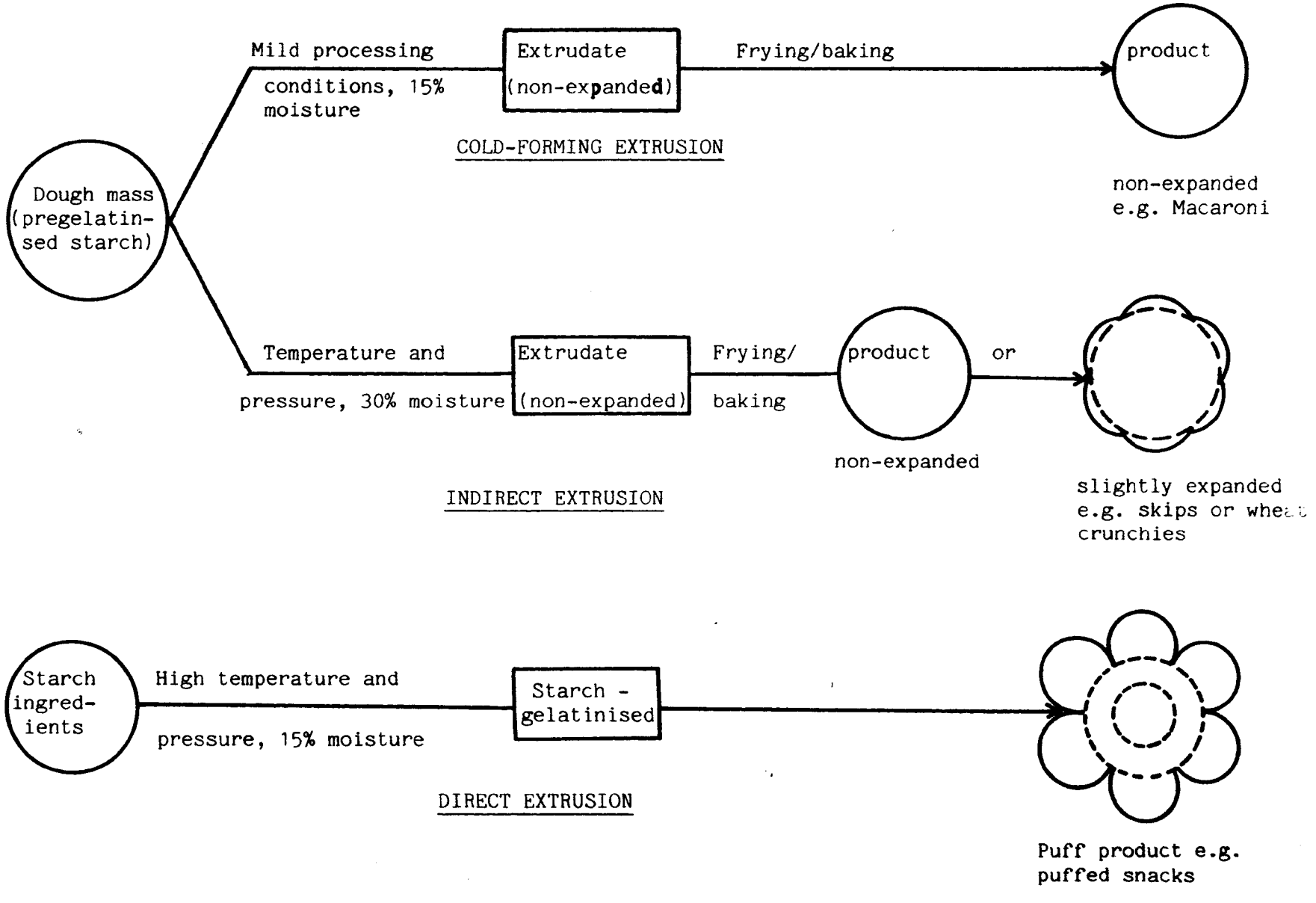
A more detailed description of each type is given in Figure 20.

3.2 The effects of processing variables on extrusion

3.2.1. Temperature and time relations in extrusion

Extrusion is a highly non-equilibrium, dynamic process, dependent on the time and temperature of the process. Once inside the extruder barrel the food material is subjected to a rapid rise of temperature followed by a slower fall as the extrudate leaves the die (Reinders et al., 1976). Under such circumstances the food material attains the desired temperature within a few seconds and is then held at that temperature for a period of 5 to 50s, depending on the extrusion process. This period of time is known as the residence time, which is dependent on the screw speed and moisture content of the sample (Zuilichem et al.,

Figure 20. Types of extrusion.



1973). A correct balance of these variables is necessary to obtain a desirable product.

A typical temperature-time regime as found during extrusion processes are shown in Figure 21.

3.2.2. Moisture and temperature relations in extrusion.

The importance of moisture-temperature relationships in extrusion is best illustrated in the variety of products which may be produced from cereal raw materials as shown in Table 5.

Table 5. Temperature-moisture relation for some types of products

Feed moisture (%)	Product moisture (%)	Extruding temperature (°C)	Product
31	30	52	Macaroni
25	25	80	Ready to eat cereal
20-35	15-30	150	Soft-moist product (pet foods)
20	4-10	180	Dry cereal product (textured plant protein)
12	2	200	Puffed snacks

For a highly expanded product, a low feed moisture content and a high extrusion temperature is required, whereas a pasta type product needs a high moisture and low extrusion temperature.

The effect of increasing and decreasing moisture content of feed materials on the product properties during high and low temperature extrusion respectively, can be summarised below (Table 6).

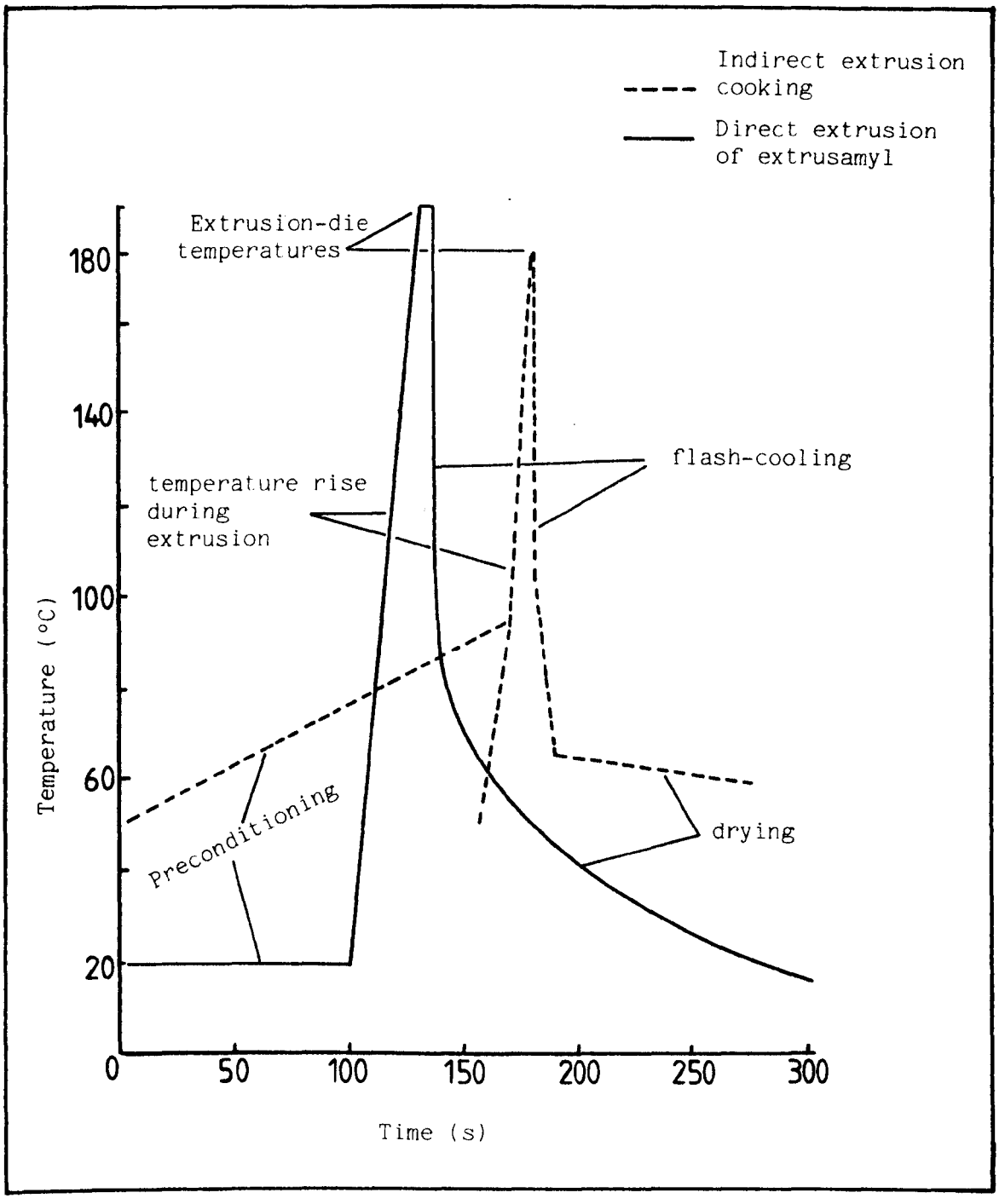


Figure 21. Example of processing conditions for direct and indirect extrusion cooking.

Table 6. Effect of moisture content on extrusion properties.

Property	High temperature Extrusion (Increasing moisture content)	Low temperature Extrusion Decreasing moisture content)
Expansion	Decreases	Thicker extrudates
Texture:		
Shearing	Decreases	Increases
Breaking	Decreases	Increases
Power consumption	Decreases	Increases
Cell structure	Smaller and less uniform	Bigger

3.2.3. Composition of raw materials

The ultimate character of the product is dependent upon the composition of the raw materials. It is, therefore, critical that the materials be carefully specified and controlled. In many cases this is easier said than done, because food materials are biological and can have considerable natural variability.

The ratio of amylose to amylopectin in starch can influence the textural properties of the product (Murray et al., 1968). For example, waxy-type starches promote puffing and give an extremely light, fragile product. Whereas, high amylose starches tend to produce harder products. For puffed snacks, 20% amylose in the starch is considered a minimum, while more than 50% amylose will result in an exceedingly hard snack.

It is common practice to add emulsifiers to the feed ingredients during extrusion. Small quantities (<1%) are added to aid in extrusion and also to give better textured product. However, too much of emulsifiers may cause problems during extrusion.

Sometimes small amounts of additives such as phosphate acetate and hydroxypropyl derivatives are incorporated with the feed materials in order to obtain the desired character of the product. The function of the additives is not well understood, but is believed to tenderize the texture of the extrudate.

In recent years modified starches are becoming more important in the snack food industry. The starches can be chemically modified to meet specific requirements for certain products.

3.3. Physicochemical changes of carbohydrate components during extrusion cooking

Only a small number of publications are available that described the effect of extrusion on potato starch granules and potato granules. During extrusion cooking, the starch granules are gelatinised, resulting in the destruction of the organized structure and solubilization of the starch (Mercier and Feillet, 1975). This is accompanied by the formation of a new structure in the presence of amylose and lipids. This structure has been observed, by x-ray diffraction studies, to be similar to the V-amylose structure of an amylose-lipid complex formed during the extrusion of potato starch with addition of oleic acid or glyceryl monostearate (GMS) (Mercier et al., 1979).

The amount of solubilized starch increases with the increase of extrusion temperature and the decrease of moisture content of starch before extrusion. The effect of extrusion temperature on various properties of extruded potato starch is shown in Figure 22.

At high extrusion temperatures, the potato starch is solubilized with the formation of linear oligosaccharides. The oligomers arise from the splitting of the amylose fraction, whereas the amylopectin fraction is as in the native starch. If the amylose forms complexes with lipid as in extruded cereal starches, then the splitting into oligomers will not occur.

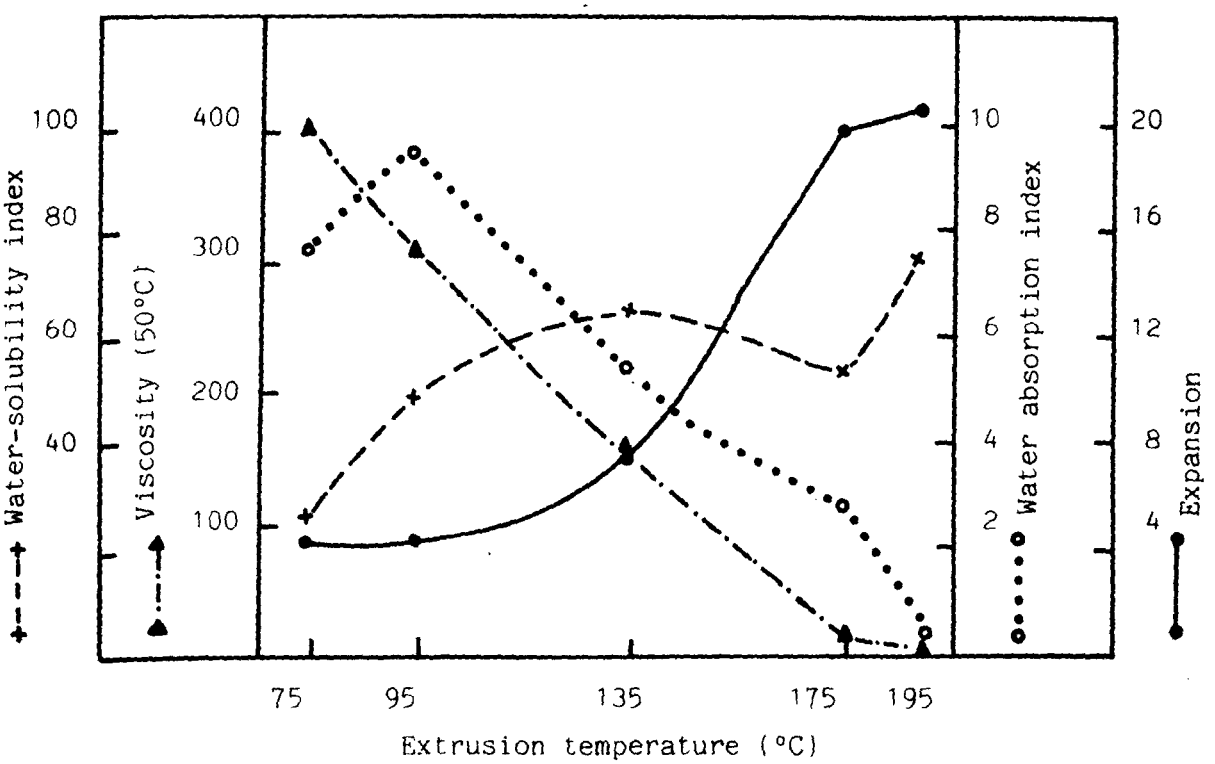


Figure 22. Effect of extrusion temperature on expansion, water-soluble carbohydrate, water absorption index and viscosity (50°C) of extruded potato starch. Initial moisture content before extrusion was 23 per cent by weight (Mercier et al., 1979).

3.4 Extrusion of potato products

The literature, other than patent literature, on extrusion cooking of potato products is sparse. Most of them are primarily related to practical problems of specific products.

The raw materials are usually dehydrated potato granules or mashed potatoes mixed with cereal or tuber starches plus additives such as emulsifiers, salts and hydrocolloids. According to Willard, 1973, the potato products can be extruded by two different types of processes. The first, is the dry collet extrusion or direct extrusion. In this process, the dry ingredients consisting of 75% granulated potato solids and 25% corn grits were moistened to 19% moisture and extruded at temperatures of 130°C to form a puffed snack resembling a French fried potato stick (Straughn et al., 1975).

The second type is an indirect extrusion process producing dried half-products which are later fried. Such a process was described by Gerkins (1965). He used dried potato flour containing approximately 10% free starch which was moistened with about 30% water containing 4.2 to 4.6% salt (NaCl). The mixture was blended to form a loose powder-like mass and extruded in a forming extruder to form pellets or strips which were then dried to a moisture content of 9%. Puffing was accomplished by frying the dried half-product in hot fat at 180°C to 210°C.

Another process described by Wisdom and Hilton, 1974, utilized potato tubers which were fabricated into potato chip-like products. The potato pieces were first blanched and dried to 35 to 45% moisture in a drier at approximately 100°C, followed by grinding the potato pieces to a dough and extruded at 95°C. The resulting strip was air dried to 12% and fried for 13 to 15s at 190°C.

Recently, potato granules have been used for making French fries. The granules are first mixed with 'French fry mix' and water in the ratio of (1:2); the dough is then extruded at low temperature to produce

chip-shaped extrudate which is cut and fried (Jericevic and Le Maguer, 1975; Ooraikul, 1977).

3.5 Extruder

The important elements of an extruder are shown in Figure 23. The feed hopper provides the opening through which food materials enter into the channel of the screw. Many of the difficulties with extrusion can be related to problems of entry of feed into the extruder. Frequently this can be overcome by cooling the feed hopper and the adjacent section of the barrel.

The barrel is the cylindrical member which fits tightly around the rotating screw. The surface is hardened in order to stand the high shear and abrasion. The size of the extruder is denoted by the internal diameter (D) and length of barrel (L). The length is very important, in that the longer the barrel, the greater the surface for heating or cooling and with the longer residence time, leads to greater control. Food extruders have varying L/D ratios, ranging from 1:1 to 25:1.

The barrel is heated electrically. Temperature control systems are placed at specific sections along the barrel and they are automatically controlled. The pressure generated in the barrel is monitored by means of pressure transducers located at appropriate points along the barrel.

The screw is the central portion of a food extruder. It is driven by an electric motor, which controls the screw speed. The extrusion screw is divided into three sections:

(i) The Feed Section accepts the food materials and conveys it to the next section,

(ii) the Compression Section, where the food material is heated, compressed and worked into a dough mass before entering and,

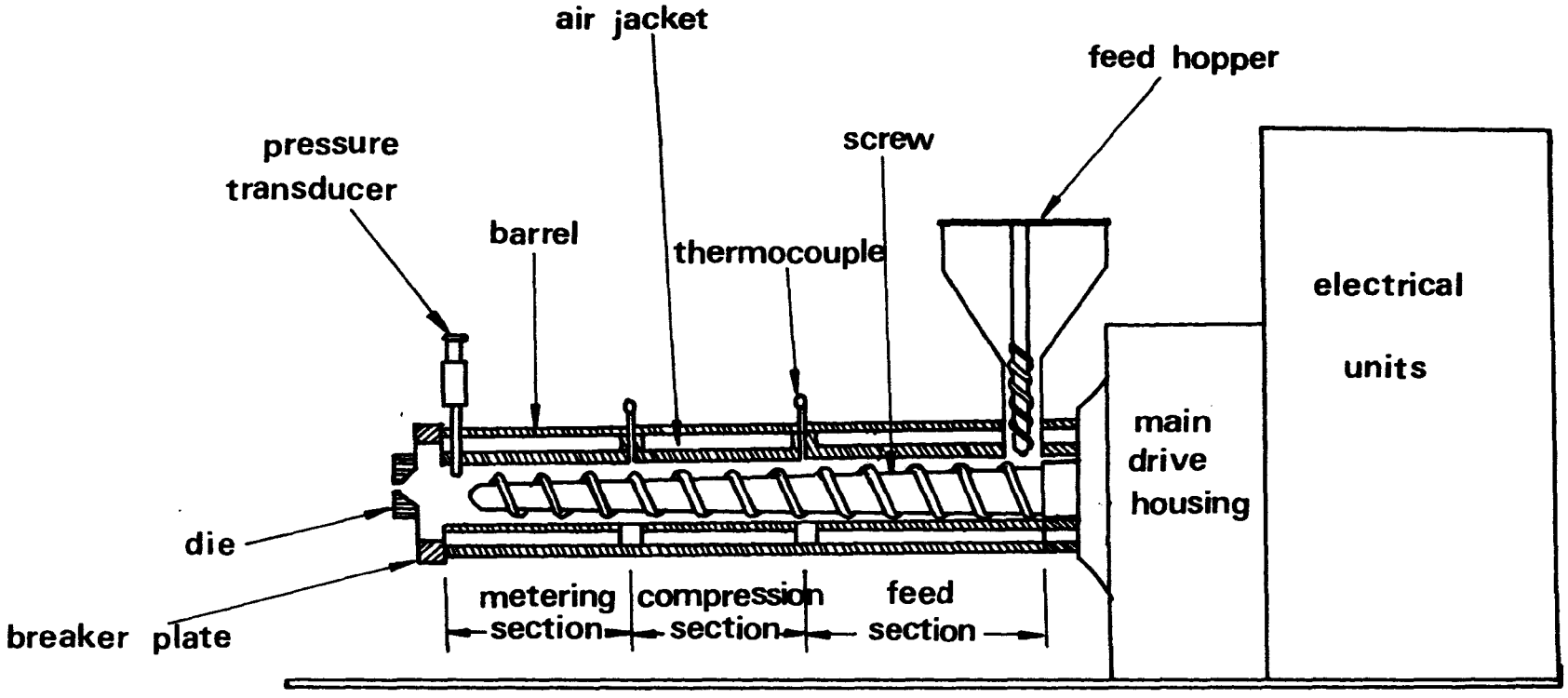


Figure 23. Component parts of an extrusion cooker.

(iii) the Metering Section, where further mixing occurs resulting in a uniform extrudate which is then forced through the die restriction.

The extrudate is shaped by the configuration of the final die. Expansion occurs as the product leaves the die because of the rapid release of pressure from the end of the extruder on emerging to ambient pressures.

3.6. Experimental

3.6.1. Materials

Potato granules and 'Potato Snack Additives' were supplied by Dornay and Smiths Foods Ltd. respectively.

3.6.2. Procedure

Extrusion cooking of potato granules was carried out using a Brabender 20 DN laboratory extruder. Potato granules and potato granules plus 'potato snack additives' with 35% moisture content were prepared using a Kenwood Chef mixer, and equilibrated for a few minutes before feeding into the extruder. The extrusion was performed under normal operating conditions i.e. with a screw speed of 100 r.p.m. and barrel temperature maintained at 70°C. The screw had a compression ratio of 1:1. The die nozzle was a slit of 25 mm x 0.5 mm.

While running, the hopper screw speed was carefully adjusted to provide the optimum feed rate and to avoid compaction and subsequent blockages. Continuous records were made of the extrudate temperature and pressure at the end of the barrel and of torque on the screw. The extruder was left operating under stable conditions for a few minutes, resulting in a continuous product flow, before any samples were taken.

The extrudates in the form of strips were cut into pieces approximately 3 cm long and fried immediately at 180°C for 10-15 s. The characteristics of the extrudates and their frying behaviour were assessed visually (Table 7).

Several extrusion trials were carried out, firstly, to establish the best conditions for extrusion (temperature and moisture) and secondly, to assess the extrusion characteristics of several batches of potato granules and the quality of the fried snacks.

To evaluate the extruder product, a number of tests were carried out. These included x-ray diffractometry, differential scanning calorimetry, extraction of water-soluble starches and the breaking strength of the extruded strips using the Instron texturometer. The procedures and results of some of the tests are presented in other sections of the thesis.

3.6.3. Determination of breaking strength of extrudates using the Instron texturometer

The measurements were taken using an Instron Universal Testing Instrument, Model 1140. A tension load cell (Type 2515-119) with a full range of 500-5000g was fixed to the instrument. Before performing any measurements the instrument was calibrated by applying a known load (500g) onto the load cell. The calibration was checked each time before using the instrument.

The tests were performed immediately after extrusion on strips 3.5 cm long. The strips were clamped at both ends by means of clippers as shown in Figure 24. For each sample an average of 6 readings was taken.

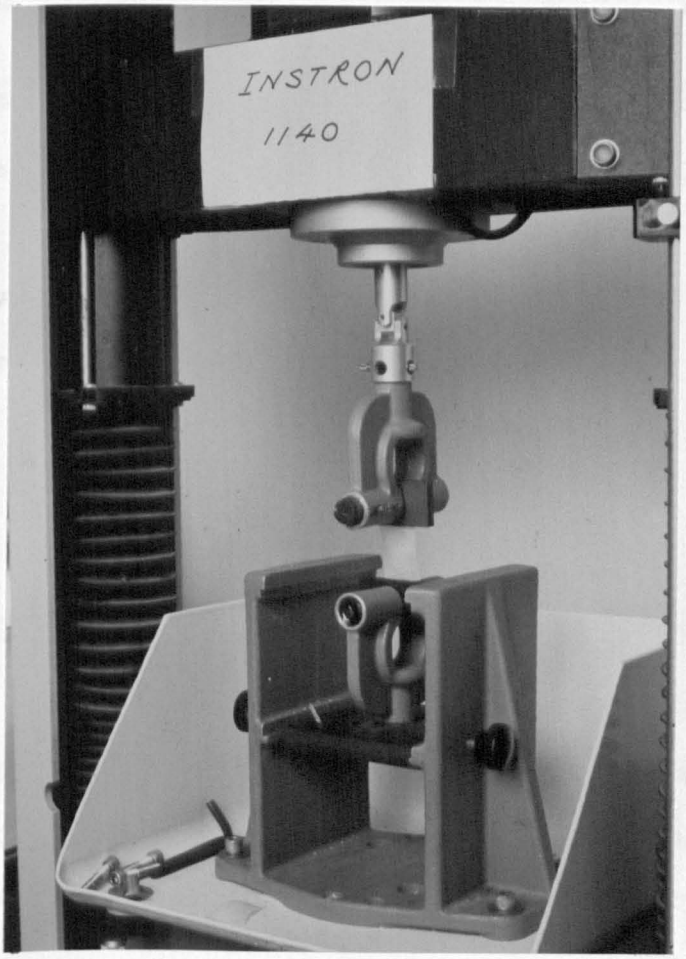


Figure 24. Determination of the breaking strength of extruded strip using the Instron texturometer.

Table 7 .

Grades for assessing the characteristics of the dough, extrudates and fried snacks .

Dough characteristic	Degree of gelling (Extrudates)
A = Moist (standard)	A = Evenly gelled (Ideal)
B = Dry	B = Over gelled
C = Very dry	C = Under gelled
D = Slightly sticky	D = Falling apart

Strip texture	Blistering (Fried snack)
A = Powdery and soft (Ideal)	A = No blistering (Ideal)
B = Thick, glassy and soft	B = Slight blistering
C = Thick, glassy and tough	C = Severe blistering
D = Very powdery (falling apart)	D = 'Flowery' product

ND - Not determined

3.7. Results and discussion

The moisture content and extrusion temperature had an important effect on the characteristics of the extrudates as shown in Tables 8 and 9 respectively. As the barrel temperature increased from 70°C to 110°C, the extrudates become overgelled, tough and glassy, especially so at 110°C. This caused an increase in breaking strength of the extrudates. At 120°C, the potato granules become so overgelled and sticky that it tended to block the die. From this study it was concluded that the ideal extrudate was obtained at a temperature of 70°C.

The reverse happened when the moisture was increased from 27.5% to 40%. At low moisture contents of 27.5% and 30%, the extrudates produced were overgelled, tough and glassy and had a high breaking strength. At 35% moisture, the extrudates obtained had the desired characteristics, they were evenly gelled and strong. At 40% moisture the extrudates were soft and weak. These results suggest that the optimum conditions for extruding potato granules are a dough consisting of 35% moisture content and an extrusion temperature of 70°C (Figures 25 and 26). These operating conditions were used for all subsequent extrusion trials.

Several batches of potato granules were extruded, and based on their extrusion behaviour, they were classified into satisfactory and unsatisfactory potato granules. The results are tabulated in Table 10. For simplicity,the different types of potato granules are denoted either by their batch number or the name of the variety of potato from which they were produced.

The satisfactory potato granules on extrusion formed a coherent strip (Figure 1) while unsatisfactory potato granules fell apart on issuing from the die (Figure 2). Microscopic observations of the extrudate showed the potato granules had been distended without rupture and on the surface a thin film could be seen binding the potato granules together. The extrudates produced from the satisfactory potato granules

Table 8. Effect of moisture content on the characteristics of extrudates.[a]

Moisture content (%)	Breaking strength (g)	Degree of gelling [c]	Strip texture [c]
27.5	408	B	C
30.0	392	B	C
35.0	310	A	A
40.0	N.D.	A	Very soft

(a) Extrusion temperature - 70°C

Table 9. Effect of extrusion temperature on the characteristics of extrudates.[b]

Extrusion temperature (°C)	Breaking strength (g)	Degree of gelling [c]	Strip texture [c]
70	300	A	A
80	330	A	A
90	350	A-B	A-B
100	396	A-B	B-C
110	420	B	C
120	N.D.	B	C

(b) Moisture content of dough - 35%

(c) Refer to Table 7 for the grades

Figure 25. Effect of moisture content on the characteristics of extrudates.

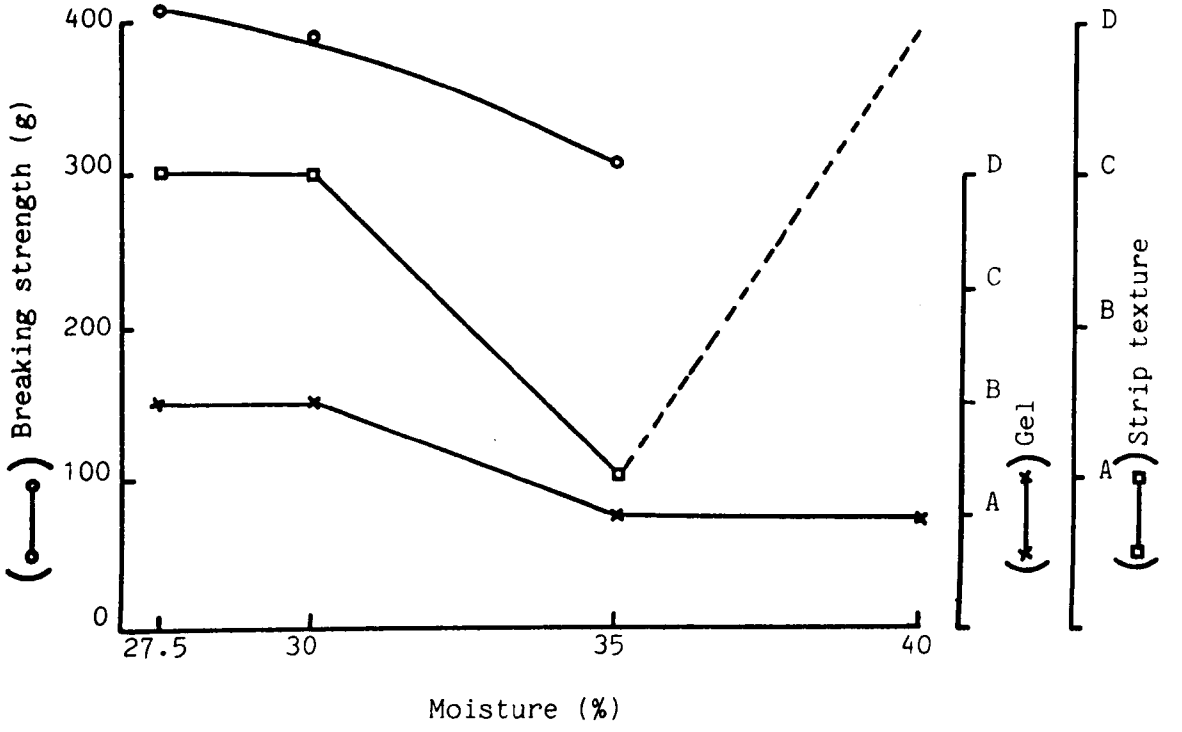


Figure 26. Effect of extrusion temperature on the characteristics of extrudates.

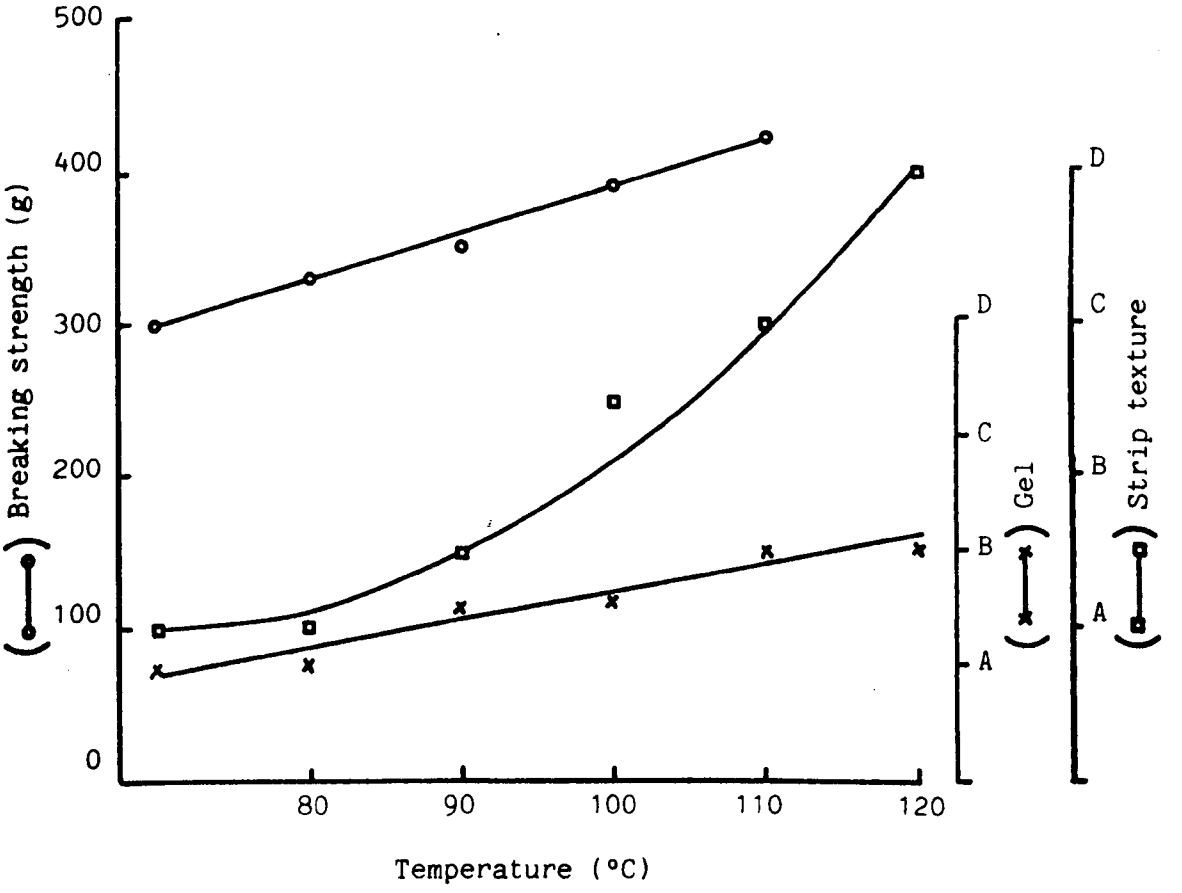
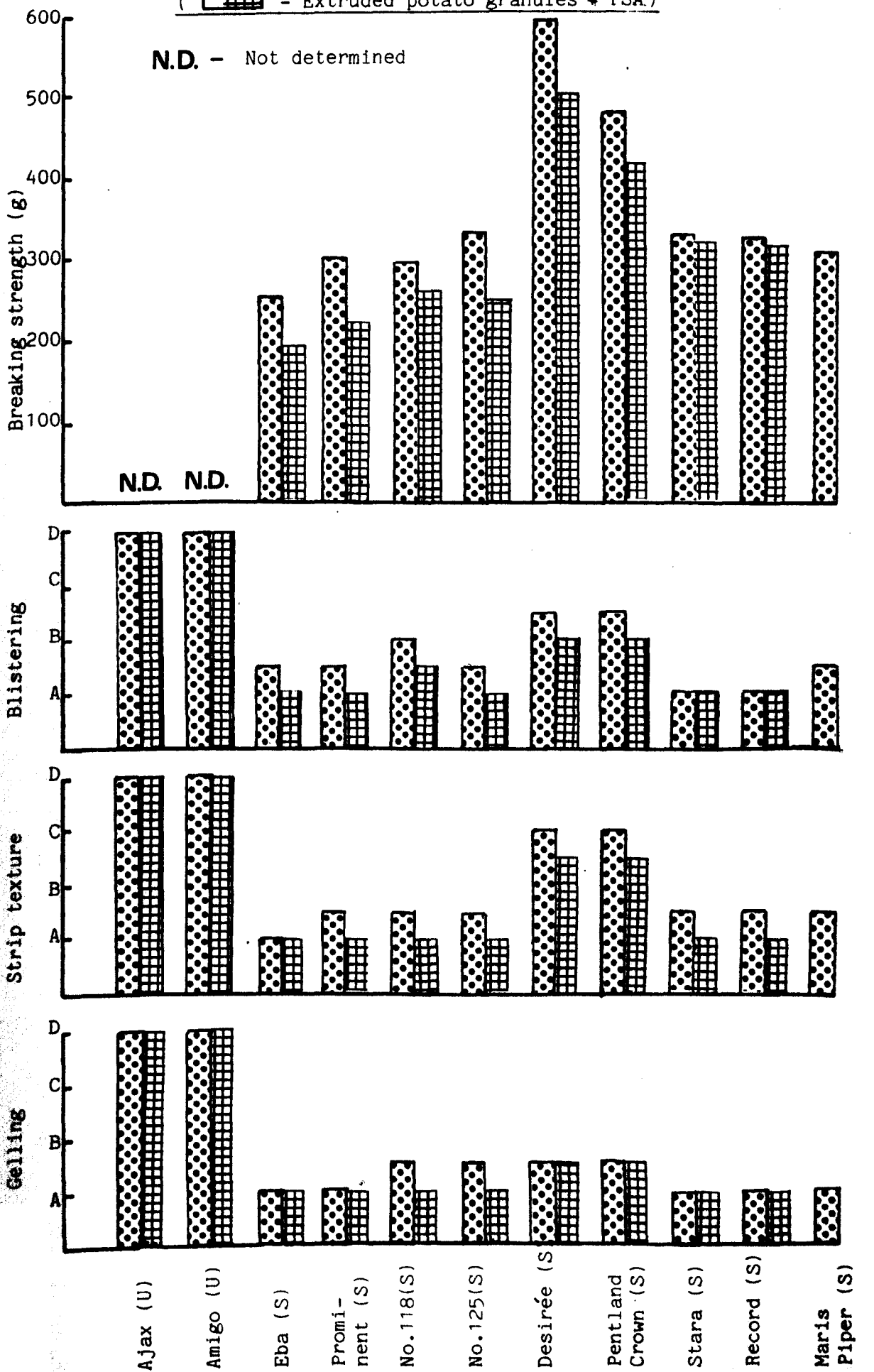


Table 10. Characteristics of extrudates (with and without addition of 'potato snack additives').

Sample	Breaking strength(g)[a]	Dough characteristic[a]	Degree of gelling[a]	Strip texture[a]	Blistering
Ajax (U)	ND	B-C	D	D	D
Ajax(U)+PSA	ND	B-C	D	D	D
Ajax (S)	310	A	A	A	A-B
Ajax(S)+PSA	265	A	A	A	A
Amigo (U)	ND	B-C	D	D	D
Amigo(U)+PSA	ND	B-C	D	D	D
Eba (S)	252	A	A	A	A-B
Eba(S)+PSA	196	A	A	A	A
Prominent (S)	300	A	A	A-B	A-B
Prominent(S)+PSA	220	A	A	A	A
Batch No.125 (S)	328	A	A-B	A-B	A-B
Batch No.125(S)+PSA	252	A	A	A	A
Batch No.118 (S)	294	A	A-B	A-B	B
Batch No.118(S)+PSA	268	A	A	A	A-B
Record (S)	320	A	A	A-B	A
Record(S)+PSA	310	A	A	A	A
Maris Piper (S)	305	A	A-B	A-B	A
Maris Piper(S)+PSA	-				
Stara (S)	330	A	A	A-B	A
Stara(S)+PSA	315	A	A	A	A
Desirée (S)	590	A	A-B	C	B-C
Desirée(S)+PSA	500	A	A-B	B-C	B
Pentland Crown (S)	480	A	A-B	C	B-C
Pentland Crown (S) +PSA	415	A	A-B	B-C	B
Record (U)[b]	ND	D	D	D	D
Maris Piper (U)	ND	D	D	D	D
Stara (U)	ND	D	D	D	D
Desirée (U)	ND	D	D	D	D
Pentland Crown (U)	ND	D	D	D	D

(a) Refer to Table 7 for the grades
(b) Addition of PSA do not improve their extrusion behaviour
(S) Satisfactory granules
(U) Unsatisfactory granules
PSA-'potato snack additives'

Figure 27. Characteristics of extrudates and texture of fried snacks.
(- Extruded potato granules)
(- Extruded potato granules + PSA)



were fried immediately and the texture of the fried snack was assessed visually for blistering. The fried snack showed approximately a 30% expansion in thickness, but only about 10% in width and length. It is believed that during frying the rapid vaporisation of the moisture at the interior as well as at the surface creates an expansion which leads to a crispy and porous product. Figure 27 contains histograms of various processing and product characteristics including gelling and blistering behaviour, strip texture and strip breaking strength.

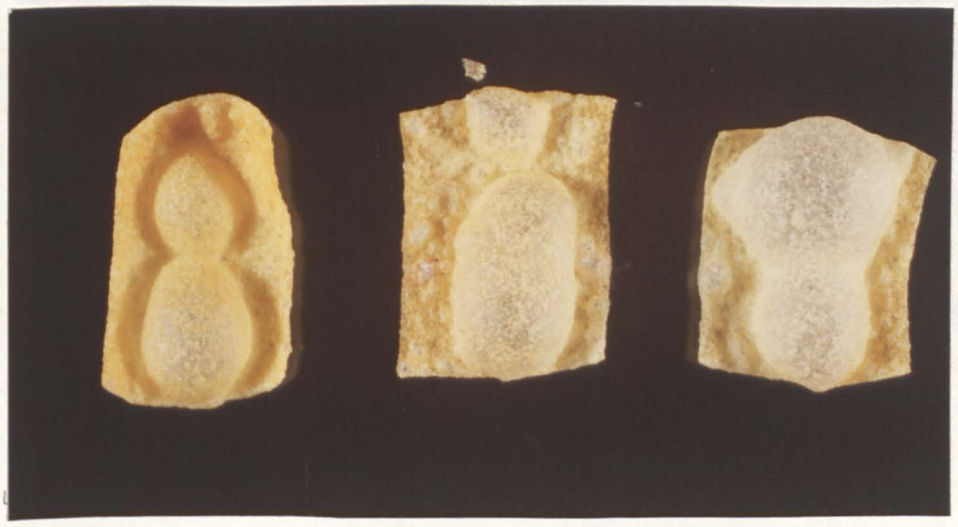
The reason why the unsatisfactory potato granules did not form a coherent strip on extrusion was later found to be due to the presence of excess glyceryl monostearate (GMS). This will be discussed in greater detail in following sections.

Among the satisfactory potato granules, Desirée and Pentland Crown produced extrudates that blistered badly on frying while others either blistered slightly or not at all. It was observed that the blisters usually occurred at the centre of the extruded strips and were symmetrical in size on the upper and lower surface of the snack (Figure 28). This is probably due to the higher moisture content in the centre of the strip than at the outer edges. When fried, the pressure conditions which develop in the interior lead to internal bubble formation which grow into substantial blisters.

The blistering effect correlated with the breaking strength of the extrudates (Figure 27). Stronger extrudates which were characterized by overgelling, by a tough and glassy appearance and by having a high breaking strength (400-600 g) were found to be more likely to blister compared to a weaker extrudate having a breaking strength of about 300 g. The significance of this will be discussed later.

Addition of 'potato snack additives' to the potato granules prior to extrusion seemed to beneficially promote the characteristics

Figure 28. Blister formation in potato snacks.



(a) Blistering occurs at the centre of the snacks.

(b) Side view of blistered snacks showing the symmetrical shape of the blisters.

(c) Front view of blistered snacks, again showing the symmetrical shape of the blisters.

of the extrudates of satisfactory potato granules, but did not materially improve the performance of the unsatisfactory potato granules. In all cases it tended to weaken the strip slightly as indicated by a reduction in breaking strength of the extrudates. The additives did, however, help to reduce blistering during frying. The additives are a mixture of many chemicals, the exact amount of each component being a trade secret. It is difficult to predict the role of the additives, but the results suggest that they both soften the extrudates and facilitate the production of an evenly expanded product during frying.

CHARACTERISATION OF THE STARCH COMPONENTS

4. Characterisation of the starch components

4.1 Introduction

In order to find out what caused the different extrusion response of differing batches of potato granules and the reason for blistering during frying, attention was naturally focused on the starch component since it constitutes more than 90% of the potato granules.

A thorough analytical study on the starch components was therefore carried out. The amylose and amylopectin contents were determined to find whether there were any significant differences among the different potato granules. Secondly, we determined the amount of free starch outside the granules and the total extractable soluble starch from the granules and extrudates. This was followed by a detailed study on the differences in molecular size of the extracted starch and lastly the differences in the amount of total phosphate and glucose-6-phosphate in the potato granules and extracted starches.

4.2 Semi-micro differential potentiometric iodine titration

4.2.1. Introduction

The interaction of starch and its component fractions, amylose and amylopectin, with iodine is perhaps the most characteristic property of these polysaccharides. Amylose interacts strongly with iodine to give a deep blue complex while, in contrast, amylopectin has only a weak affinity and gives a reddish-purple colouration. On the basis of this interaction, various methods have been devised for determining the amylose and amylopectin content of starch.

The methods, which have been reviewed in detail by Radley (1953), Kerr (1950), Schoch (1964) and Richter et al. (1968) can be classified into techniques depending on either:

(i) measuring the optical density of the iodine complex,

(ii) determining amperometrically the amount of iodine absorbed by the polysaccharide,

or (iii) potentiometrically.

Recently, an alternative to iodimetric methods has been developed for the determination of amylose/amylopectin ratio of starches. Solubilised starches in dimethylsulphoxide have been debranched with isoamylase and the resulting linear components quantitatively determined by gel permeation chromatography on a column of Sepharose CL-6B (Sargeant, 1982).

