STUDIES ON THE CONCENTRATION OF APPLE JUICE BY REVERSE OSMOSIS

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ABSTRACT

The Reverse Osmosis (RO) process and its food industry applications were reviewed. Because most of the work published in the literature on the concentration of fruit juices by RO was empirical, it was decided to select one fruit juice (apple juice) and study the retention of certain components (namely sugars and acids) when that juice was concentrated by RO.

A method was developed for the analysis of sugars and non-volatile organic acids in apple juice. In this method, acids were precipitated as their lead salts from fruit ethanolic extracts, and the sugars in the remaining supernatant and washings were participated into aqueous methanol. These preparations with internal standards were then dried and converted to their trimethylsilyl derivatives for analysis by gas-liquid chromatography. The method provided a rapid and simple procedure for the concurrent separation, identification and quantitative snalysis of sugars and non-volatile acids in apple juice.

A pilot-plant scale Abcor TM5-14 RO module was used in this study so that the results obtained could be applied to industrial processing. Preliminary experiments were conducted with dilute salt solutions to ensure that the membrane performed satisfactorily, and to monitor any changes in the operating characteristics of the membrane as the experimental work progressed. These data provide the common means for comparing different RO systems. The results obtained established that the membrane performed satisfactorily, and that the membrane characteristics (Permeate flux and % Rejection) responded as expected to changes in the operating parameters of pressure, temperature, flow rate, concentration and operating time. The membrane characteristics did not alter significantly over the time during which the experiments reported here were carried out.

A current theory (the Kimura-Sourirajan analysis) was used in an attempt to predict the membrane performance of the RO module when the system sodium chloride-water was used as test solution. The Kimura-Sourirajan analysis had previously led to the development of a set of basic transport equations which, together with the correlations of the RO experimental data, enabled the prediction of membrane performance from a minimum of experimental data. The application of this analysis to the RO system under study did not establish any significant correlations between the solute transport parameter ($D_{AM}/K\delta$), and feed concentration and operating pressure; neither were the average mass-transfer coefficient values (k) significantly correlated with feed flow rate. Experimental results obtained suggested a more complex relationship between these parameters, and the narrow range of feed flow rates under which the RO system was able to be operated meant that the Kimura-Sourirajan analysis could not be used to meaningfully predict the performance of the membrane.

A further attempt was made to predict membrane performance from a knowledge of the Taft numbers of the sugars and acids present in the juice. Experiments carried out on model solutions of sugars and acids present as single components or as complex mixtures confirmed the Taft number as a criterion for predicting the organic rejection of the RO membrane. It was also established that molecular weight was indicative of solute rejection, higher molecular weights gave higher rejection by the membrane. Results obtained further confirmed the fact that the mechanism of solute rejections by RO cellulose acetate membranes involved both preferential absorption and capillary flow of solutes through the membranes.

Finally, actual apple juice was concentrated by RO and the results obtained on permeate flux and solute rejection confirmed those found previously with model solutions of sugars and acids. It was established that apple juice (initial concentration 11^{o}Brix) could be concentrated to 35^{o}Brix at 7C

and 99 atm pressure without any significant loss of sugars and organic acids. Experiments were also carried out to assess the advantage of operating at a higher temperature (20 C), since any increase in flux would be desirable from a commercial point of view. The end-to-end flux of the TM5-14 module was found to be 16.4 l/m^2hr at 20 C compared to 11.7 l/m^2hr at 7 C when single strength apple juice was concentrated to 35^{o}Brix under maximum pressure (99 atm), an increase in flux of 40%.

The pilot plant data thus obtained for the RO module were applied to a study of the feasibility of using RO as a pre-concentration step prior to evaporation. An RO plant comprising of 296 modules (membrane area 308 m^2) with a permeate flux of 20.7 l/m^2hr was found to be feasible for concentrating the juice from 11^{o}Brix to 20^{o}Brix in 7.5 hours.

The economy of such a process was also assessed, and compared with that obtained by using a triple effect APV plate evaporator.

A comparison of the concentration costs ($ /tonne of water removed) of the two systems revealed that RO was more than twice as expensive than evaporation ($122 compared to $51) for 900 operational hours per year, thus confirming results from the published literature, which also suggested that the cost of RO was competitive with plate evaporation when operated year round (6,300 hours/year). The results found in this study indicated that the annual operating costs for RO ($142,200) were almost twice as high as the equivalent for plate evaporation ($71,500). As well, the capital investment for RO was substantially higher than that for the equivalent plate evaporator ($700,000 compared to $282,300), thus making RO very unattractive for short seasonal operation.

Thus it is concluded that the use of RO as a preconcentration technique in apple juice processing will never be realised unless capital costs are reduced considerably and operating hours are

increased substantially. On the basis of this study, it is not financially economical for the Apple and Pear Board in Hastings to consider RO for the preconcentration of apple juice when the capacity of their present evaporator is no longer adequate.

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"Đường không khó vì ngăn sông cách núi, mà khó vì lòng người ngại núi e sông"

Tặng Ba tôi và người Mẹ quá cố

Dan Le Van

September, 1978

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CHAPTER ONE

A REVIEW OF REVERSE OSMOSIS

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1. INTRODUCTION

The 'Reverse Osmosis Membrane Process' is a general and widely applicable technique for the separation, concentration or fractionation of liquid foods. It consists in forcing the liquid food to flow under pressure through a selective porous membrane. The permeate is enriched in one or more constituents while the retentate becomes more concentrated. No heating of the membrane, and no phase change in the product, are involved in the process.

Despite the rapid advances which are being made with respect to this application, the process is still at its early stages of development. The basic principles involved are still controversial and no currently available theory on the mechanism of the process is beyond question (Sourirajan, 1970).

2. OSMOSIS AND REVERSE OSMOSIS

The term 'osmosis' is used to describe the spontaneous flow of pure water into an aqueous solution, or from a less to a more concentrated aqueous solution, when separated by a semi-permeable membrane (Fig. 1).

If the pressure on the aqueous solution is increased, osmosis is impeded, and at a sufficiently high pressure it is stopped all together. This pressure is called the osmotic pressure.

A further increase in pressure on the solution reverses the direction of flow, and pure solvent is removed from the solution by passage through the membrane, leaving a more concentrated solution behind. This process has been conveniently termed Reverse Osmosis (Fig. 2).

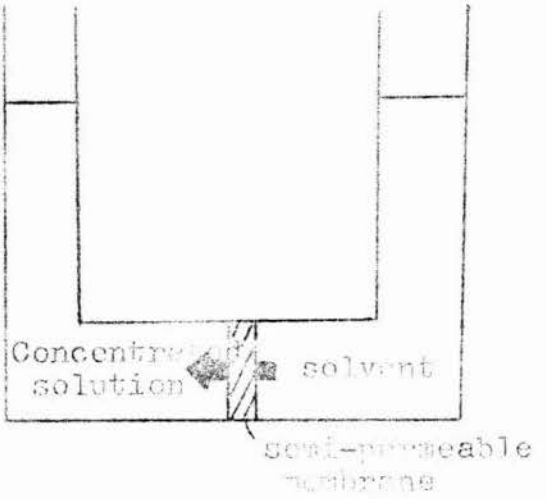


Fig. 1: Osmosis

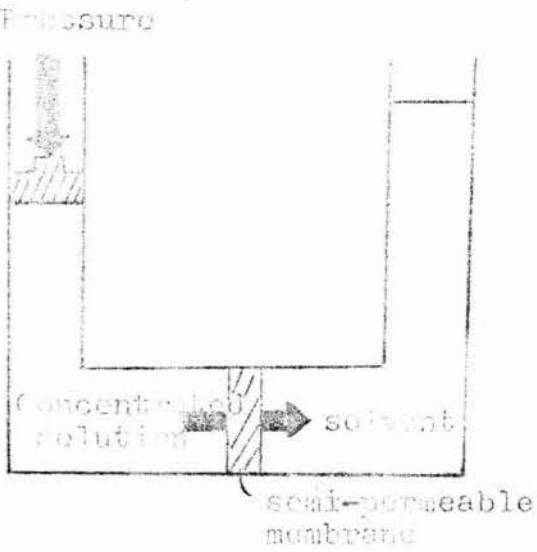


Fig. 2: Reverse Osmosis

The term 'Reverse Osmosis' has now gained such wide popular usage that it seems necessary to point out that the process is not restricted to the passage of water from aqueous solutions, nor is it restricted to 100 percent solute separation.

Neither 'osmosis' nor 'reverse osmosis' is an explanation of the mechanism of the process involved. Hence it is misleading to explain 'reverse osmosis' as the reverse of 'osmosis'. In both processes (under isothermal conditions) the preferential transport of material through the membrane is always in the direction of lower chemical potential.