Although spectrophotometric methods provide a convenient and rapid method of analysis, they are not sufficiently sensitive for accurate measurement on the semi-micro scale. Amperometric methods also appear to have the same disadvantages. The enzymic and gel chromatography method looks promising but more work is needed to establish the technique. There is little doubt that the most satisfactory methods of measuring the iodine binding characteristics of starch or its components is by potentiometric titration.

The semi-micro differential potentiometric titration technique enables the full iodine binding capacity (I.B.C.) to be elucidated. Although this technique gives much more information than colorimetric measurements, it does require specialised apparatus and is more lengthy in practice.

In this study, we chose to use the semi-micro differential potentiometric titration method as modified by Banks et al. (1971) to estimate the amount of amylose and amylopectin in starches extracted from potato granules.

4.2.2 Principle of the semi-micro differential potentiometric iodine titration method

The differential technique involves two iodine/iodide half-cells, each with a platinum electrode, which are connected by a liquid bridge. The test half-cell, t, contains the starch sample in the buffered iodide solution; and the control half-cell, c, contains buffered iodide at an identical contentration.

This experimental set-up results in an iodine concentration cell without transference i.e.

$$I_2\left[(a_{I_2})_c\right] \;\Big|\; I^{1}\,(a_{I}\text{-}) \;\Big|\; I_2\left[(a_{I_2})_t\right]$$

where 'a' represents the activity. For one electrode, the potential, E, is given by,

$$E = E_o - \frac{RT}{F} \ln\left[(a_{I_2})^{\frac{1}{2}}/a_{I}\text{-}\right] \qquad \text{where}$$

R, T and F are the Gas constant, temperature and Faraday constant, respectively. The overall potential of the cell is thus:

$$E = -\frac{RT}{2F} \ln\left[(a_{I_2})_c/(a_{I_2})_t\right]$$

The apparatus is used as a null instrument since when there is no potential between the electrodes and assuming the activity coefficient is unity, then,

$$(a_{I_2})_c = (a_{I_2})_t \ ,$$

$$\text{or} \quad \left[I_2\right]_c = \left[I_2\right]_t \ ,$$

In use, iodine is added to the test half-cell, and then the potential produced is cancelled out by addition of iodine to the control half-cell. At this point of null potential, the amount of iodine added to the control cell corresponds to the concentration of free molecular iodine in the test solution, whilst the amount of iodine bound by the starch is given by the difference between this amount and the original amount of iodine added.

Titration curves of 'bound iodine' versus 'free iodine' are then obtained as shown in Figure 29.

4.2.3. Apparatus

The apparatus is shown diagrammatically in Figure 30. Each half-cell consists of a 1 litre round-bottom flask, equipped with 4 ground glass joints which accommodate (a) the stirrer, (b) the platinum electrode (Russell pH Ltd.), (c) the liquid bridge by which the two half-cells are connected and (d) the 'Agla' syringe (Wellcome Reagents Ltd., Beckenham, Kent, England), by which iodine is added.

The stirrers, which operate continuously during the titration, are driven by a pulley system.

The liquid-bridge consists of a U-tube, having a middle arm which can be sealed by means of a glass stopcock. This simple system eliminated junction potentials and prove particularly effective. The bridge (internal volume ca.2ml) was filled by opening the stopcock on

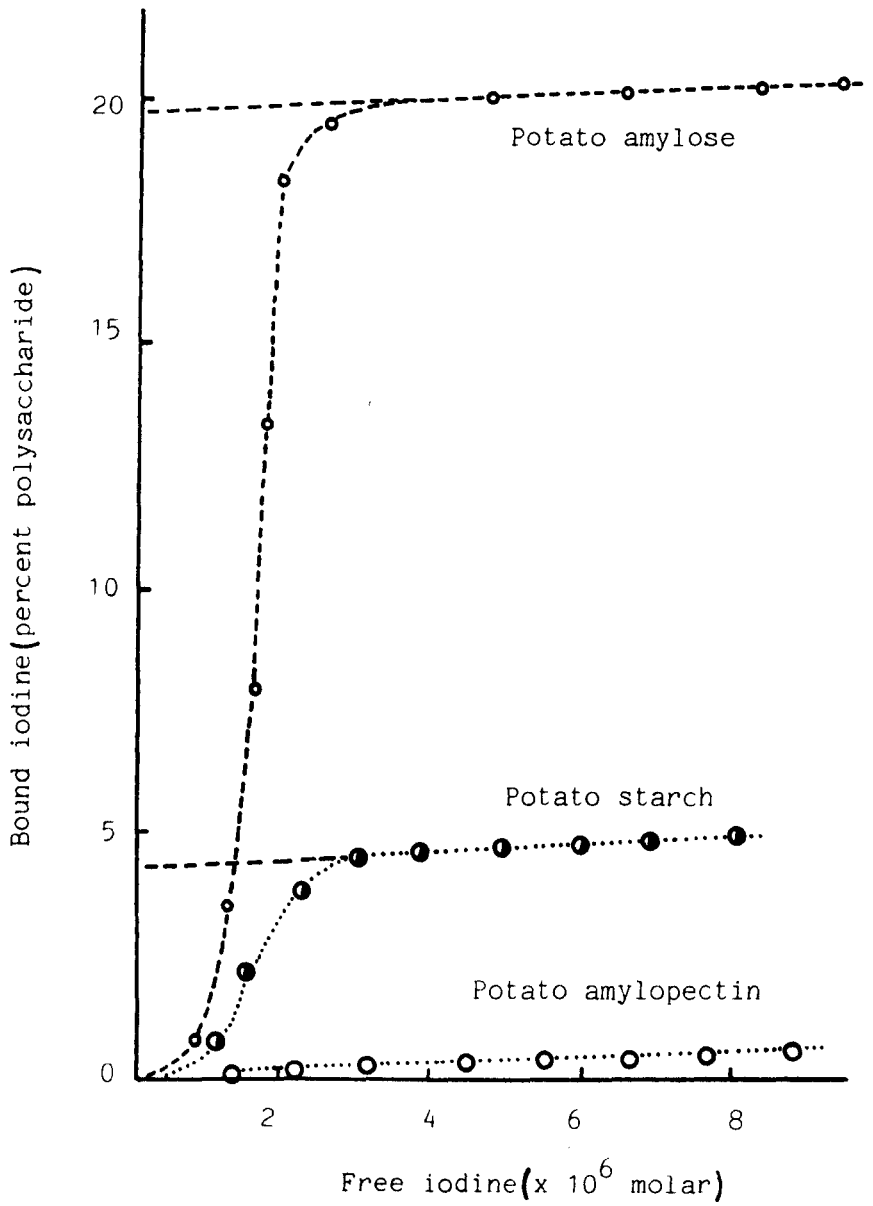
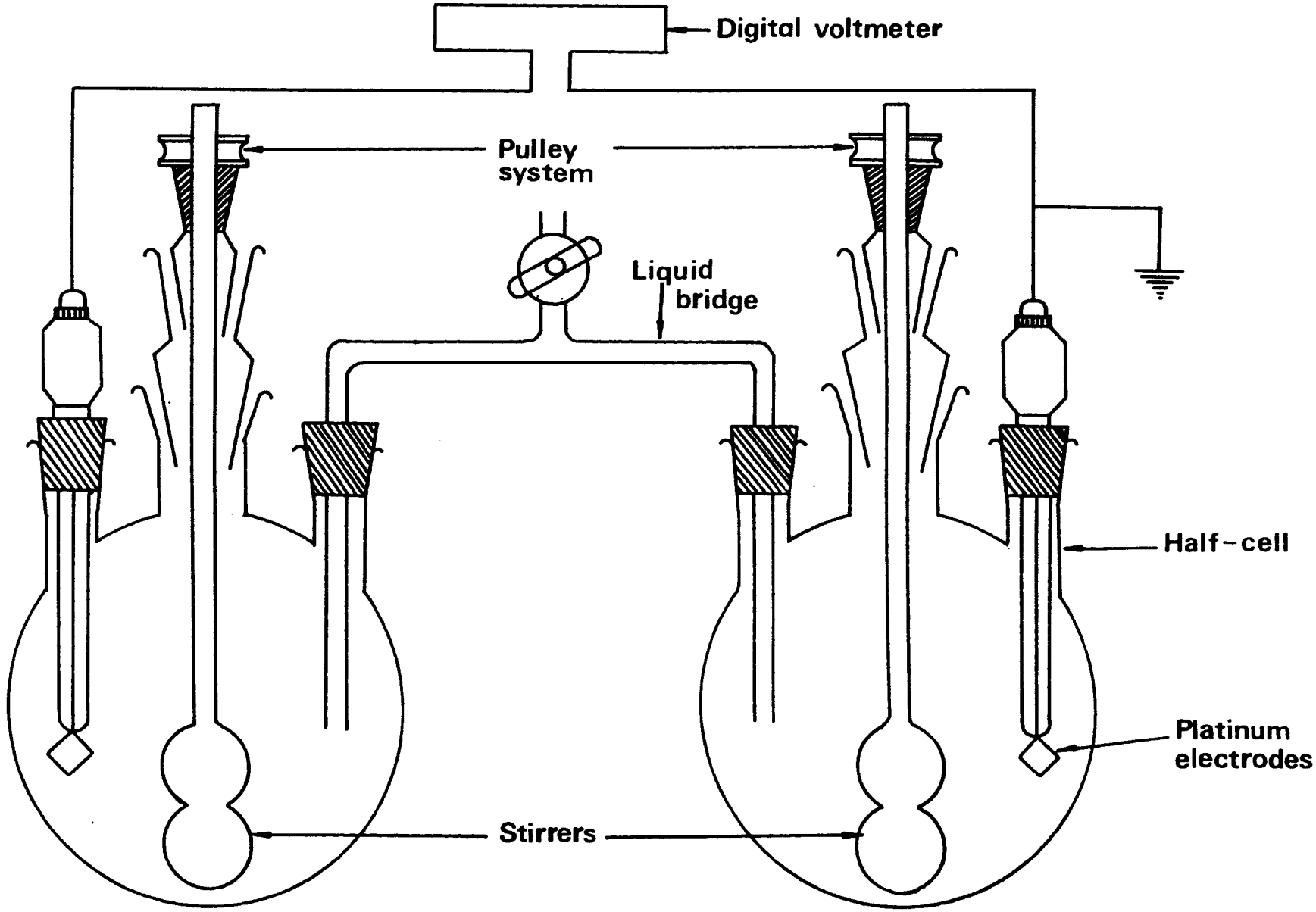


Figure 29. The iodine-binding curves of potato starch, potato amylose and potato amylopectin measured at 20°C by the technique of Banks et al., 1971.

Figure 30. Diagram of semi-micro differential potentiometric iodine titration apparatus.



the side-arm, applying sudden suction by means of a rubber bulb, and closing the stopcock as soon as the bridge was filled.

The half-cells were arranged such that the liquid levels in them were identical with the thermostat-bath liquid surface.

4.2.4.1. Materials

The starch used in the titration was extracted from potato granules as described in Section 4.2.4.2.

Reagents

Analytical grade reagents were used throughout this investigation.

(i) Stock potassium iodide solution (0.1M)

(ii) Stock iodine (0.05M) in potassium iodide (0.1M)

(iii) Sodium thiosulphate solution (0.1M)

(iv) Sodium iodate solution (0.0167M)

(v) Starch indicator solution

(vi) Iodine solution for titration (0.005M I_2 in 0.01M KI)
(Fresh iodine solution was prepared daily by tenfold dilution of the stock iodine with distilled water and this solution was kept in a brown, stoppered bottle. The dilute iodine solution was standardised regularly by means of sodium thiosulphate (0.1M), using starch as indicator. Sodium thiosulphate solution was standardised using potassium iodate).

(vii) Phosphate buffer (0.2M KH_2PO_4 and K_2HPO_4; pH 5.8)

(viii) Amyloglucosidase solution.
The enzyme (α-1:4-glucan glucohydrolase, E.C.No. 3.2.1.3.) was purchased from Sigma Chemical Company. It was dissolved in water (1mg per 1 ml) to yield a solution of activity = 14 units per 1 ml (1 unit = 1 micromole of glucose liberated per minute from soluble starch at pH 4.6 and 37°C). The enzyme solution was stored at 2°C.

(ix) Alpha-amylase solution.

α-Amylase (1,4 alpha-D-glucan glucanohydrolase E.C.No. 3.2.1.1.) was supplied by Sigma Chemical Company. A suspension containing 0.5 mg of crystalline α-amylase was diluted to 1 ml. with distilled water. The enzyme solution was stored at 2°C.

(x) Glucose oxidase-peroxidase-chromogen mixture.

Horse-radish peroxidase (3 mg) (Sigma Chemical Company), 100 mg of glucose oxidase (Sigma Chemical Company) and 50 mg ABTS* (Boehringer Corporation, U.K.) were dissolved in 100 ml. of 0.3 M Tris-phosphate buffer pH 7.0. The mixture was stored in a brown bottle at 2°C.

(xi) Hydrochloric acid (7M)

4.2.4.2. Extraction of starch from potato granules

Micronised potato granules were suspended in dimethyl sulphoxide (DMSO) to give a 5% suspension which was stirred overnight. The mixture was heated at 75°C for 3 hours, followed by homogenisation in order to solubilise as much starch as possible. The suspension was centrifuged at 10000g, the residue which contained mainly cell wall materials was discarded. Ethanol (3 vols.) was added to the supernatant to precipitate the starch. The precipitate was collected by centrifugation and washed repeatedly with ethanol to ensure complete removal of dimethyl sulphoxide. The extracted starch was freeze dried. The dried starch was redissolved in dimethyl sulphoxide and the same extraction process was repeated. The resulting dry, non-granular starch was used in the iodine titration.

4.2.4.3. Preparation of starch for iodine titration

The dry, non-granular starch was dissolved in DMSO to give a starch/DMSO solution of approximately 1%. The starch/DMSO solution

*ABTS = 2.2'-Azino-di (3-ethyl-benzthiazolin-sulphonate)

(1 ml.) was diluted with 11 ml. of distilled water and 10 ml. of the diluted starch solution was used in the iodine titration.

4.2.4.4. Titration procedure

Electrolyte solution was prepared by diluting 203 ml. of 0.1M potassium iodide and 20 ml. of 0.2M phosphate buffer (pH 5.8) to 2 l with distilled water and 830 ml. of this electrolyte solution was added to each half-cell. The cells were placed in the thermostatically controlled water bath maintained at 20 $\pm$ 0.5°C, such that the liquid level in each cell was the same as that in the bath. The liquid bridge was placed between the half-cells and filled as described previously. The cleaned electrodes were fitted in the cells and stirring was started and maintained at a rate sufficient to give rapid mixing without causing undue turbulence.

The stock solution of the sample to be titrated was prepared by diluting the polysaccharide/DMSO solution (1 ml.) with distilled water (11 ml.). The amount of starch used was 8-10 mg/840 ml. as suggested by Banks et al. (1970). A blank was prepared in a similar manner, omitting only the polysaccharide. Blank and sample solutions (10.0 ml.) were added to their respective half-cells by pipette. Thirty minutes were allowed for temperature equilibration before starting the titration.

An aliquot of 5 "Agla" units* of iodine solution (0.005M I_2 in 0.01 M KI) was added to the sample half-cell by means of an "Agla" micrometer syringe, and five minutes allowed for equilibrium to be achieved. Iodine was then added slowly by a micrometer syringe to the blank half-cell until zero potential (less than 0.01 mV) as indicated on the electronic detector (Solartron digital voltmeter-Model LM 1426). At this point, the concentrations of molecular iodine in the two half-cells were equal, and hence the amount of iodine bound by the polysaccharide

* 5 "Agla" units = 0.1 ml.)

is given by the difference in the volumes added to both sides. The addition and balancing process was repeated until the complete curve of iodine bound as a function of free iodine was obtained (Figure 29).

4.2.4.5. Determination of polysaccharide concentration

Immediately after adding the aqueous DMSO/polysaccharide solution to the sample half-cell, an aliquot (ca. 1.0 ml.) of the remaining stock solution was taken for determination of the polysaccharide concentration. This was achieved by hydrolysis of the polysaccharide to glucose using amyloglucosidase and α -amylase (the starch solution was so diluted that the polysaccharide concentration was 50-100 mg/ml.). The glucose was estimated by the glucose oxidase/peroxidase technique described previously by Colonna et al. (1981).

4.2.5. Calculation

If I_t and I_c are the amounts of iodine (in "Agla" units) added to the test and control half-cells, respectively, the amount of bound iodine $I_b = I_t - I_c$. The values of total bound iodine ($\sum I_b$) and the total free iodine ($\sum I_c$) are evaluated consecutively. $\sum I_b$ is then converted to the weight of iodine and divided by the weight of starch to obtain the milligrammes of iodine bound per 100 mg of starch, i.e.

$$\text{weight of iodine} = \frac{\sum I_b \times I_2 \text{ normality} \times 254 \times 10^3}{50 \times 2 \times 10^3} \text{ mg}$$

$$= W_{I_2}$$

If the weight of starch = WA (obtained by earlier method), then the percentage of iodine bound = $100\ W_{I_{2/WA}}$

ΣI_c is then converted to an iodine concentration in moles per litre, using the formula below:

$$[I_2]_c = \frac{(\Sigma I_c \times I_2 \text{ normality})}{50 \times 2 \times 840} \text{ moles per litre}$$

The percentage of iodine bound ($^{100W}I_{2/WA}$) is thereafter plotted against $[I_2]_c$ to obtain the iodine titration curve.

To obtain the iodine binding capacity (I.B.C.),the results obtained over a finite range of free iodine were extrapolated to zero iodine concentration according to the method of Banks et al. (1971) (Figure 29).

The amylose content was obtained from the following relation:

$$\% \text{ Amylose} = \frac{\text{Iodine binding capacity of starch at T°C}}{\text{Iodine binding capacity of amylose at T°C}} \times 100$$

The I.B.C. of amylose was taken as 19.5 (Banks et al., 1971).

$$\% \text{ amylopectin} = (100 - \% \text{ amylose})$$

4.2.6. Results

Figure 31 shows the iodine titration curves of starches extracted from potato granules. The titration was performed in duplicate and the average value was taken as the percentage amylose present in the starch as shown in Table 11.

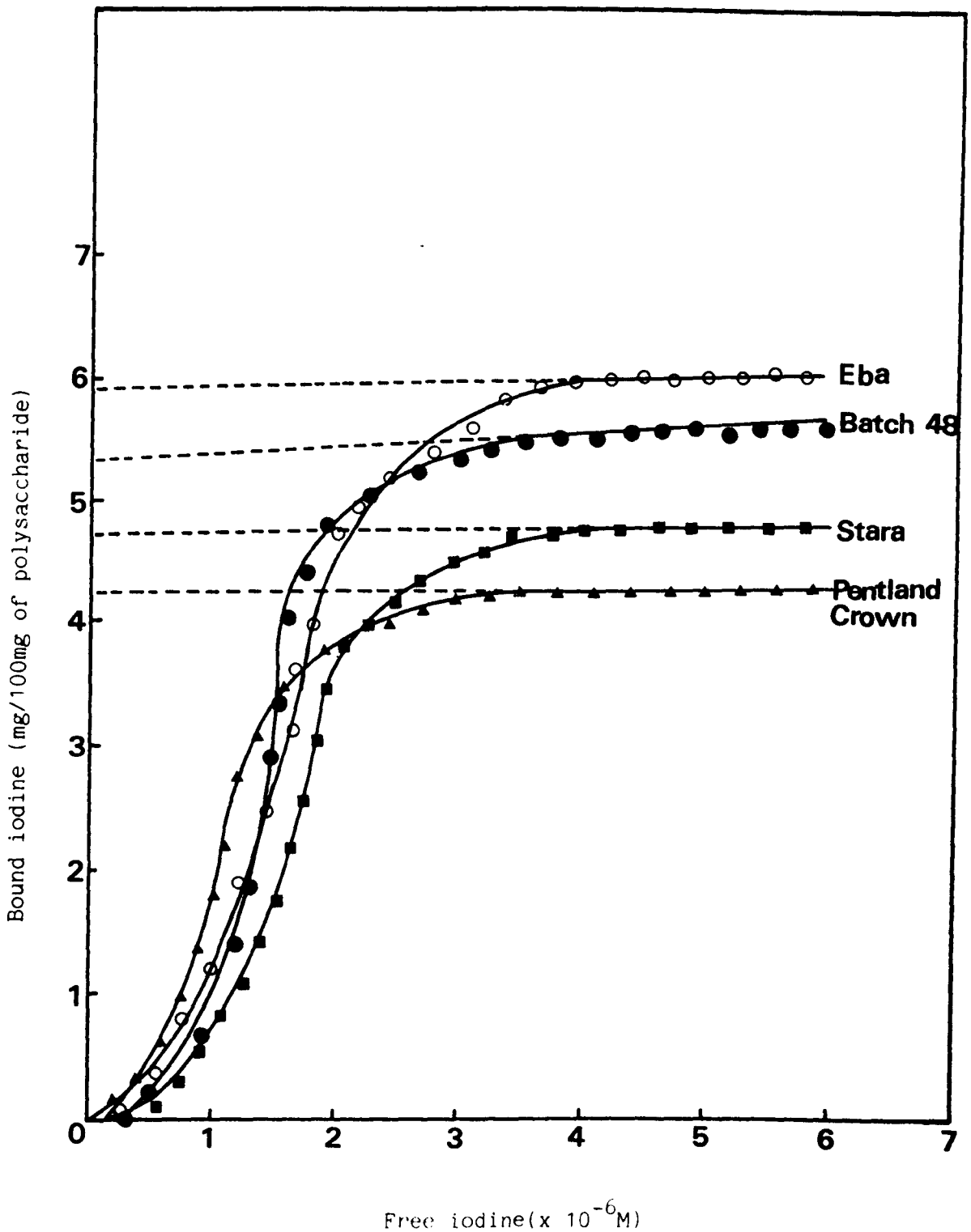


Figure 31. Iodine titration curves at 20°C of starches extracted from interior of potato granules. The dotted lines show the method of obtaining the iodine binding capacity (I.B.C.).

Table 11. The iodine binding capacity, amylose/amylopectin ratio, amylose and amylopectin contents of extracted starches from potato granules.

Potato granules	I.B.C.[a]	Amylose/ Amylopectin Ratio	% Amylose[b]	% Amylopectin
Ajax	3.70	0.23	18.97	81.03
Amigo	4.41	0.29	22.62	77.38
Eba	5.98	0.44	30.67	69.33
Prominent	4.59	0.31	23.54	76.46
Pentland Crown	4.23	0.28	21.69	78.31
Desirée	4.23	0.28	21.69	78.31
Record	4.26	0.28	21.85	78.15
Maris Piper	4.40	0.29	22.56	77.44
Stara	4.64	0.31	23.79	76.21
Batch No. 86	5.06	0.43	29.95	70.05
Batch No. 979	4.90	0.34	25.13	74.87
Batch No. 48	5.30	0.37	27.18	72.82
Batch No. 35	4.56	0.31	23.39	76.61
Batch No. 73	4.87	0.33	24.97	75.03
Batch No. 23	5.38	0.38	27.59	72.41
Batch No. 85	4.72	0.32	24.21	75.79
Batch No. 125	5.54	0.39	28.41	71.59
Batch No. 118	4.76	0.32	24.41	75.59
Batch No. 1	4.44	0.29	22.77	77.23
Batch No. 2	4.34	0.29	22.26	77.74
Batch No. 3	4.40	0.29	22.56	77.44
Batch No. 4	5.06	0.43	29.95	70.05
Batch No. 5	5.23	0.37	26.82	73.18

(a) I.B.C. = Iodine binding capacity (mg iodine bound/100 mg polysaccharide)

(b) Calculated by assuming that amylose has an I.B.C. of 19.5 (Banks et al., 1971)

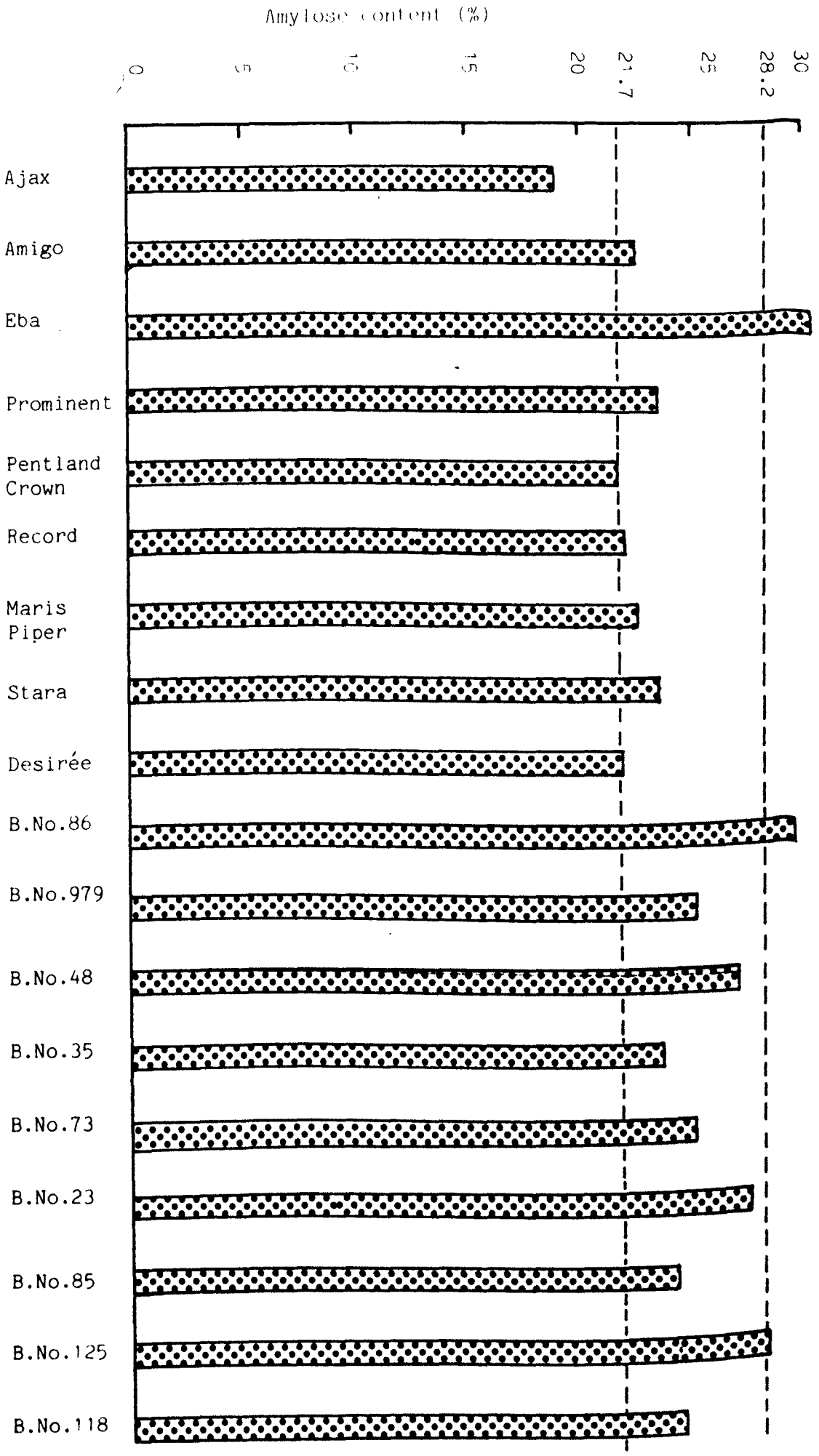


Figure 32. Amylose content of starches extracted from potato granules.

4.3. Estimation of free starch of potato granules

4.3.1. Introduction

During the production of potato granules, prevention of excessive release of starch from ruptured potato cells is of great importance to ensure acceptable textural quality of the product. A high amount of free, extracellular starch results in a gluey and sticky product (Boyle, 1975; Willard, 1975).

Various methods have been developed to estimate the amount of extra-cellular starch in potato granules. Of these only two are commonly used. Olson et al. (1953) introduced a method whereby the free starch was extracted with water at 66°C and the amount of starch extracted was estimated by the Anthrone method. Another method, known widely as the 'Blue Value Index' method was used by Mullins et al. (1955). He also extracted the soluble starch at 66°C using water and the extract was then treated with iodine. The intensity of the resulting starch-iodine blue colour gives an index of soluble starch present in the extract.

The 'Blue Value Index' is only a relative figure and no reference can be made to the actual amount of starch present nor to the proportion of amylose to amylopectin.

The aim of the present study was to try to determine whether the differences in the properties of potato granules could be due to the amount of extra-cellular free starch present. The method outlined by Mullins et al. (1955) was adopted with certain modifications.

4.3.2. Experimental

4.3.2.1. Materials

Potato granules were the same as those used in other experiments and were supplied by Dornay Foods Ltd.

4.3.2.2. Extraction of water-soluble starch from potato granules

A 250 ml. conical flask was clamped to a Griffith's flask shaker and partially submerged in a water-bath maintained at 68°C. 100 ml. of distilled water were preheated, poured into the flask and brought to 66 $\pm$ 1°C. Potato granules (1.0g) were added and the flask was immediately stoppered to prevent excessive evaporation of water. Extraction was carried out for exactly 5 min. with medium speed shaking, so that all particles were kept evenly in suspension. Exactly 10 minutes after the beginning of the extraction, the suspension was centrifuged for 20 minutes at 4000 r.p.m. in an MSE bench centrifuge. The supernatant was carefully collected and used for further analysis.

Determination of "Blue Values"

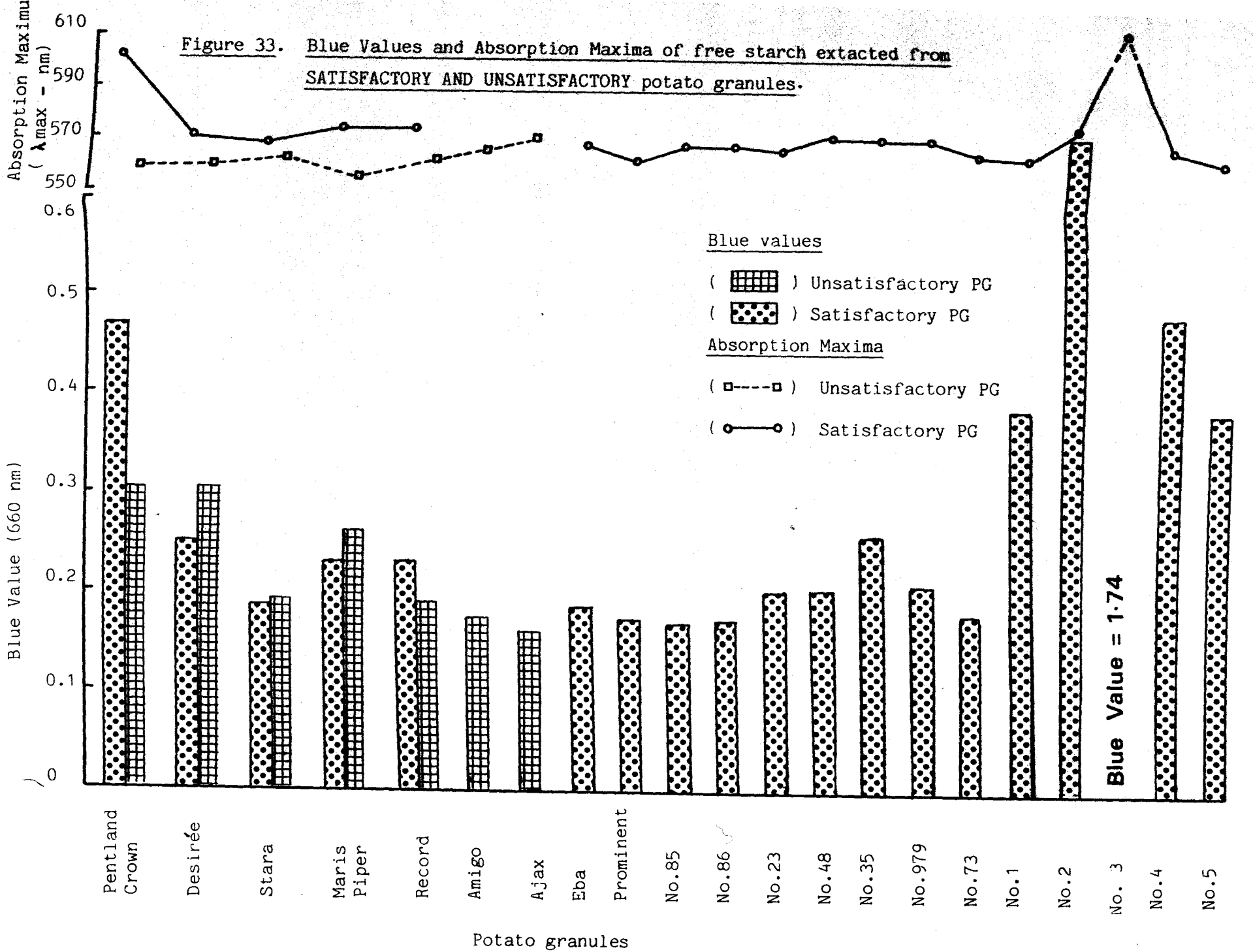
Iodine solution (0.1 ml., 0.02N) was added to 3 ml. of supernatant and 5 minutes after addition of iodine, the 'blue value' was measured by reading the absorbance at 660 mμ using a Perkin Elmer spectrophotometer. The reference solution consisted of 0.1 ml. iodine in 3 ml. distilled water.

In addition, spectra of the iodine stained extract were recorded in the visible range and the maximum absorption (λmax) was determined. The "blue values" reported are a mean of 6 independent replicates.

4.3.3. Results

The blue values of the different types of potato granules and their corresponding absorption maximum in nm. are given in Figure 33.

Figure 33. Blue Values and Absorption Maxima of free starch extacted from SATISFACTORY AND UNSATISFACTORY potato granules.



4.4. Isolation of total soluble starch from potato granules and extrudates

4.4.1. Introduction

A basic hypothesis in this project has been that the formation of a network which binds the potato granules together. Such a network is formed primarily by the interaction between starch molecules (though lipids may have some moderating effect). These starches are believed to be extracellular in nature and the amount present could well determine the strength of network formed and thus the type of extrudate that is produced.

It seemed necessary therefore to examine whether there were any differences in the total amount of extracellular starch between the satisfactory and unsatisfactory granules and, further, whether such differences correlated in any way with strip formation and blistering.

4.4.2. Experimental

4.4.2.1. Materials

Potato granules were obtained from Dornay Foods Ltd. Extruded samples were prepared as described in Section 3.6.2. The extrudates were broken up into small pieces using a 'Moulinex' grinder. Care was taken to avoid rupturing the granules.

4.4.2.2. Extraction of soluble starch

Schoch and French's procedure (1947) was used with modifications to isolate and determine the total soluble starch content from potato granules and extruded strips.

Potato granules (10g) were shaken up with 60 ml. of distilled water by agitating the mixture on a Griffith's flask shaker for 2 hours.

The slurry was centrifuged (10,000 x g for 20 min.) and the supernatant collected. The sediment was resuspended in 40 ml. of distilled water and again shaken up for 2 hours. After centrifuging the supernatant was collected and combined with the previous one.

The same procedure was repeated using 3g of ground extrudates, shaking it up with 60 ml. of distilled water for 24 h and then centrifuging. The sediment was resuspended in 40 ml. of distilled water and again shaken up for another 24 hours. After centrifuging the supernatant was collected and combined with previous one. A longer extraction time was required to break up the strips thereby freeing the extracellular starches which acted as binders.

The supernatant was treated with 3-4 volumes of methanol to flocculate the soluble starch and the mixture was heated on the steam bath for 1 hour, then allowed to settle overnight. The flocculated soluble starch was collected by centrifugation (3000 x g for 20 mins) and the starch was dispersed in 5-10 ml. of distilled water and freeze-dried. The weights of the dried samples were recorded and the percentage of soluble starch was calculated on a dry weight basis.

Duplicate extractions were carried out for each sample and the results summarized in Table 12.

4.4.3. Results

The amounts of soluble starch extracted from outside potato granules, extruded potato granule strips and extruded potato granule plus 'potato snack additives' are tabulated in Table 12. A comparison of the amounts of soluble starches extracted from satisfactory and unsatisfactory granules is shown in Figure 34.

Table 12. Soluble starch extracted from potato granules and extrudates.

Samples	Soluble starch (%)		
Potato granules	Potato granules	Extruded potato granules	Extruded potato granules+PSA
Eba (S)	1.17	4.65	4.92
Ajax (U)	1.12	4.21	4.38
Prominent (S)	1.15	4.13	4.75
Amigo (U)	1.13	4.30	4.53
Desirée (S)	1.43	5.28	5.84
Pentland Crown (S)	1.43	5.55	5.87
Maris Piper (S)	1.41	3.86	-
Record (S)	1.77	3.44	4.20
Stara (S)	1.69	3.37	3.43
Desirée (U)	1.10		
Pentland Crown (U)	1.13		
Maris Piper (U)	1.25		
Record (U)	1.49		
Stara (U)	1.53		

(S) = satisfactory granules

(U) = unsatisfactory granules

Figure 34. Total soluble starch extracted from SATISFACTORY (▦) and UNSATISFACTORY (▦) potato granules.

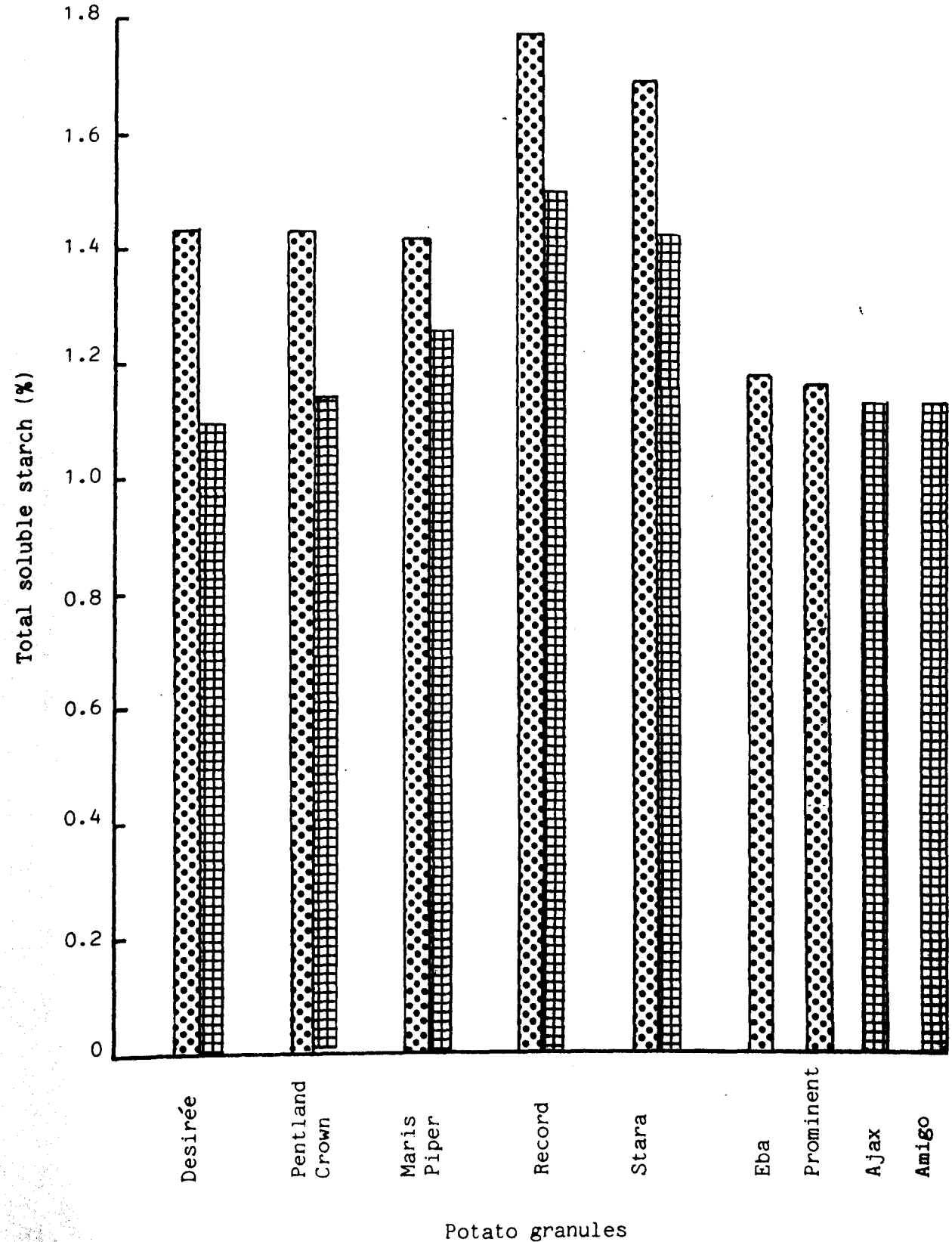
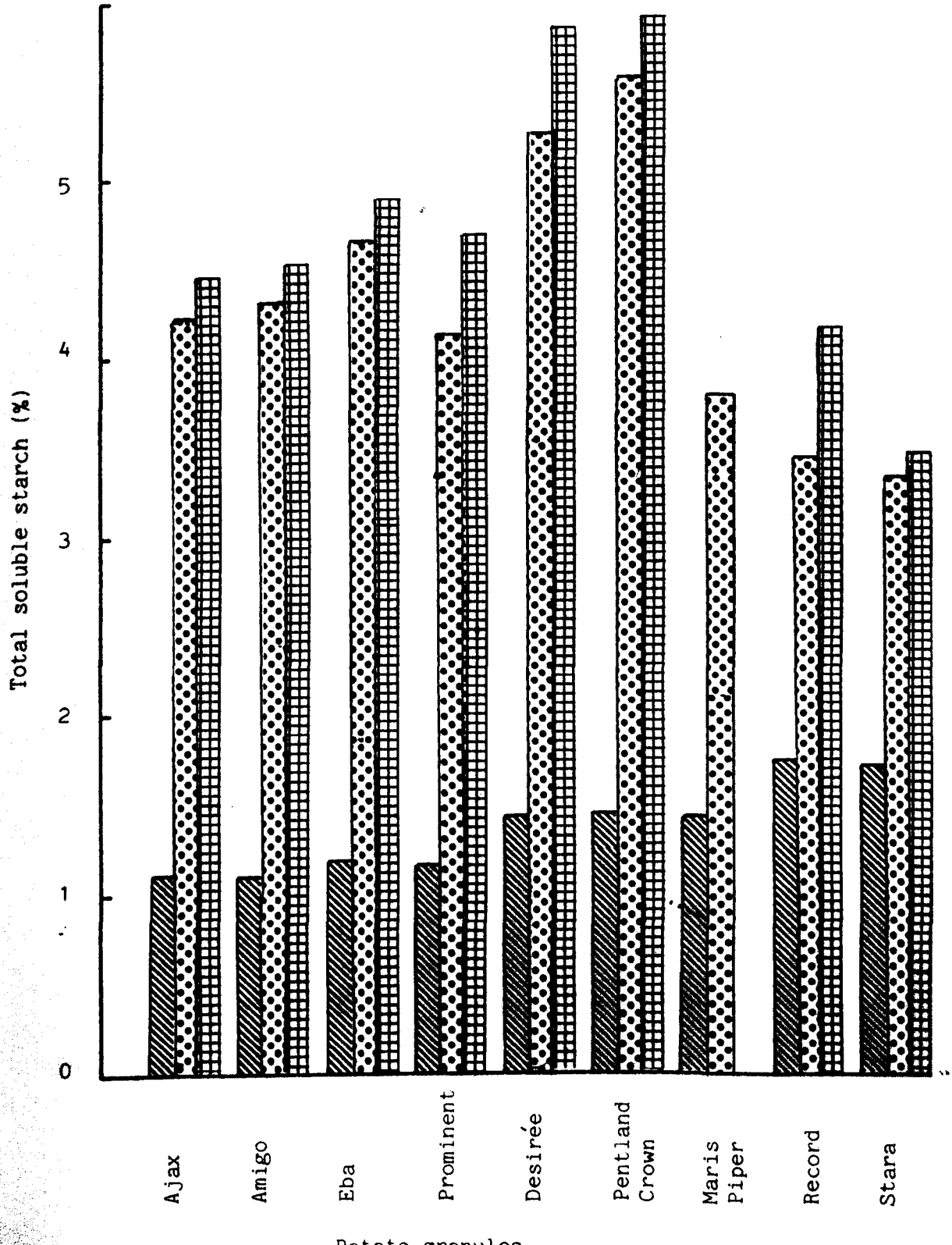


Figure 35. Total soluble starch extracted from the exterior of (i) non-extruded potato granules (▨) (ii) extruded potato granules (▩) and (iii) extruded potato granules + PSA (▦).



4.5. Gel permeation chromatography

4.5.1. Introduction

In order to gain more information about the exact nature of the extracted starches, the latter were subjected to gel chromatography. This technique has been used to separate many types of macromolecules including polysaccharides. Together with enzymatic studies it has permitted the elucidation of the fine structure of amylopectin and glycogen (Lee et al., 1968; Akai et al., 1971).

Recently, Eberman et al. (1975, Yamada et al. (1976), Bruun et al. (1977) and Biliaderis (1981) have shown that natural starches from potatoes, wheat, maize and legumes can be separated by gel chromatography into a large molecular weight amylopectin fraction and a smaller molecular weight fraction which consists primarily of amylose.

In this study the extracted starches were analysed for their percentage distribution in molecular sizes which, it was hoped, would then provide us with a better understanding of the extrusion process and the role of the extracellular starches in network formation. It was also hoped that differences between the satisfactory and unsatisfactory potato granules would be detected.

4.5.2. Experimental

4.2.5.1. Materials

Sample

The starches used in the experiment were prepared as described in Section 4.4.2.2.

Reagents

The chemicals used were of analytical reagent grade whenever possible.

(1) Sepharose CL-2B-300 (Sigma Chemical Company)

(2) Blue Dextran 2000 (Molecular wt. >2 x 10^6)
Dextran T-500 (Molecular wt. = 500,000)
Dextran T-40 (Molecular wt. = 40,000)
(Pharmacia Fine Chemicals, Uppsala, Sweden)

(3) Orcinol reagent: 1g orcinol in 1 l. of 70% (^{v}/v) sulphuric acid; the reagent was stored in brown glass bottles.