Reverse Osmosis (RO) is a general term and it is more common to speak of ultrafiltration (UF) and hyperfiltration (HF). Although UF and HF use a pressurised feed system to a semi-permeable membrane to achieve separation, there are important differences between the two, leading to different applications. The main differences are summarised in Table I.

TABLE I: Characteristics of hyperfiltration and ultrafiltration

Hyperfiltration	Ultrafiltration
Solute molecular weight generally less than 1000	Solute molecular weight generally greater than 1000
Osmotic pressures of the feed can be up to 65 atm	Osmotic pressures of the feed are generally negligible
Operating pressures are up to 100 atm	Operating pressures are up to 7 atm
Solute is retained by a diffusive transport barrier	Solute is retained by molecular screening
The chemical nature of the membrane is important in affecting transport properties	The chemical nature of the membrane is generally unimportant

Source: Kearsley (1974)

3. MEMBRANES

Reid and Breton in 1958 found that the passage of saline water over a supported dense film of cellulose acetate (CA) at elevated pressure resulted in the permeation of water with a salt rejection of 95 percent or greater (Source: Podall, 1972). The water throughput rate or flux was, however, very low (less than 0.4 ℓ/day per m^2 of membrane area).

The first practical RO membrane was developed in 1960 by Loeb and Sourirajan at U.C.L.A. They discovered an aniso-tropic membrane which had a very thin active layer with a relatively thick but very porous supporting layer. By producing an anisotropic membrane, the excessive hydrodynamic resistance inherent in previous membranes was reduced and practical flux rates become possible. The salt rejection of this membrane was comparable to the one developed by Reid and Breton but the flux was improved to about 40 ℓ/day per m^2 at comparable pressures (Podall, ibid.). A membrane of this type consists of a very thin layer of dense polymer (about 0.2 microns thick) with pores of around 4Å in diameter supported by a porous sub-layer (about 100 microns thick), with pores ranging up to 0.4 microns diameter. The Loeb and Sourirajan discovery resulted in a surge of activity aimed at the

development of RO as a practical and useful method of fluid separation. In 1964, Havens Industry announced the commercialisation of a tubular system running on sea water and utilising a resin-starved fibreglass support tube for the CA membrane (Havens Industries, 1964). In 1965, the city of Calinga (California) was the first municipality to be supplied drinking water by RO (Source: Kavanagh, 1971). In 1966, the first commercially available package systems using RO were announced by Universal Water Corporation, Havens Industries, General Atomics, Aerojet General (Kavanagh, ibid.). For UF applications, CA is being increasingly superseded by non-cellulosics with greater chemical resistance and temperature stability. However, only cellulosic RO membranes are currently available commercially. CA membranes suffer from a number of limitations, mostly attributable to the polymer properties of the membrane material. They can generally only be used with aqueous solutions. Most must be kept wet, since if they dry out, the structure tightens and they become impermeable. Temperature above 60 C have a similar effect. They are susceptible to hydrolysis outside the pH range 3-8, and are sensitive to enzyme and microbial attack. However, these difficulties have been largely overcome by the use of different materials, so that newer membranes are far more versatile.

Current suppliers of commercial RO membranes include among others, Abcor Inc. (USA), DDS (Danish Sugar Corporation, Denmark), Osmonics Inc. (USA), PCI (Paterson Candy International), Havens Industries (USA), Aqua-Chem., Inc. (USA).

4. ADVANTAGES OF REVERSE OSMOSIS

The advantage of RO over traditional methods in food processing have been discussed and tabulated by Harrison, (1970a)and are summarised in Table II.

It is evident from this table that RO opens up a large range of potential applications.

TABLE II: Some advantages of RO over traditional methods in food processing

Product Improvement Possible
Thermal damage to delicate flavouring compounds can be eliminated
Storage life and quality increased
Removal of contaminants such as salts
Sterilisation of permeate solution by retention of micro-organisms
Sweetness enhancement by acid removal
Product Handling Improvements
Reduction of liquid volume yields lower packing, freezing, storing, handling and transportation costs.
Multiple processes may be replaced by a single process type
Lower energy requirements in comparison with thermal evaporation process

Source: Harrison (1970a)

5. REVIEW OF FOOD INDUSTRY APPLICATIONS

Reverse Osmosis has been proposed as a method for the concentration of liquid foods without phase change or the application of heat. It finds its applications in two main areas of food processing : concentration and purification

5.1 Concentration

Current methods of food concentration consist of evaporation, either at atmospheric pressure or under vacuum, and freeze concentration. Both of these methods cause phase change involving costly heat transfer and possible flavour loss. Concentration of fruit juices and syrups can be accomplished by RO without phase change or thermal damage, without undue loss of solids, and with considerable amount of aroma retention at a cost competitive to evaporation. (Leightell, 1972; Merson et al., 1968; Potter 1972).

5.1.1 Egg White Concentration

On concentrating egg white by conventional methods, denaturation of the albumen proteins and foaming instability occur. This impairs its use in the baking industry, and other methods for concentration must be used.

When dried egg white is produced, glucose must be removed, prior to drying, to prevent the Maillard browning reaction and thus improve the stored product. At present, it is achieved either by controlled fermentation of the glucose, or by an enzymatic method using glucose oxidase producing gluconic acid (Harrison, 1970b).

A method has been devised (Lowe et al., 1969) using a modified RO system in which concentration and glucose reduction occur simultaneously: the glucose passes through the RO membrane with the water and is collected in the permeate rather than the final concentrated product. The glucose reduction shortens the desugaring process and thus offers potential savings.

The modification to the RO system facilitates product removal from the system, to avoid shear in the product, which would disrupt its foaming ability. Proteins are retained by the membrane because of their molecular size relative to glucose, but salts need to be added back to the concentrated product since the process lowers the ionic strength of the concentrate by their removal.

5.1.2 Maple Sap Concentration

In the production of maple syrup, maple sap needs to be concentrated 30 to 40 times, depending on the sugar content. Up to a few years ago, this was carried out by evaporation, but now RO systems have been designed for this task. The final development of flavour and colour still depends on the action of heat on the product but 75 percent of the concentration can be accomplished by RO (the other 25 percent by evaporation). The main constituents of maple sap, sugars and flavour precursors, are retained by the membrane and water is removed from the system. A 54 percent saving in cost is envisaged using this method, which makes it an attractive commercial proposition (Underwood et al., 1969).

A similar process was evolved for the concentration of wood sugar, an effluent by-product of the hardboard manufacturing industry (Kearsley, 1974). These sugars are mainly pentosans and hexosans in a wide range of molecular

weights and their recovery not only lowers the biological oxygen demand of the waste but may also provide further revenue for the industry.

5.1.3 Fractionation and Concentration of Whey

Whey is the effluent produced during the manufacture of cheese or casein, which has in the past posed very serious disposal problems owing to its high biological oxygen demand. Whey contains proteins, lactose, vitamins and minerals, and it is a useful animal feedstuff. However, its low solids content, and thus high costs during transport to the consumer, limits its usefulness, and large volumes are disposed of through the usual effluent channels.

The RO/UF processes have now provided a means of recovery of whey and its components By choice of a suitable RO membrane, whey can be concentrated, or, by using a "looser" UF membrane, can be fractionated into its component parts.

Lactose, one of the components, has a variety of uses in the food industry - from the manufacture of baby milk to dusting powders for confectionery, and whey provides a cheap and ready source of it. Whey contains, on average, about 4.5 percent lactose and this is the largest single component of whey.

For lactose production UF membranes are used, and fractionation may follow the pattern of Figure 3.

The lactose solution produced in the final UF stage may require further concentration to raise the solids content prior to recovery by crystallisation.