(4) 0.02M Iodine-potassium iodide solution

(5) 40% (^{v}/v) Perchloric acid

(6) 3M NaOH

(7) 0.01M NaCl solution containing 0.01% mercuric chloride

4.5.2.2. Preparation of starch solution

Extracted starch (20 mg) was dissolved in 2.0 ml. of 40% perchloric acid by constant stirring. After 2 hours the starch solution was neutralised with 5 ml. 3N NaOH. The solution was centrifuged and 6 ml. of the supernatant was loaded onto the column.

4.5.2.3. Gel chromatography

Gel chromatography was performed using Sepharose CL-2B, a cross-linked, alkali-stable agarose gel. The column had a gel-bed size of 2.0 x 72 cm. The sample was eluted with 0.01M NaCl solution containing 0.01% mercuric chloride. The separation was carried out at room temperature at a constant but regulated flow rate of about 18 ml./hr. Fractions of 3 ml. each were collected in a fraction collector and alternate fractions were analysed for total carbohydrates and the absorption maximum

(λ max) of the iodine-polysaccharide complexes.

The parameter Vo for the column was obtained by chromatography of Blue Dextran 2000. The peak fraction detected with Blue Dextran (absorption at 280 nm) was taken as the value of Vo.

For calibration of the column, 3 types of linear dextrans were used: Dextran T-500 (mol. wt. 500,000)

Dextran T-40 (mol. wt. 40,000)

and Blue Dextran (mol. wt. 2,000,000).

The chromatograms of the dextrans are shown in Figure 36.

Total carbohydrate in each fraction was determined by the orcinol-sulphuric acid method of Kesler (1967) using a ChemLab autoanalyser system. The reaction mixture was heated at 95°C in an oil-bath, then cooled and the absorbance monitored at 420 nm in a 15 mm continuous flow cell. The column, autoanalyser and associated equipment are shown in Figure 37.

The absorption maxima (λmax) for the fractions were obtained by mixing the 3 ml. fractions with 0.1 ml. of 0.02 M iodine solution and from the absorption spectra the λmax were measured.

4.5.3. Results

The gel chromatographic patterns of starches extracted from inside the potato granules (Ajax, Eba, Amigo and Prominent) are shown in Figure 38. Figures 39-42 consist of 3 chromatograms each. They are for starches extracted from,

(i) outside the potato granules

(ii) outside the extruded potato granules strips, and

(iii) outside the extruded potato granules plus 'potato snack additives'.

The chromatograms can be divided into 3 major regions based on the molecular sizes. Region 1 includes polymers with $\overline{MW}$ >1.5 x 10^6,

Figure 36. Calibration of column using Blue Dextran(●—●), Dextran T-500 (▲—▲) and Dextran T-40 (■—■).

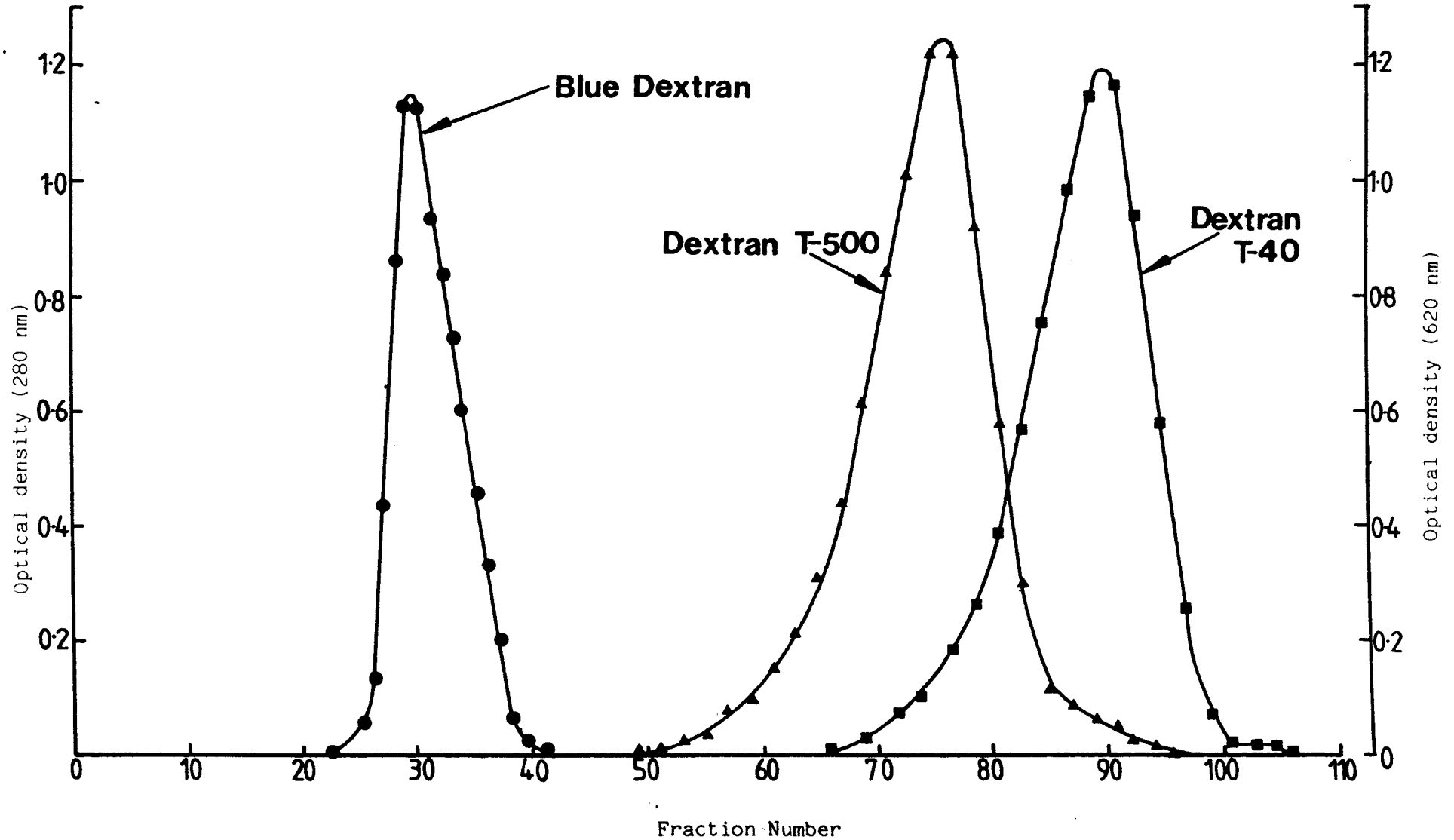
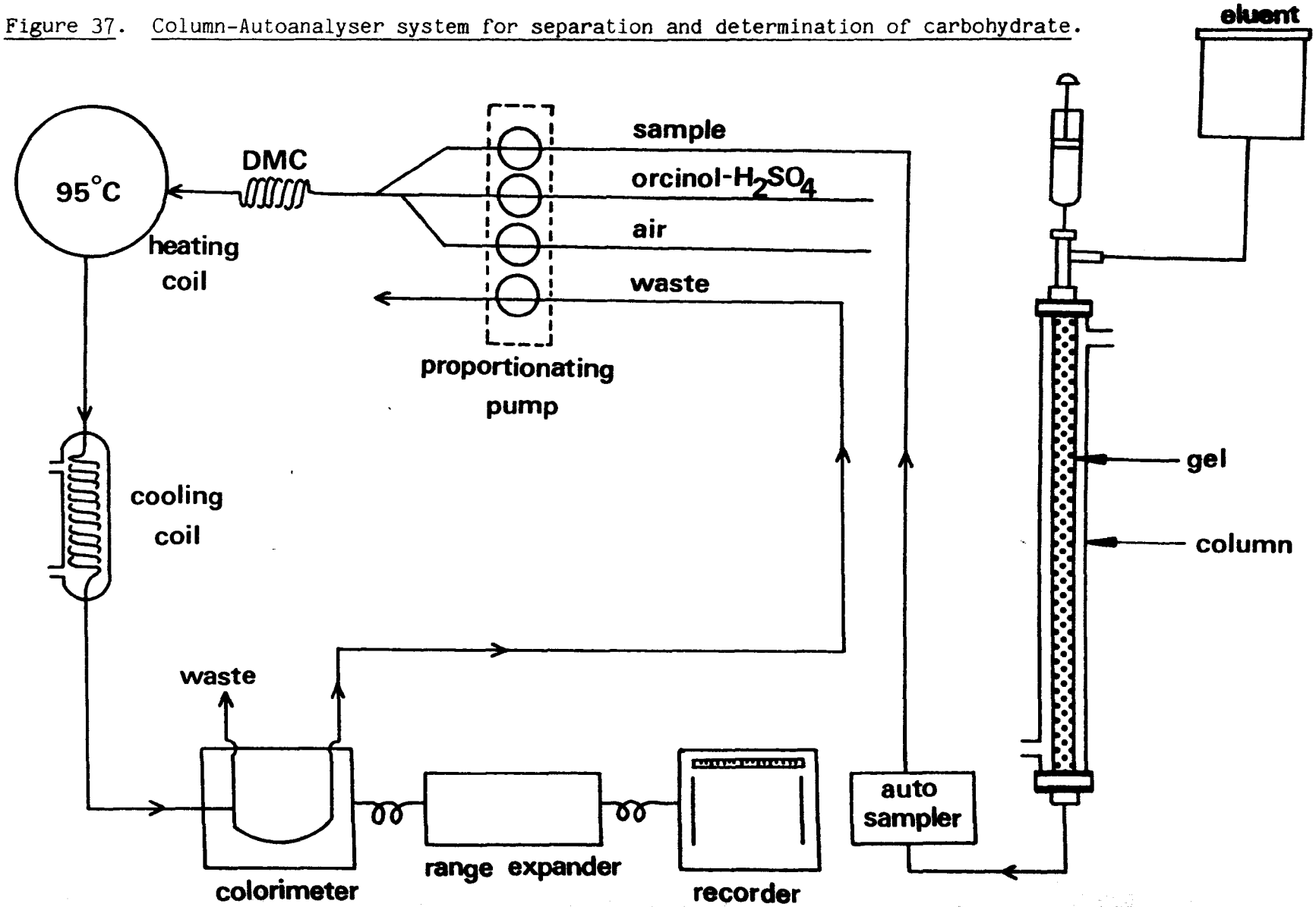


Figure 37. Column-Autoanalyser system for separation and determination of carbohydrate.



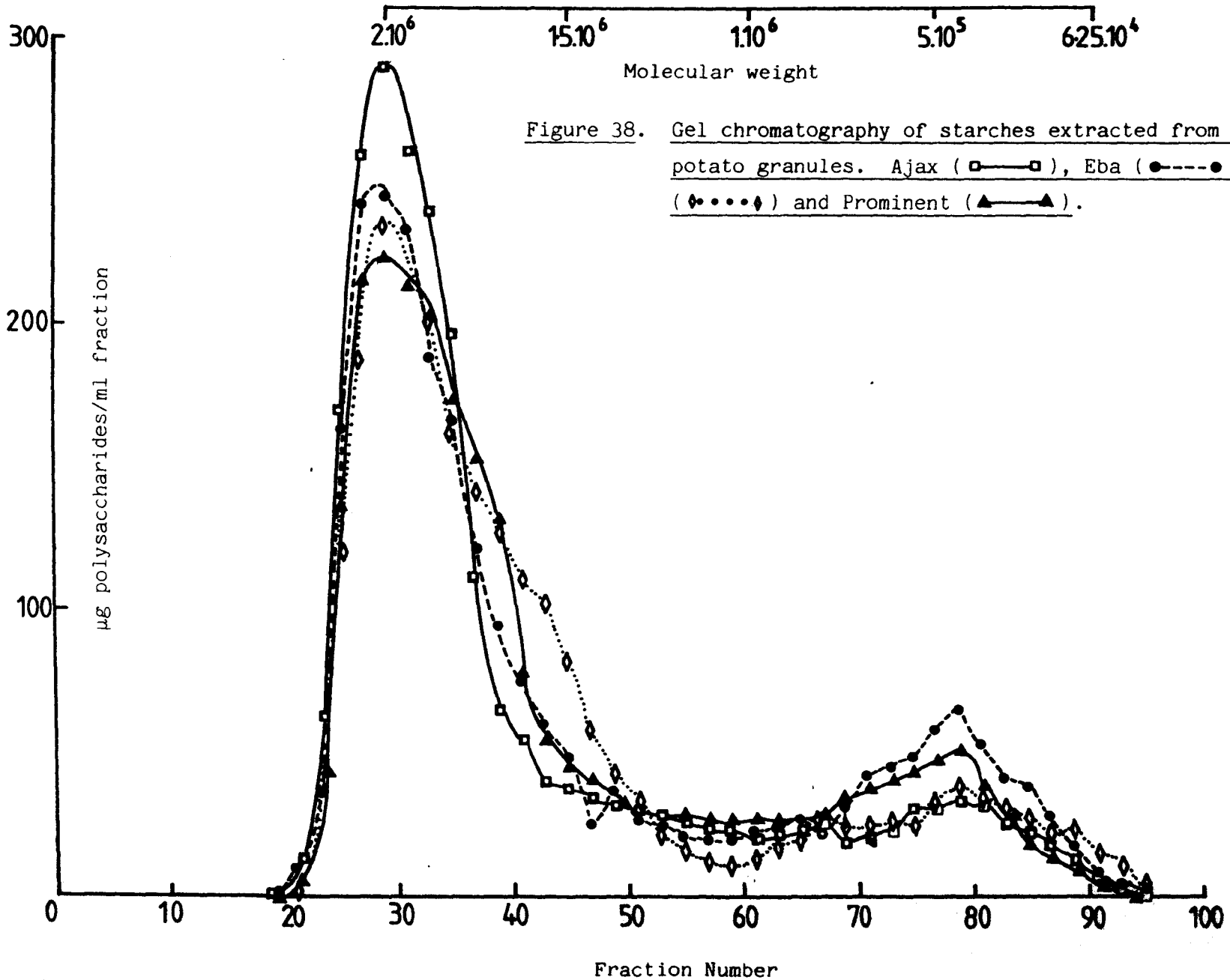


Figure 38. Gel chromatography of starches extracted from the interior potato granules. Ajax (□——□), Eba (●----●), Amigo (◊•••◊) and Prominent (▲——▲).

Figure 39. Gel chromatography of starches extracted from the exterior of (i) non-extruded potato granules (●——●), (ii) extruded potato granules (■——■) and (iii) extruded potato granules + PSA (◆- - - -◆).

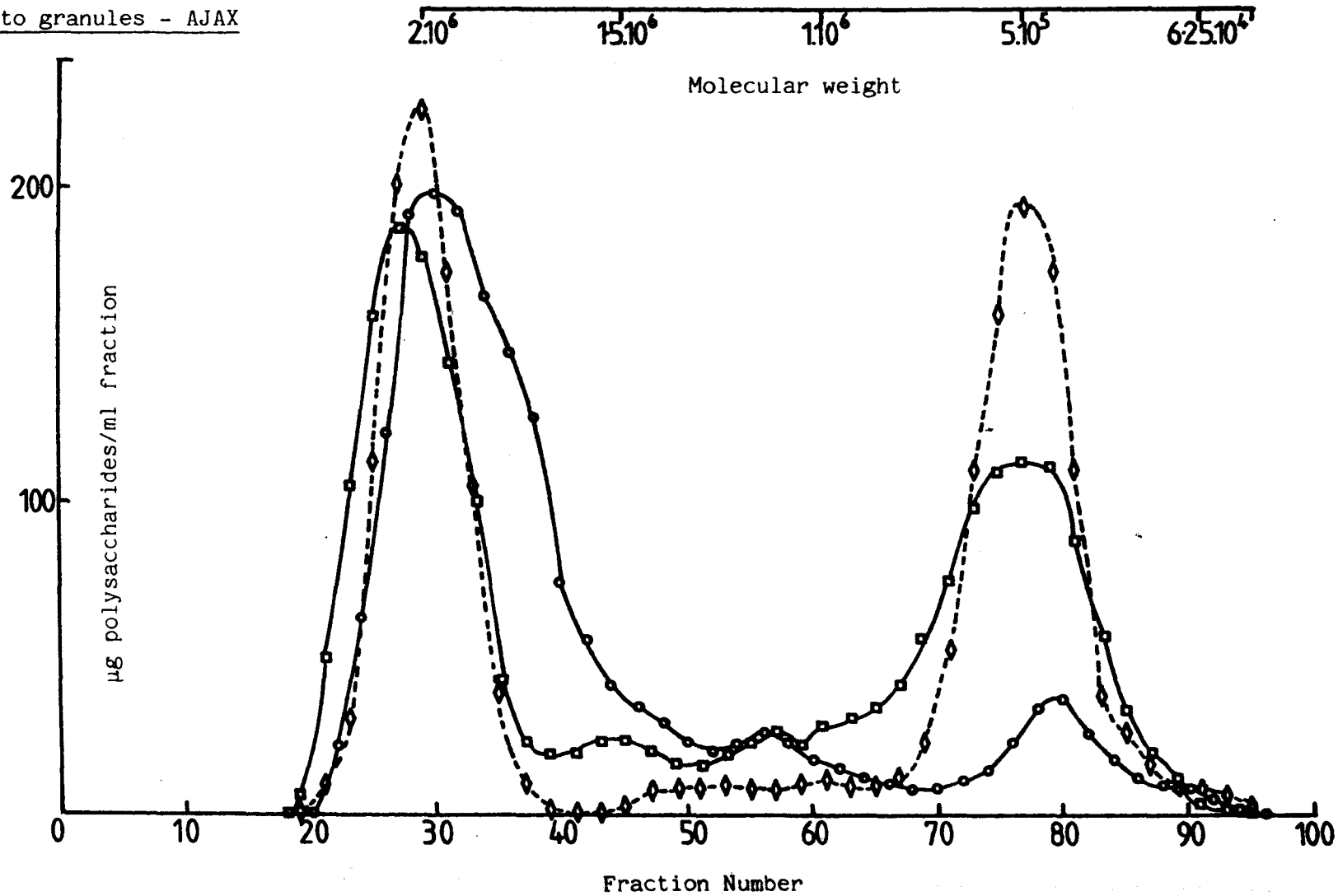


Figure 40. Gel chromatography of starches extracted from the exterior of (i) non-extruded potato granules (o——o), (ii) extruded potato granules (□——□) and (iii) extruded potato granules + PSA (♦----♦).

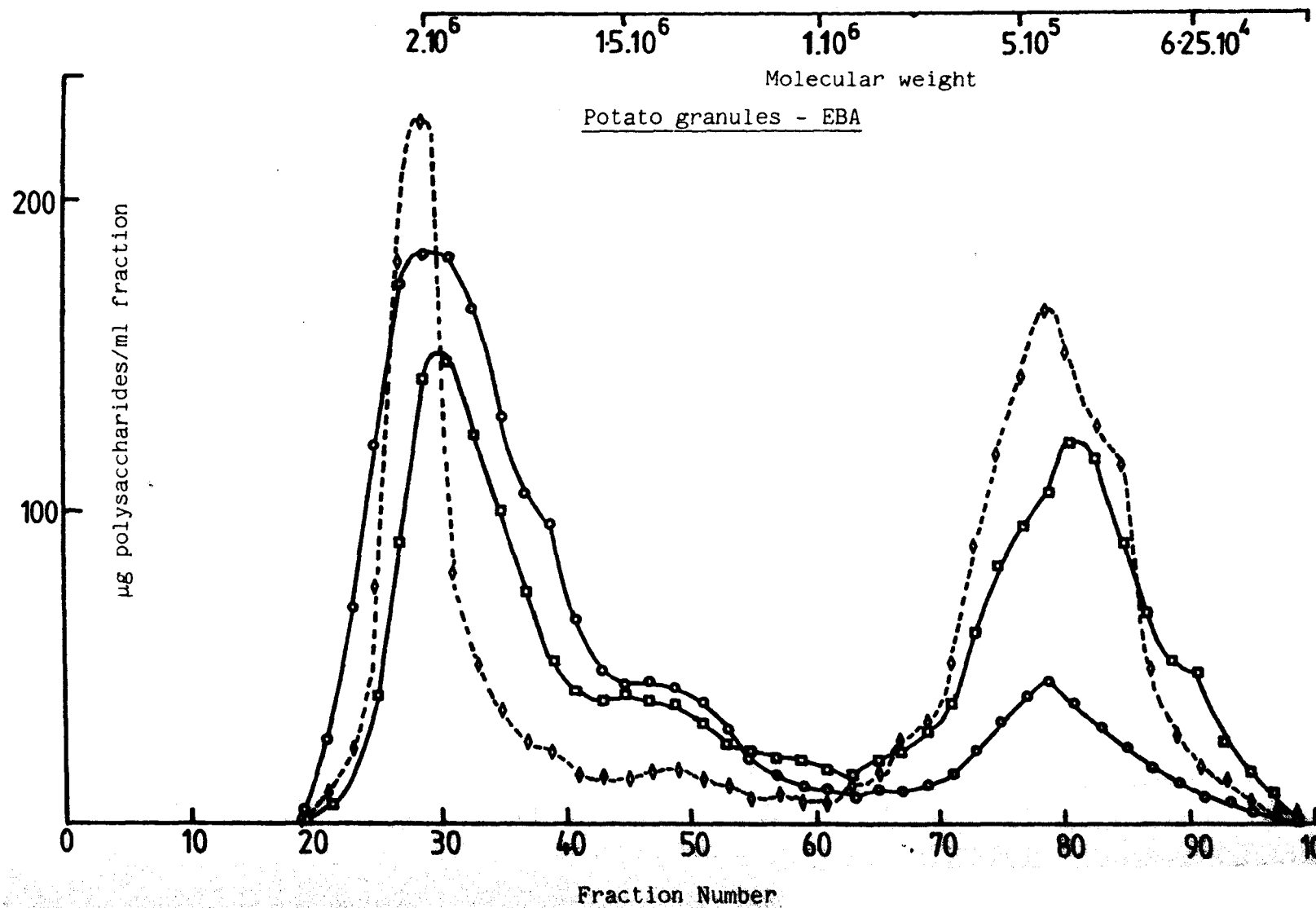


Figure 41. Gel chromatography of starches extracted from the exterior of (i) non-extruded potato granules (●——●), (ii) extruded potato granules (■——■) and (iii) extruded potato granules +PSA (♦----♦).

Potato granule - PROMINENT

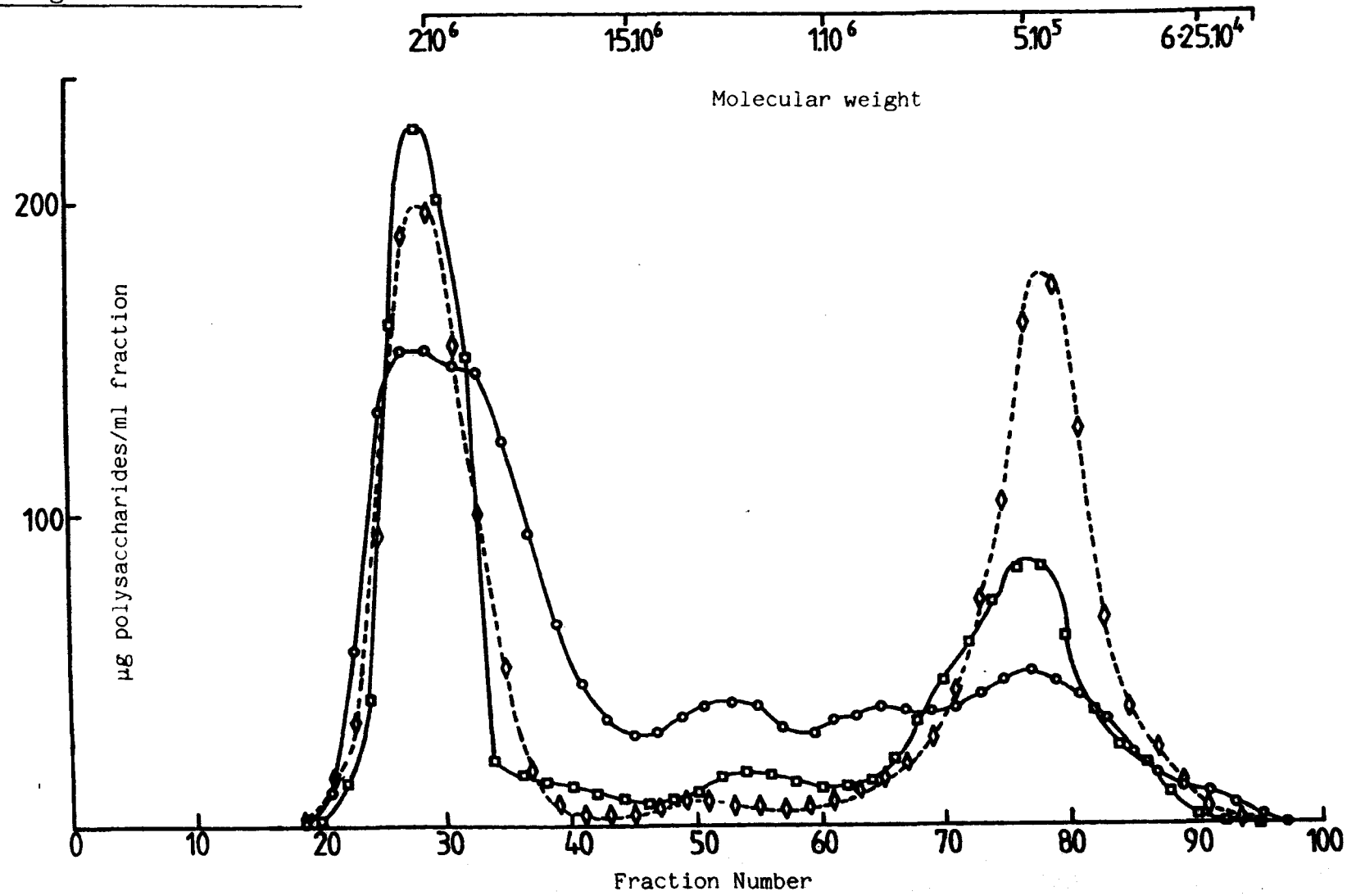
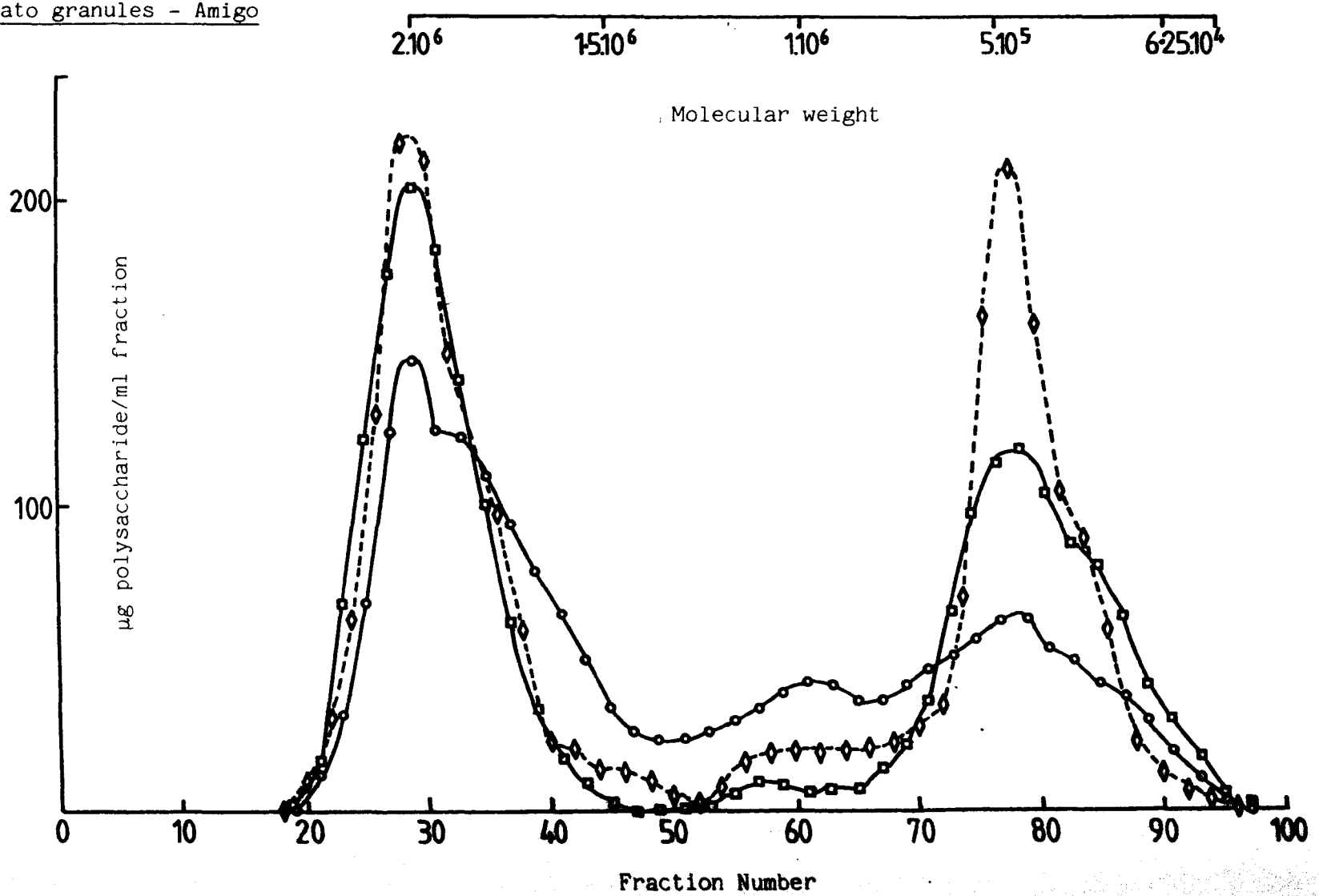


Figure 42. Gel chromatography of starches extracted from the exterior of (i) non-extruded potato granules (o——o), (ii) extracted potato granules (□——□) and (iii) extruded potato granules + PSA. (◊- - - -◊).

Potato granules - Amigo



region 2 includes polymers of $\bar{M}W$ between 1.5×10^6 - 7.5×10^5 and region 3 for polymers with $\bar{M}W < 7.5 \times 10^5$. The percentage distributions in the different molecular wt. groups (Region 1-3) were calculated from the chromatograms and the percentages are shown in Table 13.

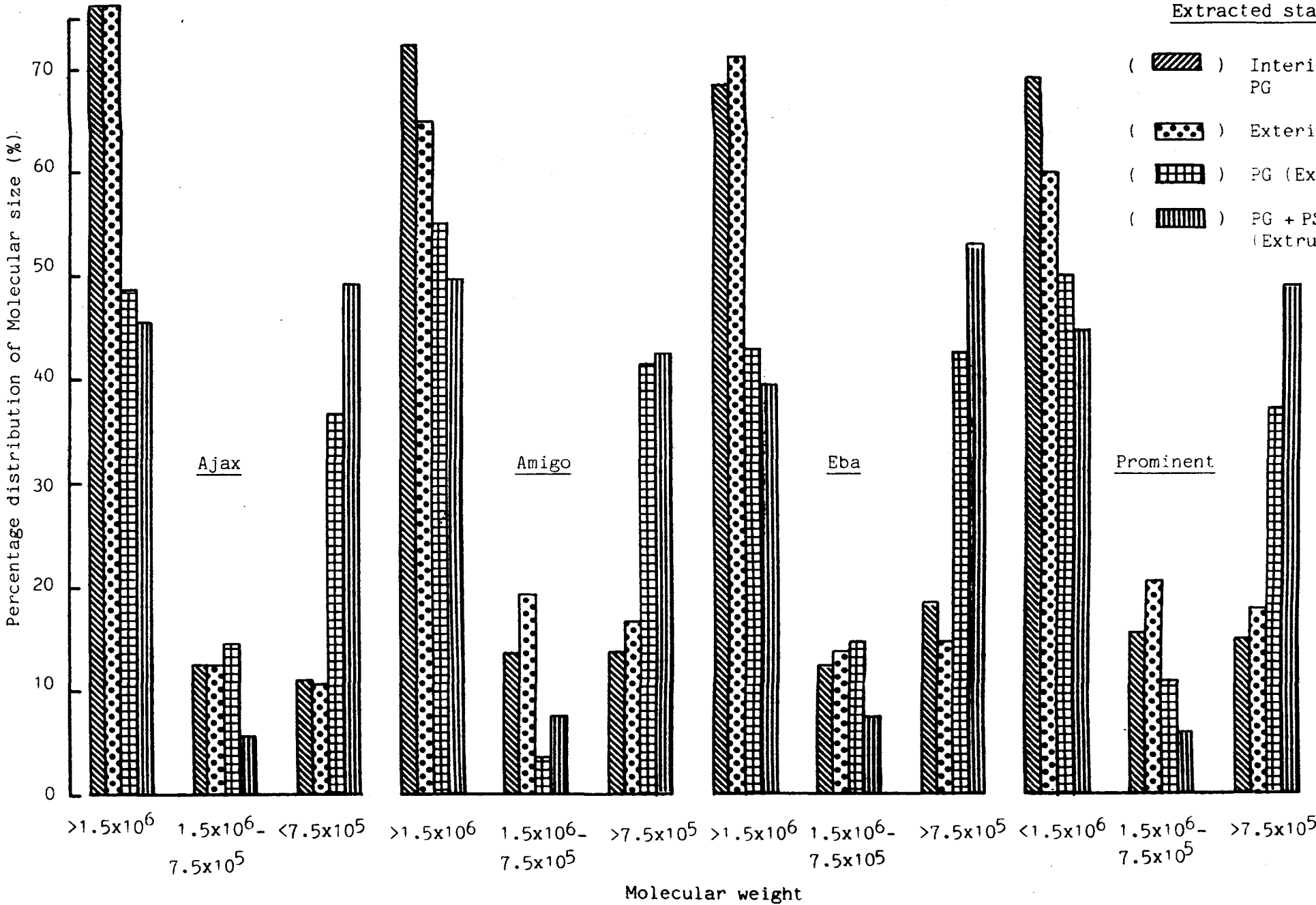
Table 13. Percentage distribution of molecular weight of extracted starches.

Sample	Distribution of molecular wt. in percentage		
	$\bar{M}W$: $>1.5\times10^6$	$\bar{M}W$: 1.5×10^6-7.5×10^5	$\bar{M}W$: $<7.5\times10^5$
Ajax (Inside PG)	76.08	12.72	11.29
Ajax (Outside PG)	76.17	12.55	11.16
Ajax (Extruded)	48.67	14.13	36.87
Ajax+PSA (Extruded)	45.64	5.55	49.35
Eba (Inside PG)	68.83	12.55	18.65
Eba (Outside PG)	71.48	13.54	14.86
Eba (Extruded)	43.38	14.22	42.50
Eba+PSA (Extruded)	39.04	7.47	53.23
Prominent (Inside PG)	69.15	15.47	15.19
Prominent (Outside PG)	60.29	20.59	18.89
Prominent (Extruded)	50.98	11.45	37.35
Prominent+PSA (Extruded)	44.71	5.84	49.57
Amigo (Inside PG9	72.68	13.43	13.57
Amigo (Outside PG)	64.17	19.27	16.58
Amigo (Extruded)	54.89	3.68	41.53
Amigo+PSA (Extruded)	49.76	7.83	42.51

PSA = 'potato snack additive'

PG = potato granules

Figure 43. Percentage distribution of molecular size of starches extracted from the interior of potato granules and exterior of potato granules and extrudates.



4.6. Starch phosphates

4.6.1. Introduction

Native starches contain variable amounts of phosphorus, up to 0.3%, but the phosphate-containing components are not identical in all starches (Kerr, 1950; Radley, 1953). In cereal starches, most, if not all of the phosphorus is present as phosphatides which are loosely bound to the polysaccharides (Schoch, 1942). However, the phosphate of tuber starches such as potato, arrowroot, tapioca and sago is attached through ester bonds to the 6-position of glucose residues (Northrup et al., 1916; Posternak, 1951).

Potato starch contains up to 0.28% of phosphorus (calculated as P_2O_5 and related to dry matter) and most of it is present in the amylopectin fraction (Sherman and Baker, 1916). The phosphorus content of potato starch depends on the variety (Veselovskii, 1940) and can be increased by high applications of phosphorus fertilisers (de Willigen, 1951).

Various investigations have been carried out to clarify the nature of sugar phosphates in some tuber and cereal starches. In potato starch, glucose-6-phosphate was initially widely accepted as the sole structure of the esterified phosphate (Gracza, 1965; Peat et al., 1952). However, Hizukuri (1970) found that only 60-70% of the bound phosphate in potato starch existed as glucose-6-phosphate and the rest occurred as glucose-3-phosphate (Takeda and Hizukuri, 1982). Other starches such as maize, waxy maize, rice and waxy rice were found to contain significant amounts of glucose-6-phosphate in their acid hydrolysates, but no evidence was found for the presence of glucose phosphate residues in wheat starch (Tabata et al., 1975).

The phosphorus content in starch is related to its rheological behaviour. Goerlitz (1960) found that the viscosity of starch paste

is increased when the phosphorus content is higher.

The object of the present investigation was to find out if there was any difference in the phosphate and glucose-6-phosphate contents between the different potato granules and extracted starches.

4.6.2. Experimental

4.6.2.1. Determination of total phosphorus

Phosphorus may be present as inorganic phosphate (ortho, meta, pyro or polyphosphate) or covalently combined with an organic moiety. To determine the total phosphate content the inorganic phosphate must first be converted to orthophosphate which can then be determined by a colorimetric method. Orthophosphate reacts with ammonium molybdate to form molybdophosphoric acid which is reduced by ascorbic acid to an intensely coloured complex known as molybdenum blue (Murphy and Riley, 1962).

4.6.2.1.1. Materials

Sample

Potato granules were supplied by Dornay Foods. Extracted starches were prepared as described in Section 4.4.2.2.

Reagents

The reagents used were of analytical-reagent grade wherever possible. Deionised water was used in the analysis.

(1) Ammonium molybdate solution, 4% ($^{W}/v$)

(2) Ascorbic acid solution, 0.1.N. The solution was prepared daily as required.

(3) Potassium antimonyl tartrate solution, 0.274% ($^{W}/v$)

(4) Reducing agent: Made up of 50ml 5N H_2SO_4, 15 ml. of ammonium molybdate solution, 30 ml. of ascorbic acid solution and 5 ml. of solution of potassium antimonyl tartrate. The solution was prepared when required.

(5) Sulphuric acid, 5N and 10N

(6) 30 per cent hydrogen peroxide

(7) Phosphate stock solution: 4.390 gm. of potassium dihydrogen phosphate was dissolved in 1 litre of deionised water. Toluene (2 drops) was added as a preservative. The concentration of the stock solution was 1.0 ml. = 1.0 mg P
A working standard solution was prepared by dilution of the stock solution.

4.6.2.1.2. Procedure for total phosphorus analysis

The method of Bertlett (1959) as modified by Radomski (1963) was employed in the conversion of inorganic phosphate to orthophosphate.

A sample (5 mg) was weighed directly into a Pyrex boiling tube with a ground glass stopper. Sulphuric acid (0.5 ml., 10N) and 0.5 ml. deionised water were added and the tube was heated in an oven at 150°C-160°C for 3 hours until charring was completed. Thirty per cent hydrogen peroxide (2-5 drops) was added to the cooled tube which was then returned to the oven for another $1\frac{1}{2}$ hours to complete the combustion and to decompose all the peroxide.

To assay for the orthophosphate, the phosphorus containing solution was transferred into a 50 ml. stoppered volumetric flask and diluted to 40 ml. with deionised water. Another flask containing 40 ml. deionised water was used as a blank. Reducing agent (8 ml.) was added to the flask and diluted to 50 ml. with deionised water and mixed. The flask was allowed to stand for 10 min. and the optical density measured at 660 mμ. The amount of orthophosphate present in each sample was determined from a standard curve.

4.6.2.2. Determination of glucose-6-phosphate

Glucose-6-phosphate was assayed by the glucose-6-phosphate dehydrogenase catalysed reduction of $NADP^+$ (Hizukuri et al., 1970). The reduction of $NADP^+$ was initiated by the addition of glucose-6-phosphate dehydrogenase and measured by the increase in optical density at 340 mμ.

4.6.2.2.1. Materials

Reagents

(1) Glucose-6-phosphate dehydrogenase (D-glucose-6-phosphate: NADP oxidoreductase E.C. No. 1.1.1.49) from the Sigma Chemical Company.

(2) $NADP^+$ (Nicotinamide adenosine dinucleotide phosphate) from the Sigma Chemical Company.

(3) EDTA

(4) Tris-HCl buffer pH 7.5 (0.225 M)

(5) Assay reagent: 0.225M Tris-HCl buffer, pH 7.5 containing 2.5×20^{-2}M $MgCl_2$; 6.54×10^{-4}M $NADP^+$ and 3.3×10^{-3}M EDTA.

(6) Glucose-6-phosphate from the Sigma Chemical Company.

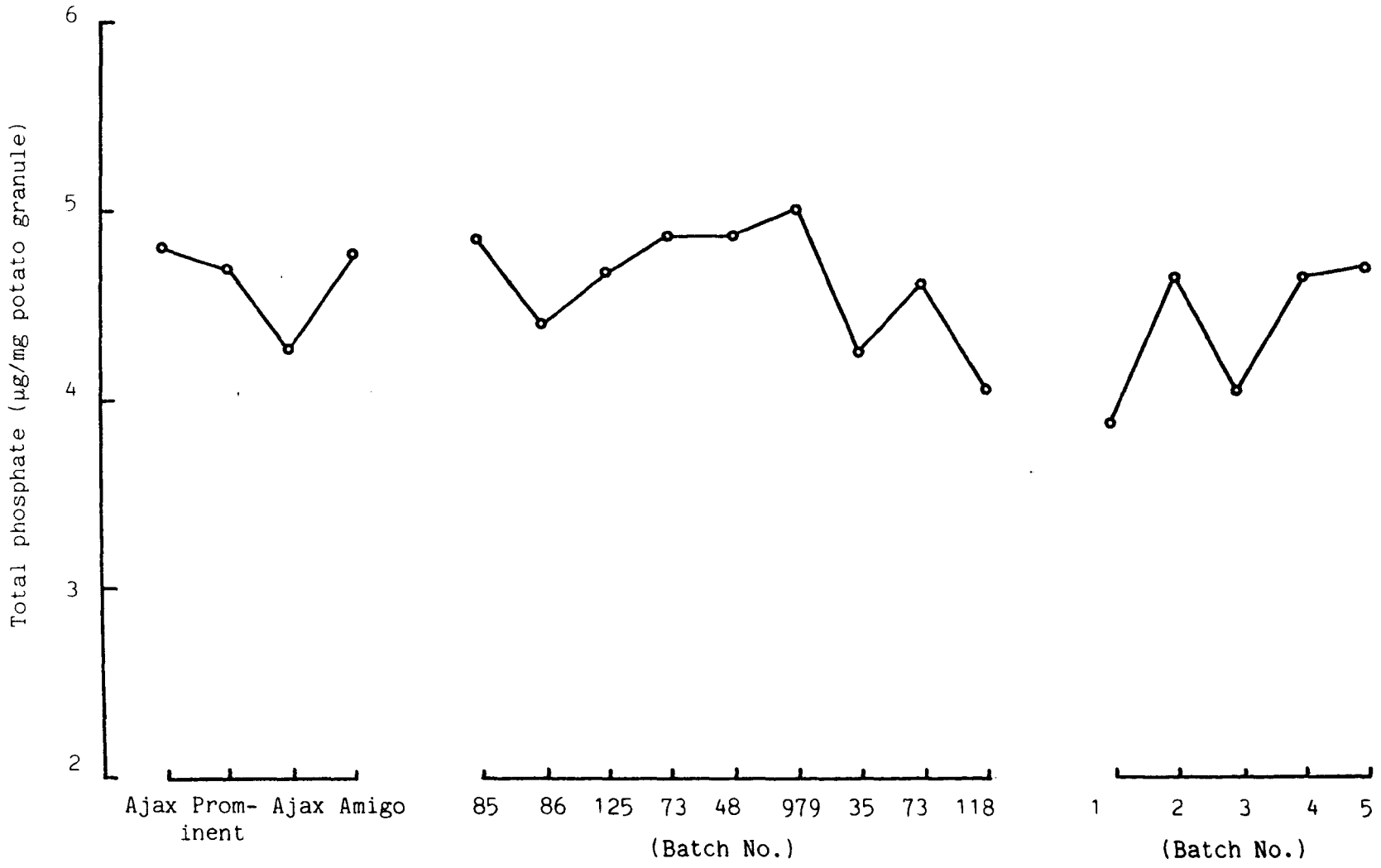
4.6.2.2.2. Assay for glucose-6-phosphate

The assay reagent (1.0 ml.) was added to 2.0 ml. of sample solution in a test-tube followed by 50 μl of glucose-6-phosphate dehydrogenase. After standing for 10 min. the increase in optical density was measured at 340 mμ against a reference blank containing the complete components except $NADP^+$. The amount of glucose-6-phosphate in each sample was calculated from a standard curve.

4.6.3. Results

The total phosphate contents present in potato granules are shown in Figure 44. The total phosphate and glucose-6-phosphate contents

Figure 44. Total phosphate content of potato granules.



Total phosphate and glucose-6-phosphate contents in starches extracted from potato granules and extrudates

Extracted starches	Total phosphate (μg)/mg starch	Glucose-6-phosphate (μg)/mg starch
Ajax (outside)	4.24	4.84
Ajax (extruded)	2.21	6.78
Ajax + PSA (extruded)	31.10	2.73
Ajax (inside)	8.40	3.04
Eba (outside)	4.42	5.02
Eba (extruded)	1.60	3.08
Eba + PSA (extruded)	17.4	2.42
Eba (inside)	7.6	3.74
Prominent (outside)	4.57	3.52
Prominent (extruded)	2.48	2.95
Prominent + PSA (extruded)	29.1	4.97
Prominent (inside)	6.9	2.33
Amigo (outside)	4.38	3.92
Amigo (extruded)	3.62	4.84
Amigo + PSA (extruded)	40.01	5.02
Amigo (inside)	8.10	3.17
Batch No. 118 (outside)	2.21	6.16
Batch No. 118 (extruded)	1.85	6.16
Batch No. 118 + PSA (extruded)	20.20	3.96
Batch No. 118 (inside)	9.20	2.42
Batch No. 125 (outside)	1.66	4.80
Batch No. 125 (extruded)	1.45	4.80
Batch No. 125 + PSA (extruded)	20.50	3.94
Batch No. 125 (inside)	8.90	2.40

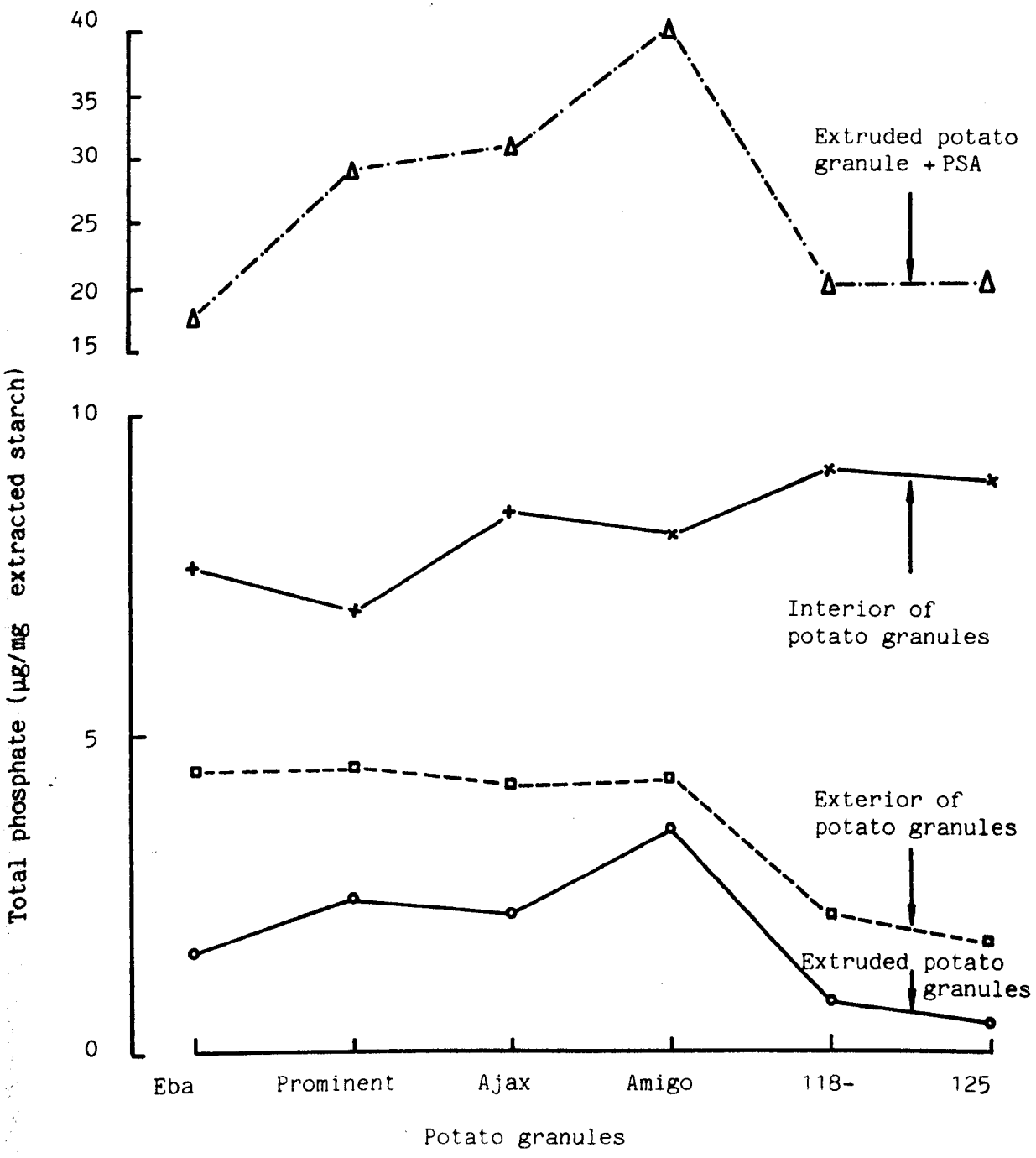
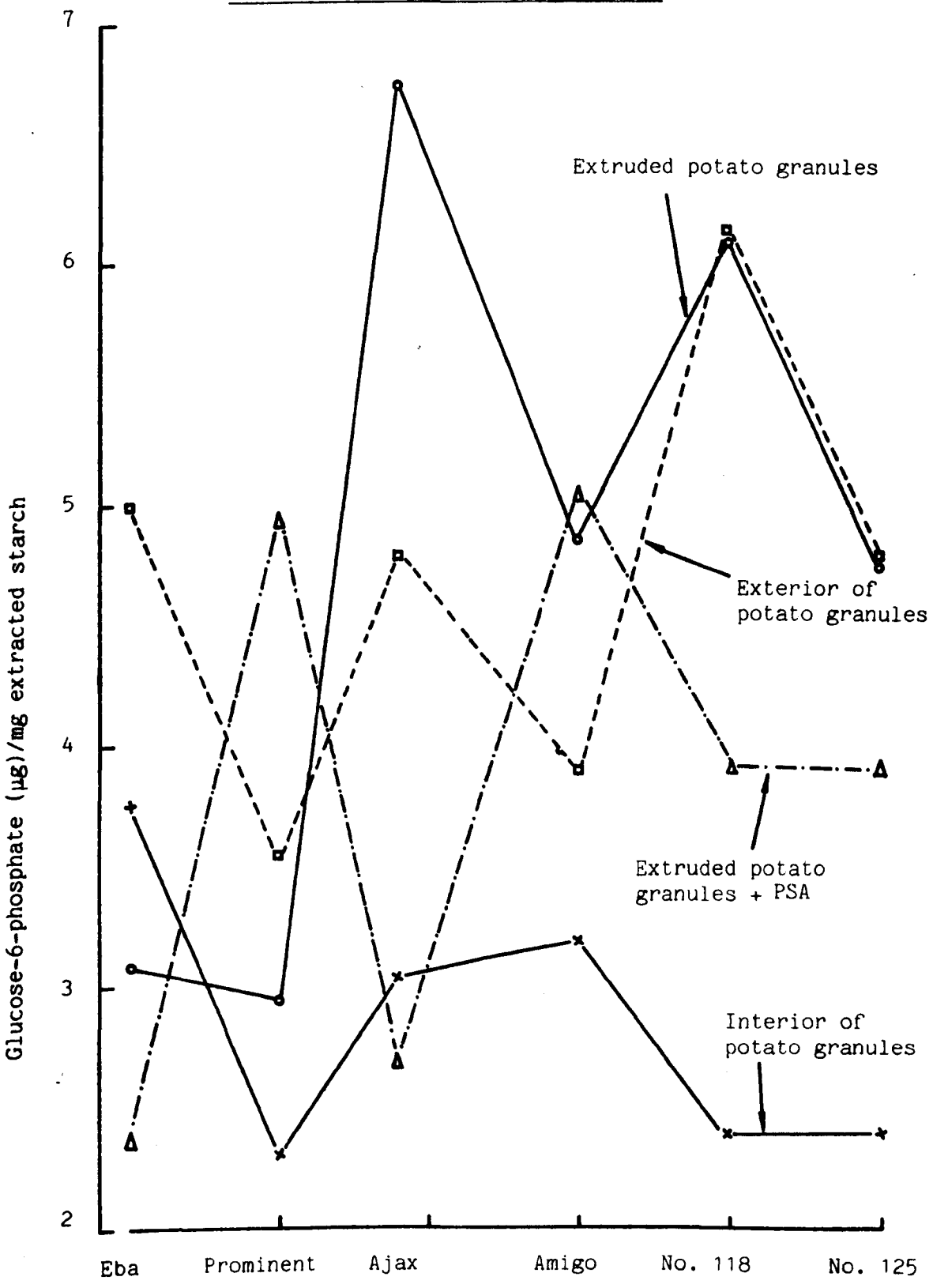


Figure 45. Total phosphate content of extracted starches from the exterior of (i) non-extruded potato granules (□----□), (ii) extruded potato granules (○——○), (iii) extruded potato granules + PSA (Δ-·-·-Δ) and (iv) the interior of potato granules (×——×).

Figure 46. Glucose-6-phosphate content of extracted starches from the exterior of (i) non-extruded potato granules (▫----▫) (ii) extruded potato granules (o——o), extruded potato granule + PSA (Δ-·-·-Δ) and (iii) the interior of non-extruded potato granules (×——×).



of extracted starches from (i) outside potato granules (ii) inside potato granules (iii) extruded potato granules and extruded potato granules plus PSA are shown in Figures 45 and 46, respectively.

4.7. Discussion

Amylose-Amylopectin Content

The amount of amylose present in most of the starches extracted from potato granules varies from 22-28% as shown in Figure 32. These results are in fair agreement with those reported for native potato starches by Badenhuizen (1959) (20-24% amylose) and Hadziyev and Steele (1979) (25% amylose). However, the starch extracted from Ajax contained a very low amylose content of 19% and 2 other samples, Eba and No. 86, both contained a high amylose content of 30% each.

The extreme amylose contents in the 3 samples are probably due to the different varieties of potatoes, though the possibility of

analytical artefacts during the preparation of the Ajax sample cannot be wholly ruled out. The possible artefacts are retrogradation during the final stages of sample preparation for titration and the titration itself and the presence of lipid in the starch, both of which have been reported to affect the iodine binding capacity of the amylose (Rundle and French, 1943A; Schoch, 1942). All the samples used in this experiment were extracted and prepared in the same manner as described earlier and if retrogradation were to occur it would affect all the samples and not Ajax alone. The reproducibility of duplicate titrations was good with an error of $\pm$ 1% amylose content. As to the presence of lipid, the extraction procedure of Banks and Greenwood (1970), using DMSO and ethanol was supposed to remove all the lipid. Ajax was later found to be different from the others in having excess GMS, some being tightly bound with the starch and this might not have been completely removed by the solvent during the extraction. Our measured conclusion is therefore that the differences recorded are real and significant.

The high amylose contents of Eba and No. 86 are likely to be a characteristic of the different varieties of potatoes. Eba is a high starch variety containing about 28% solids, while Batch No. 86 was produced from a mixture of varieties. Johnston et al. (1968) found that even among samples from the same variety of potato, the amylose content could vary up to 2% depending on the size of starch granules, maturity, growth and storage conditions.

Early work suggested that a correlation did exist between, the amylose content and extrusion behaviour of potato granules: the unsatisfactory potato granules (Ajax and Amigo) were found to have less amylose than the good granules (Eba and Prominent). This was not confirmed when more samples of potato granules were analysed. The results of amylose and amylopectin contents are shown in Table 11.

Several workers have reported that the amylose content is important in controlling the quality of the extruded product (Feldberg, 1969; Mercier and Feillet, 1975; Murray et al. 1968 and Bhuiyan and Blanshard, 1982). In all these cases native starches were processed by the direct extrusion method during which the starch granules underwent gelatinisation. In this project, a different process was involved in which pregelatinised starch (potato granules) was indirectly extruded and expansion was achieved during subsequent frying. The results in this study suggested that the amylose content is not a critical factor in determining the quality of the extruded products.

Free starch (Blue values)

The 'Blue Value' results show that the majority of the potato granules have rather low blue values of between 0.19-0.30, except Pentland Crown (0.47), and their absorption maxima (λ max) lie between 560-570 nm. The low blue values were probably due to the presence of GMS which competed with iodine to form the amylose-lipid complex. The lipid once inside the amylose helix is not readily replaced by iodine (Senti and Erlander, 1964), which will reduce the amount of free amylose for binding with iodine, resulting in a pale blue colour (Bourne et al., 1960). The decrease in blue values with increasing monoglyceride levels had been reported by Hoover et al. (1982), who found that the greatest decrease in blue values was with the addition of 0.2% GMS; beyond this level the decrease was negligible.

The presence of GMS also resulted in a cloudy supernatant which affected the absorbance reading. The λ max of between 560-570 nm is very similar to that of the amylopectin-iodine complex which has a λ max of 530-570 nm, as compared to the λ max (620-660 nm) of the amylose-iodine complex (Richer et al., 1968). This observation suggests that the blue values that we measure are due to the amylopectin-iodine complex

as most of the amylose is already complexed with the GMS. The blue values and absorption maxima of potato granules from Batch No. 1-5 are higher than the others. This is because less GMS was used during the add-back process. As a result more potato granules may have been broken, releasing a larger quantity of free starch for binding with iodine.

There is no correlation in blue values between the satisfactory and unsatisfactory potato granules. However, the λ max of the unsatisfactory potato granules were 10 nm lower (560-570 nm) and also the extracted supernatants were oily and cloudy in appearance, which suggest that the unsatisfactory granules were likely to contain more GMS. The investigations show that the blue value method is less reliable when GMS is present in the potato granules and, moreover, it does not give us a clear indication of the actual amount of starch present.

Total soluble starch

Results from the total soluble starch extractions shown in Figure 34, indicate that the unsatisfactory granules have less soluble starch than the satisfactory granules, from the same variety. According to the hypothesis previously stated, the extracellular soluble starch is very important in forming the network which is necessary in the production of a coherent strip during the extrusion. Therefore, initially it seemed possible that the presence of smaller amounts of soluble starch in the unsatisfactory granules might explain why they behaved poorly during extrusion.

However, the low level of soluble starch in unsatisfactory potato granules might not simply reflect inherent qualities of the granule but be a consequence of the presence of excess GMS which would form a complex with the amylose fraction in the extracellular soluble starch as well as with those inside the potato granules. The starch-lipid complex

is less soluble in water and more difficult to extract (Schoch, 1965; Lonkhuysen et al., 1974). This view is supported by earlier observations made during the determination of blue values, where the extraction from unsatisfactory granules have lower λ max values and were more oily in appearance. A further possibility which should be considered is that there may be differences in the cell wall of the granules which control the flow of GMS and low molecular weight polymers in and out of the granules, respectively. The significance of the cell wall will be studied in the next section.

More soluble starch was extracted from the extrudates, especially those produced from Pentland Crown and Desirée as shown in Figure 35. The increase from potato granules as compared with extrudates in soluble starch, varied from a low value of 100% in Stara to almost 290% for Pentland Crown and 270% for Desirée. It was both noticeable and interesting that the extrudates produced from Pentland Crown and Desirée both blistered badly on frying. It is believed that during extrusion, soluble starch of low molecular weight is being expressed out of potato granules to form a network. Microscopic observations have shown that the network was in the form of a thin film on the surface of the extrudates as well as in between the granules which bind them together. Mercier et al. (1979) found that during extrusion of potato starch, there was an increase in water soluble starch content and this soluble fraction was shown to be low molecular weight, linear oligomers.

With the addition of potato snack additives (PSA) there was a slight increase in extractable soluble starch (4-10%), even though the extruding conditions were the same as before. At this juncture it is difficult to understand the role of PSA during extrusion. However, from the results and observations, we suggest that the increase in soluble starch could be attributed to the presence of Ca^{2+} and Na^{+} in the PSA. It is known that the Ca^{2+} will form a gel network with the

pectin by cross-linking with the free carboxyl groups. The Na^+ can also react with the free carboxyl groups and in so doing it curtails the cross-linking reaction of Ca^{2+} (Glicksman,1969). This will improve the solubility of the pectin and affect the permeability of the cell wall. Preliminary extrusion trials carried out, showed a slight increase in soluble starch content of extrudates produced from potato granules with higher amounts of Na^+, compared to the one with higher Ca^{2+} content.

The amount of soluble starch extracted from potato granules correlated with their extrusion behaviour. Satisfactory potato granules have more soluble starch than the unsatisfactory potato granules. With respect to the blistering effect, it seems that extrudates with a greater amount of soluble starch were more likely to blister.

Gel permeation chromatography

Starches extracted from potato granules have similar chromatographic patterns (Figure 38), consisting of a high and narrow peak at $\bar{M}_w \sim 2.10^6$, which is the exclusion peak and a low curving peak between molecular weights 1.10^6-1.10^4. The carbohydrate material of the exclusion peak has an absorption maximum (λ max) of between 540-560 nm, which suggests that the material consists mainly of amylopectin while the fractions from the retarded peak have a λ max of between 600-620 nm, which means that the latter material is comprised mainly of amylose. These results are similar to those obtained for native potato starch by Eberman *et al*. (1975).

The chromatograms in Figure 38 show that the starch from Ajax seems to have a higher percentage of high molecular weight materials ($\bar{M}w > 1.5 \times 10^6$) whereas the starch from Eba has a higher percentage of low molecular weight materials ($\bar{M}w < 7.5 \times 10^5$). This result agrees with the amylose content of Eba (30%) and Ajax (18%).

Chromatograms of starches extracted from outside potato granules

and extrudates shown in Figures 39-42 were quite similar to the chromatograms of starches extracted from inside the potato granules (Figure 38), except that the exclusion peak was smaller while the retarded peak was larger. The presence of the exclusion peak suggests that amylopectin is also present in the extractable soluble starch, which probably arises from the ruptured potato granules. In all cases, during extrusion there seemed to be an increase in the low molecular weight polymers in the extracted starch. This agrees with the general hypothesis that amylose is being expressed out of the potato granules during extrusion. The chromatograms also show a slight increase in the low molecular polymers with the addition of potato snack additives.

Besides the 2 main components, some polymers of intermediate molecular sizes ($\bar{M}_w$ 1.5×10^6 - 7.5×10^5) are also present as shown in Figure 43. The fractions gave a purplish coloration with iodine and the λ max is between 570-580 nm. Overall the results do not show any major differences in molecular size distributions of the extracted starches from different potato granules and extrudates. However, it indicates quite clearly that the starch that is being expressed during extrusion is amylosic in nature and this forms a network resulting in a coherent structure.

Phosphate content

Potato granules have a phosphate content of about 0.4-0.5%, as shown in Figure 44. The amount is higher than the previously quoted value of 0.28% for potato starch (Harris and MacWilliams, 1963). This is probably due to the different types of samples (potato granules instead of potato starch) and method of analysis. The phosphate content shows little difference between the satisfactory and unsatisfactory potato granules.

Figure 45 shows that the starches extracted from inside the potato granules contain about 0.7-0.9% phosphate, which suggests that there is a large concentration of amylopectin inside the potato granules. Whereas the soluble starch from outside the potato granules and extrudates have 0.45% and 0.15-0.35% phosphate content, respectively. From earlier results, we found that these soluble starches contain more amylose than amylopectin, which may explain why the phosphate contents are lower. With the addition of PSA (which contains dicalcium phosphate), the phosphate content of the extracted starches is increased to 3-4%. It is likely that the phosphate is not incorporated into the potato granules during extrusion, but is trapped in the network of soluble starch which is easily extracted with water.

Most of the phosphate is esterified to the C_6 position of the amylopectin molecule (Gracza, 1965) and this is reflected by the presence of high amounts of glucose-6-phosphate (0.2-0.6%) in the extracted starch (Figure 46). The variation in the glucose-6-phosphate content in the different extracted starch fractions seems to show no correlation with any extrusion properties.

STUDIES ON THE CELL WALL MATERIAL OF POTATO GRANULES

5. Studies on the cell wall material of potato granules

5.1. Introduction

As mentioned earlier the potato granules can be envisaged as a mass of gelatinised starch enclosed by the cell wall. This cell wall, both provides rigidity to the cell and controls the permeation of molecules in and out of the cell and diffusion of water. This important function has been thought to affect the textural properties of the raw and cooked potato tissue. The topic has been reviewed recently by Reeve (1977).

Because of the importance of cell wall in controlling the properties of potato granules, it was decided to analyse the cell wall polysaccharides, both quantitatively and qualitatively, to assess whether there was any correlation in the composition of cell wall polysaccharides with extrusion behaviour of the potato granules.

5.2. Experimental

5.2.1. Materials

Potato granules used in this experiment were supplied by Dornay Foods Ltd.

Chemicals

(i) D-glucose, D-galactose, D-mannose, L-rhamnose, D-xylose, L-arabinose, D-fucose and meso-inositol were purchased from the Sigma Chemical Company.

(ii) Acetic anhydride (A.R. grade) was refluxed over anhydrous $CaSO_4$ and redistilled.

(iii) Pyridine (A.R. grade) was dried over KOH pellets for at least one week before use.

All other chemicals used were of A.R. grade or the highest purity available.

(iv) α-Amylase (Pancreatic) was purchased from Fluka, AG, Switzerland.

(v) Amyloglucosidase (Rhizopus sp.) was purchased from the Sigma Chemical Company.

(vi) Xylanase and cellulase were a gift from Dr. Comtat (CERMAV, Grenoble, France).

(vii) Aniline oxalate was prepared by mixing together 400 ml. of 2% ($^{v}/v$) aniline in absolute ethanol with 600 ml. of 2.5% ($^{w}/v$) of oxalic acid.

5.2.2. Extraction of cell wall materials

5.2.2.1. Extraction of cell wall material from potato granules using 90% aqueous DMSO

Potato granules were suspended in 90% aqueous DMSO and stirred vigorously overnight. The thick emulsion was then centrifuged at 18,000 g for 20 min. which yielded an opalescent aqueous-organic phase containing starch. The residue was dispersed in aqueous DMSO, stirred overnight and centrifuged as before. The same procedure was repeated 3 more times. The organic layers from the 5 extractions were combined together, dialysed and freeze-dried. The insoluble residue was washed several times with distilled water, dialysed and freeze-dried. The dried sample was used as the cell wall material. The presence of any starch in the extracted cell wall material was checked by its reaction with I_2/KI solution.

5.2.2.2. Extraction of cell wall material from potato granules using a mixture of α-amylase and amyloglucosidase

Potato granules were first suspended in distilled water and then treated with α-amylase and amyloglucosidase at 45°C for 48 h using sodium azide as a bactericide. The quantity of enzyme required depended

on the amount of potato granules. The digestion was carried out in a 'digestion cell' and the product formed, which was mainly glucose, was constantly removed by pressing it through a Millipore filter (pore size = M.W. 10^4) at a pressure of 3 psi. The digest was collected, centrifuged and the residue washed with water, dialysed and freeze-dried. The dried residue was treated with fresh α- amylase and amyloglucosidase for another 36 hrs. to remove any remaining starch. The final residue, obtained after centrifugation, dialysis and freeze-drying was essentially starch free as indicated by a negative reaction with iodine solution. The dried residue is the cell wall material. The extraction scheme is shown in Figure 47.

To check the absence of starch in the extracted cell wall material, portions of it were treated separately with cellulase and 2N H_2SO_4.

5.2.3. Analysis of cell wall polysaccharides

The cell wall material was first hydrolysed to give the sugars which were then reduced and acetylated to their alditol acetates, before injection into the gas liquid chromatography (GLC).

Two types of hydrolytic procedures were used to hydrolyse the cell wall material to the sugars.

5.2.3.1. 2N Trifluoroacetic acid (TFA) hydrolysis

Only supernatant fractions were subjected to this type of hydrolysis. Dried sample (10 mg) was suspended in 2 ml. of 2N TFA and heated at 100°C for 4 hrs. After hydrolysis, 1 mg of meso-inositol was added as internal standard, the mixture was then diluted with distilled water and concentrated using a Buchi rotary evaporator. During the process a few drops of ammonia solution were added to neutralise the mixture. The reduced mixture was later reduced and acetylated.

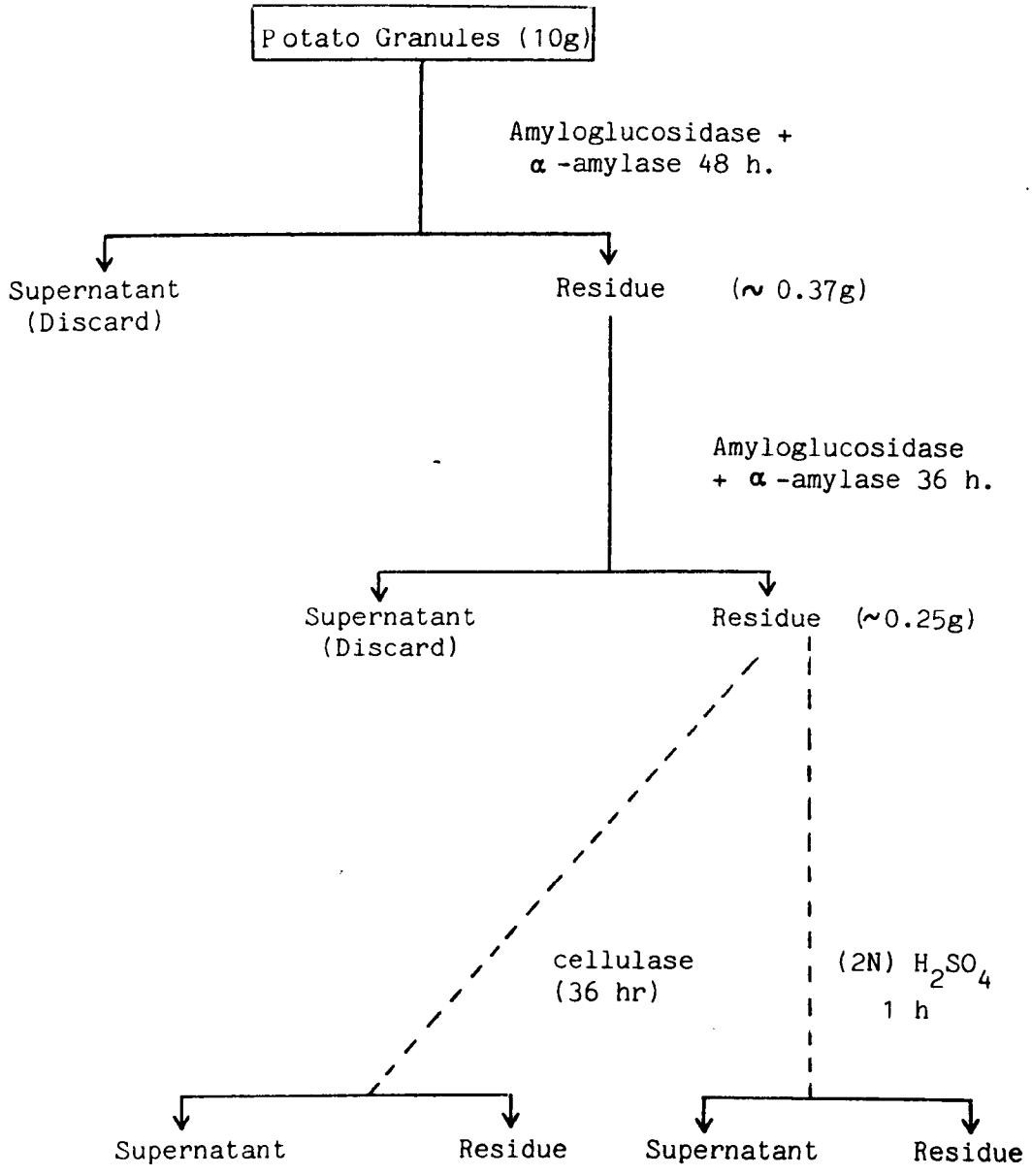


Figure 47. Scheme for sequential extraction of cell wall material from potato granules using enzymes.

5.2.3.2. 72% H_2SO_4 hydrolysis (Saeman hydrolysis)

The hydrolytic procedure is a modification of the Saeman procedure (1954).

Cell wall material (10 mg) was wetted with 0.2 ml. of 72% H_2SO_4 and left at 30°C for 1.5 h or overnight at room temperature. Agitation with a glass rod ensured complete dissolution. It was then diluted with distilled water to give 2N H_2SO_4, 1 mg of meso-inositol was added as internal standard and the tube was sealed and hydrolysis was carried out at 100°C for 6 hrs.

After hydrolysis, the hydrolyate was washed into a beaker, diluted with distilled water and neutralised with $BaCO_3$. The mixture was allowed to stand for 1 h and then filtered through fluted filter paper (Whatman No. 42). The filtrate was evaporated to dryness on a rotary evaporator and later reduced and acetylated.

5.2.3.3. Reduction and acetylation of the sugars

The solution of aldoses was treated with sodium borohydride ($NaBH_4$), for 2 h at room temperature to reduce the hemiacetal groups. Excess borohydride was destroyed by treatment with acetic acid until a neutral pH was obtained. The solution was evaporated to dryness under vacuum. The boric acid liberated was removed by codistillation with methanol. The alditols obtained were then treated repeatedly with a mixture of methanol plus 1% HCl and evaporated to dryness. This was followed by treatment with acetic anhydride (1 ml.) and pyridine (1 ml.) and heated at 100°C for 1 h to permit acetylation. Excess acetic anhydride was destroyed by adding distilled water and evaporating to dryness. The dried alditol acetate derivatives obtainedwere then ready for analysis.

5.2.3.4. Gas-liquid chromatography analysis

The neutral sugars released on acid hydrolysis of the CWM were determined as their alditol acetates. For GLC, a Packard-Becker 417 instrument fitted with a flame-ionisation detector was used. Separations were performed on glass columns (2m x 0.15 cm) containing 3% of ECNSS-M on Gas Chrom. Q (100-200 mesh) at 185°C with a carrier-gas flow rate of 60 ml/min. The dried samples were first dissolved in chloroform prior to injection. Peak areas were calculated with a 3880 A Hewlett-Packard integrator. Typical GLC chromatograms of a mixture of neutral sugars are shown in Figures 48 and 49.

5.2.3.5. Paper chromatography

The chromatography was performed on Whatman No. 1 filter paper, using the following solvent system: ethyl acetate-pyridine water or (8:2:1). The inorganic ions present in the mixture of sugars were removed by deionization with Amberlite ion-exchange resin. The experiment was performed for 20 h and the chromatograms were developed by spraying them evenly with aniline oxalate and drying in an oven at 80°C. The sugars were revealed as dark brown spots on a light background (Figure 50).

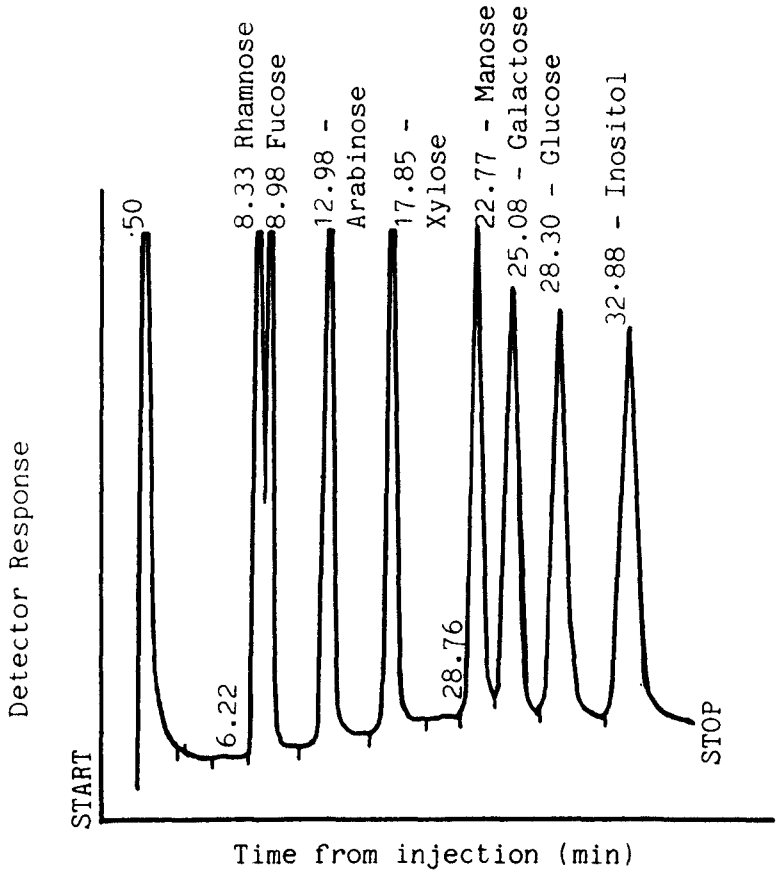


Figure 48. Separation of standard neutral sugars by gas liquid chromatography.

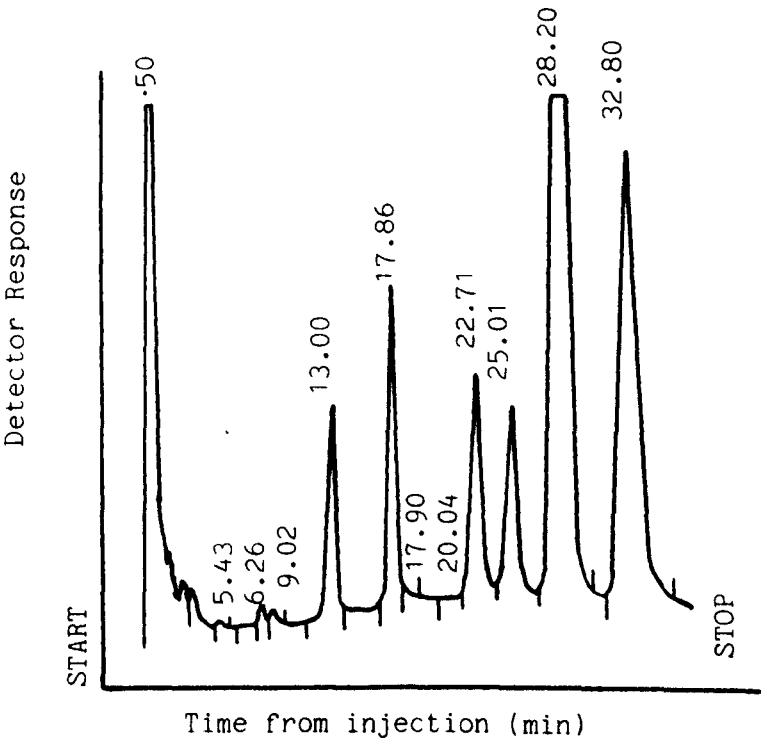
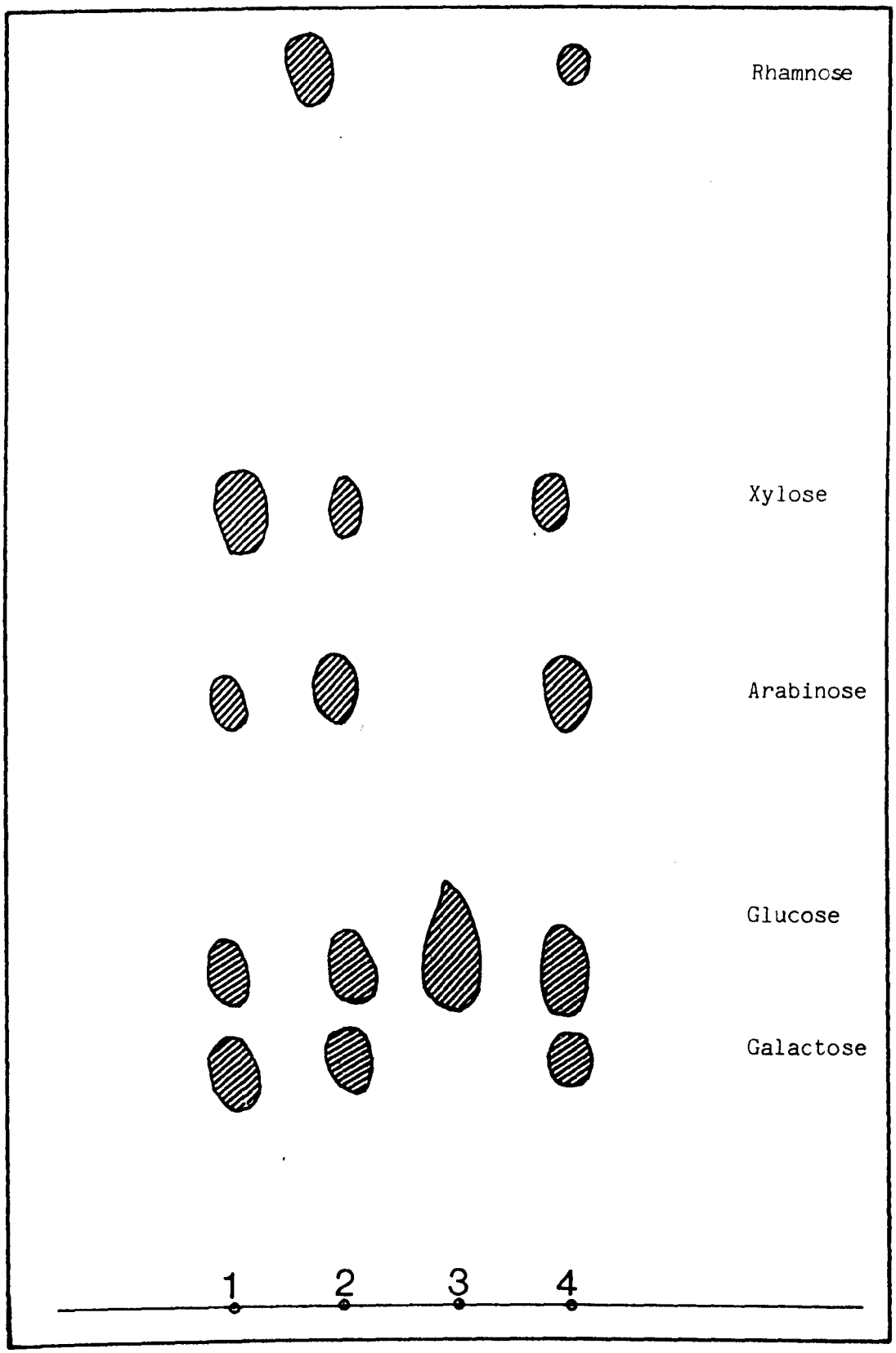


Figure 49. Separation of the alditol acetates of cell wall material by gas liquid chromatography.

Figure 50. Paper chromatogram of neutral sugars present in cell wall material.



5.2.4. Results and discussion

The high starch content in potato granules made the isolation of cell wall material very difficult. The same problem was experienced by Ring and Selvendran (1978) and Mullen and Bateman (1975), when they tried to extract cell wall material from potato tubers. These workers used aqueous DMSO to solubilise the starch.

Two methods for solubilising the starch were examined: (i) using aqueous DMSO and (2) using a mixture of α-amylase and amyloglucosidase. Aqueous DMSO was less efficient in removing the gelatinised starch from the potato granules as indicated by the amount of extracted cell wall material (~ 5.3% dry weight) obtained. In addition, DMSO solubilised small quantities of non-starch polysaccharides such as arabinose and xylose (Table 15A). A mixture of α-amylase and amyloglucosidase was also used to digest the starch and was found to effectively remove about 97% by weight of potato granules leaving approximately 2.5% of cell wall material (Table 15A), while the supernatant fraction contained almost 100% glucose. The 2.4% cell wall material was less than the amount of cell wall material extracted from potato tuber (5.6% dry wt.) by Hoff and Castro (1969). The 5.6% of cell wall material also included the skin of the tuber and pectic material from the middle lamellae.

The extracted cell wall material was free of starch as indicated by a negative reaction with iodine. Results from Table 15C show that the supernatant fraction obtained after cellulase action on cell wall material contained almost 100% glucose, suggesting that cellulose is present in the cell wall. After hydrolysis using 2N H_2SO_4, the supernatant contains less glucose than the residue fraction, indicating that cellulose and glucans (other than starch) are present in the cell wall material.

There is little difference in the amount of cell wall material extracted from the 5 types of potato granules (Table 15). Their neutral sugar compositions also show minor differences (Table 15B). Glucose

Table 14. Neutral sugar compositions of cell wall fractions extracted from potato granules of different varieties

Cell wall fractions of potato granules	Monosaccharides (Molar Ratio)						
	Rhamnose	Fucose	Arabinose	Xylose	Mannose	Galactose	Glucose
(A)							
Method 1: Using Aqueous-DMSO							
Residue fraction	T	T	1.5	0.5	0.4	4.1	93.2
Supernatant fraction	-	-	0.8	0.2	-	0.6	98.4
Method 2: Using Enzymes							
Residue fraction	-	T	2.2	1.6	2.1	2.0	92.0
Supernatant fraction	-	-	-		-	-	100.00
(B)							
Cell wall fractions of potato granules extracted using Method 2.							
PG (var. Pentland Crown)	-	T	2.2	1.6	2.1	2.0	92.0
PG (var. Ajax)	-	T	1.8	2.8	1.7	1.4	92.3
PG (var. Eba)	-	T	2.4	2.8	1.8	3.6	89.4
PG (var. Stara)	-	T	2.8	3.1	2.4	2.4	89.3
PG (var. Desirée)	-	T	2.0	2.8	2.2	2.1	91.0
(C)							
Fractions obtained after cellulase and (2N) H_2SO_4 treatment							
Supernatant (cellulase treatment)	-	-	-	-	-	-	100
Residue (cellulase treatment)	-	-	2.6	3.5	2.2	1.9	89.8
Supernatant (H_2SO_4 treatment)	T	T	5.2	8.1	1.5	6.1	79
Residue (H_2SO_4 treatment)	-	-	1.5	2.3	2.8	-	93.5

T = Trace amount

constitutes about 90% of the total neutral sugars present with minor quantities (~ 2% each) of galactose, mannose, xylose, arabinose and a trace amount of fucose. The type of neutral sugars present in the cell wall extract is in agreement with earlier findings by Le Tourneau, 1956; Hoff and Castro, 1969 and Jarvis et al., 1978.

Even though the quantity of cell wall materials and their composition of neutral sugars show only minor differences, it does not mean that functionally the cell walls of the different potato granules will behave in the same way. Even with the same constituents, the architecture and organisation of the cell walls could be very different. The architecture of the cell wall of the granule is an area of ignorance. We can, however, say from the model proposed by Keegstra et al. (1973), the cell wall has a complex structure and may be expected to have a very pronounced influence on the properties of the potato granules during extrusion.

Table 15. Cell wall material extracted from potato granules

Potato granules (varieties)	Cell wall material (% dry weight)
Method 1: Using Aq. DMSO	
PG (var. Pentland Crown)	5.30
Method 2: Using Enzymes	
PG (var. Pentland Crown)	2.58
PG (var. Ajax)	2.35
PG (var. Eba)	2.30
PG (var. Stara)	2.12
PG (var. Desirée)	2.54

MOLECULAR ORDER OF STARCH IN POTATO GRANULES

6. Molecular order of starch in potato granules

In parallel with studies of the starch and cell wall components of potato granules, attention was directed to the molecular order of the starch components with the intention of determining whether super-molecular order was responsible for the extrusion response of the potato granules and the blistering effect of the extrudates. The evaluation of the molecular order is governed by the technique used. Three techniques were chosen for this study, each having its own purpose.

(i) The x-ray diffraction technique was used to examine the changes in intramolecular order of the starch in potato granules occurring during the add-back process and subsequent extrusion. The x-ray patterns and relative crystallinities of satisfactory and unsatisfactory potato granules were also examined.

(ii) Differential scanning calorimeter(D.S.C.)was found useful in studying the interactions of GMS with the starch in potato granules before and after extrusion. The thermograms of satisfactory and unsatisfactory potato granules were compared to demonstrate any differences.

(iii) Infra-red spectroscopy was used to investigate the structure and conformation of the starch molecules in potato granules.

6.1. Differential scanning calorimetry (D.S.C.)

DSC is designed for the measurement and characterization of the thermal properties of material. When a phase transition suchas melting, evaporation or crystallisation occurs in the sample material, an endothermic or exothermic reaction takes place. The change in power required to maintain the sample holder at the same temperature as the reference holder (i.e. its programmed temperature) during the transition is recorded as a peak (Figure 51). The peak area indicates the total energy involved in the transition. It is important to emphasize, however, that the enthalpy so obtained is not determined under equilibrium conditions.

6.1.1. Theory

Differential scanning calorimetry is a technique based on the original principles of the differentialthermal analyser (D.T.A.). The main difference between D.S.C. and D.T.A. is that the area under the output curve of the D.S.C. is directly proportional to the total amount of energy (Q) transferred in or out of the sample, whereas in D.T.A., the output curve is directly proportional to the temperature difference ($\triangle T$) which occurs between the sample and the reference material during any physical or chemical change. The D.S.C. curve is recorded with the chart abscissa indicating the transition temperature and the peak area measuring the total energy transfer to or from the sample.