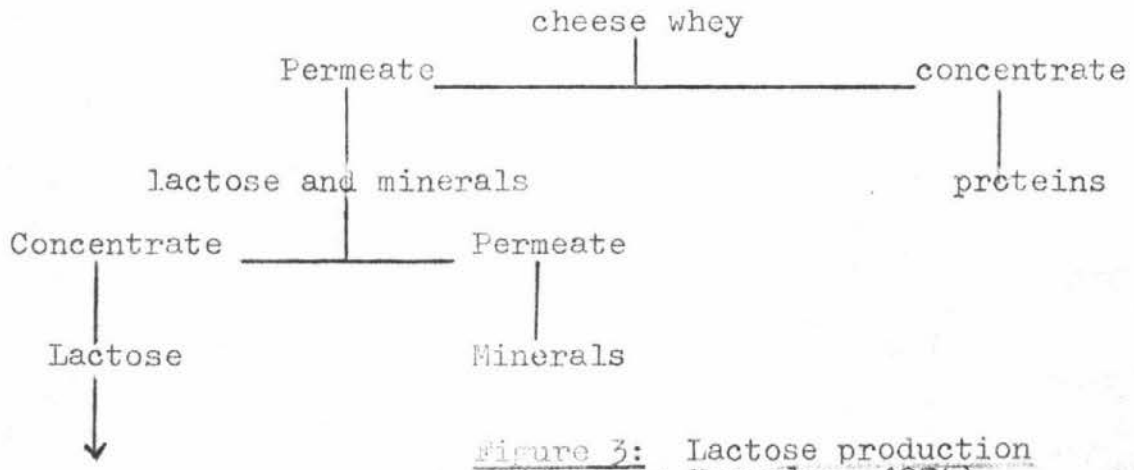


Figure 3: Lactose production
(Source: Kearsley, 1974)

5.2 Purification

Another type of application which takes advantage of the unique properties of RO is purification, or the removal of some undesirable solutes with the permeate. The membrane will allow salts and small amounts of acids such as lactic and acetic acid to pass, while retaining sugars and other high molecular weight substances.

Fractionation and concentration of cottage cheese whey has been reported by Marshall et al., (1968), in which lactic acid and salts have been removed, leaving a concentrated solution of purified lactose and undenatured protein.

RO has also been used for the cleaning and concentration of enzymes. Dilute aqueous solutions can be concentrated at low temperatures, and with an appropriate choice of membrane porosity, undesirable low molecular weight solutes can be removed at the same time (Smith, 1974).

Another purification example is the removal of acid such as malic acid, to make fruit juice sweeter (Merson et al., 1968).

6. REVIEW OF FRUIT JUICE CONCENTRATION BY REVERSE OSMOSIS

Work done in this area is sparse and results are sometimes conflicting. This is not only due to the different types of membranes used and the various experimental conditions encountered, but also to the particular type of juice studied. Progress in the making of newer and superior membranes has been fast, but as yet, no ideal membrane has been developed to cope with the various requirements involved in the concentration of fruit juices.

Fruit juices can be considered to be complex mixtures of sugars, acids, flavouring compounds and pectic substances in solution. Merson and Morgan (1968) have published work on apple and orange juice concentration. The authors used a cellulose acetate membrane cast according to the method developed by Manjikian and Loeb (Manjikian, 1967). The membrane made was supported on a sintered stainless steel

surface 2.5 cm wide, 2.5 cm deep and 43.2 cm long. The permeate was analysed for solutes, and the volatile aroma in both the feed and permeate liquid was analysed chromatographically.

It was found that the minor constituents of the juice were largely responsible for satisfactory flavour, and the success of the process largely depended on the behaviour of these during RO. It is therefore important that these molecules be retained by the membrane in sufficient quantities to give a good concentrate quality. The nature of the flavouring varied from juice to juice, and some molecules were retained better than others. Pectins present in the juice increased the viscosity, which had an important effect on the pumping requirements needed to circulate the feed. Increased viscosity normally hindered the removal of accumulated solids from the surface of the membrane, but conditions used in the laboratory minimised this effect. It was found that clarified apple juice, having a viscosity of 1.4 cp gave the same permeation rate as the whole juice, having a viscosity of 2.0 cp when they were circulated at 1 m/sec and maintained at 14° Brix.

It was found from glc analysis that many of the volatile components leaked out of the membrane to some extent, and this effect could be reduced by using tighter membranes, with subsequent loss of permeation, which would increase the product cost. They observed that economic factors will dictate a flow rate at which some aroma loss occurs. At the other extreme, the membrane cannot have such a high flow rate that solids are lost. It was possible to lose some malic acid without harming the taste, since pH was not abruptly changed with small changes in acid content. The flavour of the reconstituted juice was reported to be less intense than the fresh material, but was still judged to be very good as the full spectrum of the apple aroma was well above the threshold concentration.

Clarified apple juice is reported to cause very little membrane fouling (Leightell, 1972). To obtain a four-fold concentration, operating pressures of the order of

102 atm are required because of the high (20.4 atm) osmotic pressure (Table III). Sustained high flux operation at this pressure is reported to be currently not attainable (Roosmani et al., 1974).

TABLE III: Typical osmotic pressures for different foods

Substance	Approximate concentration %	Approximate osmotic pressure psi	atm
Whey	6 - 7	100	6.8
Orange juice	11	230	15.7
Apple juice	14	300	20.4
Grape juice	14-18	300	20.4
Pineapple juice	14	300	20.4
Maple sap	4 - 5	100	6.8

Source: Leightell (1972)

Merson and Morgan (1968) carried out similar work to apple juice, on orange juice. The juice was reamed from California Valencia oranges and seeds and large pulp particles removed by passing through an 80 mesh screen. The juice was then concentrated in the same way as apple juice using a tubular design RO unit supplied by Havens Industries of San Diego, California. The oil content of the juice was 30 ppm.

The aroma of orange juice is considerably more complex than that of apple juice. This is because much of the aroma resides in an oil phase present in the juice in the form of an emulsion. These aroma molecules are mostly hydrocarbons and are only sparingly soluble in water. They are insoluble in the CA membrane and hence are easily retained. This was shown by the retention of volatiles in the permeate being very low, e.g. the concentration of limonene was 100 times more in the feed than in the permeate. As in apples, however, some very important flavour compounds are water-soluble esters, alcohols, and aldehydes. In spite of some loss of these during concentration by RO, the flavour of four-fold concentrates produced was judged to be excellent. With RO, the aroma retention depends upon the "tightness" of the membrane, being higher for a membrane with a low permeation rate.

In commercial evaporation of orange juice, all the water-soluble aroma compounds are completely stripped off. To compensate for this, commercial practice is to add peel oil and to overconcentrate, e.g. to 58 °Brix, and then cut back to 42 °Brix with fresh juice. Thus, in a drink reconstituted to 10.5 °Brix, only 8 or 9% of the original water-soluble flavour is present. By contrast, concentrating four-fold through a membrane by RO results in a drink with at least 25% of the original flavour, even if the membrane is very open.

Essence recovery is used commercially for concentrating apple juice. With a tight membrane, RO may be able to produce an equally flavourful concentrate with a single operation. Furthermore, the flavour may be more stable during storage because it has never been separated from the juice and has not been subjected to rigorous thermal processing (Merson et al., ibid.).

Feberwee and Evers (1970) investigated the influence of both the molecular weight of the organic solute and its solubility in the cellulose acetate membrane on the degree of separation. Water-soluble organic materials were chosen ranging in molecular weight from 58-585. The pressure difference across the membrane was 100 atmospheres in all experiments. It was found that the retention of the organic solutes was primarily dependent on their molecular weight, and not on their solubility in the membrane. For compounds with a molecular weight of less than 100, retention was poor, while compounds with a molecular weight of 300 or more were almost completely retained. Between these extremes, retention increased steadily with increasing molecular weight. The authors concluded that concentration of food liquids by RO is therefore likely to result in the loss of important low molecular weight, water soluble flavour components.

Gherardi et al., (1972) studied the influence of some variables in the concentration of apple juice, orange juice and grapefruit juice, with special emphasis on the chromatograms obtained from the volatile fractions of the concentrate and permeate.

Two Abcor modules made of CA membranes were used and could handle pressures up to 100 atmospheres, with a total useful surface area of about 1 m^2. They found that the permeate flow rate increased with increasing applied pressure, while it was independent of variation in the capacity of the pump. Permeate flow decreased with increasing concentration of liquid foods. The authors reported that losses of solute into the permeate were not noticeable until the concentration reached 20 °Brix. With much higher concentrations, however, growing quantities of sucrose and citric acid begin to appear in the permeate, finally becoming quite considerable. The cause of this was attributed to a real and characteristic saturation of the membrane by various solutes, which accumulated on the surface with resultant negative effects, not only on the speed of permeation, but also on the semi-permeability on the same membranes.

The losses of ascorbic acid were limited largely to the final stages of the concentration process, proving that RO is a good method for concentrating this particular heat sensitive material.

With apple juice aroma, fairly considerable losses were noted in the permeate. However, in spite of this, the product after concentration still had a characteristic aroma and above all a distinct freshness due to the presence in the correct proportion, even though in small quantities, of almost all the volatile components peculiar to apple.