Figures 52 and 53 show the other major difference between D.T.A. and D.S.C. In D.S.C, the sample and reference cells are connected to individual heaters and thermal sensors. The control system is divided into two control loops. One is for average temperature control. This permits the temperature of the sample and the reference to be increased at a predetermined rate, which may also be recorded. The second loop ensures that if a temperature difference develops between the sample

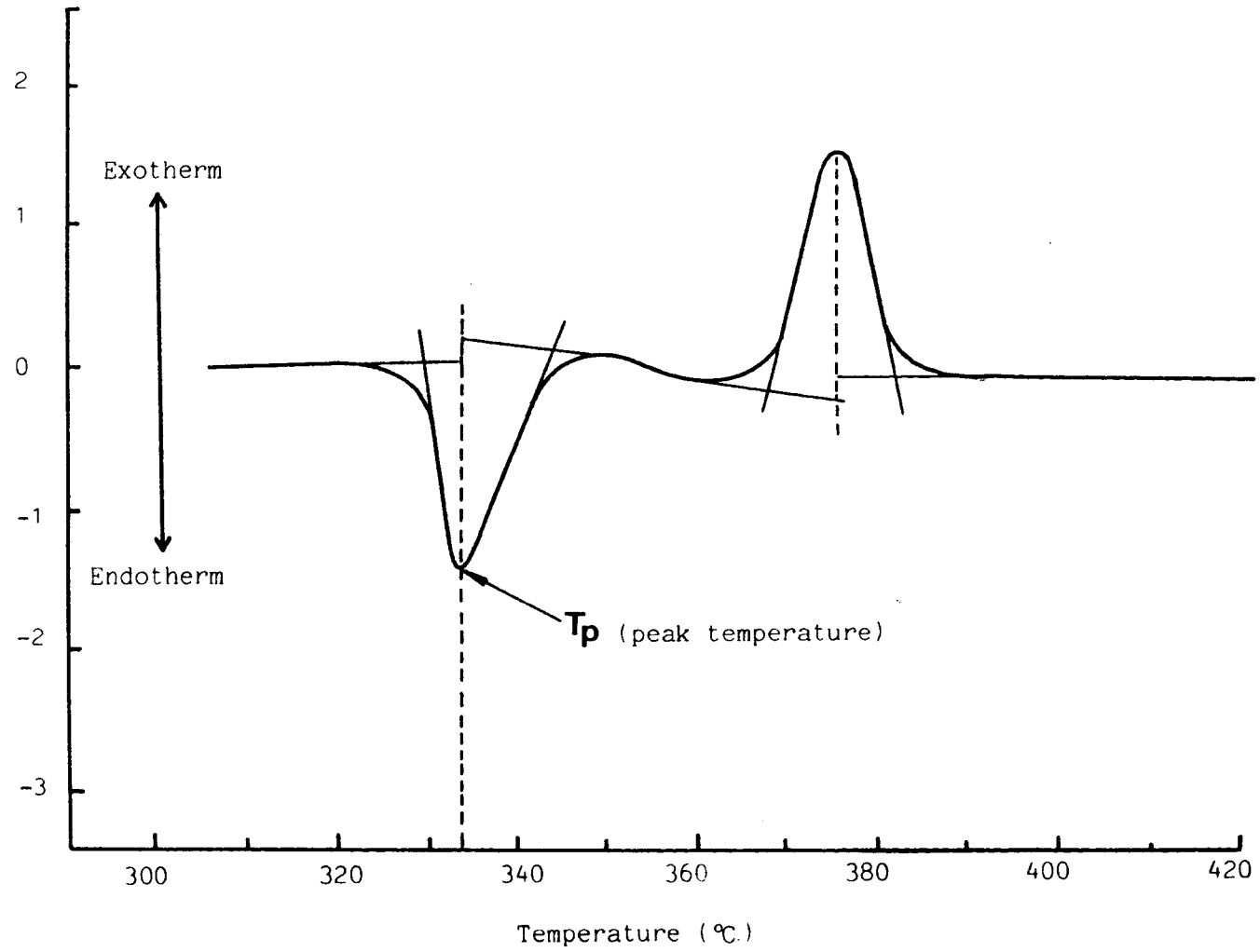


Figure 51. Conventions for presentation of thermal analysis data.

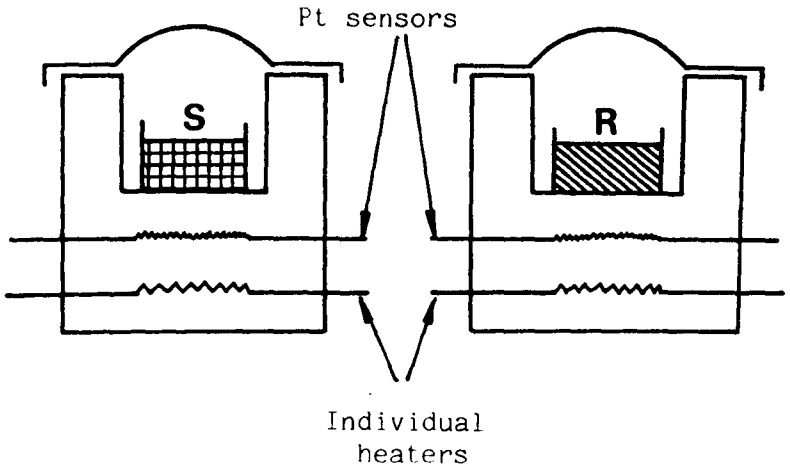


Figure 52. D.S.C. sample holder (Schematic).

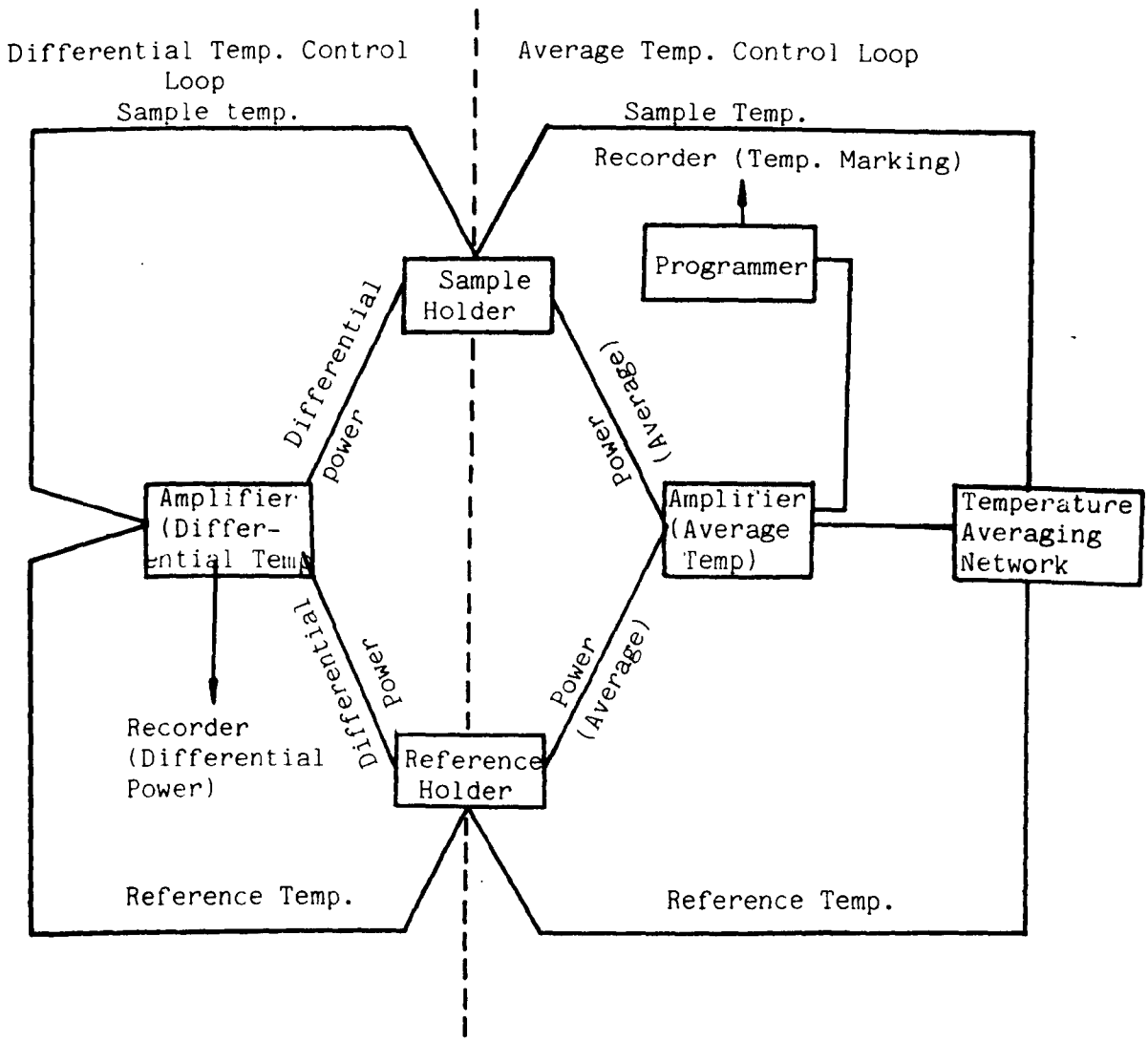


Figure 53. Schematic representation of D.S.C. control loops.

and the reference, because of an exothermic/endothermic process, the power input is adjusted to remove this difference in the form of an exo/endothermic peak.

6.1.2. Experimental

6.1.2.1. Materials

Potato granules were supplied by Dornay Foods Ltd. Extruded samples were prepared as in Section 3.6.2. They were air dried and then ground using a 'Moulinex' grinder before being used in the experiment. To remove lipids, the samples were extracted with absolute methanol in a Soxhlet extractor for 24 h (Mikus et al., 1946).

6.1.2.2. Preparation of potato granules - GMS complex

GMS (0.5 g) was allowed to swell in 9.5 g of water to give the cubic phase; 0.025 g of sodium caseinate was added and this mixture was sonicated for 2 min to give a homogeneous dispersion. Varying amounts (0.5 g, 1 g and 2 g) of this dispersion were mixed with water to give 4 g in total; potato granules (1.4 g) were then added and the suspensions were freeze-dried. The lipid contents of the freeze-dried samples were 0.7, 1.4 and 2.8% ($^{w}/w$), respectively.

6.1.2.3. Method

(Preparation of samples for D.S.C. analysis)

Starch samples (200 mg) of known moisture content were intimately mixed with an appropriate amount of distilled water in small glass bottles with air tight lids to obtain a starch/water ratio of 1:1 (on dry wt. basis).

Portions ($\sim$30 mg) of the well mixed starch-water mixtures were

transferred into previously weighed special stainless steel sample containers (Kit no. 319-0218) using fine glass rods. The capsules were immediately sealed using a Perkin Elmer Quick Press and the sample weight was determined.

A Perkin Elmer D.S.C.-2 was used in this study. The sample capsule was placed on the sample holder with an empty capsule as the reference. Samples were heated at a rate of 5°C/min over a temperature range of 30°C to 150°C. The instrumental sensitivity was 0.5 mcal/sec. The recorder was set with a chart speed of 20 mm/min and a full scale deflection of 20 mV. A stream of dry nitrogen was allowed to flush through the D.S.C. head at 25 psi, throughout the experiment. An experimental set usually consisted of 3-4 runs. In the first run the sample capsule was heated until 150°C and then allowed to cool at room temperature for 10 min before the second run was made. The same procedure was repeated for run nos. 3 and 4, respectively. The water content in each sample capsule was found by carefully puncturing holes on the capsule and determining from loss in weight after heating at 130°C after 2 hrs.

Calibration of the D.S.C. has been described by Hegg et al. (1978). The calibration coefficient for $\triangle H$ calculations was derived from the known heats of fusion of gallium and indium.

6.1.3. Calculations

The endotherms and exotherms obtained in the experiment were analysed quantitatively and the range of temperature during which they occurred were noted. The peak areas were determined by finding out their weights and converting them to cm^2, from which the heat of transition, $\triangle H$, were calculated using the equation:

$$-\triangle H = \frac{K \times R \times A}{M \times S}$$

Where

K = calibration constant which is 1

R = energy in mcal/sec/cm

A = peak area in cm^2

M = sample weight in mg

S = chartspeed in cm/sec

$-\Delta H$ is expressed as cal/g dry starch. For each sample the mean of 3 determinations was obtained. The transition temperatures were estimated to be accurate within $\pm$ 1°C and the enthalpies within $\pm$ 5-8%.

6.1.4. Results

The thermograms of the potato granule-GMS complex are shown in Figure 54. Each thermogram consisted of 2 endotherms at approximately 50°C (M_L) and 107°C (M_{A-L}). When the potato granule-GMS complex was reheated, an exotherm appeared at 64°C (Mx), together with the other 2 endotherms. On subsequent reheating the exotherm decreased in size and this was accompanied by a shift to a lower temperature (Figure 55). The enthalpies of the 2 endothermic transitions and single exothermic transition of the potato granule-GMS complex are shown in Figures 56 and 57.

When the unsatisfactory potato granules were heated, their thermograms showed 2 endotherms at 53°C and 107°C (Figure 58), while the thermograms of the satisfactory potato granules, extruded potato granules and extruded potato granules + PSA showed only 1 endotherm at 107°C (Figure 59). The enthalpies of the endothermic transitions of satisfactory and unsatisfactory potato granules are shown in Table 16 and a plot of these enthalpies is shown in Figure 60. Table 17 give the enthalpies of the endothermic and exothermic transitions of extruded potato granules

Figure 54. D.S.C. thermograms of defatted potato granules and potato granule - GMS complex (0.7%, 1.4% and 2.8% added GMS).

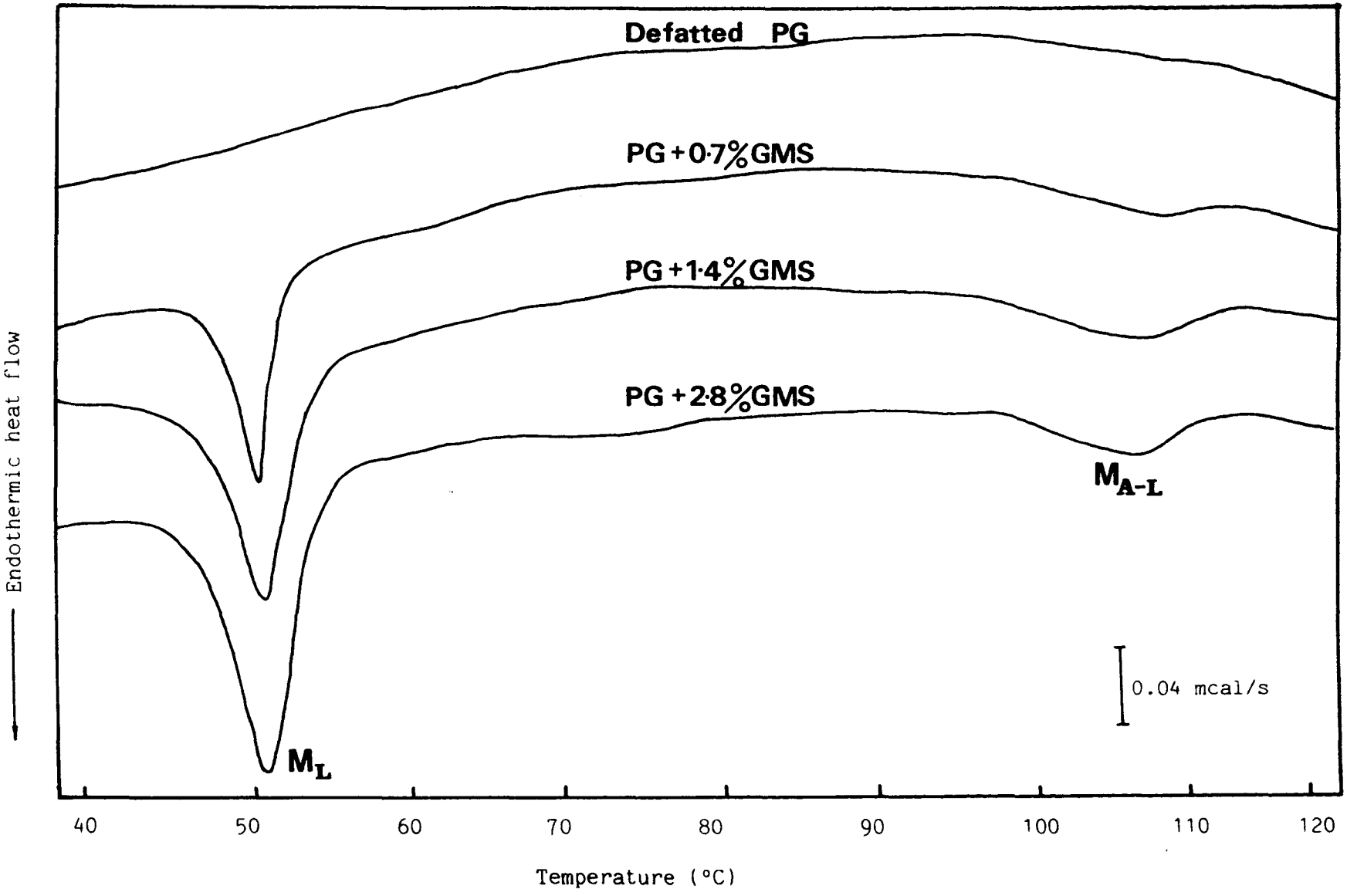
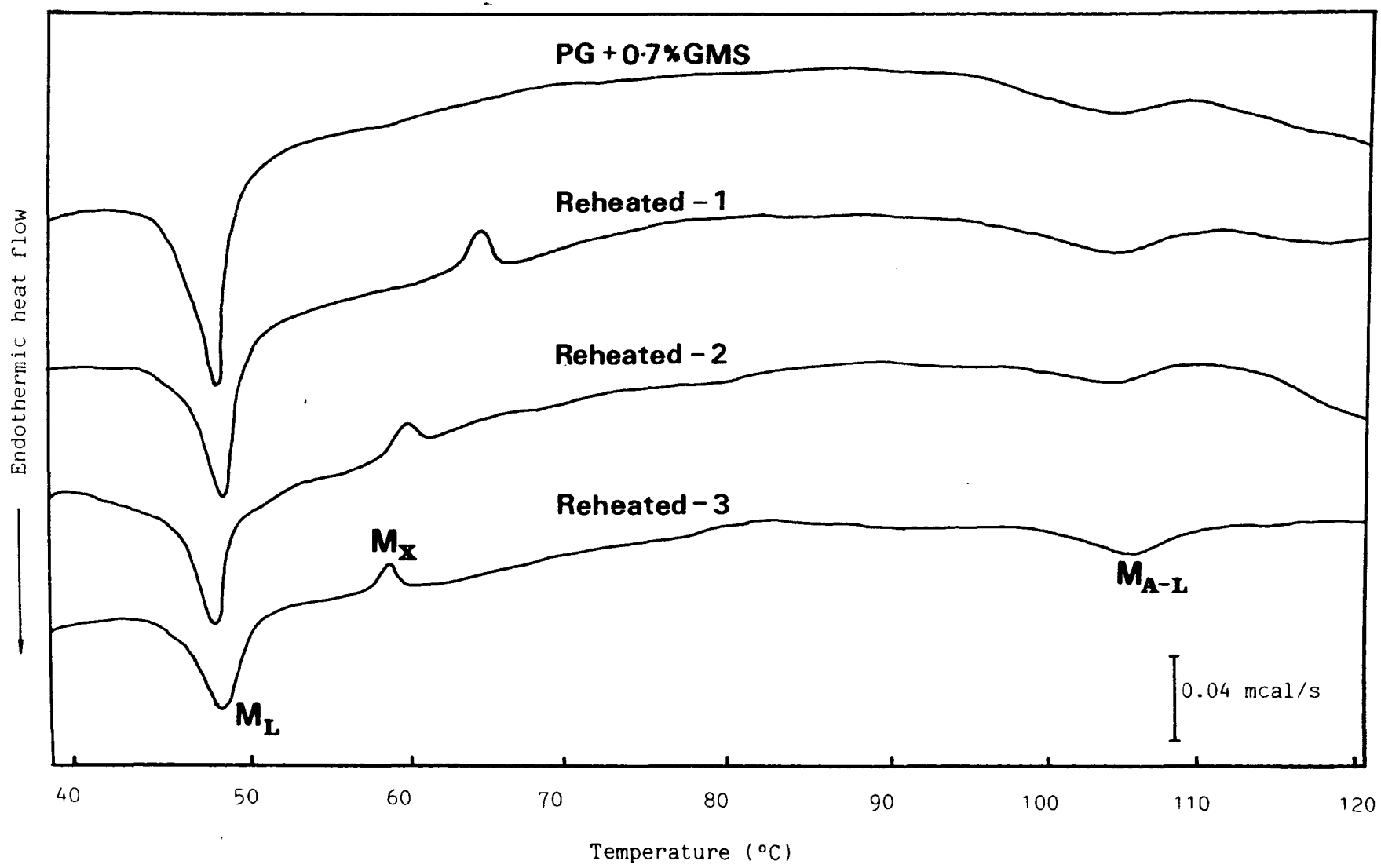


Figure 55. D.S.C. thermograms of potato granule-GMS complex (0.7% GMS) during initial heating and subsequent reheating.



Enthalpies of M_L, M_{A-L} and Mx transitions of potato granule-GMS complex (0.7, 1.4 and 2.8% added GMS)

Amount of GMS added (wt. - %)	M_L transition		M_{A-L} transition		Mx transition[a]	
	Tp (°C)	ΔH (cal/g)	Tp (°C)	ΔH (cal/g)	Tp (°C)	ΔH (cal/g)
Defatted potato granules	-	-	-	-	-	-
No GMS added	-	-	107	0.16	-	-
0.7%	51	0.89	107	0.30	64	0.22
1.4%	52	2.05	106	0.69	65	0.31
2.8%	52	4.44	106	1.04	65	0.23

(a) - Appears on reheating

Enthalpies of M_L, M_{A-L} and Mx transitions of potato granule-GMS complex (0.7% GMS) during initial heating and subsequent reheating

Sequence of runs	M_L transition		M_{A-L} transition		Mx transition	
	Tp (°C)	ΔH (cal/g)	Tp (°C)	ΔH (cal/g)	Tp (°C)	ΔH (cal/g)
Initial heating	51	0.89	107	0.30	-	-
Reheating (1)	50	0.22	106	0.33	64	0.22
Reheating (2)	50	0.17	107	0.35	60	0.13
Reheating (3)	50	0.11	107	0.30	58	0.10

Figure 56. Enthalpies of M_L, M_{A-L} and Mx transitions of potato granule - GMS complex (0.7, 1.4 and 2.8% added GMS).

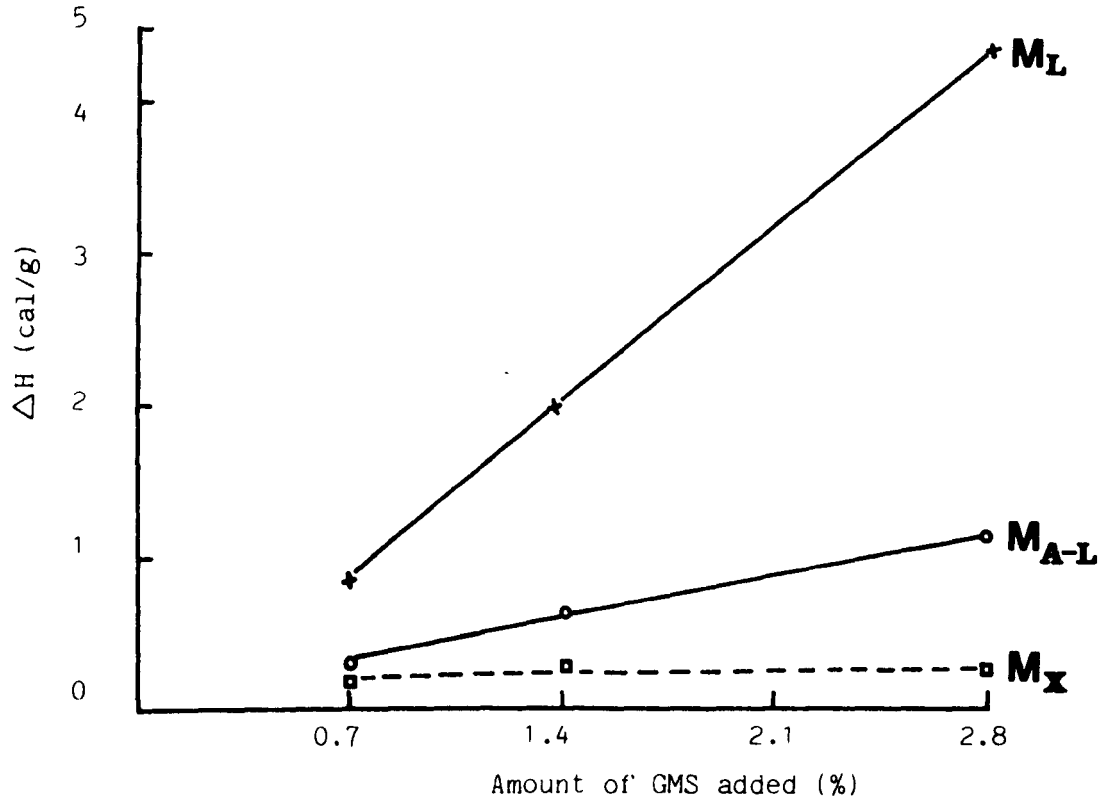


Figure 57. Enthalpies of M_L, M_{A-L} and Mx transitions of potato granule -GMS complex (0.7%) during initial heating and subsequent reheating.

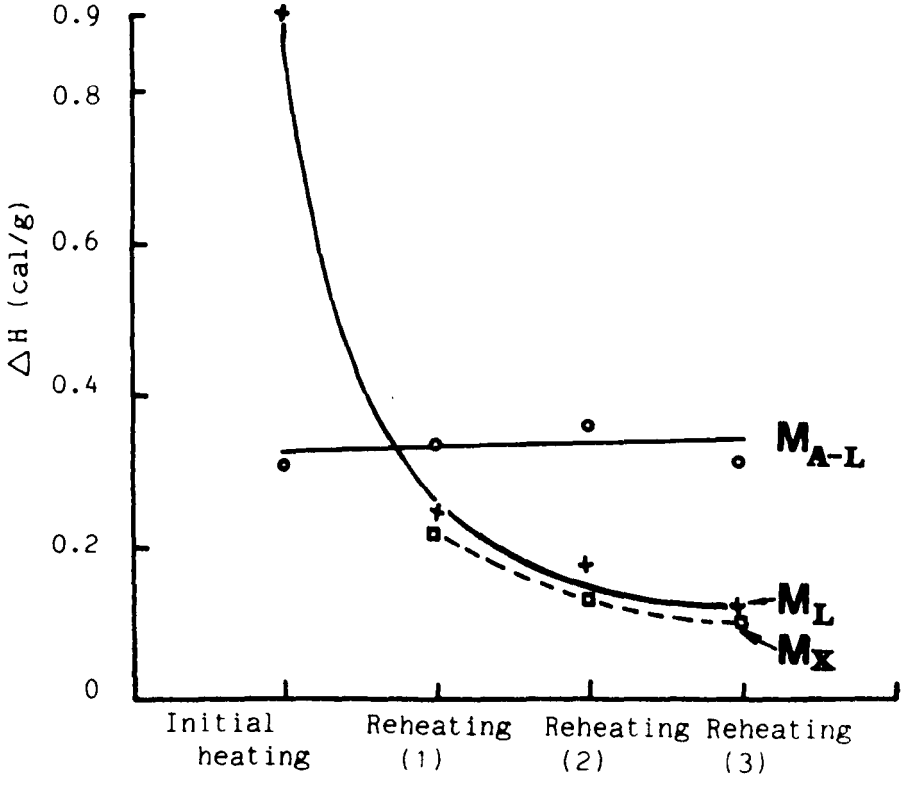


Figure 58. D.S.C. thermograms of UNSATISFACTORY potato granules.

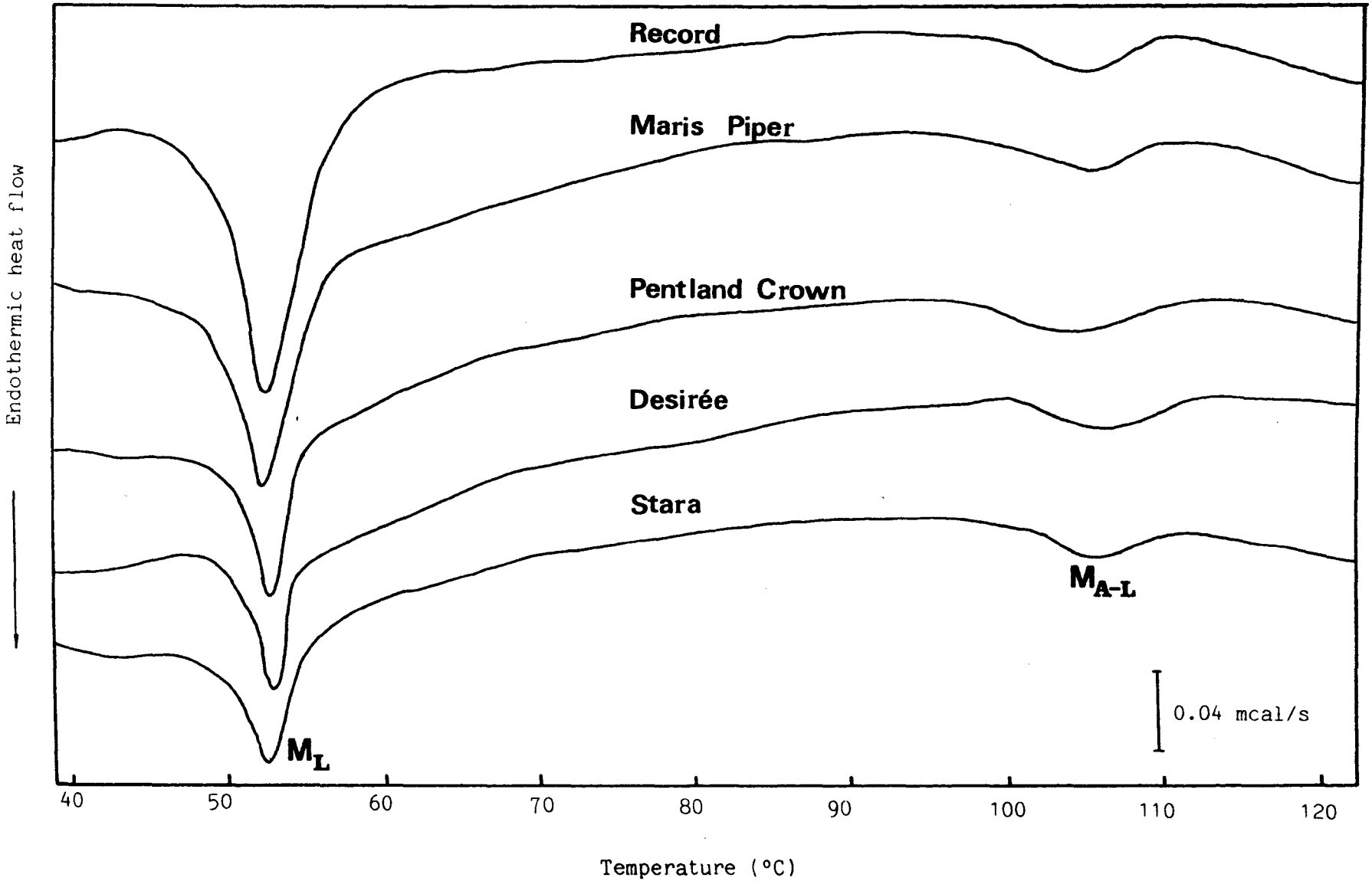
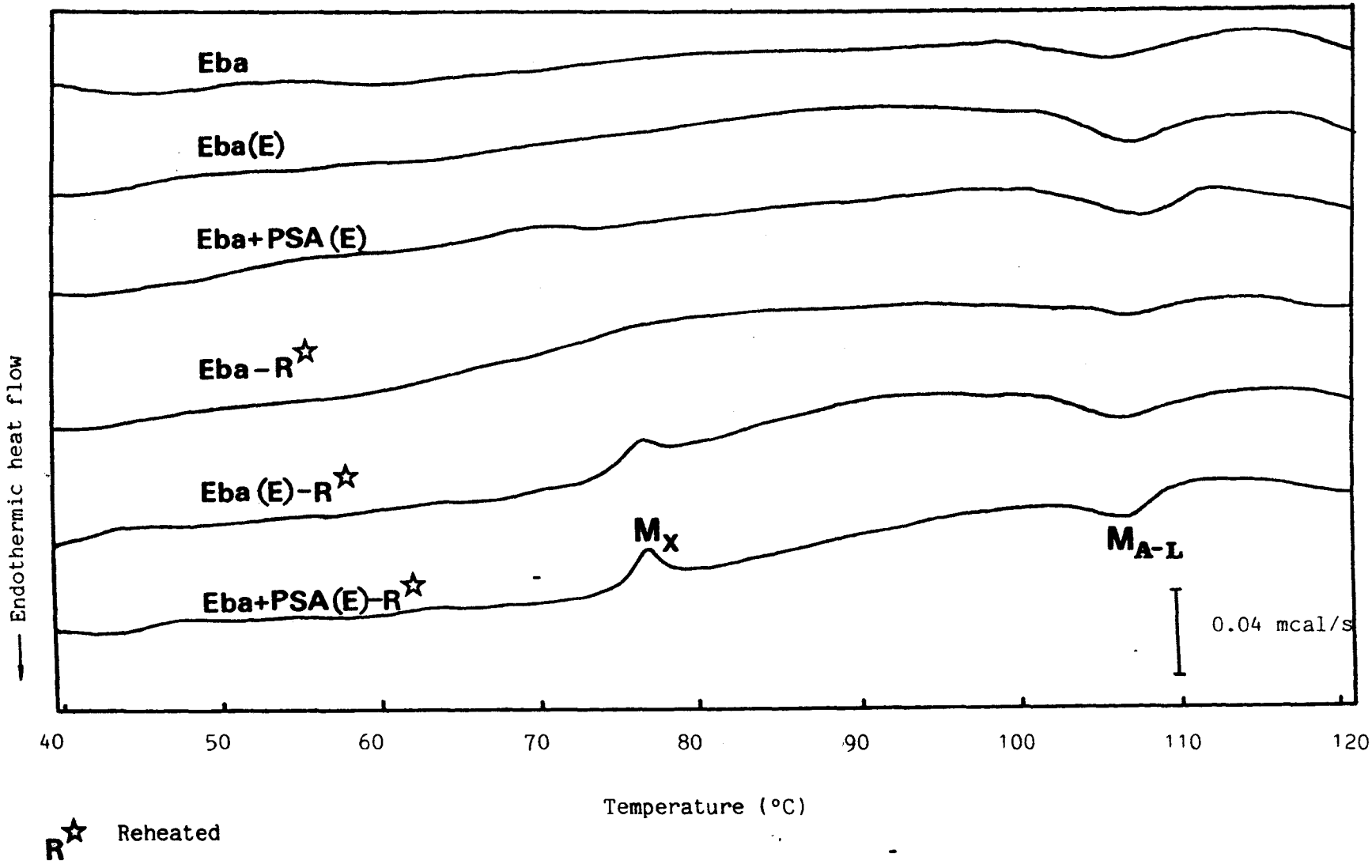


Figure 59. D.S.C. thermograms of potato granules, extruded potato granules and extruded potato granules +PSA during initial heating and reheating.



and extruded potato granules plus PSA.

Unsatisfactory potato granules were stored at 20°, 30° and 44°C and analysed by D.S.C. at intervals of 3, 12 and 15 weeks. Their thermograms showed 2 endothermic transitions at 53°C and about 107-112°C. The enthalpies of these transitions were recorded in Figures 61 and 62.

Table 16. Enthalpies of M_L and M_{A-L} transitions of satisfactory and unsatisfactory potato granules.

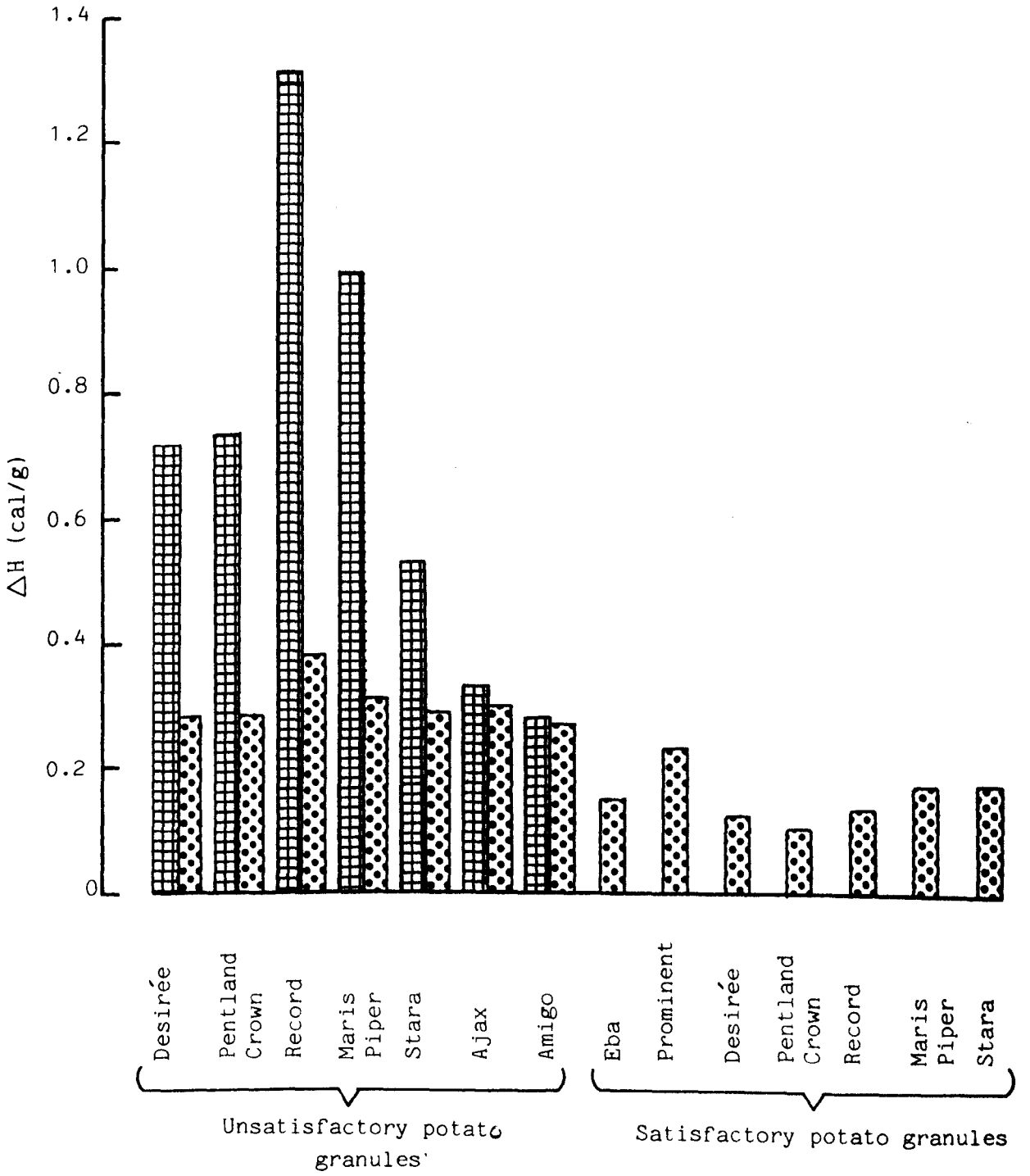
Potato granules	Free Fat[(a)]	M_L transition		M_{A-L} transition	
		Tp(°C)	△H(cal/g)	Tp(°C)	△H(cal/g)
Unsatisfactory potato granules					
Pentland Crown (U)	-	53	0.73	107	0.28
Desirée (U)	-	53	0.71	107	0.28
Record (U)	1.86	53	1.31	107	0.38
Stara (U)	-	53	0.53	107	0.29
Maris Piper (U)	-	53	0.99	107	0.31
Ajax (U)	0.74	54	0.33	108	0.30
Amigo (U)	0.49	54	0.28	108	0.27
Satisfactory potato granules					
Eba (S)	0.25	-		108	0.15
Prominent (S)	-	-		107	0.23
Pentland Crown (S)	-	-		107	0.10
Desirée (S)	-	-		108	0.12
Record (S)	0.22	-		108	0.13
Stara (S)	-	-		107	0.17
Maris Piper (S)	-	-		108	0.17

(a) - Free fat analysis was carried out by Dornay Foods.

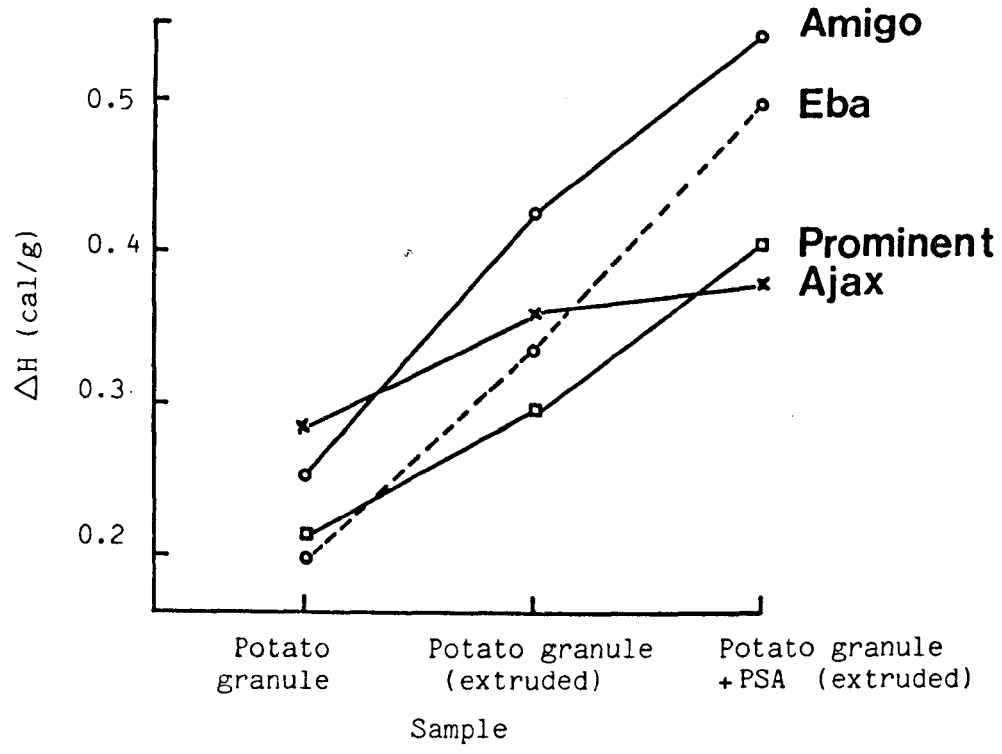
(U) - Unsatisfactory

(S) - Satisfactory potato granules

Figure 60. Enthalpies of M_L (▦) and M_{A-L} (▩) transitions of SATISFACTORY and UNSATISFACTORY potato granules.



Enthalpies of M_{A-L} transitions of potato granules, extruded potato granules and extruded potato granules +PSA



Enthalpies of M_{A-L} transitions of potato granules, extruded potato granules and extruded potato granules +PSA

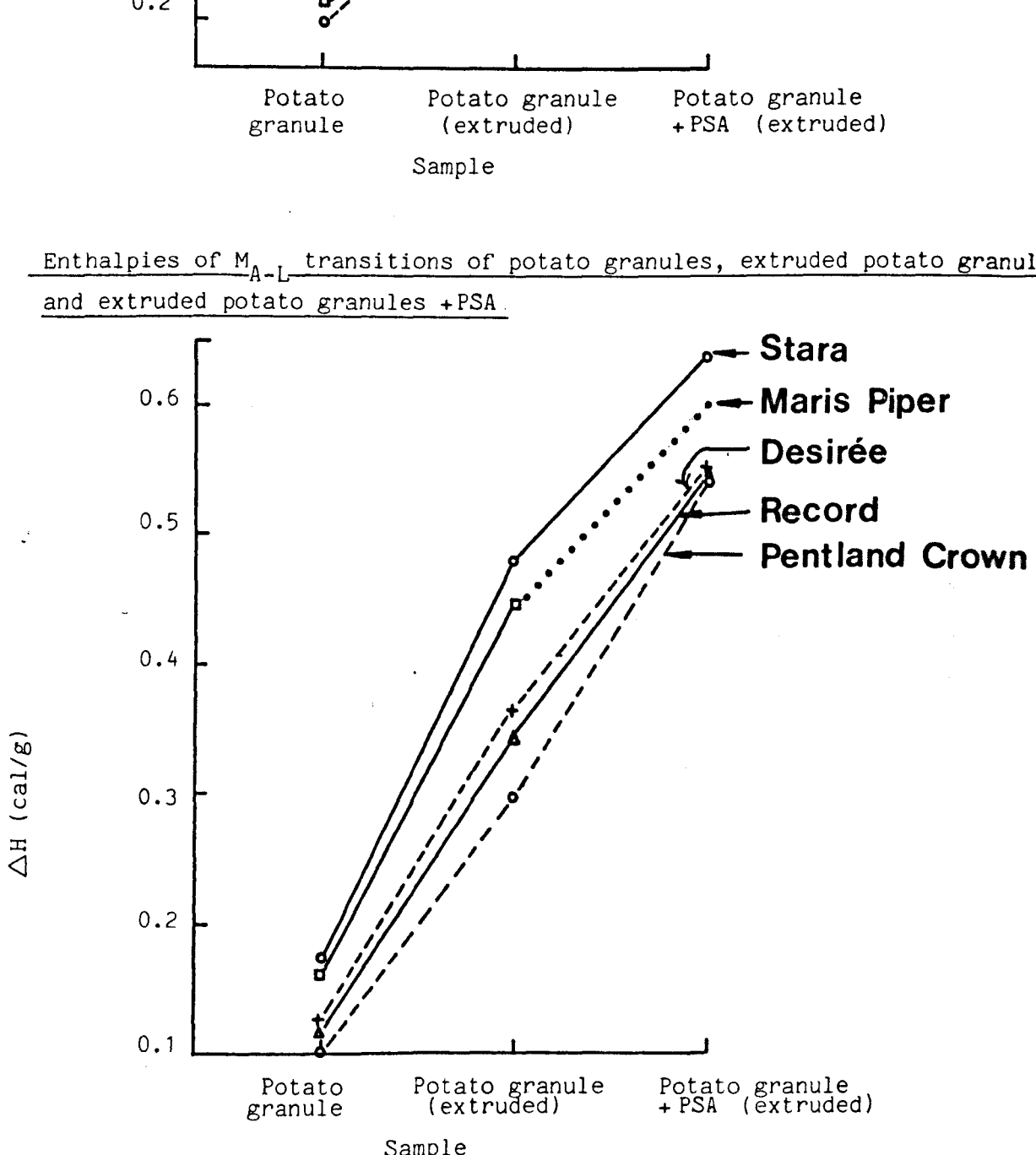


Table 17. Enthalpies of MA-L and Mx transitions of extruded potato granules and extruded potato granules plus PSA.