More satisfactory results were obtained with the grapefruit and orange juices, as the oil-soluble (water insoluble) flavour components were better retained by the membrane. One of the major drawbacks of RO pointed out by Cherardi was the slow speed of permeation at the higher concentrations. This was due to the increase in osmotic pressure with concentration, the effect of concentration polarisation, and the occlusion of pores of the membranes with subsequent loss of permeability.

Thus to overcome this problem it would be necessary to ensure turbulence of the feed inside the membrane. With better designed membranes to withstand higher external pressures, it is hoped that these problems colud be overcome and provide more interesting results in the area of the concentration of fruit juices.

Peri et al., (1973) investigated some aspects of the concentration of orange juice by RO (retention and permeation rate). The concentration was carried out with a laboratory DDS (De Danske Sukkerfabrikker, Copenhagen) unit having 3600 cm^2 membrane surface area. The juice was clarified by centrifugation and successfully concentrated by RO at 5-7 C, at pressures ranging from 30 to 70 atm and with different membrane types DDS 880 (55% NaCl rejection), 990 (91% NaCl rejection) and 999 (99% NaCl rejection) raising the concentration up to about 25 °Brix. Results obtained indicated high retention (98-100%) of sugar, acids, phenolics, nitrogen and ash and retention of of 30 to 100% of volatile aromatic constituents (calculated from aromagrams for membranes 880 and 990). The permeability was found higher than that reported in the previous litterature, particularly with the membrane type DDS 990.

Peri (1973) subsequently calculated the costs of the concentration of orange juice by RO, based on permeation rate values obtained using the DDS assembly as above. The values referred to a 2,3 and 4-fold concentration with a working period of 60 and 120 days/year, 20 hr/day in a continuous operation with 8 stages in series. For a period of 60 days/year, the costs are Lira 3690/tonne, 4781/tonne and 6972/tonne treated juice, corresponding to a 2, 3 and 4-fold concentration. For a period of 120 days/year, the costs are Lira 2140/tonne, 3333/tonne and 4522/tonne respectively. Peri (ibid.) concluded that these figures, based on conservative cost and performance estimates,are competitive with comparable concentration techniques such as freeze-concentration or evaporation with cut-back and aroma recovery.

Schobinger et al., (1974) carried out studies on the behaviour of the aromas of cider during concentration by RO at room temperatures, as compared to a conventional thermal process by evaporation. Samples of commercial cider were concentrated either in a pilot-plant single stage Unipektin evaporator (3 passages) or at room temperature in a laboratory RO unit (DS 995, Copenhagen) to yield concentrates of 25 and 23 °Brix respectively. At various stages in the concentration cycle, the titratable acidity, alcohol content, total extract and extractable aroma were determined. Concentration with RO was found not to give better results than conventional evaporation. The CA membrane used allowed the majority of the aroma compounds to pass through the membrane with the water and ethanol. As regards organic acids, Schobinger et al. (ibid) reported that malic as well as lactic diffused through the membrane with increasing concentration. Citric acid, on the other hand, appeared to be retained experimentally. A slight quantity of sugar (0.2 g/ℓ) was also detected in the permeate beyond the value of 20 °Brix for the extract. On the basis of these results, the concentration of apple cider by RO is not recommended.

Pompei and Rho (1974) concentrated Passion Flower juice by RO using three different membrane types DDS 990, 995 (97% NaCl rejection) and 999. They obtained better aroma retention than was the case with apple cider. Tests were carried out at 6 C at different operating pressures (40, 50 and 70 atm) with the three membranes, each having a surface area of 0.36 m^2. Analyses of permeates and concentrates obtained showed high retention of sugars (>99%), acidity (97% total acids), nitrogen compounds, polyphenols, potassium, and notably volatile aroma constituents. 95% of passion flower aroma is reported to consist of ethyl-butyrate, ethyl-caproate, n-hexyl butyrate and n-hexylcaproate. Pompei and Rho found retentions of these in the three respective membranes in the order of 32.5%, 41.5% and 70%. The authors added that the reconstituted juice was not organoleptically different from the original juice with respect to aroma and freshness.

Peri and Pompei (1975) studied the partial concentration of grape juice to 25 °Brix using three DDS membranes

(DDS 990, DDS 995 and DDS 999), and evaluated the influence of the operating conditions and the type of membrane on the permeability, and the retention, of some of the constituents of the juice, particularly sugars, acids and total phenols. Their work was very similar in nature to the one published earlier (Pompei and Rho, 1974). All the tests were carried out at a temperature of 6 C, at three different pressures (50, 60 and 70 atm). Each membrane had an effective surface area of 0.36 m^2. The juice used came from a white grape of the Pinot variety. It had earlier undergone clarification treatment (gelatine - tannin - bentonite) and had been kept at low temperature, with the preparation of a sparkling wine in view. At the time of the tests, the juice was slightly fermented and had a residual sugar level of about 10%. The juice was concentrated at a pressure of 70 atmospheres. The authors found that the permeability tended towards zero for a sugar concentration of about 26% and that retention of the sugars by the three membranes were identical and almost total, while alcohol retention was nil.

With respect to phenols, they found that simple phenols permeated through the membrane, while the more complex flavour molecules were completely retained. The authors concluded that the 990 membrane, which is the most porous used, was best for concentrating grape juice, since it had comparable retention to the more compact one, and was much more permeable.

Sourirajan, (1970) in an entirely different approach, laid out the physico-chemical criteria for the isothermal RO separation of water from binary aqueous solutions based on Loeb-Sourirajan type porous CA membranes. This approach gave rise to the Kimura and Sourirajan analysis of RO experimental data (See Chapter Three, Section 2) which led to a set of basic transport equations that could be used to predict membrane performance for a large number of binary aqueous solutions from data obtained for a simple appropriate reference solution system. Matsuura and Sourirajan (1971) extended their investigations to the separation of some organic solutes in aqueous solution using CA membranes. The systems studied were glucose-water (0.1 to 1.5 M), maltose-water (0.3 to 0.11 M)

lactose-water (0.04 to 0.22 M), ethylene glycol-water (0.2 to 1.5M), propylene glycol-water (0.2 to 0.8 M), and ethylene glycol-propylene glycol-water (total molality ~ 1.0 M) in the concentration range studied. The correlations of data for the single solute systems were found similar to those reported for the system sodium chloride-water. Results obtained with the mixed solute system showed that the prediction technique developed for aqueous solution systems containing mixed inorganic solutes with a common ion is applicable for systems containing non-ionic mixed organic solutes.

Matsuura et al.(1973) later studied the RO concentration of fruit juices using a similar approach. They presented the physico-chemical criteria for the RO separation of inorganic ions, alcohols, aldehydes, ketones, esters, acids, sugars and non-polar substances with respect to the separation of fruit juice components using porous CA membranes. RO cells of the flow-type were used, each having an effective film area of 9.6 cm^2. Equations of RO transport applicable to the processing of fruit juices were derived by the authors and found applicable for the determination of osmotic pressures of the juice solutions. Experimental data on the osmotic pressures of commercially available apple juice, pineapple juice, orange juice, grapefruit juice, grape juice and tomato juice and their concentrations were also given. The authors' system of analysis could be used to predict membrane performance for the RO concentration of fruit juices provided the following conditions were satisfied :

(i) osmotic pressure of solution is proportional to mole fraction of solute;
(ii) solute concentration in product is small compared to that of water;
(iii) longitudinal diffusion of solute is negligible in the process using a flow-type cell apparatus;
(iv) the solute transport parameter ($DAM/k\delta$) is independent of feed concentration (see Chapter Three, Section 2) ;
(v) molar density of solution is constant, and it is essentially that of pure water;
(vi) membrane pore structure does not change during the process.

Experimental data on the processing capacities of some typical CA membranes for the concentration of the above juices were finally given by the author.

Matsuura et al (1974a) carried out further studies on RO for concentration of fruit juices using non-flow type CA cells which had a film area of 9.6 cm^2. They showed that low temperature (7 C) RO treatment of membrane permeated apple juice waters resulted in significant recovery of aroma compounds which escaped through the membrane during the primary concentration process. The authors suggested a two-stage process. In the first stage, the objective was to recover most (>99%) of the sugars present in the juice. In the second stage, most of the flavour components were recovered and analyses showed that this was more so at 7 C than at 25 C. They also found that the lower processing capacity at the lower operating temperature (2363 ℓ/day m^2 at 25 C compared to 1100 ℓ/day m^2 at 7 C) was compensated by higher aroma recovery in the concentrate (the concentrations of aroma compounds in the concentrate were 23.5% and 50.5% higher respectively compared with the concentration in the feed).

In a recent study on RO recovery of flavour components from apple juice waters, Matsuura et al,(1975) used the non-flow type CA cell (surface area = 9.6 m^2) for the first stage concentration of apple juice and the permeate obtained was subsequently concentrated using the flow type cell (effective film area = 13.2 cm^2) made from laboratory aromatic polyamide membranes. Earlier work (Matsuura et al., 1974b) had indicated that polar organic solutes of the type present as flavour components in fruit juices were much better separated with aromatic polyamide membranes than with CA membranes with about the same average pore size. The authors verified that a higher operating pressure together with a lower operating temperature resulted in a relatively higher recovery of flavour components in the concentrate during the RO treatment of apple juice waters. They concluded, however, that due to the lower processing capacities of the polyamide membranes studied (314 ℓ/day m^2 as compared with 1300 ℓ/day m^2 for CA membranes), further development was needed for more productive aromatic polyamide membranes if recovery of flavour components

from apple juice permeate was done on a commercial scale.

7. CONCLUSION

From this review of the litterature, it can be concluded that RO, as a technique for the concentration of fruit juices, should be favourably regarded above all because of the advantages it shows regarding the qualitative characteristics of the final concentrates. With the exception of apple cider, advantages in concentrating fruit juices such as apple, orange, and grapefruit juice can be summarised as follows:

(i) Good retention capacity for sugars, organic acids, mineral salts and nitrogeneous substances (Peri et al., 1973; Pompei and Rho, 1974; Peri and Pompei, 1975; Matsuura et al., 1973).

(ii) The possibility of preserving almost entirely the natural content of ascorbic acid (Gherardi et al., 1974).

(iii) The possibility of keeping, at a respectable level, the various volatile aromatic compounds in a single stage RO process (Merson et al., 1968; Peri et al., 1973; Pompei and Rho, 1974; Gherardi et al., 1974) or as a two-stage recovery process (Matsuura et al., 1974a; 1975).

On the other hand, the drawback and difficulties which are still encountered, and which severely limit this new technique, are such that its use on an industrial scale for the concentration of fruit juice seems at the moment premature. However, it is hoped that the improvement of existing membranes or the development of new membranes (e.g. aromatic polyamide membranes) will eliminate this problem to a large extent and thus make this interesting technolgical process available for wider applications.

Because most of the work published in the literature to date on the concentration of fruit juices by RO is empirical, it was decided to select one fruit juice (apple juice) and attempt to predict (using currently available theories) the retention of certain components (namely sugars and acids) when the juice was concentrated by RO. A pilot scale Abcor TM5-14 module was used (the plant is described in detail in Chapter Three, Section 1, page 51) so that the results

obtained would be of value from a commercial point of view. Preliminary work consisted of concentrating simple solutions containing one or more sugars or acids in an attempt to reveal whether or not there was any interaction between these components. Finally, actual apple juice was concentrated by RO, and the results obtained compared with the work done on model solutions.

CHAPTER TWO

THE DEVELOPMENT OF A METHOD FOR ANALYSING SUGARS AND NON-VOLATILE ORGANIC ACIDS IN NEW ZEALAND GRANNY SMITH APPLES

SECTION I

A REVIEW OF THE POSSIBLE METHODS

1. INTRODUCTION

The first requirement in this study was for a method which would determine (both qualitatively and quantitatively) sugars and acids present in aqueous solutions. Because in many cases the level of sugar and/or acid in the solution would be very low, the method selected would need to be sensitive and precise. If possible, the method should also be relatively quick and simple, as many solutions would need to be analysed.

2. POSSIBLE METHODS

The official methods for analysis of total sugars and acids in fruits and fruit products are published by the Association of Official Analytical Chemists (A.O.A.C., 1975). In brief, total acidity in the juice is determined by titrating the juice (250 mℓ) with alkali (0.1 N) using phenolphtalein as the indicator. Total sugars can be determined by the Nelson-Somogyi method of colorimetric copper reduction.

While A.O.A.C. methods are useful as a quick check on the overall amount of sugars or acids in a given sample of juice, they could not be used for the separation and identification of sugars and acids present in complex mixtures in apple juice.

Thin layer chromatography (tlc) has been used to separate and identify the sugars present in many tropical fruits (Chan et al., 1975 a,b) and the acids present in Canadian apple juice (Ryan, 1972).

In both cases, tlc is used in conjunction with or prior to gas-liquid chromatography (glc) as a qualitative test. Tlc cannot be used as a quantitative procedure because of its limited accuracy at the lower concentrations, the limit of detection being about 5 µg in the case of acid (Ryan, 1972). Tlc has also failed to positively separate

acid components having close R_F values (Heatherbell, 1975 a). While ion-exchange has been successfully used to separate organic acids present in chinese gooseberry fruit, it failed to separate any of the sugars (Heatherbell, ibid.).

A recent method for the separation, identification and quantitative analysis of common fruit sugars and non-volatile organic acids was developed by Heatherbell (1974). In this method, acids were precipitated as their lead salts from fruit ethanolic extracts, and the sugars in the remaining supernatant and washings partitioned into aqueous methanol. These preparations with internal standards were dried and converted to their trimethylsilyl derivatives for analysis by glc. Total sugars and total acids determined by this procedure gave comparable results with those obtained using standard A.O.A.C. procedures.

This method has many advantages over other methods in that it offers a rapid and simple way of quantifying sugars and acids at the same time. The method permits identification of most fruit acids and the quantitative determination of a wide range of common fruit acids and sugars. Therefore, Heatherbell's procedure was adopted in this study and used for the analysis of sugars and organic acids present in apple juice.

SECTION II

ANALYSIS OF SUGARS AND NON-VOLATILE ORGANIC ACIDS IN GRANNY SMITH APPLES BY GAS-LIQUID CHROMATOGRAPHY

1. INTRODUCTION

Gas chromatographic methods have recently superseded existing analytical methods for carbohydrate and acid analysis. The advantages of gas-liquid chromatography (glc) over "classical" methods such as paper, thin-layer and ion-exchange chromatography are many. Firstly, the estimation of the amount of sugar and acid is part of a separation-identification procedure (McNair et al., 1968). Secondly, glc is a very sensitive method of analysis as monosaccharides of less than one pmol have been detected (Clamp, 1974). Thirdly, another advantage of glc is its flexibility. The type of liquid phase and percentage loading, oven temperature and programming rate, carrier gas flow, etc. can be varied to separate almost any combination of organic solutes. The only limitation is that the chemical handling procedure should quantitatively transfer to the final injection procedure all the constituents. Trimethyl-silyl (TMS) derivatisation pioneered by Sweeley et al (1963) has laid out a firm basis for quantitative work using glc. Finally, reliability and repeatability can be achieved provided peak areas can be accurately integrated.

Recent work on glc as an analytical procedure has led to the rapid and concurrent recovery of sugars and acids in fruits (Heatherbell, 1974). Many New Zealand fruits have been successfully analysed for sugars and organic acids using this method (Heatherbell, 1974, 1975a, 1975b).

The object of this work is a further investigation into glc as a quantitative method for analysing sugars and organic acids with special reference to New Zealand Granny Smith (GS) apple as raw material. This, in the end, will provide a direct and convenient method to separate, identify and quantitate GS apple sugars and non-volatile acids so

that their fate can be followed during the concentration of GS apple juice by Reverse Osmosis.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1 Gas Liquid Chromatograph

2.1.1 GLC Equipment

The gas-liquid chromatograph used was a Varian Aerograph model 2100 with dual column and differential electrometer. The columns can be balanced and operated with Flame Ionisation Detectors (FID) and/or Electron Capture detectors (EC). For this work, a single column with FID was used. The pen recorder used was a RIKADENKI dual pen recorder. The chromatograph was connected to a Varian model 485 electronic digital integrator for determination of peak areas.

The flow of carrier gas, hydrogen and air was regulated by fine controllers and metering valves, with a rotameter in the carrier gas line.

The column oven could be operated by direct dialing up to a temperature of 400 C with $\pm$ 1 C repeatability. Temperatures could also be set at different modes : isothermal, programmed at a preselected rated rate to a preset limit at which it could be held or cooled down.

2.1.2 Column preparation and conditioning

A 1.8 m x 3.2 mm I.D. U-shaped glass column packed with 5% SE-52 on 80/100 mesh Varaport 30 was used.

The column was prepared by dissolving the correct amount of liquid phase in a suitable solvent (n-hexane) and placing in a round bottom flask. The weighed amount of solid support (Varaport 30) to give a Final 5% SE-52 was then added. The flask was connected to a rotary evaporator and the solvent slowly evaporated at room temperature until just damp. It was then immersed in a 60C bath under full vacuum to evaporate all the solvent. A small piece of

glass wool was then placed in one end of the column and a vacuum pulled on that end while adding the dry packing in small quantities through the open end. Full packing was achieved by vibrating and gently tapping the column. After the support had settled, the open end of the column was plugged (McNair et al., 1968).