Sample (Potato granules and extrudates)	MA-L transition Tp (°C)	MA-L transition △H (cal/g)	Mx transition[a] Tp (°C)	Mx transition[a] △H (cal/g)
Ajax (U)	108	0.30	-	-
Ajax (E)	108	0.37	78	0.34
Ajax+PSA (E)	108	0.39	78	0.25
Amigo (U)	109	0.27	-	-
Amigo (E)	109	0.44	77	0.31
Amgigo+PSA (E)	109	0.55	78	0.36
Eba (S)	109	0.20	-	-
Eba (E)	109	0.34	77	0.18
Eba+PSA (E)	109	0.50	77	0.35
Prominent (S)	108	0.23	-	-
Prominent (E)	108	0.30	73	0.30
Prominent+PSA (E)	108	0.41	74	0.29
Desirée (S)	108	0.12	-	-
Desirée (E)	107	0.36	75	0.17
Desirée+PSA (E)	107	0.55	75	0.18
Pentland Crown (S)	107	0.10	-	-
Pentland Crown (E)	107	0.31	71	0.20
Pentland Crown+PSA (E)	107	0.55	76	0.17
Record (S)	108	0.13	-	-
Record (E)	107	0.35	74	0.24
Record+PSA (E)	108	0.55	75	0.11
Stara (S)	107	0.17	-	-
Stara (E)	108	0.48	74	0.29
Stara+PSA (E)	108	0.64	73	0.07
Maris Piper (S)	108	0.17	-	-
Maris Piper (E)	107	0.45	74	0.63

(U) - Unsatisfactory potato granules
(S) - Satisfactory potato granules
(E) - Extrudates
PSA - Potato Snack Additives
(a) - Appear on reheating

Effects of storage time and temperature on the enthalpies of M_L and M_{A-L} transitions of UNSATISFACTORY potato granules (DESIRÉE).

Temperature (°C)	Storage time (week)	M_L transition Tp (°C)	M_L transition ΔH (cal/g)	M_{A-L} transition Tp (°C)	M_{A-L} transition ΔH (cal/g)
44	3	54	0.49	107	0.31
30	3	53	0.46	107	0.28
20	3	53	0.71	107	0.18
20	12	53	0.45	111	0.31
44	15	54	0.41	112	0.36
30	15	54	0.31	112	0.30
20	15	54	0.46	112	0.33

Effects of storage time and temperature on the enthalpies of M_L and M_{A-L} transitions of UNSATISFACTORY potato granules (RECORD).

Temperature (°C)	Storage time (weeks)	M_L transition Tp (°C)	M_L transition ΔH (cal/g)	M_{A-L} transition Tp (°C)	M_{A-L} transition ΔH (cal/g)
44	3	54	1.23	107	0.42
30	3	54	0.92	107	0.27
20	3	54	1.31	107	0.37
44	15	55	0.87	112	0.61
30	15	55	0.76	112	0.38
20	15	55	1.19	112	0.42

Figure 61. Effect of storage time and temperature on the enthalpies of M_L ( ) and M_{A-L} ( ) transitions of UNSATISFACTORY potato granules (DESIRÉE).

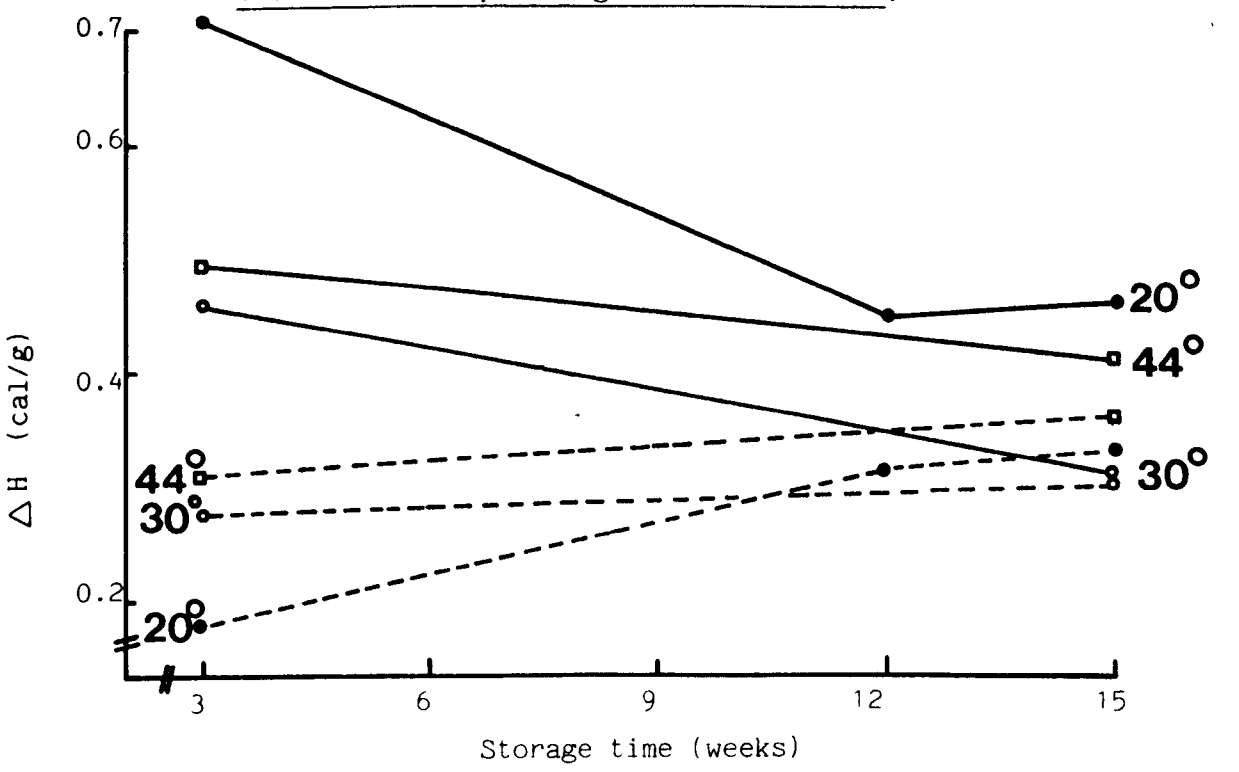
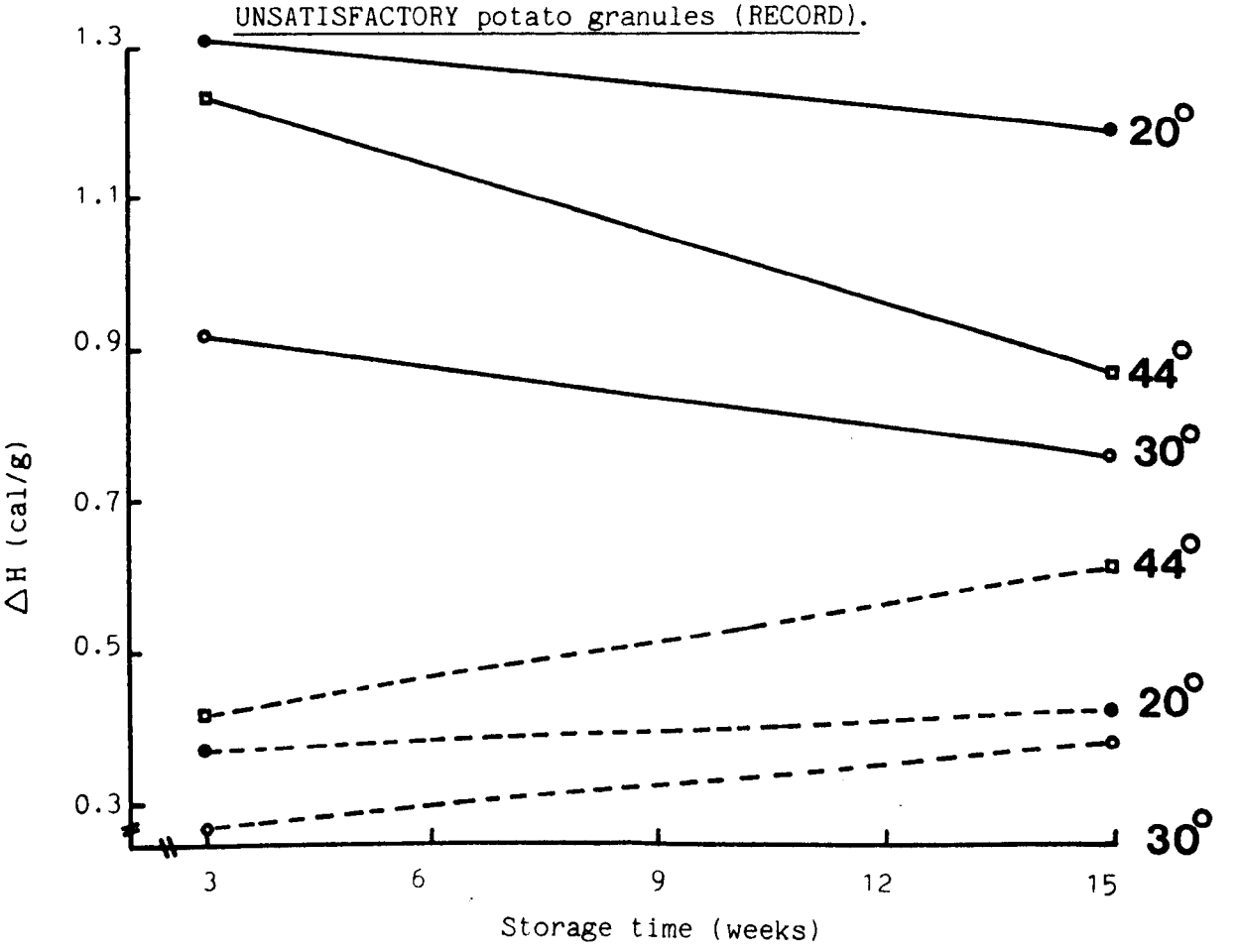


Figure 62. Effect of storage time and temperature on the enthalpies of M_L ( ) and M_{A-L} ( ) transitions of UNSATISFACTORY potato granules (RECORD).



6.2. X-ray diffraction

The physical and chemical behaviour of a polymer is often dependent upon the proportion of chain segments that is in the ordered state, i.e. the polymer crystallinity. A method was devised by Wakelin et al. (1959), using the x-ray diffraction technique to measure the amount of this order in a semicrystalline polymer. The method was later modified by Statton (1963) and subsequently has been found to be valuable for evaluating the crystallinity and the degree of molecular organisation within starch granules.

6.2.1. Basic principles of x-ray diffraction

The intensity of the x-rays scattered over all angles by a given assemblage of atoms is dependent on their state of order or disorder. If the crystalline and amorphous scattering in the diffraction pattern can be separated from each other than the integral total scattering of these 2 components can be used as a basis for observing and comparing subsequent changes of either the crystalline or amorphous fraction.

In this method the x-ray primary beam traverses a collimator, penetrates and is then scattered by the specimen of polymer under examination. The diffraction patterns of unknown, standard crystalline and amorphous sample are recorded on a chart, taking care that the differential intensity measurements encompass an angular range that is of sufficient size to include most of the crystalline peaks.

The scattering intensities of the amorphous (Ia), crystalline (Ic) and unknown specimen (Iu) are measured and compared point by point at small angular increments over the whole angular range under examination.

It is important that the angular increment, generally not more than 0.5° = 2θ, be small enough to sample the relatively sharp crystalline peaks as well as the broad amorphous fluctuations.

6.2.2. Experimental

6.2.2.1. Materials

Potato granules were the same as those used in other experiments. Some were prepared under 3 different processing conditions,

(i) cooked, kept at 60°C for 1 h and granulated at 25% moisture and dried,

(ii) cooked, granulated at 33% moisture, kept at 4°C overnight and dried,

(iii) cooked, riced, kept at 4°C overnight and dried.

The extruded samples were prepared as in Section 3.6.2. The samples of potato granule-GMS complex were the same as those used in D.S.C. studies.

6.2.2.2. Method

(Preparation of sample and x-ray analysis)

Satisfactory x-ray patterns were obtained only when samples were properly prepared and mounted. Samples of potato granules and ground extrudates used in the experiment were of uniform size (90μ or less) obtained by sieving them through a 170 mesh sieve. All samples were equilibrated to the same moisture content by storing them in a desiccator containing saturated potassium sulphate solution, which gave a relative humidity of 97% (~ 38% moisture content).

The sample holder consisted of a sheet of aluminium, 3.7 x 3.7 x 0.13 cm thick, with a rectangular window of size 1.0 cm wide and 2.0 cm long. The sample compartment was filled by adding an excess of starch powder which was packed into place with 2 glass slides to form a slab of powdered starch with a smooth surface. The sample in its holder was mounted vertically on the specimen stage as shown in Figure 63.

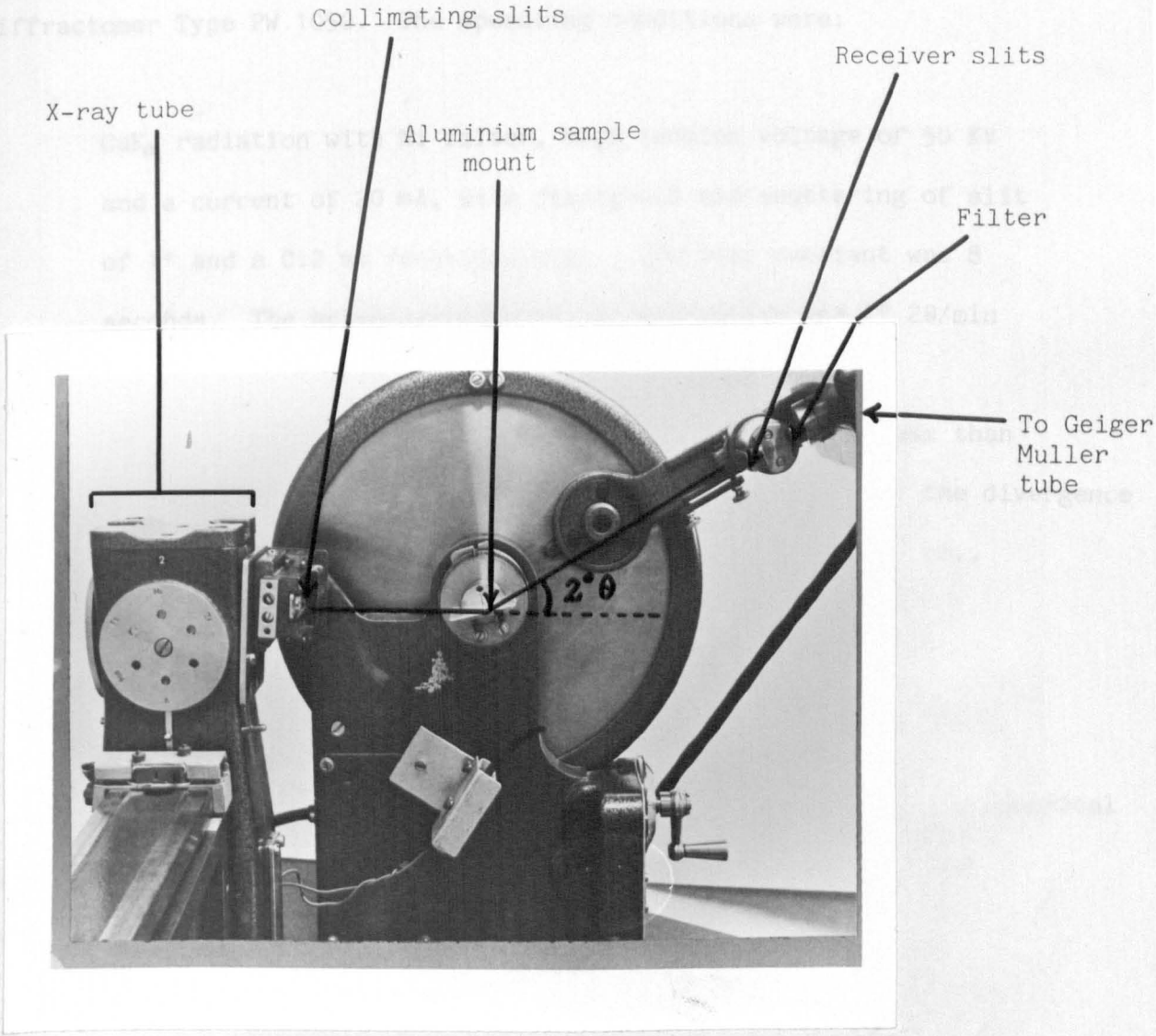


Figure 63. Powder sample holder of x-ray goniometer (safety cover removed).

The relative humidity inside the camera was regulated with a piece of cotton wool, soaked with saturated potassium sulphate solution and placed underneath the sample holder.

X-ray diffraction patterns were obtained with a Philips X-ray Diffractomer Type PW 1050. The operating conditions were:

CuK_α radiation with Ni filter, high tension voltage of 50 KV and a current of 20 mA, with divergence and scattering of slit of 1° and a 0.2 mm receiving slit. The time constant was 8 seconds. The scanning speed of the goniometer was 1° 2θ/min and the chart speed was 80 cm/min.

A normal run is from 2θ = 4° to 30°. For 2θ less than 10°, the high tension voltage was lowered to 32 KV and the divergence and scatter slits were 1/4° and receiving slit was 0.1 mm., other conditions being the same.

6.2.3. Treatment of data

Wakelin et al. (1959) suggested a method which provides a numerical comparison of an unknown sample to the most amorphous and the most crystalline extremes of a polymer species.

The intensity of the x-ray diffraction was measured at equal increments along the x-ray recorder trace. These increments have the boundaries at the same 2θ values in the traces for all samples of a polymer species. The more increments used the more exact will be the determination. In this experiment an increment of 2mm was chosen. The positions were chosen to coincide with as many peaks in the pattern as possible. These reference positions were used to obtain the intensity data for the amorphous (Ia) and crystalline (Ic) extremes and the unknown (Iu) as shown in Figure 64.

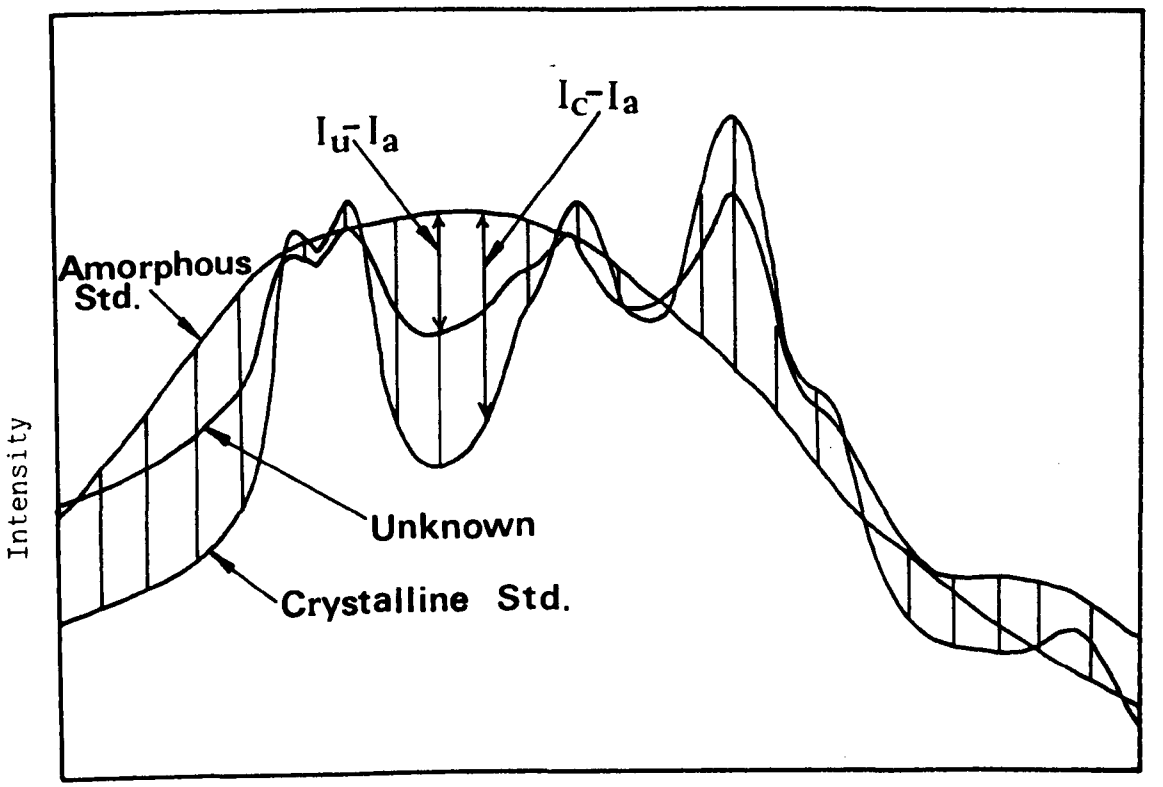


Figure 64. X-ray intensity curves of an unknown, amorphous and crystalline standard showing some of the intensity differences used to calculate the crystallinity index (Statton, 1963).

Some normalisation of the intensity data was usually necessary because of the difficulties in obtaining identical x-ray patterns of different samples. This can be accomplished rapidly and accurately by the computer. The normalisation requires the basic assumption that the number of counts recorded will be the same for a given mass of starch sample and a given exposure no matter whether the sample is crystalline or amorphous. This assumption is valid since it is based on the fact that the x-ray recorder registers only the result of interaction of x-rays with atoms, the state of aggregation of the atoms will determine the location and phase of the scattering but will not affect the total intensity. Thus, amorphous scattering can be treated in the same way as crystalline diffraction. This assumption permits us to normalise x-ray diagrams for 2 samples having different masses or exposure times using the following method. The area under the curve of intensity versus diffraction angle for one of the standards is obtained by conventional numerical integration. The data for the unknown are handled similarly to obtain the area under its curve. The ratio of these areas is found and then used as a multiplier for each of the data for the unknown. These new, normalised data are then used to determine the crystallinity index.

The normalized data were analysed mathematically by 2 methods after correcting for the background radiation.

In the regression method, the scattering intensities at intervals of $2\theta = 0.2°$ were measured, for the crystalline and amorphous standards and the unknown, and these data were used to calculate the regression line letting $Y_{2\theta}$ = (U-A) and $X_{2\theta}$ = (C-A). The slope is therefore the relative crystallinity.

In the integration method, the ratio of the absolute values of the difference between the unknown and the amorphous standard (U-A) and the crystalline and amorphous standard (C-A) were used to obtain

the relative crystallinity (C)

where $$C = \frac{(U-A)}{(C-A)}$$

According to Wakelin et al. (1959), the integral method gave higher values. From a mathematical point of view, the regression method is less likely to be affected by "rogue" readings and therefore was selected for use.

6.2.4. Results

Figure 65 shows the diffraction patterns of potato samples taken during different stages in the 'add-back' process. The peak angles and 'd' spacings of the patterns are given in Table 18. The samples of the potato granule-GMS complex were also used and their diffraction patterns are given in Figure 66. Figures 67, 68 and 69 contain x-ray patterns of satisfactory potato granules, unsatisfactory potato granules and extrudates, respectively. The effect of moisture content on the crystallinity of potato granules can be seen in their diffraction patterns (Figure 70).

Table 19 gives the percentage crystallinity of potato granules and their extrudates.

Figure 65. X-ray diffraction patterns of potato samples taken from different stages in the 'add-back' process.

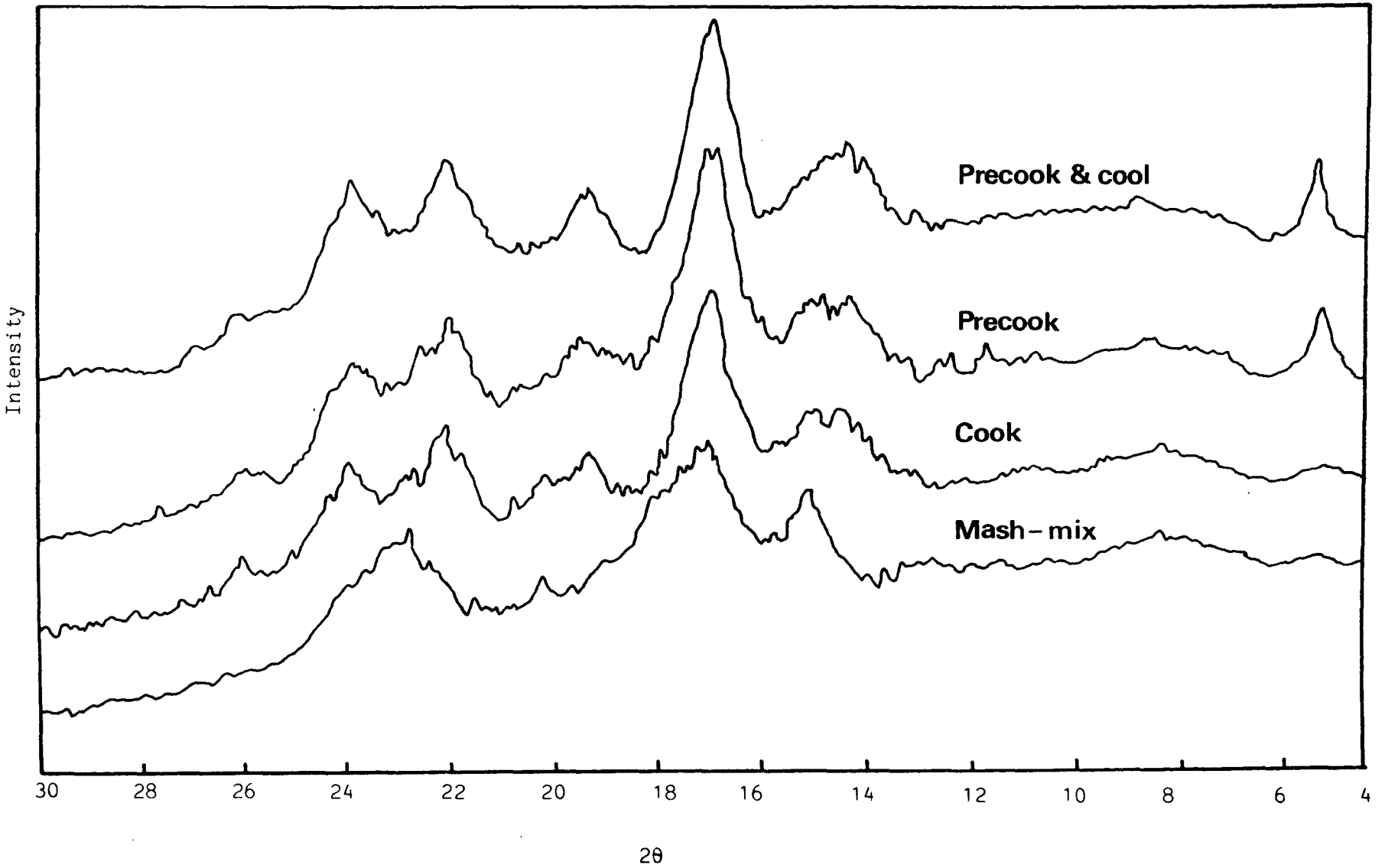


Table 18. Prominent peaks in the x-ray diffraction patterns of potato samples.

Potato samples at different stages of 'add-back' process											
Pentland Crown Starch		Precook		Precook and cool		Cook		Mash-mix		Potato granules	
Intensity scale(a)	2θ	Intensity scale	2θ	Intensity scale	2θ	Intensity scale	2θ	Intensity scale	2θ	Intensity scale	2θ
S	5.60	w^+	5.60	w^+	5.60	w^-	5.60	w^-	5.60	w^-	5.62
W	9.90	w^-	11.73	w^-	11.50	w^+	15.00	w^-	12.62	w^-	11.31
W^-	11.58	w^-	12.39	m	14.39	s	17.00	m	15.08	m^+	15.09
W^-	14.15	m	14.39	s	17.15	w^+	19.15	s^-	17.23	s^-	17.20
W	15.15	m	15.12	m^-	19.42	w^-	20.15	w	20.23	w^-	18.06
S	17.35	s	17.15	m	22.15	m	22.08	m	22.77	w	20.21
W^+	20.00	m^-	19.54	m	24.00	w	22.69			m	23.05
M	22.23	m	22.08	w^-	26.23	m^-	23.85				
m^-	24.15	m	24.00	w^-	27.00	w^+	26.00				
		w^-	27.77								

(a) Intensity scale: strong (s), medium (m), weak (w), less than (-), more than (+)

Figure 66. X-ray diffraction patterns of potato granule-GMS complex (0.7%, 1.4%, 2.8% GMS).

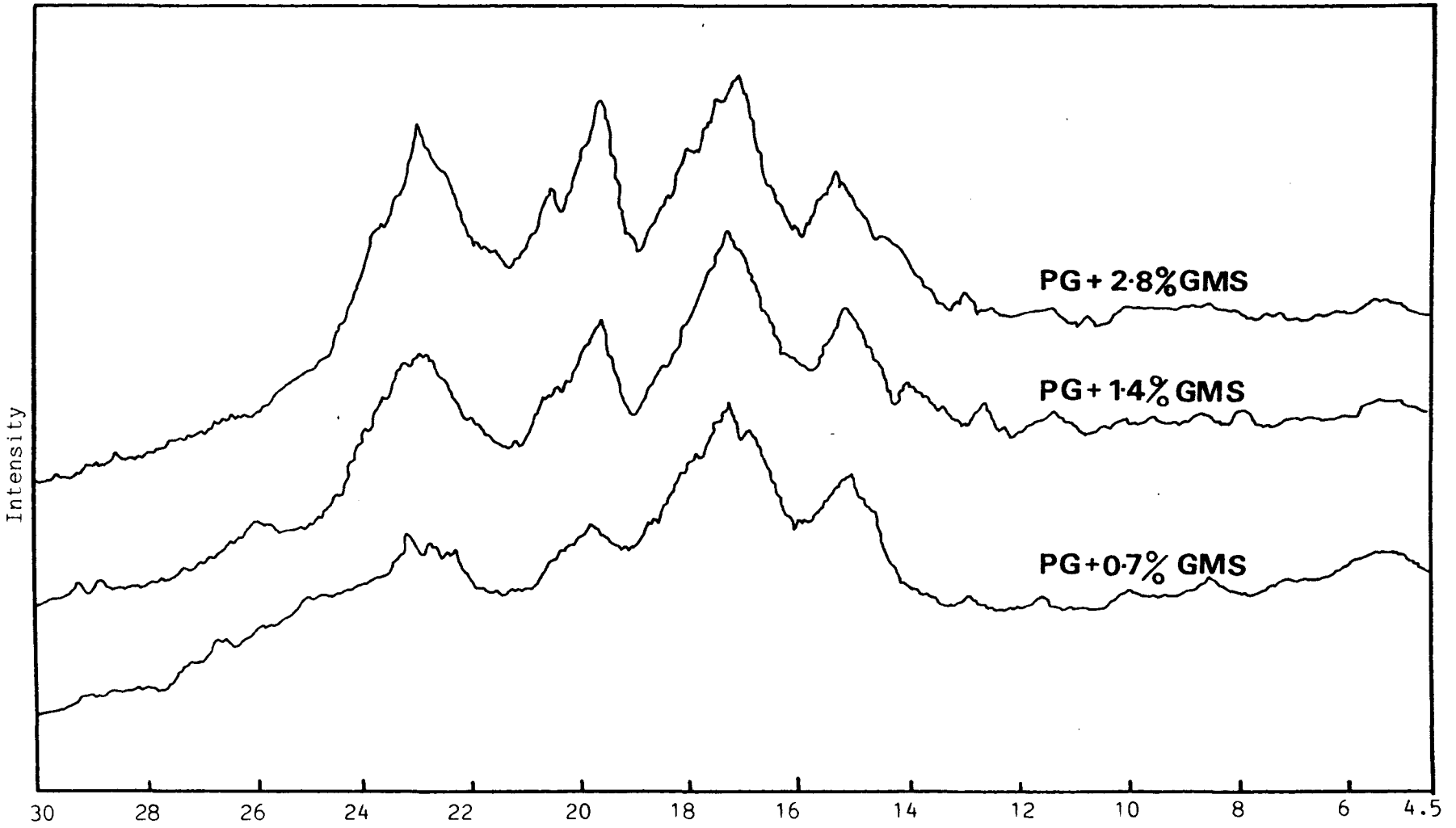


Figure 67. X-ray diffraction patterns of SATISFACTORY potato granules.

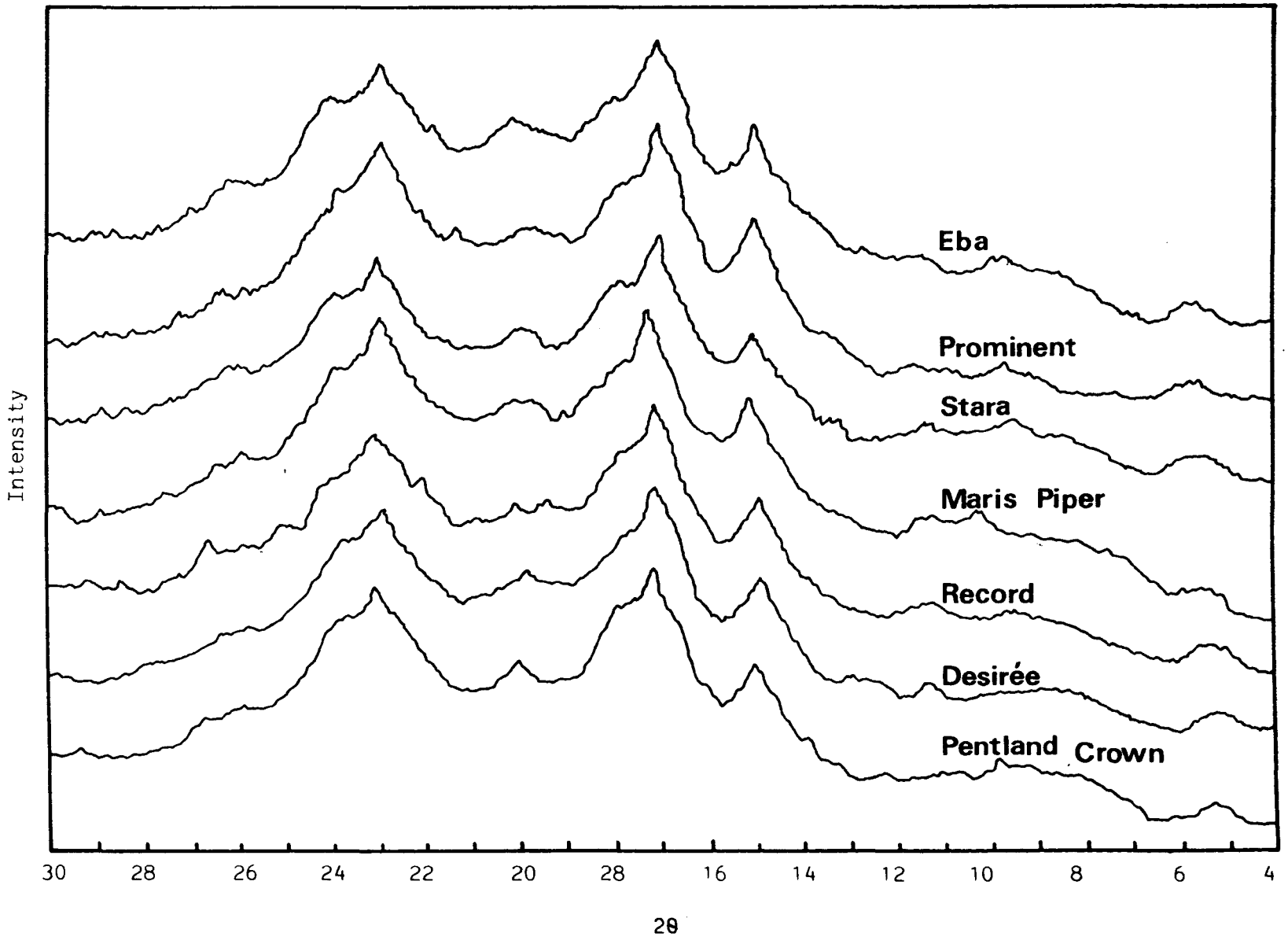


Figure 68. X-ray diffraction patterns of UNSATISFACTORY potato granules.

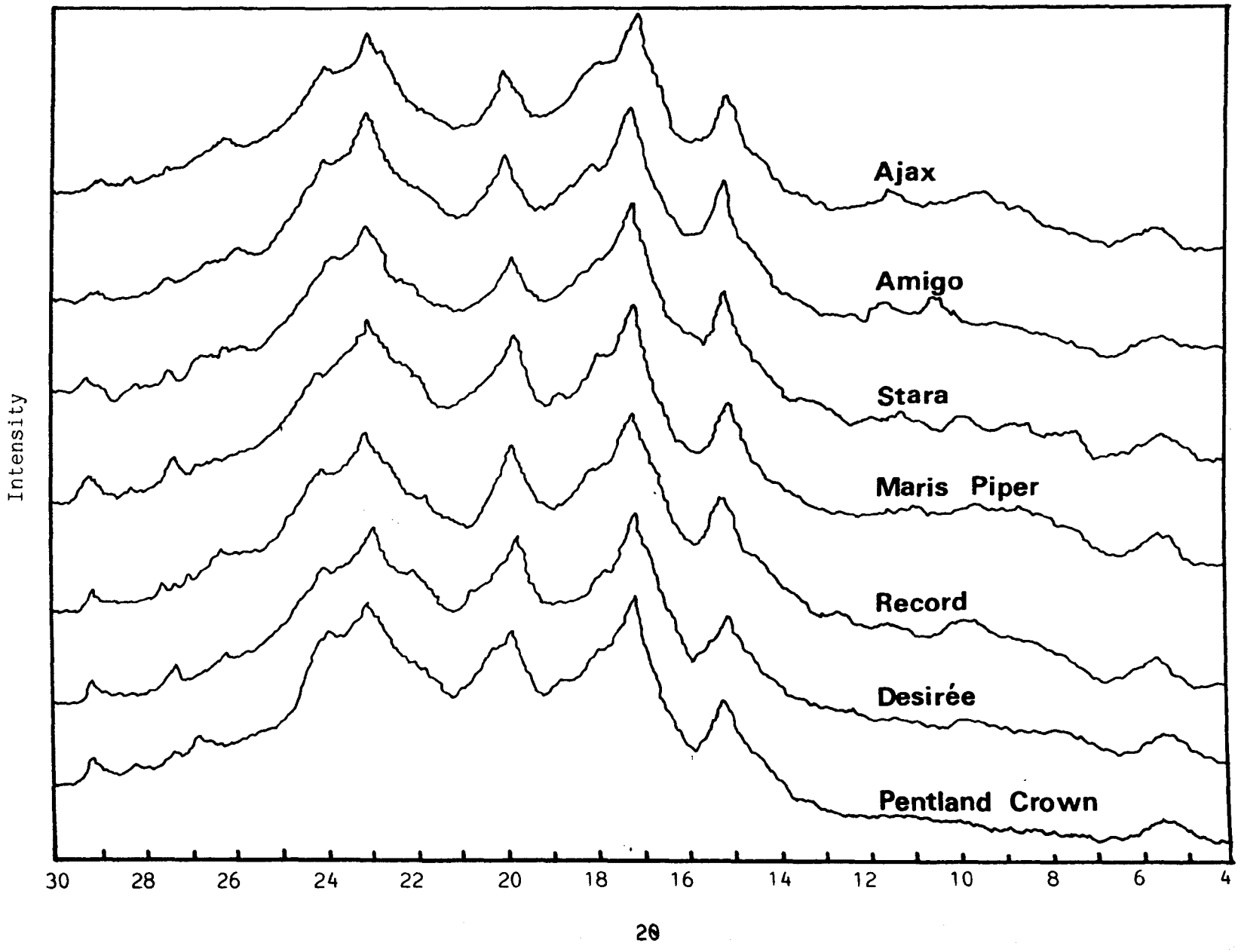


Figure 69. X-ray diffraction patterns of extruded potato granules and extruded potato granules +PSA .

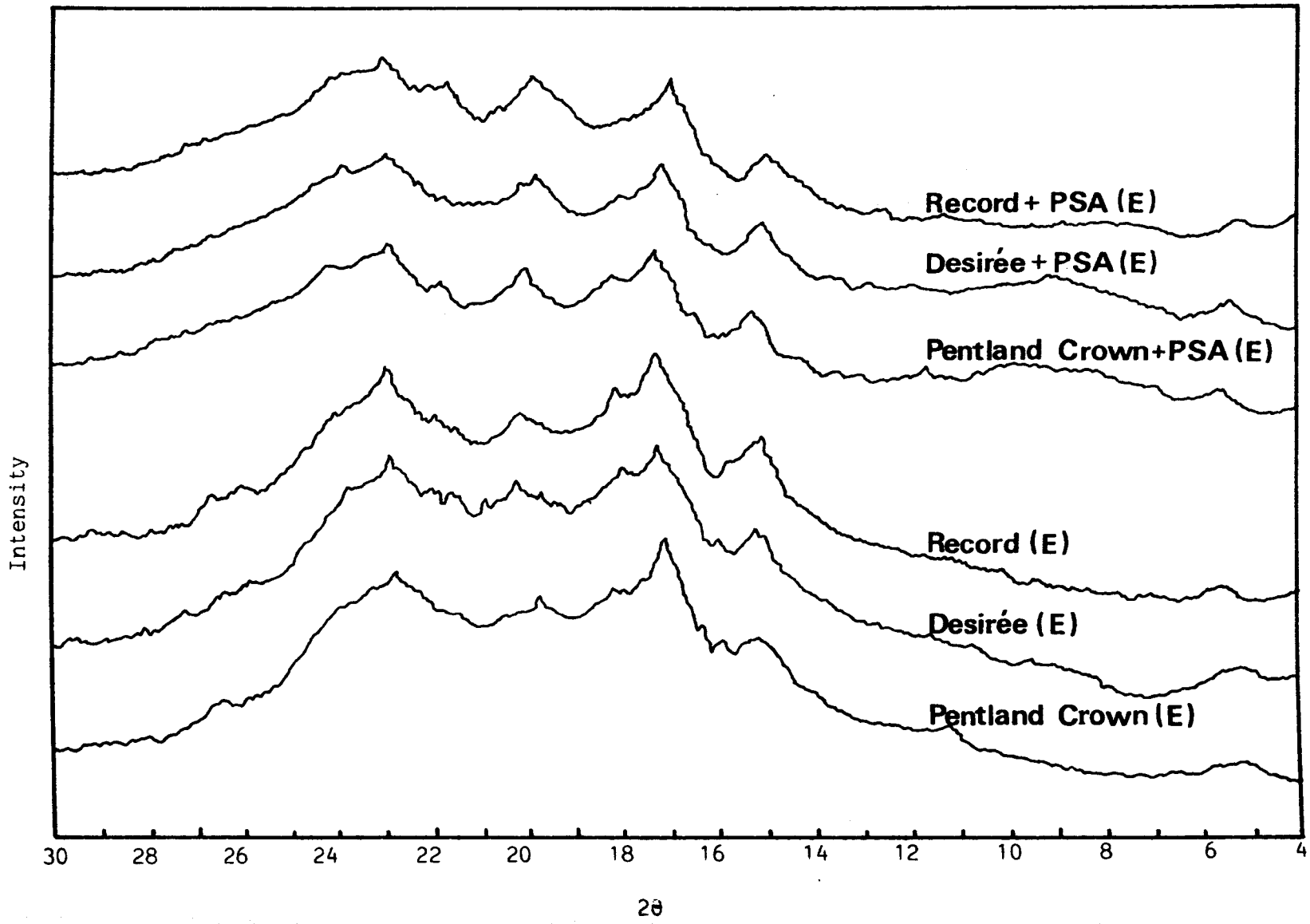


Table 19. Relative percentage crystallinity of potato granules and extrudates.

Sample	(%) crystallinity		
	Potato granule	Extruded potato granule	Extruded potato granule+PSA
Eba (S)	100.00	75.21	73.59
Prominent (S)	84.69	76.50	67.32
Ajax (U)	96.00	73.18	60.25
Amigo (U)	100.00	77.98	69.44
Precook potatoes	78.06		
Precook (and cool) potatoes	68.42		
Cook potatoes	63.62		
Mash-mix	62.30		
Satisfactory potato granules			
Pentland Crown (S)	81.47	74.51	56.59
Desirée (S)	75.29	73.65	54.27
Record (S)	81.67	72.75	62.99
Maris Piper (S)	74.87	77.06	
Stara (S)	75.61	67.13	55.62
Unsatisfactory potato granules			
Pentland Crown (U)	100.00		
Desirée (U)	81.88		
Record (U)	90.39		
Maris Piper (U)	86.81		
Stara (U)	58.27		

(S) = Satisfactory

(U) = Unsatisfactory

6.3. Infra-red spectroscopy

6.3.1. Introduction

Infra-red spectroscopy was first used by Samec (1953, 1956, 1957) to study the differences between starches and the changes occurring during the ageing of starch gels. He showed that native, gelatinised and alcohol precipitated starches gave different spectra with distinct absorption bands, and during ageing of starch gels there was an increased formation of hydrogen bonds.

Recently, Vasko and Koenig (1972) and Koenig and Vasko (1970) also used the same technique to investigate the structure and conformation of polysaccharides both in the solid state and in solution. The study led to the assignment of the 1295 cm^{-1} band to a unique folded chain conformation of amylose and amylopectin; the 790 cm^{-1} and 1256 cm^{-1} bands to the metastable conformations within non-crystalline portions of the polymer and the 855 cm^{-1} bands to the crystalline contribution from the polymer.

Vasko and Koenig (1972) also suggested that the infra-red technique was capable of picking up long range crystalline order which is too low to be detected by x-rays.

It was therefore decided to use this technique to investigate whether any differences in the spectra of the different samples could be detected with respect to their crystallinity and the chain-folding of the starch molecules.

6.3.2. Experimental

6.3.2.1. Materials

Potato granules were supplied by Dornay Foods Ltd. Extruded samples were prepared as in Section 3.6.2.