The column was finally placed in the oven and conditioned at 245 C overnight. The oven was then cooled to 225 C and the column conditioned with a small carrier gas flow rate (10 mℓ/min.) until stable.

2.1.3 GLC Conditions

Best operating conditions were obtained with:

Injector temperature: 250 C
Detector temperature: 250 C
Nitrogen carrier flow rate: 30 mℓ/min
Hydrogen flow rate: 25 mℓ/min
Air flow rate: 250 mℓ/min

The oven temperature was programmed from 165 C to 245 C at 4 C/min for the sugars and from 100 C to 225 C at 6 C/min for the acids.

2.2 Centrifuges and ancilliaries

A MSE centrifuge was used for the 250 mℓ bottles and 50 mℓ centrifuge tubes. A BTL lab-bench centrifuge was used to sediment solids from the TMS-derivatives contained in the 3 mℓ vials.

A BTL mechanical shaker was used to ensure good mixing and to accelerate silylation inside the vials.

A Varian Aerograph Ultrasonic was also used when more thorough mixing was required.

2.3 Vials and connections

The 3 mℓ vials (Pierce Chemical Co.) had Teflon-lined screw caps. The vials were attached to a modified

"Quickfit" tubing adaptor connected to a Buchi rotavapor by plastic screw caps also lined with teflon silicone rubber seals.

Samples were stored under vacuum over P_2O_5 until silylated.

2.4 Syringes

5 and 10 $\mu\ell$ syringes were used for glc injection. A 500 $\mu\ell$ syringe was used to add "TriSil" or "TriSil Z" (Pierce Chemical Co.) into the 3 mℓ vials for silylation purpose.

All syringes were from S.G.E. (Scientific Glass Engineering Ltd., Melbourne, Australia).

2.5 Saturated Lead Acetate Solution

This was prepared by dissolving neutral lead acetate (approx. 16 g) in water (100 mℓ).

2.6 Internal Standards

Inositol (meso)-inactive used for the sugars was from BDH (British Drug House Ltd, Poole, England).

D-Tartaric acid used for the acids was also from BDH.

2.7 TMS reagents

TriSil for the acids were obtained in 50 mℓ vials and TriSil Z for the sugars in 25 mℓ vials. Both reagents were from Pierce Chemical Co., Rockford, Illinois.

2.8 Other Chemicals

Glucose, fructose, sorbitol and sucrose were obtained from BDH as were succinic, malic, citric, ascorbic, galacturonic and glucuronic. Phosphoric acid of the highest purity available was used. Quinic acid was obtained from Sigma Chemical Co., St.Louis, USA.

2.9 Sample Preparation

Whole apple or apple juice was stored at 4 C before analysis. Peeled fruit or juice (50 mℓ) was transferred to a Waring blender and 95% Ethanol (150 mℓ) was added and the mixture blended for 5 min, giving a final concentration of approximately 80%. After standing for 1 hour the extract was centrifuged at 2000 g for 10 min. The supernatant was decanted and the residue washed twice with 80% Ethanol (25 mℓ). Supernatant and washings were combined and diluted to 250 mℓ with 95% EtOH.

2.10 Sample determination

5 mℓ aliquots of prepared sample were transferred to a 50 mℓ centrifuge tube. Tartaric acid (10 mg as 1 mℓ of 1% solution in 95% EtOH) was added, followed by 85% EtOH (10 mℓ) and saturated lead acetate solution (1 mℓ) to precipitate the acids. After mixing thoroughly, the extract was allowed to stand for 45 min or longer, and then centrifuged at 800 g for 7 min. Complete precipitation of the acids was checked by adding a drop of lead acetate solution into the supernatant. The latter (containing the sugars) was decanted, the residues were washed three times with 85% EtOH (1 x 10 mℓ followed by 2 x 5 mℓ) and the combined supernatant and washings were partitioned between chloroform-methanol-water (120 mℓ of 8:4:3 v/v). The latter step was used to prevent any possible interference from pigment and lipid materials in the sample. Lead salts during each washing were carefully resuspended using a spatula and ultrasonic bath. The lower methanol-chloroform layer containing negligible amount of sugar was discarded. The upper methanol layer was made up to 100 mℓ with 80% EtOH, 1 mℓ aliquots transferred to 3 mℓ vials, inositol added (0.2 mℓ of 0.1% w/v) and the sample evaporated to dryness on a rotary evaporator.

The precipitate containing the acids was washed with diethyl ether (5 mℓ), centrifuged, the ether decanted and residual ether evaporated before oven drying at 100 C for 1 hour. Dried precipitate was transferred to the 3 mℓ vials for silylation. Samples were stored under vacuum over P_2O_5 until silylated.

2.11 Preparation of TMS derivatives

Sugars in the 3 mℓ vials were silylated by adding TriSil Z (300 μℓ), shaking for 5 min, heating at 70 C for 20 min and then shaking for 15 min to ensure complete reaction.

Lead Salts in the 3 mℓ vials were derivated by adding TriSil (1.5 mℓ), shaking thoroughly for 5 min and heating at 50 C for 30 min.

Solids in the vials were sedimented out by centrifuge and typically 0.5-1.0 μℓ of the clear solution directly injected into the gas chromatograph. Sample size, conditions and sensitivity level were adjusted to keep major peaks on scale.

2.12 Preparation and determination of standard

All sugars were dried over P_2O_5 under vacuum prior to weighing. D-fructose, D-glucose, D-sorbitol and sucrose were accurately weighed to make up 1% (w/v) standard solutions in 80% EtOH. Calibration curves were obtained for each sugar over the concentration studied by chromatographing varying amounts of sugar (0.1 to 2.0 mg) with constant amounts (200 μg) of inositol.

Standard acid solutions were similarly prepared by dissolving crystalline acids in 80% EtOH. The concentration of each acid was studied within the approximate range commonly found in fruit. Aliquots (5 mℓ) of a standard acid solution were transferred into 50 mℓ centrifuge tube, tartaric acid (10 mg as 1 mℓ of 1% (w/v) solution) added and the solutions treated in the same manner as described in Section 2.10. Calibration curves plotting weight of acid/weight of standard ($W_1:W_s$) against the corresponding area ratio $A_1:A_s$ were prepared. Concentrations studied were from 0.04 to 1.0% ($W_1:W_s$ of 0.2 to 5.0) for the acids.

In addition, model solutions of mixtures of sugar

and acid standards at a W_1:Ws of 1.0 were prepared for recovery analyses, first by direct injection of the TMS derivatives and secondly through the entire analytical procedure. These model solutions simulate GS apples containing a 1% (w/w) concentration for each acid and 2% (w/w) for each sugar on a fresh weight basis.

Calibration curves were prepared by plotting Weight solute/Weight standard (W_1:Ws) against the corresponding area ratios (A_1:As).

2.13 Calculations

Relative response factors (K) for sugars and acids were calculated as:

$$K = \frac{A_1 : As}{W_1 : Ws}$$

These were used to calculate the amount of a given acid or sugar by:

$$\text{Weight of unknown} = \frac{\text{Weight of internal std} \times \text{peak area}_{\text{unknown}}}{\text{Appropriate K value} \times \text{peak area}_{\text{internal std}}}$$

In the case of fructose and glucose, two peaks each appear, therefore, the peak area of sugars is the sum of the two peaks.

3. RESULTS AND DISCUSSION

3.1 Qualitative analysis

The principal purpose here is to separate and positively identify the significant sugar and acid components in the apple material. The Granny Smith (GS) variety was chosen because it accounts for 80% of the apples processed into juice by the N.Z. Apple and Pear Board processing factories (Gyde, 1976).

Preliminary analysis of a representative GS sample without internal standard revealed the presence of 4 sugars being presumably fructose, glucose, sorbitol and sucrose. Inositol was chosen as internal standard for the

sugars because it had not been reported in GS apples, it was readily available in pure form and was chemically stable and solid at room temperature; and it gave a completely resolved peak close to the mid-point in an unoccupied region of the chromatogram. A typical glc separation of TMS derivatives of the sugars present in GS apples is shown in Figure 4. Comparison of the relative retention times of the unknown peaks in Figure 4 with those of pure crystalline sugars (from Table I) established and confirmed the presence of α and β-D-fructose, α and β-D-glucose, D-sorbitol and sucrose.

A similar "blank" was run for the acids in GS apples and comparison of the retention times of the peaks showed the possible presence of the following acids: phosphoric or succinic, malic, citric, quinic, p-coumaric, ascorbic, glucuronic and/or galacturonic. Here identification of the acids presented some difficulty due to the close resolution of some peaks on the chromatogram. Tartaric acid was chosen as internal standard for the acids because it had not been reported in GS apples and its lead salt is completely insoluble in water or ethanol (Merck, 1960). Typical glc patterns of non-volatile acids present in GS apples are shown in Figures 5 and 6. Comparison of the retention times of the acid peaks with those of authentic acids on SE-52 column (Table V) suggested that peak 1 in Figure 5 could be either phosphoric or succinic, due to their very close retention time (0.46 and 0.49 respectively). The problem was overcome by "spiking" peak 1 with an equal amount of TMS derivatives of pure phosphoric or succinic. It was observed that succinic did not build up on top of peak 1 but in fact gave a second peak next to the original one. On the other hand, pure phosphoric co-chromatographed with the unknown peak, giving a single peak twice the size of the original one. This established that peak 1 was in fact phosphoric acid. Using the same technique, it was found that the main non-volatile acid in GS apples is malic, with lesser amounts of phosphoric, citric, quinic and ascorbic and trace amounts of galacturonic. Peak 6 did not correspond to p-coumaric and peak 9 of Figure 2 was also

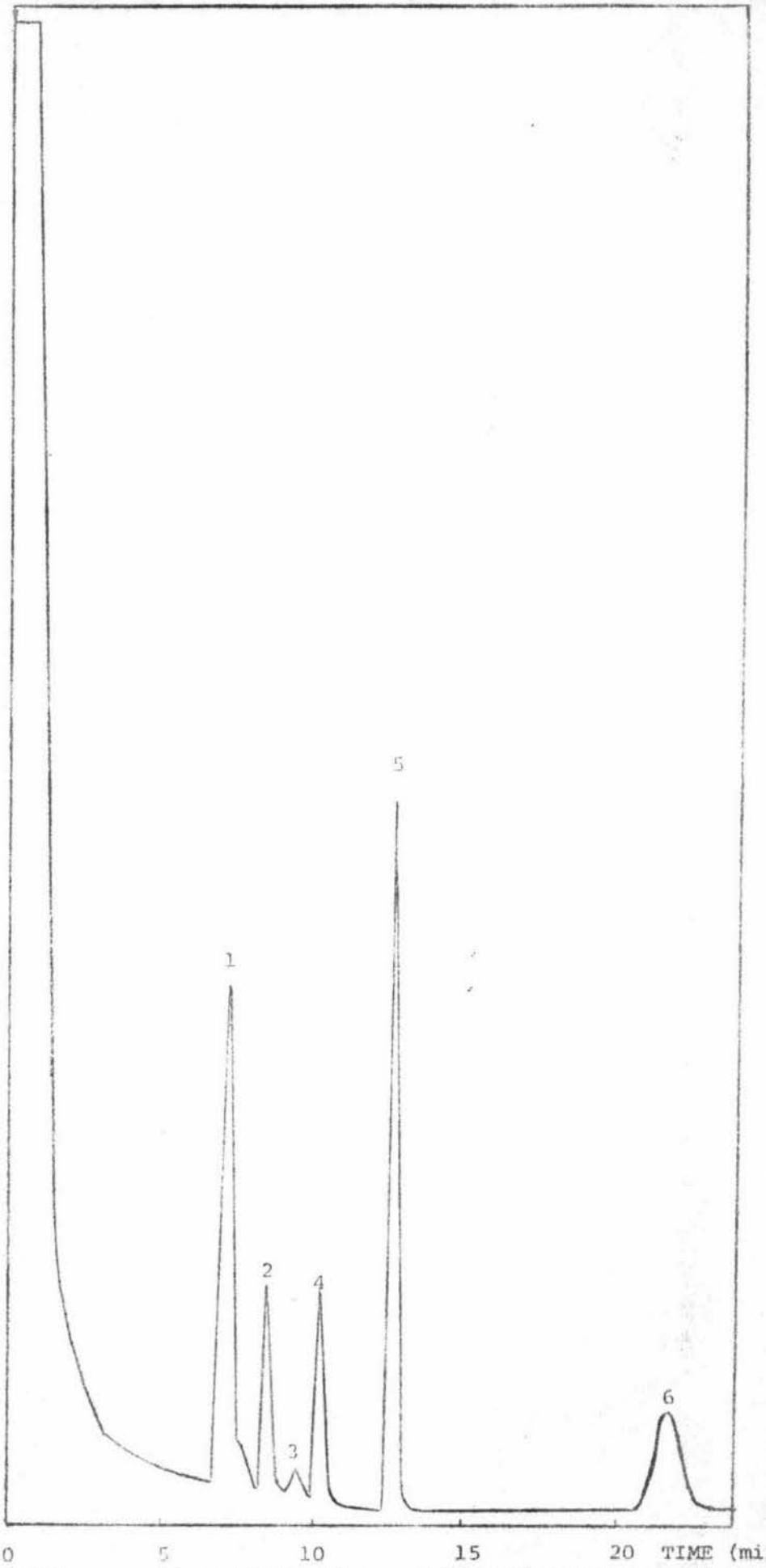


FIG. 4; GLC separation of TMS ethers of GS apple sugars on SE-52 column: 1, α + β-D-fructose; 2, α-D-glucose; 3, D-sorbitol; 4, β-D-glucose; 5, Inositol (internal standard); 6, Sucrose.

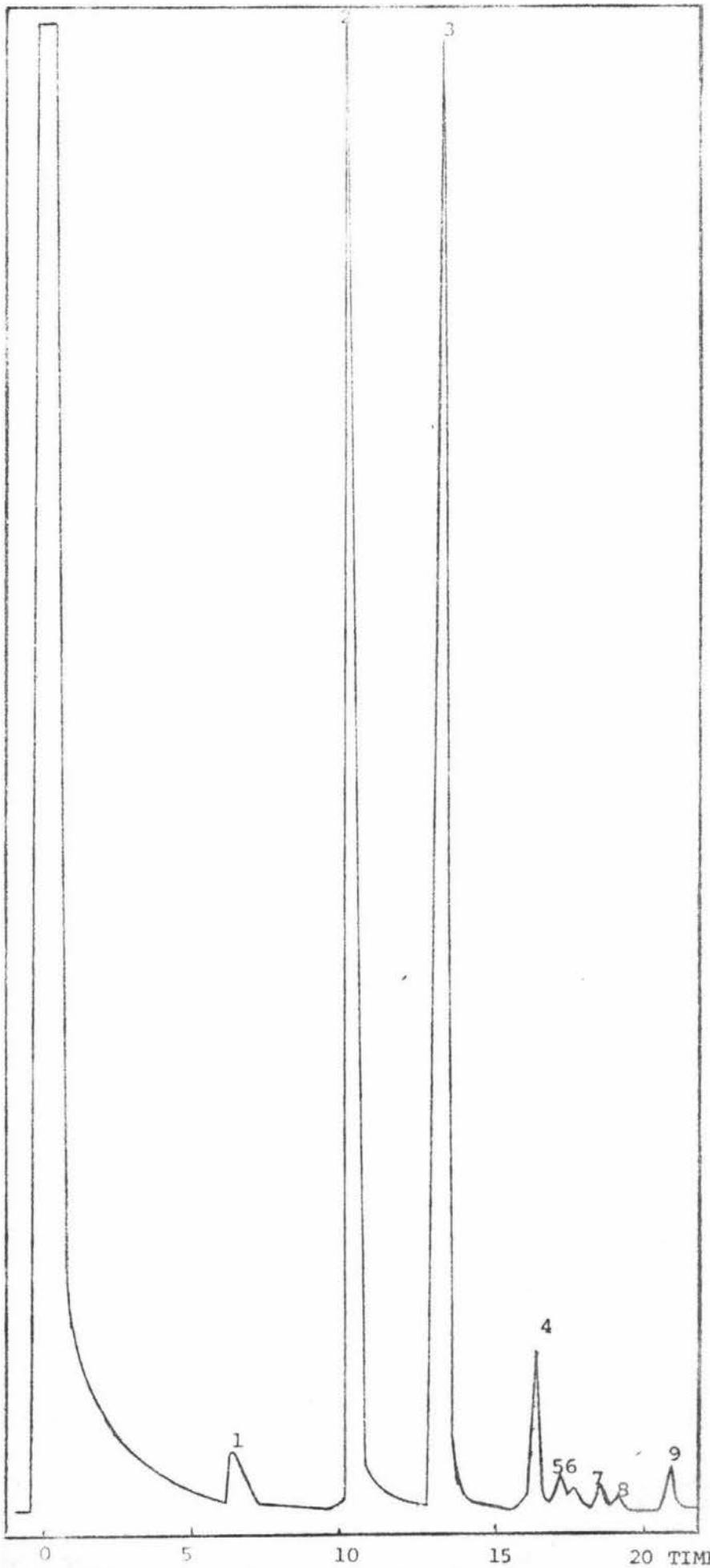


FIG. 5: GLC pattern of organic acids in GS apples:
1, Phosphoric; 2, Malic; 3, Tartaric (int. std.);
4, Citric; 5, Quinic; 6,9, Unidentified;
7, Ascorbic; 8, Galacturonic.