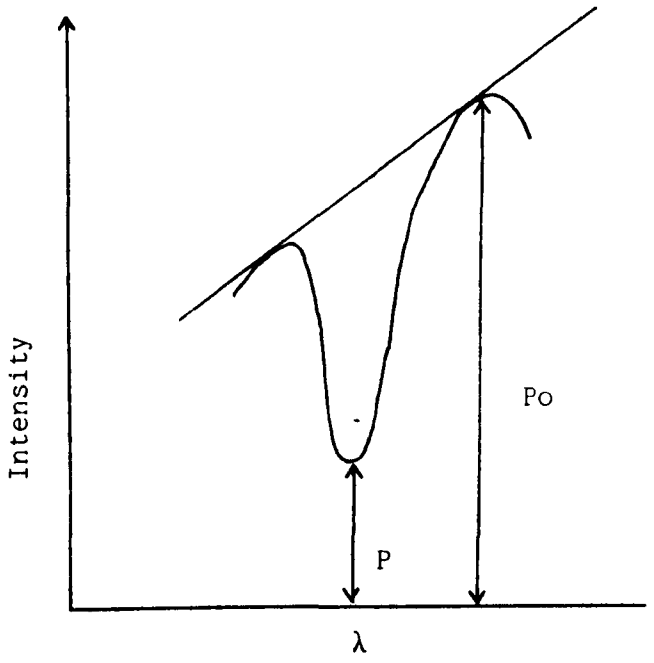
6.3.2.2. Method

All infra-red samples were examined using the potassium bromide pellet technique. All pellets were prepared in the same manner. A weighed portion of the powdered starch sample (0.075 g) was thoroughly mixed with a weighed quantity (0.925 g) of potassium bromide (KBr) powder in a mullite mortar. The KBr was powdered infra-red quality obtained from BDH Chemicals Ltd., Poole, U.K. The sample - KBr mixture was ground for 20 min. A known amount of the mixture (43 mg) was transferred to a partially assembled die and leveled with a small spatula. The plunger was inserted and rotated in both directions and at the same time a slight pressure was applied. The plunger was carefully removed and the steel disk inserted into the chamber. The steel plunger was reinserted and the remainder of the die assembled. The die was evacuated before the pressure was applied. A hydraulic laboratory hand press was used to apply a pressure of 10 tons on the plunger for 5 mins while the system was under vacuum. After releasing the press the plunger and steel disk were carefully removed and a transparent pellet of ca. 0.25 mm thickness and 13 mm diameter was obtained. The pellet was placed carefully on a sample holder and inserted in the spectrometer for analysis.

Spectra in the frequency range of 4000-650 cm^{-1} were measured using a Perkin-Elmer double beam infra-red spectrometer (Model 683) fitted with a NaCl prism.

6.3.3. Results

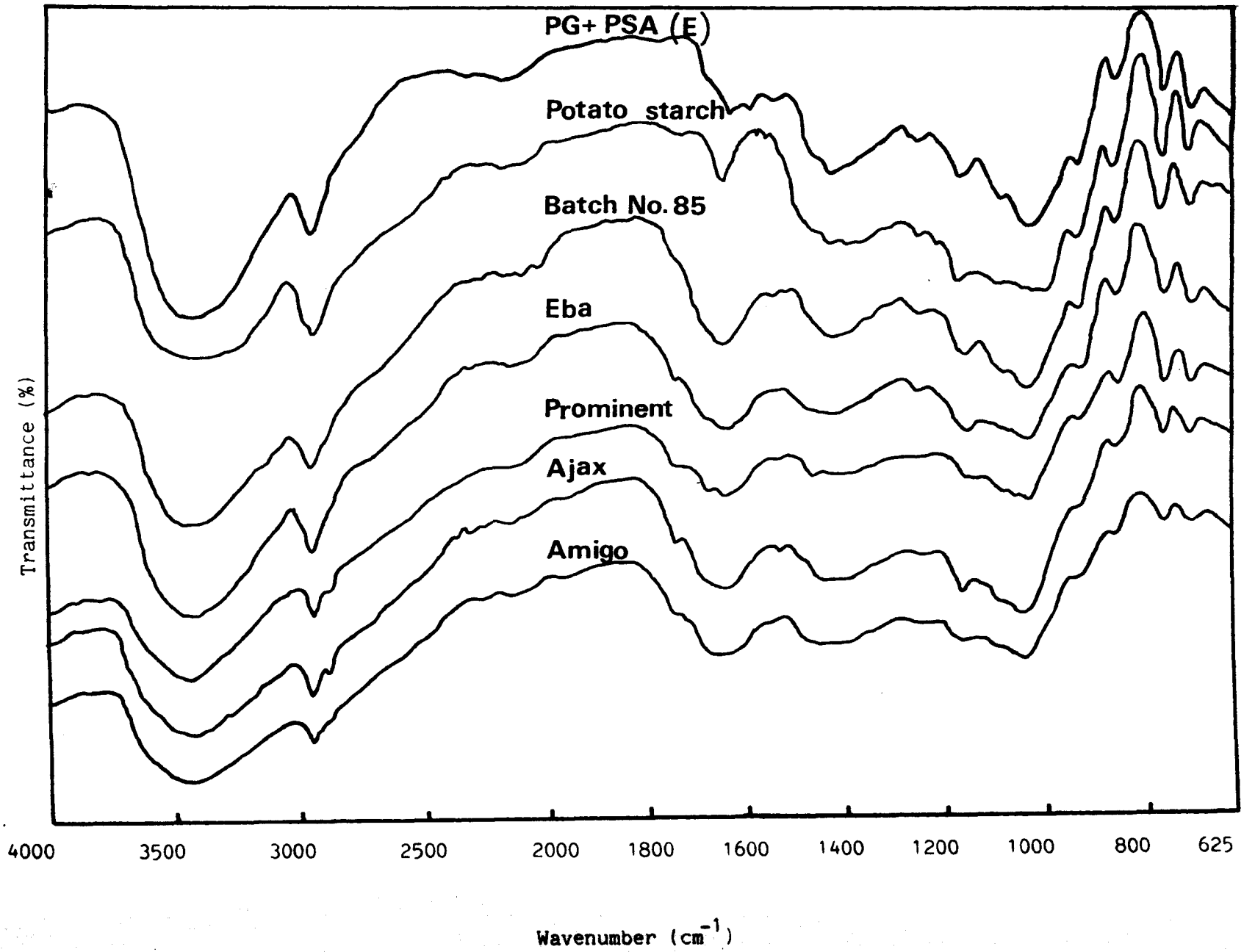
For qualitative analysis of the spectra, the base-line or ratio method was used as illustrated below:



A straight line was drawn at the base of the band and the intensities 'P' and 'Po' were measured at the absorption peak. The difference in intensities between 'Po' and 'P' was calculated and then converted to absorbance value.

Infra-red spectra of potato granules are shown in Figure 71, and the absorbance values of the absorption bands at wavelengths; 935, 855 and 760 cm^{-1} are given in Table 20.

Figure 71. Infra-red spectra of potato granules, potato starch and extrudates.



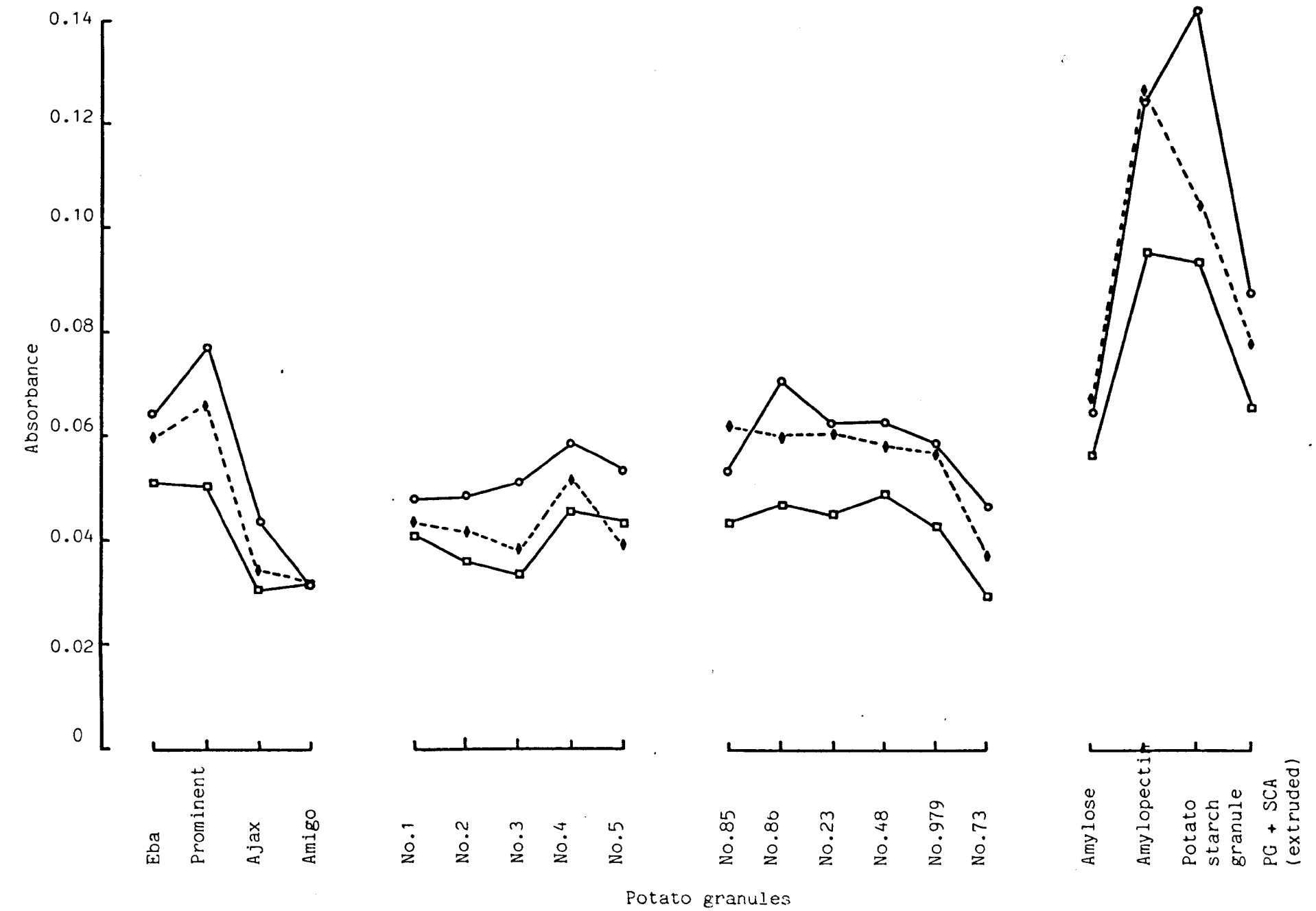

Absorbance values at different wavelengths; 935 cm^{-1} (o——o), 855 cm^{-1} (♦- - - -♦) and 760 cm^{-1} (□——□)
Absorbance
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0
Eba
Prominent
Ajax
Amigo
No.1
No.2
No.3
No.4
No.5
No.85
No.86
No.23
No.48
No.979
No.73
Amylose
Amylopectin
Potato starch granule
PG + SCA (extruded)
Potato granules

Table 20. Absorbance values of the absorption bands at different wavelengths.

Samples	Absorbance value		
Potato granules	935 cm^{-1}	855 cm^{-1}	760 cm^{-1}
Eba (S)	0.060	0.051	0.064
Prominent (S)	0.067	0.050	0.077
Ajax (U)	0.034	0.030	0.043
Amigo (U)	0.031	0.031	0.030
Batch No. 1	0.043	0.042	0.048
Batch No. 2	0.042	0.036	0.048
Batch No. 3	0.038	0.033	0.051
Batch No. 4	0.051	0.046	0.058
Batch No. 5	0.039	0.043	0.054
Batch No. 85	0.062	0.043	0.053
Batch No. 86	0.060	0.047	0.071
Batch No. 23	0.061	0.045	0.062
Batch No. 48	0.058	0.049	0.063
Batch No. 979	0.057	0.043	0.058
Batch No. 73	0.037	0.029	0.047
Amylose	0.067	0.057	0.065
Amylopectin	0.127	0.096	0.126
Potato starch granules	0.105	0.094	0.143
Extruded (PG + PSA)	0.077	0.066	0.088

(S) Satisfactory potato granules
(U) Unsatisfactory potato granules

6.4. Discussion

Differential scanning calorimetry

The phase transitions which starches undergo on heating in the presence of water have been studied in recent years by the technique of differential scanning calorimetry. When native starches are heated at high water content (volume ratio, v, >0.7) a single gelatinisation endotherm (called the G transition) was observed in the temperature range of 65-75°C (Stevens and Elton, 1971, Hollinger et al., 1974, Donovan, 1979, Biliaderis et al., 1980). The G transition was not observed during the heating of potato granules. This is not surprising because the potato starch granules had already been gelatinised during the add-back process. Instead an endotherm was observed at 55°C (designated as M_L) during the heating of unsatisfactory potato granules, but not for satisfactory granules (Figure 58). The same endotherm (M_L) was also observed during the heating of the potato granule-GMS complex (Figure 54). However, defatted unsatisfactory granules do not show this endotherm. The results strongly suggest that the M_L transition is due to the melting of GMS and that unsatisfactory potato granules contain excess GMS.

When starches are heated in limited amounts of water ($0.45 < v < 0.7$), the melting of the starch crystallites occurs as a separate transition at a temperature considerably higher (80°-90°C) than those observed for the gelatinisation transition (Donovan, 1979, Eliasson, 1980, Biliaderis et al., 1980). Again, this endotherm was not observed for both satisfactory and unsatisfactory potato granules, because all the starch crystallites had already been melted during the cooking of the potatoes. However, an endothermic transition (designated as M_{A-L}) was observed at a higher temperature of about 107°C. The enthalpies of this transition were bigger for the unsatisfactory potato granules (Figure 60). This transition can be reduced or eliminated by extraction

of potato granules with methanol. This same endotherm was also obtained on heating the potato granule-GMS complex (Figure 54). A similar high temperature endotherm at about 100°C was also observed when maize and wheat starches were heated, but not potato or waxy maize starches (Donovan and Mapes, 1980; Eliasson, 1980; Kugimiya et al., 1980). However, when potato starch was heated with lipid such as lysolecithin, the endotherm appeared (Eliasson et al., 1981), and the x-ray pattern of the dried sample showed some weak lines characteristic of a V-type starch-lipid complex (Kugimiya et al., 1980). The formation of the starch-lipid complex can be seen as an exotherm, simultaneously with and immediately following the gelatinisation endotherm. In most cases it could not readily be distinguished especially in potato granules. On the above evidence, the M_{A-L} transition were identified as arising from the melting of the crystalline phase of the V-type amylose-lipid complex.

The enthalpies of the M_{A-L} transitions were slightly larger for the unsatisfactory potato granules compared to the satisfactory granules (Figure 60). Indeed, it seemed that the unsatisfactory potato granules have excess GMS which can form a complex with almost all the available starch on the potato granule surface and perhaps some in the interior of the granules having gained entrance by diffusion, while any not complexed will appear as the M_L endotherm at 51°C. From this study, it seemed clear that the unsatisfactory extrusion response of some potato granules was in reality due to the excess GMS. This was confirmed by free-fat analysis which showed a significantly higher free fat content in unsatisfactory potato granules.

When the extrudates produced from satisfactory potato granules were heated, only the M_{A-L} transition was observed, similar to the one given by satisfactory potato granules (Figure 59). The enthalpies of this transitionwere slightly bigger than those of the potato granules. This suggests that the extrusion process promotes the formation of the starch-lipid complex either by expressing out more soluble starch which

then complexes with GMS or reordering of the starch molecule for complex formation. The enthalpies increased slightly when potato snack additives were added (Figure 59). PSA contains GMS which was able to bind with more starch. However, because of the small size of the M_{A-L} endotherm and the sloping baseline at high temperature, the actual determination of the enthalpy was rather difficult.

The storage of unsatisfactory potato granules at different temperatures (20, 30 and 44°C) caused a decrease in the enthalpies of the M_L transition, but the decrease was not proportional to the increase in size of the M_{A-L} enthalpies (Figure 61 and 62). This might be due to the GMS forming some complexes with amylopectin and other cell components. The slight increase in the M_{A-L} enthalpy indicated that during storage, changes occurred which resulted in the formation of some amylose-lipid complex.

An exotherm was also observed when extrudate and potato granule-GMS complex were reheated again after the first heating and cooling. The exotherm (designated as Mx), occurred at about 64°C, together with an M_{A-L} transition as shown in Figure 55. The size of the exothermic peak did not seem to be related to the GMS concentration (Figure 56). On subsequent reheating and cooling, the enthalpies decreased, accompanied by a progressive shift towards the lower temperature region. A limited investigation was mounted to resolve the mystery of this peak by heating up a series of samples containing possible components of potato granules such as pectin, cellulose, amylose, amylopectin and cell wall material, individually, and together, and with GMS, but in all cases no exotherm was observed.

X-ray diffraction

The production of potato granules involves changes in molecular organisation of the starch fraction which is reflected in their x-ray

diffraction patterns (Figure 65). Native potato starch has a typical B-pattern according to the classification of Katz and van Itallie (1930, with the characteristic peak at 2θ = 5.6°. The precooked potato starch also has a B-pattern, but with a smaller 2θ = 5.6° peak, while the cooked potato showed a predominantly A-type pattern with a very small 2θ = 5.6° peak. Both the mash-mix and potato granules had strong A-patterns. The conversion of B- to A- type pattern as a result of heating potato starches, had also been reported by Sair and his co-workers (Sair and Fetzer, 1944; Sair, 1946, 1967). They found that the x-ray pattern of potato starch can be changed from the B-type to A-type by heat-moisture treatment (starch with 27% moisture is heated in a sealed container at 90-100° for 16 h). The changes in the x-ray patterns indicate that the crystallites have either melted or recrystallized or at least have undergone reorientation. In the potato granules, these changes also involve a decrease in the degree of crystallinity, from about 100% in native starch to about 62.3% in mash-mix, shown in Table 19.

The x-ray patterns of potato granules were basically of the A-type (Figure 67). The principal indices of the patterns were 2θ = 15.2°, 17.1°, 19.5°, 23.2° which correspond to interplanar spacing of 5.88, 5.24, 4.62 and 3.91°A, respectively. These values agreed well with those given by Zobel (1964). There was a difference in x-ray patterns between the satisfactory and unsatisfactory potato granules in that the unsatisfactory granules have a stronger peak at 2θ = 19.5°. Somewhat surprisingly the 3 samples of potato granules prepared under different processing conditions all gave a strong A-pattern. It was anticipated that, that sample in particular, which had only been cooled, riced and then preserved at 4°C overnight would exhibit the B-pattern as a substantial component. In the event this was not observed, the A-pattern dominant after drying, the B-pattern being almost non-existent.

The potato granule-GMS complex also showed a very strong peak

at 2θ = 19.5° (Figure 66) which is quite characteristic of the V_h-pattern (Zobel, 1964). However, not all the peaks of the V-pattern are visible which is probably due to the strong A-pattern superimposed on the weak V-pattern of the starch-lipid complex. The x-ray results showed a correlation with the DSC results, in both cases the unsatisfactory potato granules had higher levels of GMS and starch-lipid complex than the satisfactory granules.

The percentage crystallinity data in Table 19 did not show any distinguishable differences between the satisfactory and unsatisfactory potato granules. But it seemed as though the unsatisfactory granules had a slightly higher degree of crystallinity, which is a result of the stronger peak at 2θ = 19.5°.

The x-ray patterns of the extrudates were essentially of the A-type (Figure 69), but the patterns were weaker than those of the potato granules. There was also a general decrease in degree of crystallinity (Table 19). This was due to the disorganisation of the starch macromolecules during extrusion into a less organised structure, but still retaining the general molecular order. The V-amylose pattern was very weak, denoted by a small peak at 2θ = 19.50°. Its obscurity could be due to the strong scattering from the amorphous structure or to the fact that the x-ray technique is not sensitive enough to pick up small quantities of the starch-lipid complex. The addition of additives tend to decrease the degree of crystallinity and gave rise to a more amorphous structure. The role of the additives is not adequately understood. However, it seemed reasonable to say that the additives had the clear ability to disorganise the starch macromolecules during extrusion.

The effect of moisture content on the intensity of the diffraction pattern was also studied. A dry potato granule sample (~ 7% moisture) gave a rather amorphous pattern without any distinguishable peak (Figure 70). The amorphous 'halo' centered near 2θ = 17.5°. As the moisture

content was increased the intensities of the diffraction peaks became stronger. The strongest pattern was obtained with potato granules that had been equilibrated at a relative humidity of 97% or 37% moisture. The same observations were reported by Guilbot et al. (1961); Sterling (1960)and Hizukuri et al. (1964). Working with potato starch, Nara et al. (1978) found that the relative crystallinity of potato starch at 40% moisture was 1.61 times the crystallinity at 24% moisture. These observations suggest strongly that water molecules play a major role in the crystalline organisation of hydrated potato starch.

Infra-red spectroscopy

The infra-red spectra of different potato granules were quite similar and each spectrum consisted of several absorption bands at wavelengths of 2900, 1640, 935, 855, 760 and 710 cm^{-1} (Figure 71). The bands at 2900 and 1640 cm^{-1} are due to the vibrational modes of water, those at 935 and 760 cm^{-1} to the α-D-glucopyranoside ring, the 855 cm^{-1} band due to the cyrstalline contributions from the polymer, while the 710 cm^{-1} band as yet has not been characterised. Three other bands (1295, 1256 and 760 cm^{-1}) were expected, but in fact were not observed. They are due to chain folding and metastable conformations of the polysaccharides, respectively (Koenig and Vasko, 1970; Vasko and Koenig, 1970). These 3 bands were observed in studies using preparations of amylose and amylopectin. Thus their absence in the spectra of potato granules was not altogether surprising as potato granules are a mixture of polymers.

To compare the differences between the spectra, a quantitative analysis in terms of absorbance values was made for the absorption bands at 935, 855 and 760 cm^{-1}. The results are shown in Table 20. These three absorption bands were chosen because they provided more information on the structure and nature of the starch, whereas the 2 bands at 2900

and 1640 cm^{-1} are only due to water. There was no distinct difference in absorbance values between the satisfactory and unsatisfactory granules. Samples such as Ajax and Amigo had lower absorbance values for all the 3 bands compared to Eba, Prominent and No. 85. The significance of this is not well understood. It is possible that the excess GMS that was present in Ajax and Amigo affected the molecular vibrations and oscillations of the atoms & molecules by altering their spatial arrangement, valence forces and intermolecular forces, thus modifying the intensity of the absorption bands.

Quantitative analysis of carbohydrate materials using infrared spectroscopy is difficult, due to the problem of preparing samples having similar weights. Moreover not all the absorption bands have been characterised yet because of the limited preliminary structural information available from other physical techniques.

ROLE OF WATER IN POTATO GRANULES DURING EXTRUSION AND FRYING

7. Role of water in potato granules during extrusion and frying

Results in Section 3.7 showed that the amount of water present during the extrusion of potato granules had an important influence on the extrudates produced and probably their frying characteristics as well. The role of water and its physical state, whether it is bound or free in the potato granules is not known. It was therefore essential to examine the state of the water in potato granules. The differences in bound water content might, for example, account for the different extrusion response of the potato granules and the blistering effect of the extrudates.

The investigation was carried out using a pulsed NMR spectometer, firstly, to determine the amount of bound water in the potato granules before and after heating and secondly, the changes in the water mobility in terms of spin-spin relaxation time (T_2) during the heating of a satisfactory and an unsatisfactory potato granule sample.

7.1. Introduction

Magnetic resonance is a phenomenon found in systems which possess both magnetic moments and angular momentum. The nucleus is composed of both protons and neutrons. If all protons and all neutrons are paired then the resultant nuclear spin is zero. However, if either a neutron or a proton, or both, are unpaired then the nucleus will possess a non-zero magnetic moment.

The spin quantum number of a nucleus is denoted by symbol I. Quantum mechanics shows that for a nucleus with spin I there are 2I + 1 possible values of magnetic moment given by:

$$\mu = m \gamma h$$

where h = Planck's constant

γ = magnetogyric ratio

m = I, I-1,.....-I+1, -I

In the absence of external fields all 2I+1 nuclear spin states will have the same energy. Application of a magnetic field, $\underset{\sim}{Bo}$, to a system of spins, produces an interaction energy of value $-\underset{\sim}{\mu o}\ \underset{\sim}{Bo}$. The consequence of this is that the states are split into 2I+1 energy levels each separated by an energy $E = \gamma \hbar Bo$.

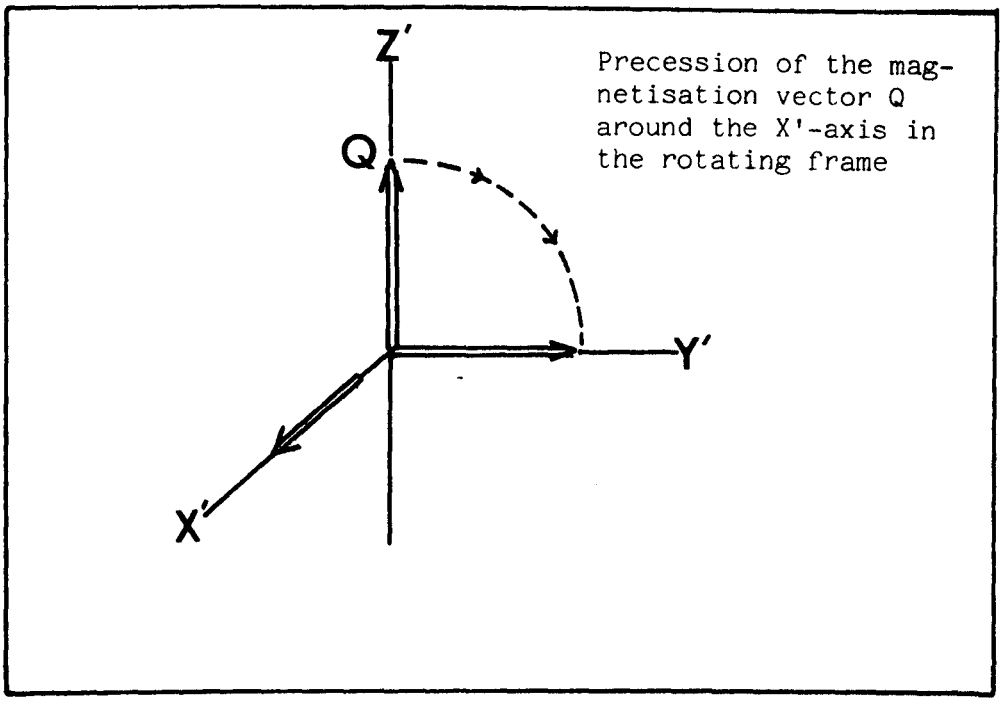
The existence of such a set of energy levels is detectable by the N.M.R. experiment.

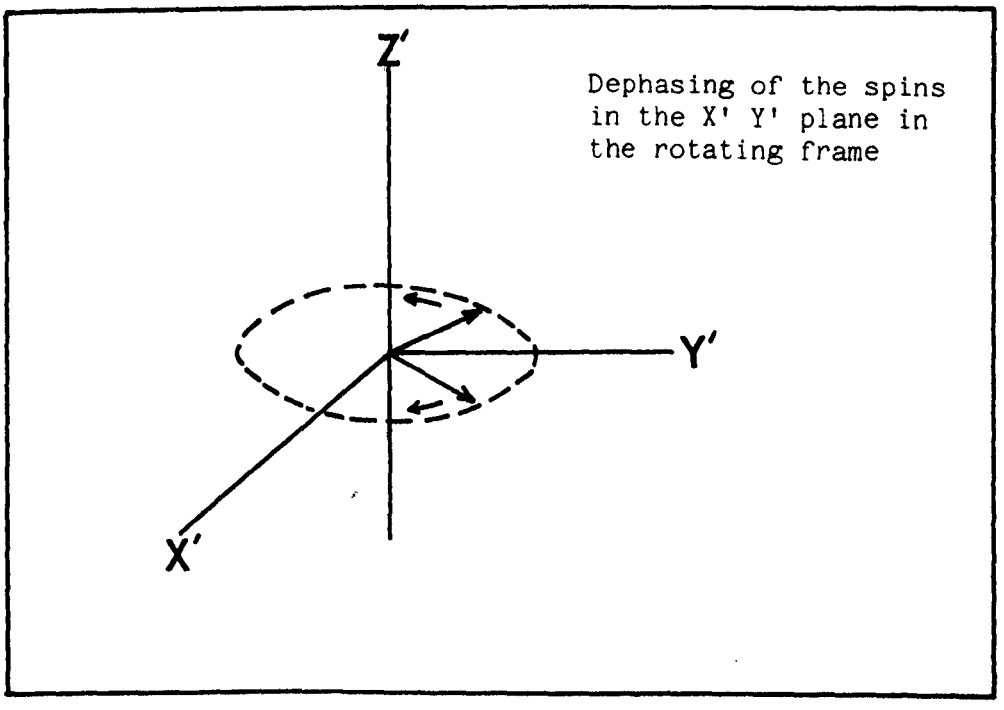
7.1.1. Pulsed NMR

The pulsed NMR technique consists of applying very short (few μs) and strong radio frequency (R.F.) pulses via a transmitter coil placed orthogonally to a polarising magnetic field B. The sample is positioned centrally in this coil. The transient response of the macroscopic magnetization Q of the spin system is recorded after the completion of the H_1 pulse, by monitoring the signal induced in a receiver coil. Often the sample coil is used in both transmission and receiving modes. The signal induced in the coil is applied to an RF amplifier, the band width of which may be reduced to improve the signal noise level. The amplified signal is phase detected at the RF frequency, ωo (or diode detected during setting up procedures) and is directly displayed on an oscilloscope screen, or stored digitally in a signal averager for further processing or constant display.

The next macroscopic magnetization Q of the spin is initially aligned along the z'-axis, defined Bo, at equilibrium. The subsequent motion of the macroscopic magnetization vector Q, may most easily be shown by utilizing a frame of reference having a set of cartesian axes x', y' and z', which rotate about the laboratory frame of reference Z-axis (coincident with the z'axis) at an angular frequency ωo. However, application of the circularly polarized R.F. field H, which operates along the x' axis for a time t_w, the pulse length, causes the magnetisation vector to precess about the x' axis in the y'-z' plane (Figure

Figure 72.


Z'
Q
Y'
X'
Precession of the magnetisation vector Q around the X'-axis in the rotating frame


Z'
Y'
X'
Dephasing of the spins in the X' Y' plane in the rotating frame

72). The reason for this is that the effective z'-component of magnetization in the rotating frame is zero and therefore, when viewed from the rotating frame, the magnetization vector precesses about the only field that it experiences, the H_1 in the x' direction. Q precesses from the x'-axis through an angle θ which depends only on the pulse length. Two pulse lengths are normally used which give rotations of $\theta = 90°$ or $\theta = 180°$. Thus immediately after the completion of the pulse, Q lies along the y' and z' axes respectively; these pulses are referred to as 90° and 180° pulses. The component of Q in the y' direction is monitored by the receiver after the application of each pulse, although the reference phase may be adjusted to monitor the magnetization in any direction in the x'-y' plane. After the application of a pulse, the magnetisation returns to equilibrium by the two relaxation processes T_1 and T_2 which are referred to as spin-lattice relaxation and spin-spin relaxation times respectively.

The observed time constant of a free induction decay (FID) is generally denoted by T_2^* and $T_2^{*-1} = T_2^{-1} + \gamma \Delta B$, where T_2 is the true spin-spin relaxation time and ΔB is the field inhomogeneity.

It is possible to eliminate the contribution from the field inhomogeneity during measurement of T_2 by using a Carr-Purcell (1954) pulse sequence as modified by Meiboom and Gill (1958). The Carr-Purcell technique consists of tilting the magnetization through 90° by applying a radio-frequency magnetic field perpendicular to Bo as described earlier. After a time, t, a 180° pulse is applied, also along the x' axis. This results in a spin echo (Hahn, 1950) at a time 2τ due to rephasing of spins which have been dephased as a result of being in different local fields due to inhomogeneity of the applied field.

This experiment assumes that over the time scale of the experiment, nuclear exchange between chemically shifted sites and diffusion between points of different field strengths are negligible. The 180° pulse

is followed by a train of 180° pulses, each separated by a time 2τ. Ideally the echo signal heights trace out the true spin-spin relaxation decay. The Meiboom-Gill modification requires a 90° phase shift between the initial 90° pulse and the subsequent 180° pulses; the train of 180° pulses is, in effect, applied along the y' axis (Figure 72). This again results in a train of spin echoes, the decay envelope of which is T_2. This sequence, however, compensates to the first order for possible RF inhomogeneities.

7.1.2. Experimental

7.1.2.1. Materials

Potato granules were supplied by Dornay Foods Ltd.

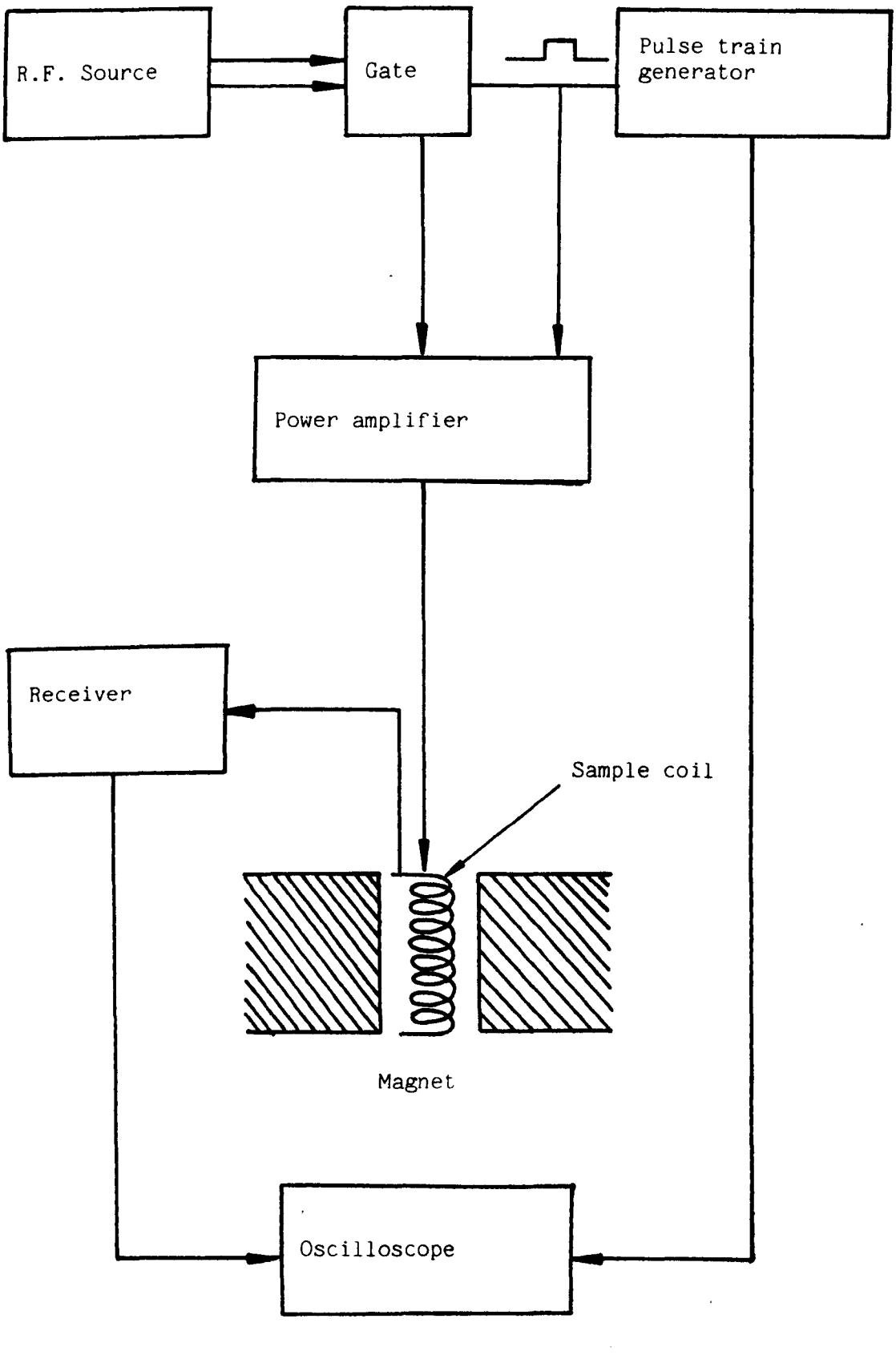
7.1.2.2. Apparatus

A block diagram of the pulsed NMR spectometer is shown in Figure 73. It was designed and constructed in the Food Science section of the Department of Applied Biochemistry and Food Science, University of Nottingham. The instrument was fitted with a sample temperature control facility to permit the measurement of relaxation times over a wide range of temperature (-60°C to +100°C).

7.1.2.3. Description of pulsed NMR spectrometer

A Carr-Purcell Meiboom-Gill (CPMG) train of pulses is fed to the sample coil via a poweramplifier. The resulting free induction decay and spin echoes are fed to alow noise amplifier and applied to a linear phase - coherent demodulator. The amplitude peaks of the resultant envelopes carry the information about the spin-spin relaxation time (T_2) of the sample.

Figure 73. Block diagram of NMR spectrometer.



The envelope peak amplitudes are signal averaged and punched onto paper tape which is subjected to computer analysis to obtain the values of T_2.

7.1.2.4. Method

The following investigations were carried out:

(a) The bound water contents for potato granules were determined before and after heating up to 90°C for 10 min.

(b) The T_2 values for a satisfactory (Eba) and an unsatisfactory (Ajax) sample of potato granules were determined at different temperatures from 20° to 90°C and with water contents ranging from 35 to 65%.

7.1.2.5. Sample preparation

Potato granules with the required moisture contents were prepared in specially made glass tubes of diameter 4 mm and length 6 cm . A constant sample height of 10-12 mm was used. The samples were carefully packed as uniformly as possible to minimize inhomogeneity. All the samples were equilibrated overnight at 5°C, and precautions taken to avoid loss of moisture from the samples during this period.

7.1.2.6. Procedure

The sample tube was positioned centrally in the sample coil and a maximum amplitude was achieved by carefully tuning the magnet after setting a 90° pulse. After a while a 180° pulse was set and the spin echo was adjusted to a suitable amplitude. Then a whole Carr-Purcell Meiboom-Gill sequence (90°, τ, 180°, 2τ) was initiated. The FID and

the spin echoes thus obtained were fed to a low noise amplifier and applied to a phase coherent demodulator.

The envelope peak amplitudes were displayed on the oscilloscope screen, signal averaged and punched onto paper tape which was subsequently processed for the T_2 values and the initial highest amplitude.

An electronic temperature control was used to set up the different temperatures; for temperatures below room temperature (20°C) liquid nitrogen was used.

To determine the bound water content, the initial T_2 amplitude was found for samples of known water content (50 g H_2O and 50 g starch) at 20°C and then after freezing to -10°C. The ratio of these two T_2 amplitudes gave the bound water content. The same operation was repeated after heating the potato granules to 90°C for 10 min and cooling down to room temperature.

7.1.3. Results and discussion

The amount of bound water in potato granules before and after heating to 90°C and their differences are shown in Table 21. The potato granules were heated to 90°C to simulate the conditions during extrusion. The bound water content of potato granules varied from 23 to 40%, compared to 23 and 25%, present in hydrated dough as reported by Daniels (1974) and Davies and Webb, (1969), respectively. The large variation in bound water content could be due to the lipid binding with the starch in potato granules. There was no clear difference in bound water content between the satisfactory and unsatisfactory potato granules. However, all the unsatisfactory granules seemed to show a slight decrease in bound water after heating, while the satisfactory granules generally showed an increase with the exception of a few (Figure 74). The same phenomena were observed for the satisfactory and unsatisfactory granules at different moisture levels (Figures 75 and 76), respectively. This effect could be attributed to the presence of higher amounts of V-amylose in the unsatisfactory potato granules, which has a more open structure compared to A-amylose. As a result the bound water could be more easily freed during heating.

It is quite likely that the bound water was not the factor influencing the extrusion response or the blistering effect as was first thought. During the frying of the extrudate it was observed that the blisters formed almost immediately as the extrudate was dropped into the oil. It seemed to suggest that it was the vaporisation of the free water out of the extrudate that caused the blisters to form. This view was supported by the fact that water binding energy of free water was much less than bound water, a difference of 150 cal/mol H_2O was reported by Soewarno, 1981, using tapioca flour with 63% moisture.

Table 21. Percentage of bound water of potato granules before and after heating.

Potato granules	Bound water (Before heating, %)	Bound water (After heating, %)	Change in bound water, %
Unsatisfactory potato granules			
Ajax (U)	23.0	21.5	-1.5
Amigo (U)	29.8	28.6	-1.2
Desirée (U)	34.8	33.5	-1.3
Pentland Crown (U)	23.3	22.2	-1.1
Maris Piper (U)	27.6	21.3	-6.3
Stara (U)	32.6	31.4	-1.2
Record (U)	27.0	23.9	-3.1
Satisfactory potato granules			
Eba (S)	33.1	36.9	4.0
Prominent (S)	25.1	32.8	7.7
Desirée (S)	30.3	31.8	1.5
Pentland Crown (S)	35.6	29.0	3.4
Maris Piper (S)	27.7	26.5	-1.2
Stara (S)	30.9	26.2	-4.7
Record (S)	29.8	27.5	-2.3
Batch No. 1	38.1	29.7	1.7
Batch No. 2	26.2	19.6	-6.6
Batch No. 3	30.1	16.7	-13.4
Batch No. 4	34.7	27.7	-7.0
Batch No. 5	37.2	31.1	-6.1
Batch No. 85	41.1	43.6	2.5
Batch No. 86	34.0	37.4	3.4
Batch No. 125	30.2	30.6	0.4
Batch No. 23	26.3	34.8	8.5
Batch No. 48	38.2	31.5	-7.3
Batch No. 35	30.5	41.8	11.3
Batch No. 73	35.7	39.7	4.0
Batch No. 118	38.3	47.4	9.1

Figure 74. Bound water content of potato granules at room temperature (▨) after heating to 90°C (▦) and the change in bound water before and after heating (⁘).

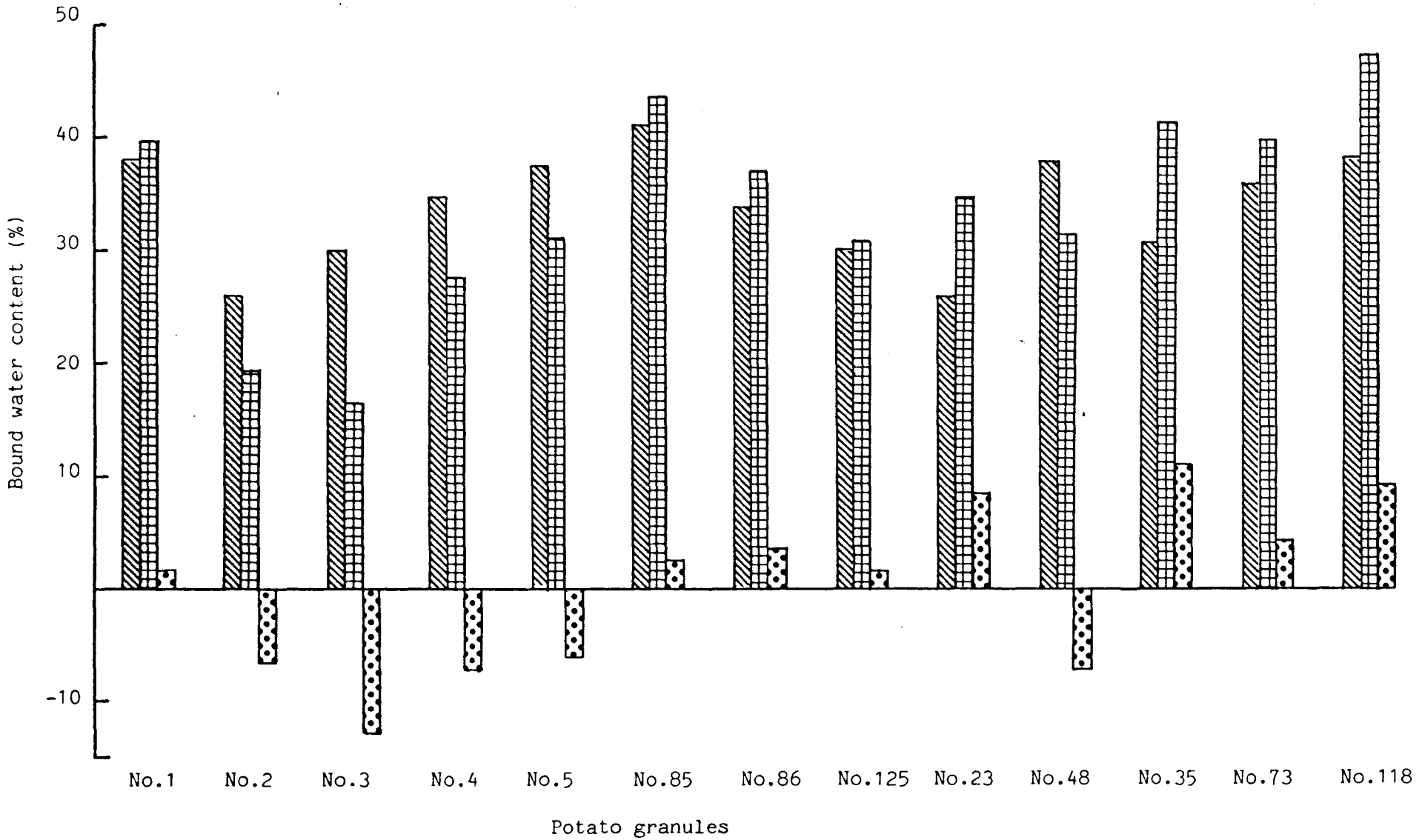


Figure 74. Bound water content of potato granules at room temperature (▨), after heating to 90°C (▦) and the change in bound water before and after heating (▩).

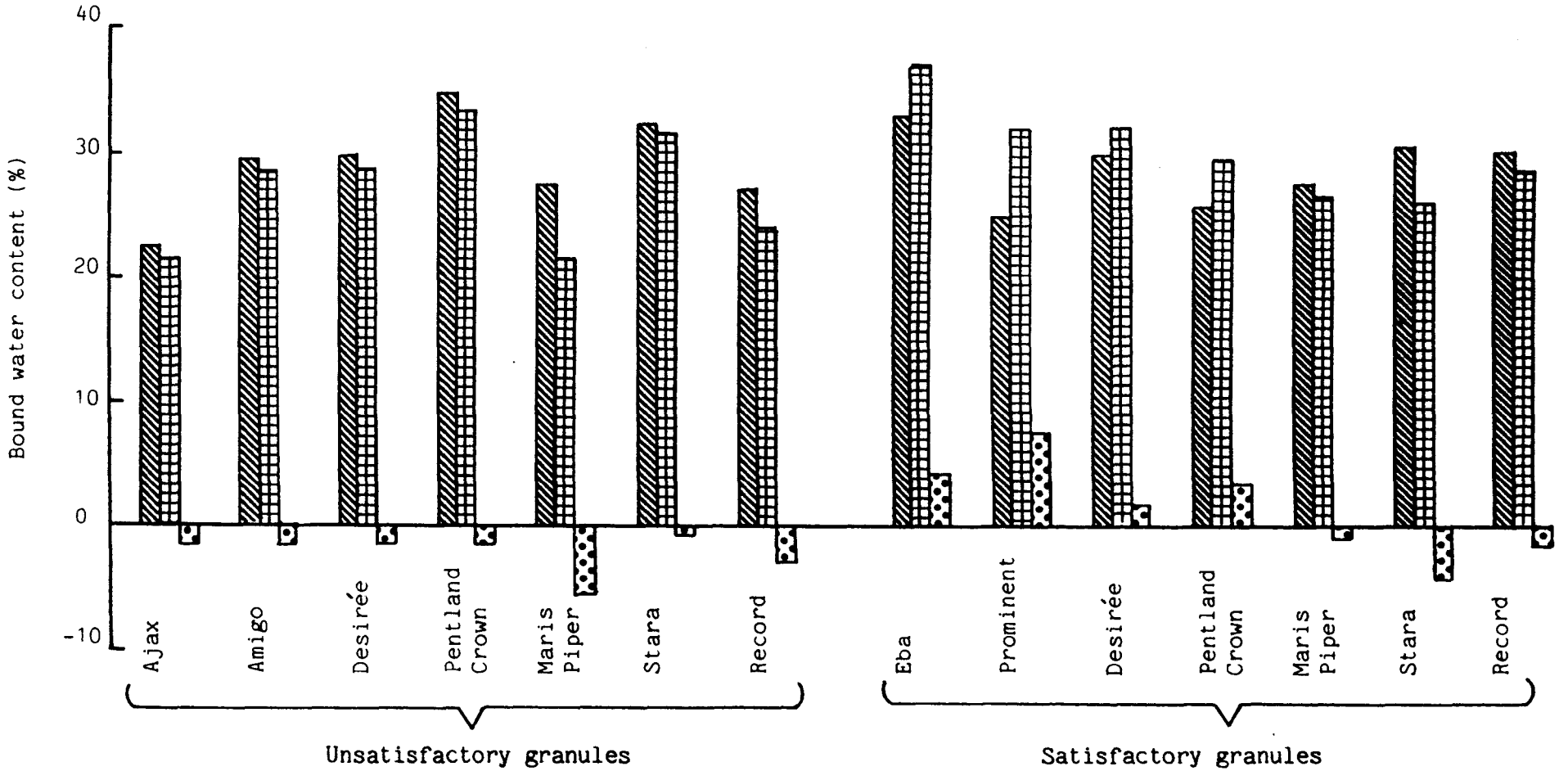


Figure 75. Bound water content of SATISFACTORY potato granules - EBA (at room temperature, after heating to 90°C and the change in bound water after heating) at different moisture levels.

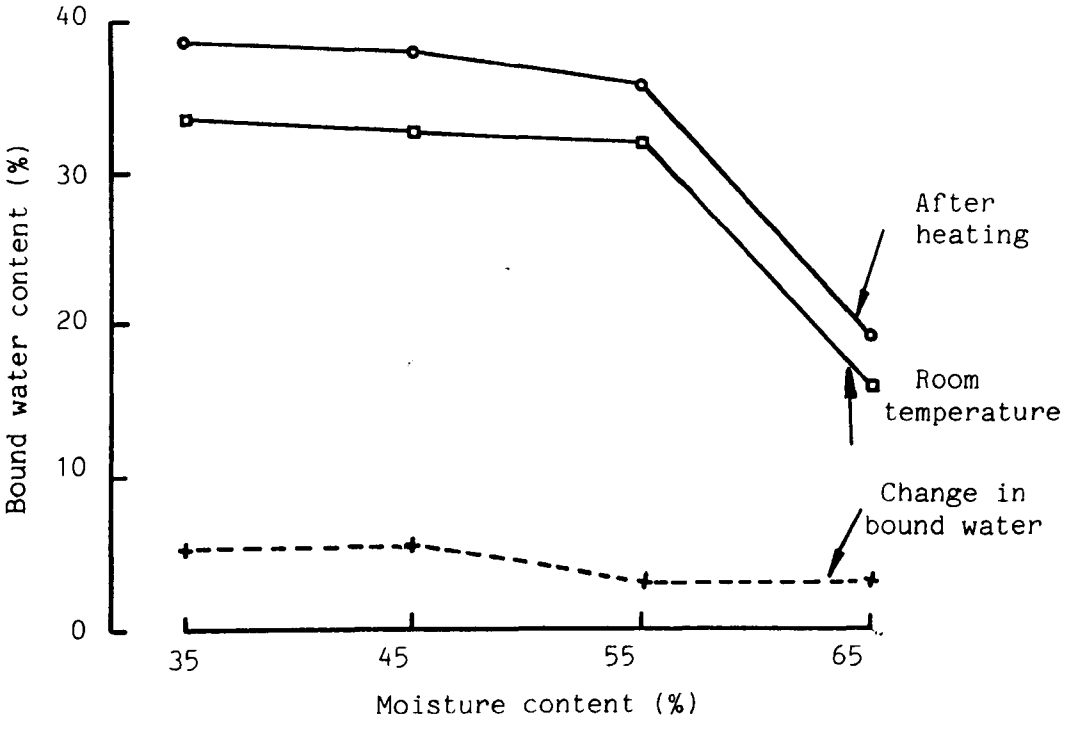
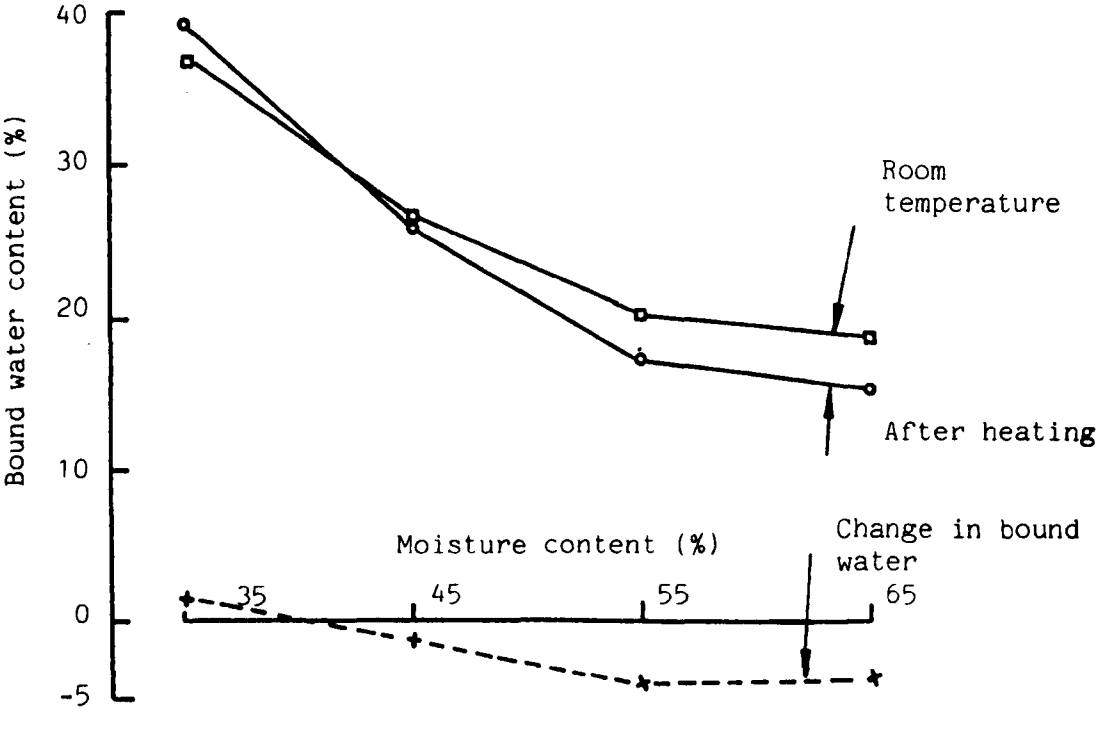


Figure 76. Bound water content of UNSATISFACTORY potato granules - AJAX (at room temperature, after heating to 90°C and the change in bound water after heating) at different moisture levels.

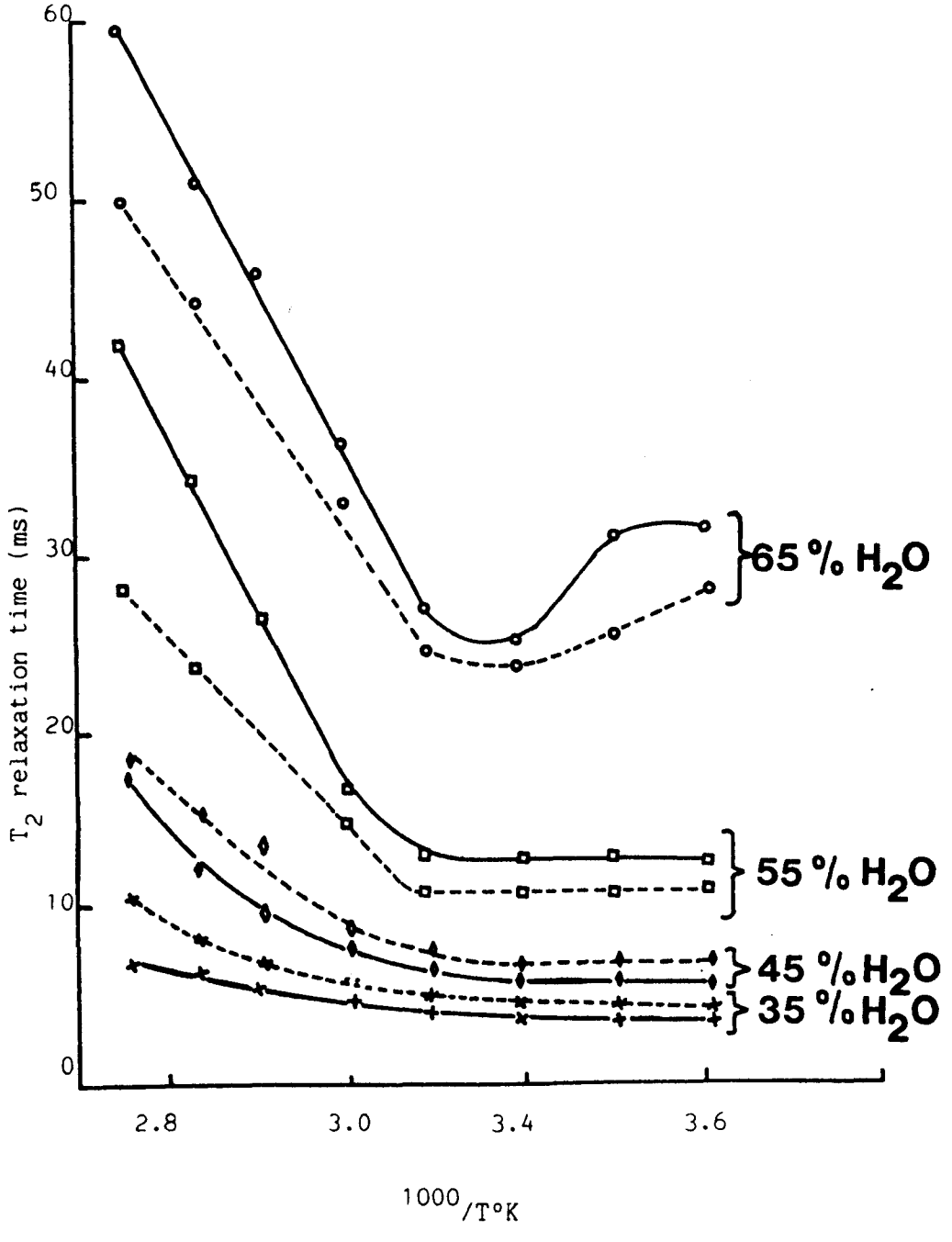


The variations of spin-spin relaxation time (T_2) with temperature and moisture content of satisfactory and unsatisfactory potato granules are illustrated in Figure 77. T_2 is a measure of the strengthof water binding and the values increased with increasing moisture content as reported by Leung et al., 1976. At 65% moisture, the T_2 decreased until 50°C and on further heating it rose rapidly. At moisture contents between 55% and 35%, the T_2 remained fairly constant until 50°C and then started to increase as the temperature rose. The increase was faster at 55% moisture than at 45% and 35% moisture. These results imply that the water molecules are more mobile at temperature above 50°C and above at higher moisture content of 65% and 55%. The satisfactory granules seemed to have a longer T_2 than the unsatisfactory granules at 65% and 55% moisture, but the trend was reversed for the 45% and 35% moisture content. Based on these results, during the extrusion of potato granules (at 70°C and 35% moisture), we would expect a longer T_2 for the unsatisfactory potato granules compared to the satisfactory granules. A longer T_2 impliesa shorter correlation time and more mobility of the water molecules. This effect is more likely to be caused by the presence of excess GMS in the unsatisfactory potato granules.

Figure 77. Temperature and concentration dependence of N.M.R. T_2 relaxation times of potato granules with varying water contents.

Unsatisfactory potato granules - AJAX

and satisfactory potato granules - EBA



8. General discussion

It is evident that in the experimental sections, a considerable number of avenues have been explored with the aim of determining the reasons for the twin problems of inadequate strip formation and blistering. Many of these have proved fruitless. There are, however, some very positive leads and these will now be collated and the whole picture examined.

(I) Strip formation

The studies with D.S.C. and x-ray diffraction (and supported subsequently by lipid analysis) have shown that the presence of an excess of GMS prevents strip formation and cohesion of granules. Such, of course, is the reason for its use in potato granules production since its addition prevents coalescence and sticking together of granules and yields a free flowing powder. The molecular basis for its effectiveness is now clear. V-amylose (amylose-lipid complex) is a single helix, complete in itself, whereas both A- and B- amyloses are double helices. Structure formation in a starch gel whether it be B-amylose or A-amylose (as in potato granules) of necessity demands cross-link formation through the helices. The V-amylose structure does not demand the same and indeed exists as an entity by itself.

The presence, therefore, of excess GMS at the surface of the granules will both "saturate" any surface amylose present converting such molecules to single helices of V-amylose with no capacity to crosslink, and, at the same time will likewise saturate any further amylose which may be expressed from the interior of the granules during the extrusion process.

At first sight then it is surprising that further GMS is one component of the potato snacks additives and is deemed to be essential. However, when we examine the position in detail there may

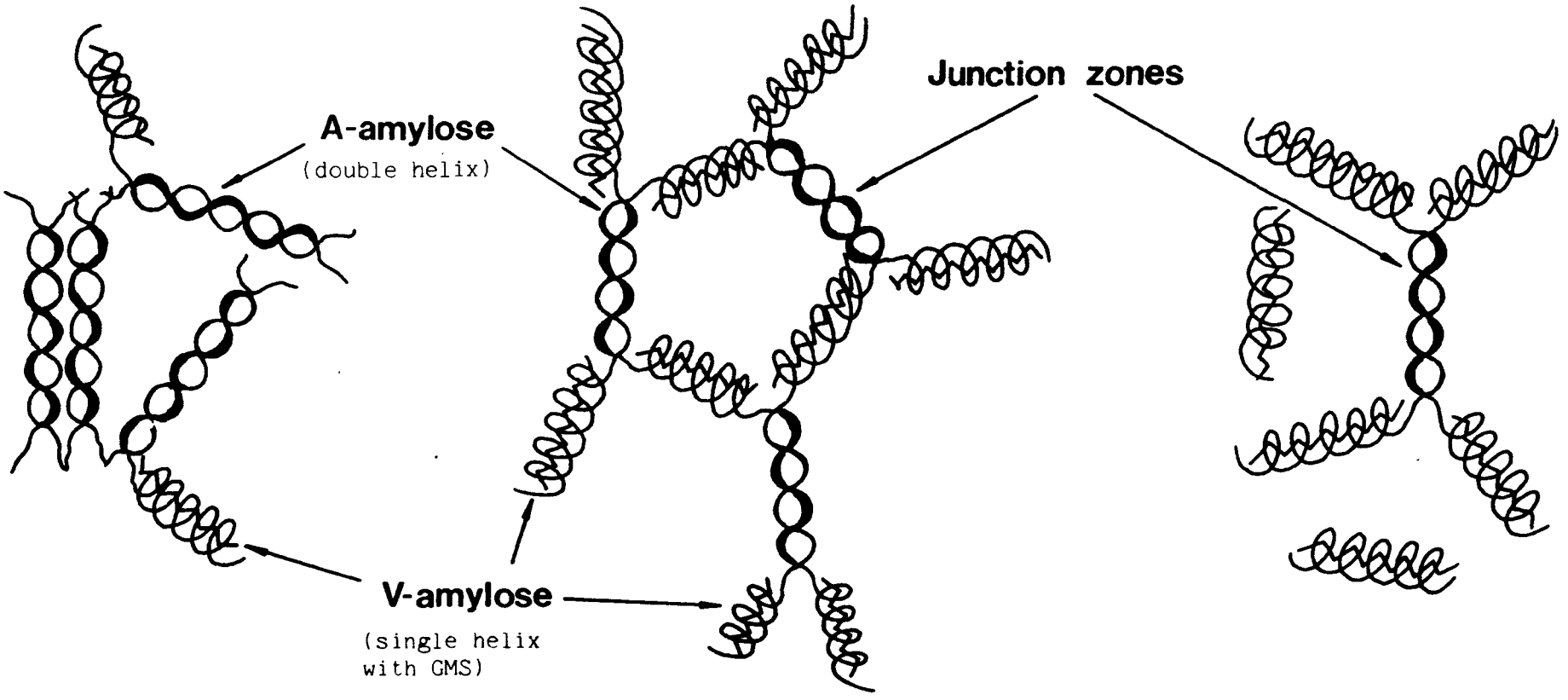
be some justification for this claim, though other possibilities cannot be ruledout. We may consider the process of extrusion and strip formation (and the role of GMS) as follows,

(i) Granules, in which the surface amylose is <u>just</u> saturated by GMS (and hence show no M_L peak on the D.S.C. thermogram) are extruded and amylose from the granule interior is expressed and forms a coherent network between the granules thereby binding them together.

(ii) The strength of this intergranular network is important. Too strong a network would of course lead to a strip which might show only minimal expansion on frying and possess the wrong textural properties. Such a strip has incidentally been produced through the addition of exogenous amylose to the mix prior to extrusion. The addition, however, of <u>excess</u> GMS at this stage would prevent formation of a coherent network. However, an intermediate level would lead to a loosely knit network which would both have adequate strength to form a ribbon but be sufficiently flexible to permit satisfactory expansion. These different situations are illustrated in Figure 78.

(iii) Supporting evidence for this general picture emerges from a number of areas. The D.S.C. thermograms of satisfactory granules, extruded granules and extruded granules + PSA show a progressive increase in the size of the M_{A-L} peak at 107°C. This clearly shows that satisfactory strip formation is accompanied by the formation of further amylose-lipid complex. It is

Figure 78. Effect of varying GMS contents on the structure of amylose gels.



(a) 'LOW' GMS content

(b) 'CORRECT' GMS content

(c) 'HIGH' GMS content

also interesting that the studies of x-ray crystallinity of strip, formed with or without PSA, shows that the former case exhibits a lower order - presumably because there is less x-ray order in the V- than in the A-form. It is possible, however, that other additives in the PSA may hinder the redevelopment of A-type crystallinity.

It is perhaps natural to ask whether it might not be possible to use potato granules with a somehwat higher GMS content and at the same time omit the GMS from the potato snack additives. On reconsidering the hypothesis given above about the mechanism of strip formation it will be seen that it is important to have the correct amount of GMS in the right place at the right time. For example, what might be deemed to be the correct overall quantity of GMS for granule AND snack production if supplied at the point of granule production might fail because, instead of there being sufficient to prevent aggregation of granules during production and then a residue available to control the texture of strip formation, this latter reservoir might disappear between granule production and extrusion by diffusion into the potato granules. (There is some evidence of this from the storage studies of granules with excess GMS). This might subsequently interfere with the expression of amylose from the interior of the granule or lead to an unsatisfactory texture of the resultant strip. Only further careful experiments under controlled conditions could show whether this was so.

(II) Blistering

At one stage in the project when it was realised that the potato granules were present in the A-starch form, it was suggested that the

B-form might be produced under certain conditions and with its higher water content might be responsible for blistering. However, the attempted preparation of granules via a route which, it was surmised, would be an extreme of any found in production (e.g. holding the moist-mix at 4°C overnight, prior to drying), did not lead to significant B-amylose formation or to blistering. This hypothesis was therefore discarded.

A number of other ideas and observations, as well as experimental evidence have led to what is believed to be a much firmer proposal.

(a) There is no correlation between the bound water content and blistering. If there were, we might have expected this correlation to be evident at the end of the frying process when the "free" water would already have been driven off and vaporisation of "bound" water might be expected to occur. Careful observation showed that in the frying process, which might require 15 s overall, the blistering commenced about 4 s after immersion in the hot oil, at a time when thermocouple measurements showed that the strip had attained a temperature of about 100°C, a figure it retained for a further few seconds before finally rising to the hot oil temperature of 180°C. The blistering therefore appears to be arising from the vaporisation of substantially "free" water.

(b) A study of the blisters has shown that they are symmetrical in their structure and nucleation of the bubble must therefore occur from the centre of the strip. Furthermore, the walls of the blister can be shown by microscopic examination to be composed of potato granules and not of a film of extruded macromolecules.

(c) There is no correlation between the presence and absence of blister formation with macromolecular order, cell wall composition, polysaccharide composition etc. The only correlation that appears is that a high level of total soluble starch (i.e. starch on the exterior of the granules) appears to be related to the capacity to blister. (The tendency to blister was also found to be somewhat related to cold Brabender measurements performed by Dornay Foods Ltd). Such samples with this high free soluble starch content and blistering tendency are also characterised by a lower elasticity of the strip and greater resistance to rupture under tension (i.e. having a higher breaking strength). The picture emerges, therefore that where there is an abundant and well developed intergranular network of polysaccharide, the tendency to blister is enhanced.

(d) Although the frying process is designed to develop the texture of the product by vaporising the water present which leads to modest puffing, blistering is clearly a situation where water vapour is unable to escape as fast as it is produced and therefore generates a somewhat higher pressure than normal leading to blister formation. It is therefore reasonable to conclude that samples which blister in fact possess a lower permeability to water vapour than non-blistering strip.

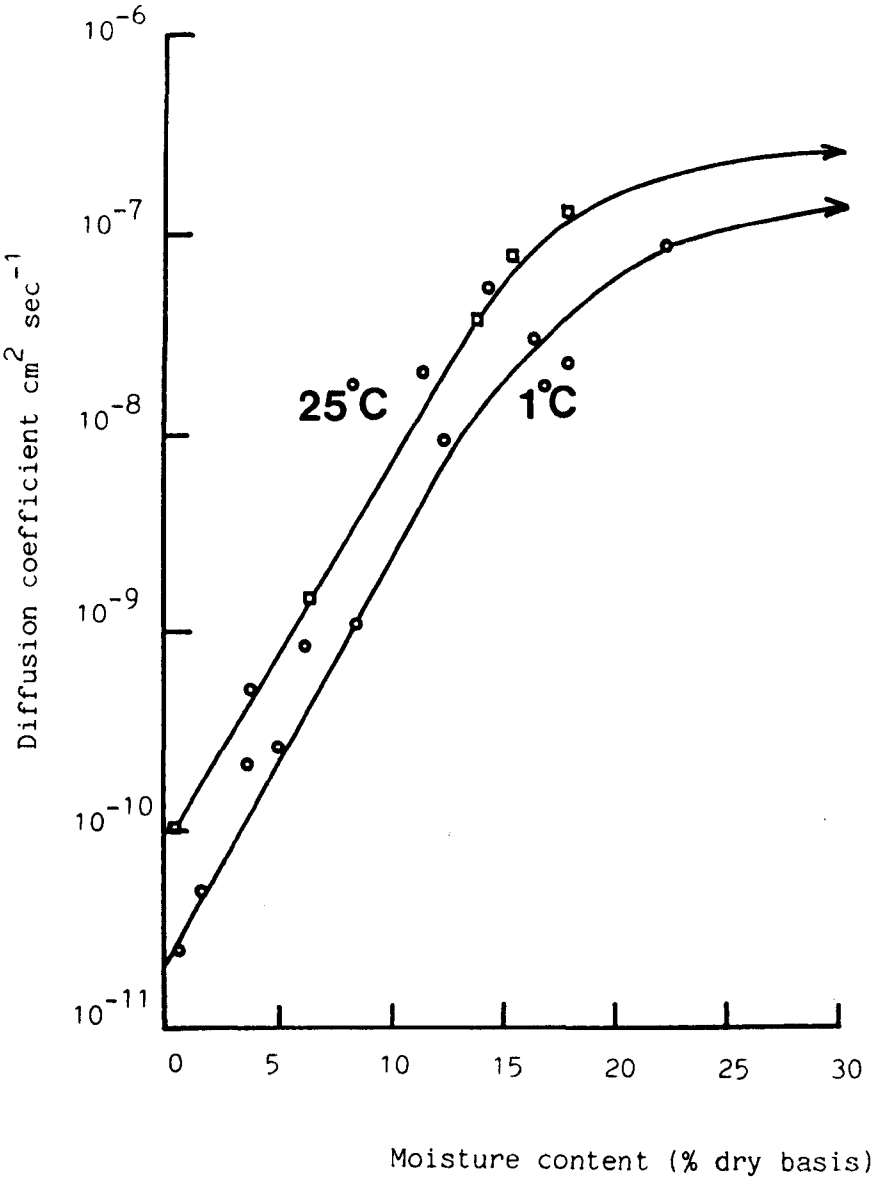
(e) Such a system offers an interesting example of the interaction of mass and heat transfer and using suitable assumptions a mathematical model has been developed (See Appendix 1) based on the above picture.

The broad assumptions that have been made are:

(i) That the water distribution in the freshly extruded strip is non-uniform. Although the extrusion temperature is only about 70°C, it is obvious that evaporative cooling from the surfaces of the strip is occurring after issue from the extruder die. Such a situation would suggest that the highest water content will be at the centre of the strip. Furthermore, water is added to the formulation just prior to entering to the extruder and mixed in to form a moist dough. The water content is then only 35% and from a study of Fish's data (Fish, 1959) on the diffusion coefficient of water on cooked potato tissue and gelatinised potato starch granules (Figure 79), it would appear that the diffusion coefficient would not permit full equilibration of the water uniformly throughout the whole macromolecular matrix inside as well as outside the granules during its progress through the extruder. If that be so, then the water concentration outside the granules will be somewhat higher than in their interior. Again, measurements of the water content of extruded strip immediately after cooking give values of between 28-29%, which suggests that any water diffusion processes are going to be quite slow and of the order of $\sim 10^3$s. One area of ignorance and uncertainty is how the diffusion coefficient may increase with temperature.

(ii) In contrast, we assume that the rate of heat transfer to the centre of the strip is rapid. This is reasonable both on physical grounds and experimental measurements

Figure 79. Diffusion of water in starch gel.



which support the view that this takes place with a time constant of <10 s.

The mathematical model shows that, with the above assumptions, the behaviour observed is consistent with the physical processes that are envisaged.

(a) For example: blistering is the result of high pressure being generated within the strip as a result of the vaporisation of water. The increase in pressure is dependent on the permeability of the "film".

(b) If the "film" is impermeable then the pressure and density in the strip will increase linearly with time during frying, without limit, whereas, if the "film" is permeable then the pressure and density become bounded and will settle to a uniform and constant value with time.

(c) The free (rather than the bound) water is responsible for the blistering phenomenon as the diffusion of bound water from within the granules to the exterior is a much slower proces..

(d) The highest pressure is localised at the centre of the strip.

We might attempt to make one or two practical deductions:-

(a) We would anticipate that there would be an inverse correlation between the blistering behaviour and the permeability, a high permeability being associated with

a low blistering behaviour.

(b) It would appear that blistering and poor strip formation are the two extremes of the operating region where potato snacks can be produced. Poor strip formation reflects an inadequate network, blistering, an over-strong network - therefore we would not normally expect the problems to coincide. However, it does need to be remembered, that the addition of PSA does lead to the production of extra free soluble starch, but the GMS prevents this being turned into an over-strong network. Therefore it might be possible to overcome blistering in certain materials by marginally increasing the GMS content of the extrusion "mix".

(c) Since blistering is a consequence of excessive water vapourisation, it might be thought that the problem could be 'alleviated' by reducing the water content of the dough-mix. However, other factors come into play. A dough of low water content is more viscous and therefore will be subjected to more "work" during passage through the extruder, such being the precise conditions which might enhance further expression of polysaccharide from the interior to the exterior of the granules. If this were the case, blistering might be exacerbated.

Conversely, marginally increasing the water content, (> 40%), because it lowers the viscosity and the working of the dough, might reduce the total soluble starch and minimise blistering.

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APPENDIX

Appendix 1.

Mathematical model of the blistering process

Introduction

The general hypothesis which has been described in the main discussion (see Section 8) depends on the appropriate interrelations of mass and heat transfer at a given time in the frying of the extruded strips.

To mathematically describe the process contributing to the phenomenon has the virtue of requiring a precise analysis of events and permits one to draw conclusions on physical considerations which might not be immediately obvious yet which may subsequently be susceptible to experimental test.

A porous membrane was chosen as the basic model to derive the equations governing the process. The mathematical manipulations were kindly performed by Dr. S. Hibberd and Dr. J.T. Holden of the Department of Theoretical Mechanics, Nottingham University.

Physical considerations

The relevant dimensions of the extruded strips are as follows:- width 2.5 cm.; thickness (which is probably most important) about 0.5 mm (500 microns). Since each granule has, typically, a diameter of 100 microns, the strip is about 5 granules thick.

The extrudate is fried in oil at 180°C for 10-15 s. It has been observed that the blistering took place early in the frying process (after 4 s). Experiments have shown that during frying there was a rapid rise in temperature to about 100°C and remained at that temperature for a short period of time (1-2 s), then followed by a further increase to the temperature of the oil. The formation of blisters tended to

be approximately symmetrical in that a similar size blister usually appeared in the same position on each side of the snack. There also seemed to be a higher incidence of blister formation near to the centre of the snack rather than towards the edges.

Porous membrane model

It is reasonable to assume that during frying the water in the extrudate (28-29%) is rapidly vapourised. The time scale over which heat enters the extrudate is given by:

$$t = 0 \ (d^2/D)$$

where d = half thickness of extrudate (strip)

D = thermal diffusion coefficient

0 = order

Most of the heat entering the extrudate will probably be due to conduction through the potato granules, rather than through the interstitial matrix or by convection. Taking $D = 1.5 \times 10^{-3}$ cm^2 s^{-1}, which is the value for water, then the appropriate time scale is $t \approx$ 0.4 s, which is consistent with our observation.

From examination of the frying process it is apparent that blistering takes place at the early stage during frying and presumably it is the free water, rather than the bound water which is responsible for the phenomenon. We would also anticipate that the diffusion of bound water from within the granules to the exterior is a much slower process, a typical diffusion coefficient for the escape of water is $D \approx 10^{-7}$ $cm^2 s^{-1}$, which gives a time scale for the release of this bound water of $t \approx 10^3$ s. However, some bound water is released during the 10-15 s of frying, since the ultimate moisture content is about 5%.

A possible mechanism which causes blistering would appear to be the formation of high pressure within the fried extrudate as a result

of the vaporisation of free water. The water vapour will expand and any obstruction to its escape will result in blister formation.

Two factors seem to determine the formation of blisters:

(i) The internal or water vapour pressure within the extrudate.

(ii) The strength of the network holding the granules together to form the extrudate.

This conjecture is supported, in part, by the observations that if the extrudate is left for a sufficiently long period it will not blister when fried. The conditioning period allows the free water to evaporate and thus reduce the likelihood of any high internal pressure and also enhance the formation of a stronger network by retrogradation.

A simple model which may prove useful is based on the following assumptions:

(I) That the dominant restrictions to this vapour movement are deemed to be the top and bottom surfaces of the extrudate. Such a "film" resistance represents the reduced permeability of the outer layers of the strip.

(II) The interstitial spaces between the potato granules are comprised of water vapour and air with an average local pressure 'P' and density 'ρ' . Outside the initial warming up period ($\approx$ 0.4 s) the system could be considered as isothermal and an appropriate equation of state might be:

$$P = K\rho \text{ where } K = RT \quad \ldots\ldots (1)$$

in which R = universal gas constant

T = ambient temperature within the extrudate during frying (100°C)

(III) The flow of water vapour and air is restricted by the upper and lower surfaces of the extrudate. We might assume that the flow rate through the surface is proportional to the pressure difference across the surface. This implies that the internal gases are restricted by a porous membrane across which the condition,

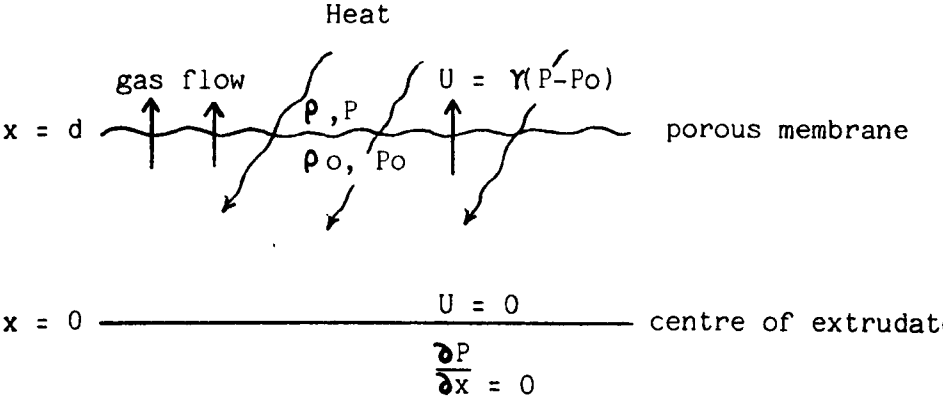
$$U = \gamma(P - P_o) \qquad \cdots\cdots\cdots\cdots \qquad (2)$$

at the surface must hold.

U = internal gas velocity

P-Po = pressure difference across membrane.

γ = permeability parameter



Porous membrane model

(IV) The heating causes the formation of water vapour from free water and volume expansion of any interstitial gases. Some equations governing this model are as follows:

In the first instance we assume a one-dimensional flow field perpendicular to the large flat surface of the extrudate with coordinate 'x' measured from the centre. The equation representing the conservation of water vapour/air mass is:

$$\frac{\partial P}{\partial t} + \frac{\partial (\rho u)}{\partial x} = \text{source} = \lambda \qquad \ldots\ldots\ldots \quad (3)$$

Where ' λ' represents the rate of increase of air/water vapour mass due to heating.

An equation for the motion of the internal gases is given by a momentum balance,

$$\rho \left(\frac{\partial u}{\partial t} + \frac{u \partial u}{\partial x}\right) = -\frac{\partial P}{\partial x} + \text{viscous forces}$$

Neglecting the viscous terms and making the reasonable assumption of low flow velocities, gives an equation of motion,

$$\rho \frac{\partial u}{\partial t} = -\frac{\partial P}{\partial x} \qquad \ldots\ldots\ldots\ldots \quad (4)$$

The boundary conditions associated with equations (3) and (4) are the assumed symmetry at the centre (x = o) yielding

$$u = 0 \ , \frac{\partial P}{\partial x} = 0 \quad \text{at } x = 0 \qquad \ldots\ldots\ldots \quad (5)$$

and the outer surface condition,

$$u = \Upsilon (P - Po) \qquad \text{at } x = \pm d \quad \ldots\ldots \quad (6)$$

Values for 'λ' will be difficult to estimate since the rate of heat input into the snack which leads to vapour formation is not easy to estimate. The assumed condition (2) could be investigated experimentally and a value for Υ can be determined.

Impermeable membrane

We now consider the conditions and governing equations in the case of an impermeable membrane.

In the absence of any gas flow within the extrudate then equations

(3) and (4), reduce simple to

$$\frac{\partial P}{\partial x} = 0 \text{ and } \frac{\partial P}{\partial t} = \lambda$$

whilst (1) gives $P = K\rho$

Solving this system for an assumed constant value for λ, gives,

$$\rho = \rho o + \lambda t \text{ and } P = Po + K\lambda t \quad \cdots\cdots\cdots (7)$$

where $Po, \rho o$ are the initial (ambient) values of pressure and density, respectively. The results (7) correspond to a uniform pressure and density which increases linearly with time without limit. In this special case in which there is no vapour movement the outer boundary condition plays no active role.

Permeable membrane

With gas movement through the extrudate then the outer surface boundary condition will play an important role. We can easily show that the vapour pressure governed by this system is no longer unbounded and we can calculate this ultimate limiting pressure. Looking for the long time (steady) solution, equations (3) and (4) simply give:

$$\frac{\partial(\rho u)}{\partial x} = \lambda \quad \text{and} \quad \frac{\partial P}{\partial x} = 0$$

Solving this will give P = constant = P_∞, say, and $Pu = \lambda Kx$

Making use of symmetry condition (5) and surface condition (6) will give,

$$\frac{P}{\infty}\left(\frac{P}{\infty} - Po\right) = \frac{\lambda K d}{\gamma}$$

from which P_∞ is given by,

$$\frac{P}{\infty} = \frac{Po}{2}\left[1 + \frac{(1 + 4\lambda K d)^{\frac{1}{2}}}{\gamma P_o^2}\right] \quad \cdots\cdots\cdots (8)$$

Thus the ultimate pressure reached is bounded; note that as $\gamma \longrightarrow 0$, corresponding to an increasingly impermeable membrane, the pressure as expected becomes unlimited as before. The resulting pressure is uniform which suggests that break-up could occur anywhere. An unsteady state analysis would give the variations in pressure with position before the pressure ultimately settles to a uniform, constant value. The symmetry at the centre line ensures that the pressure satisfies $\frac{\partial P}{\partial x} = 0$, indicating the likelihood of a maximum occurring at the centre.

Small-time scale analysis

To try and gauge some of the questions mentioned earlier, the physical behaviour of the model was examined for small times after immersion of extrudate into the hot oil. In the initial stages the density of the vapour will not be greatly different from the initial density and gas velocities will be very small. Hence we can assume:

$$\rho - \rho_o = \rho' << 1 \quad \text{and} \quad u << 1 \quad \text{initially.}$$

Under these assumptions the governing equations (3) and (4) can be linearised to give

$$\left.\begin{aligned} &\frac{\partial u}{\partial t} + \frac{k}{\rho_o}\frac{\partial \rho'}{\partial x} = 0 \\ \text{and} \quad &\frac{\partial \rho'}{\partial t} + \rho_o \frac{\partial u}{\partial x} = \lambda \end{aligned}\right\} \quad (9)$$

whilst the boundary conditions become,

$$u = o \quad \text{at } x = o \quad \text{and } u = \gamma k \rho' \text{ at } x = d \qquad \ldots\ldots\ldots \quad (10)$$

Equation (9) can be more conveniently written in characterstic form:

$$\frac{d}{dt}\left(\rho' - \lambda t + \frac{\rho_o}{\sqrt{k}}u\right) = 0 \quad \text{along} \quad C^+ : \frac{dx}{dt} = \sqrt{k}$$

and $$\frac{d}{dt}\left(\rho' - \lambda t - \frac{\rho_o}{\sqrt{k}}u\right) = 0 \quad \text{along} \quad C^- : \frac{dx}{dt} = \sqrt{k}$$

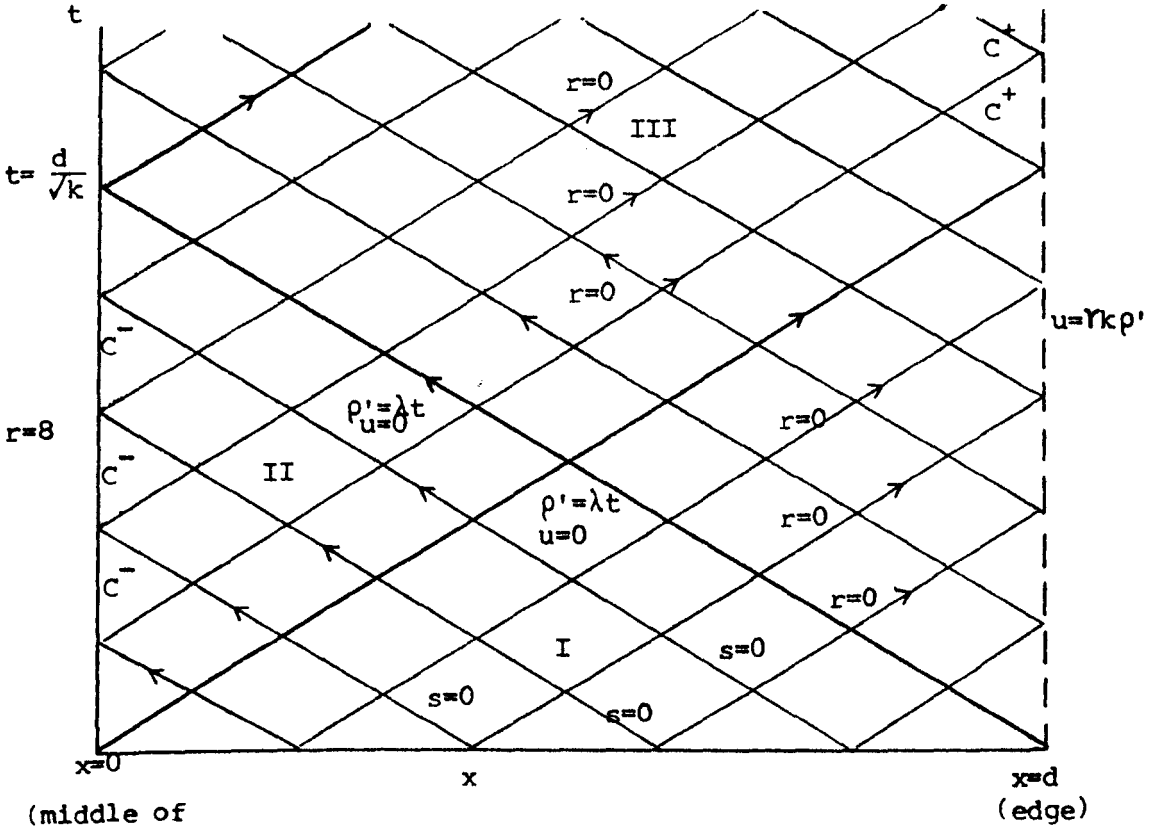
Defining Riemann invariants r and s by,

$$r = \rho' - \lambda t + \frac{\rho_o}{\sqrt{k}}u \quad \text{and} \quad s = \rho' - \lambda t - \frac{\rho_o u}{\sqrt{k}} \quad \ldots\ldots (11)$$

then r = constant along $C^+ : \frac{dx}{dt} = \sqrt{k}$

and s = constant along $C^- : \frac{dx}{dt} = -\sqrt{k}$ } (12)

The properties (12) state that all characteristics are straight and consequently the analytic solution is obtainable by construction.



In terms of the Riemann invariants,

$$u = \frac{\sqrt{k}}{\rho_o}\frac{(r-s)}{2} \quad , \quad \rho' = \lambda t + \frac{(r-s)}{2}$$

At the centre x = o, we have u = o, which gives the conditions that

$$r = s \qquad \ldots\ldots\ldots\ldots \qquad (13)$$

At the edge, x = d, we have $u = \Upsilon k \rho'$ which gives

$$\frac{\sqrt{k}}{\rho_o}\frac{(r-s)}{2} = \lambda t + \frac{(r+s)}{2}\Upsilon k$$

i.e.
$$s = -\frac{2\Upsilon\lambda k t + \left(\frac{\sqrt{k}}{\rho_o} - \Upsilon k\right) r}{\Upsilon k + \sqrt{k}/\rho_o} \qquad \ldots\ldots\ldots \qquad (14)$$

It is easy to show that within regions marked I and II, where r = o and s = o, will give

$$\rho' = \lambda t \qquad \text{and} \qquad u = 0$$

Within region III, r = o so at x = d,

$$s = \frac{-2\lambda\Upsilon k t}{\Upsilon k + \sqrt{k}/\rho_o} = \frac{-2\lambda t}{1 + \frac{1/\Upsilon\rho_o}{\sqrt{k}}}$$

This leads to a solution within region III of,

$$\left.\begin{aligned} u &= \left(\frac{\sqrt{k}}{\rho_o}\right)\frac{2\lambda\Upsilon\rho_o\sqrt{k}}{1+\Upsilon\rho_o\sqrt{k}}\left[t + \frac{(x-d)}{\sqrt{k}}\right] \\ \rho' &= \lambda t\left[1 - \frac{\Upsilon\rho_o\sqrt{k}}{1+\Upsilon\rho_o\sqrt{k}}\right] + \frac{d-x}{\sqrt{k}}\cdot\frac{\lambda\Upsilon\rho_o\sqrt{k}}{1+\Upsilon\rho_o\sqrt{k}} \end{aligned}\right\} \qquad (15)$$

At the edge x = d,

$$\left.\begin{aligned} u &= \frac{\sqrt{k}}{\rho_o} \cdot \frac{2\lambda\rho_o\sqrt{k}}{1+\gamma\rho_o\sqrt{k}}\, t \\ \rho' &= \lambda\left[1 - \frac{\gamma\rho_o\sqrt{k}}{1+\gamma\rho_o\sqrt{k}}\right] t \qquad \text{for } t < \frac{2d}{\sqrt{k}} \end{aligned}\right\} \quad (16)$$

The density increases linearly with time but at a rate reduced from the impermeable case by a factor depending on the permeability parameter From (15) it is clear that the highest pressures are achieved at the centre of the region. Calculations for times greater than shown are possible by continued construction but then the model is probably invalidated by values of pressure too large for the linear analysis.

The small time scale analysis does confirm that the highest pressures will be at the centre of the extrudate and the rate of increase in pressure will depend considerably upon the value of the permeability parameter (γ).

Further experimental work is in progress to determine some of the parameters, λ and γ, and a full scale analysis will be conducted to check the validity of the proposed mathematical model.