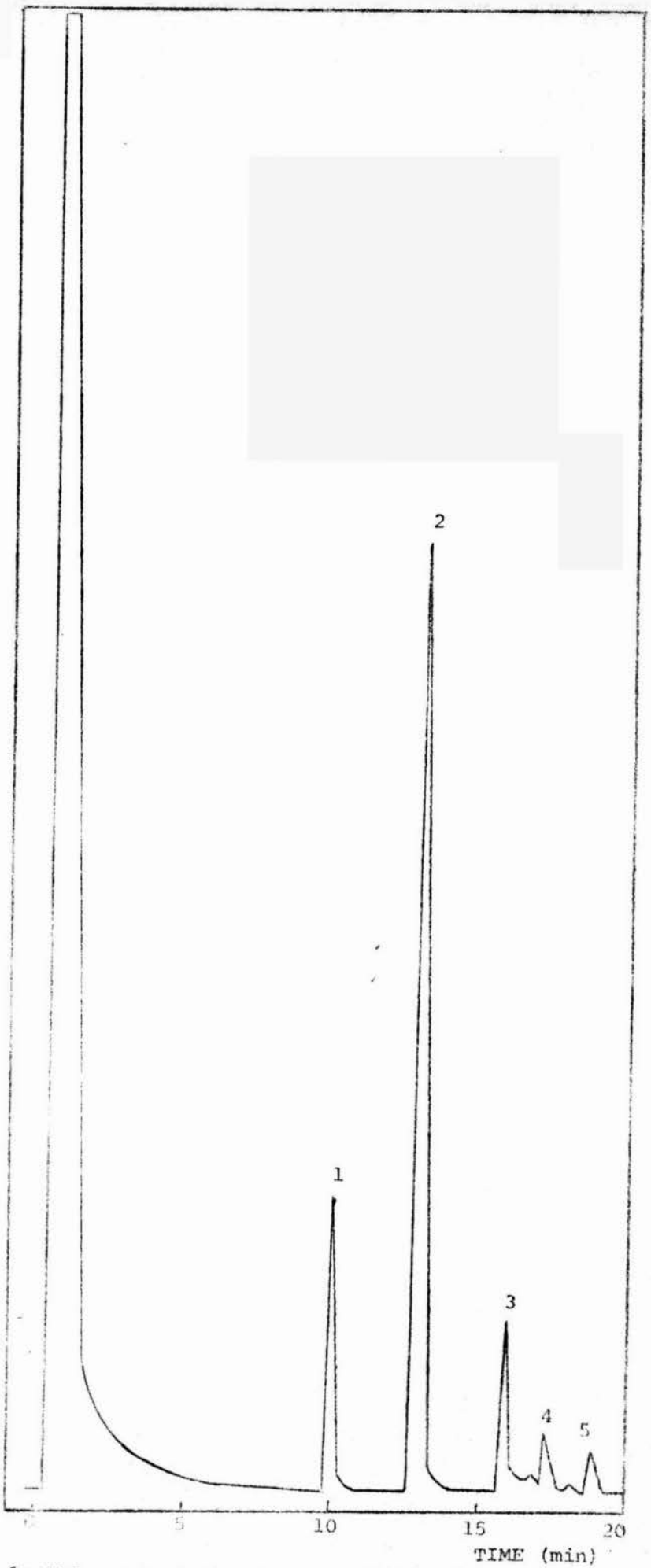


FIG. 6: CLC pattern of organic acids in GS apples:
1, Malic; 2, Tartaric (internal standard);
3, Citric; 4, Quinic; 5, Ascorbic.

unidentified. Comparing Figures 5 and 6, it is interesting to note that the relative amounts of the non-volatile acids can change remarkably depending on the sample analysed. Thus, in Figure 6, there was no phosphoric and galacturonic but a relatively larger amount of citric, quinic and ascorbic. This is likely to be due to a difference in maturity of the fruit analysed: galacturonic has been reported to exist only in mature or over-ripe apples (Hulme, 1970) while quinic has been reported mostly in peel and young fruit (Ulrich, 1970).

On the basis of the qualitative results obtained, it was concluded that the main non-volatile organic acids of interest in GS apples were: phosphoric, malic, citric, quinic and ascorbic. These acids in fact constitute 97% of the peak area detected.

TABLE IV: Relative retention time of TMS derivatives of sugars on SE-52

Sugar	Retention time
D-fructose	0.56
α-D-glucose	0.67
D-sorbitol	0.75
β-D-glucose	0.82
Inositol (internal standard)	1.00
Sucrose	1.81

TABLE V: Relative retention time of TMS derivatives of non-volatile organic acids on SE-52

Acid	Retention time
Phosphoric	0.46
Succinic	0.49
Malic	0.77
Tartaric(internal std)	1.00
Citric	1.25
Quinic	1.32
p.Coumaric	1.38
Ascorbic	1.43
Galacturonic	1.46
Glucuronic	1.53

3.2 Quantitative analysis

3.2.1 Effect of Reaction time

Reaction time studies established that conversion of crystalline sugars to their TMS derivatives was complete after a 5 min shake followed by a gentle mixing for 20 min at 70 C in a water bath and a final 15 min shake to ensure complete reaction.

For acids, a 5 min shake followed by 30 min at 50 C completed TMS derivatisation of simple mixtures. For more complex synthetic mixtures a further 15 min shake may be necessary.

3.2.2 Effect of TMS reagents

Preliminary work using TriSil as silylating reagent for sugars resulted in low recovery of the individual sugars from a synthetic mixture. It was later established that this was due to the effect of residual moisture in the vials even after the samples were taken to dryness on a rotary evaporator. Since complete drying of the samples is often arduous and time consuming, the problem was overcome by using TriSil Z instead of TriSil to derivatise sugars. TriSil Z has been reported as suitable for quantitative work involving carbohydrates either in dry or moist conditions (Pierce Handbook of Silylation, 1972). Experiments confirmed this and led to the use of TriSil Z for sugars in the final sample preparation procedure.

3.2.3 Effect of storage on TMS-derivatives

Repeated injection of the same TMS derivative over a period of time established in the case of sugars a slow loss of TMS-fructose and sucrose with time. Samples were best analysed within 6 hours of silylation.

3.2.4 GLC conditions

Studies on the effect of glc conditions established that length of chromatographic run rather than recovery was significantly affected by temperature programming rate : too low a temperature program (e.g. isothermal or at 1 C/min) gave satisfactory separation of the components at the expense

of a lengthy run. On the other hand, a fast programme rate of temperature rise (e.g. 8 or 10 C/min) eluted the peaks quickly but the chromatogram was crammed and inaccuracy arose due to overlapping peaks. Best oven conditions for good separation in reasonable time were obtained as follows: for sugars; 165-245 C at 4 C/min; for acids 100-225 C at 5 C/min.

3.3 Recovery of sugars or acids by direct injection

A set of standard calibration curves was prepared for each of the sugars and acids studied. These curves are depicted in figures 7 and 8 respectively. In both cases, linearity between peak area ratio and weight ratio was observed over the concentration range studied. Each point on the graphs was the average of 4 or more determinations. Best accuracies were obtained at a $W_1:W_s$ of unity. Extending the range too far (e.g. $W_1:W_s = 10$) may lead to non-linearity due to either loss or enrichment of the solute with respect to the internal standard. The response factors K calculated from the slopes of the calibration curves gave the values for sugars and acids listed in Table VI.

TABLE VI: K factors for crystalline sugars and acids as their TMS derivatives

Sugar/Acid	Detector response K*
D-fructose	0.52
D-glucose	0.78
D-sorbitol	0.82
Sucrose	0.58
Phosphoric	0.78
Malic	0.86
Citric	0.70
Quinic	1.02
Ascorbic	0.91

*Average of four determinations

A mixture of sugar standards made with various amounts of crystalline sugars and a constant amount of inositol was analysed for individual sugar recovery and

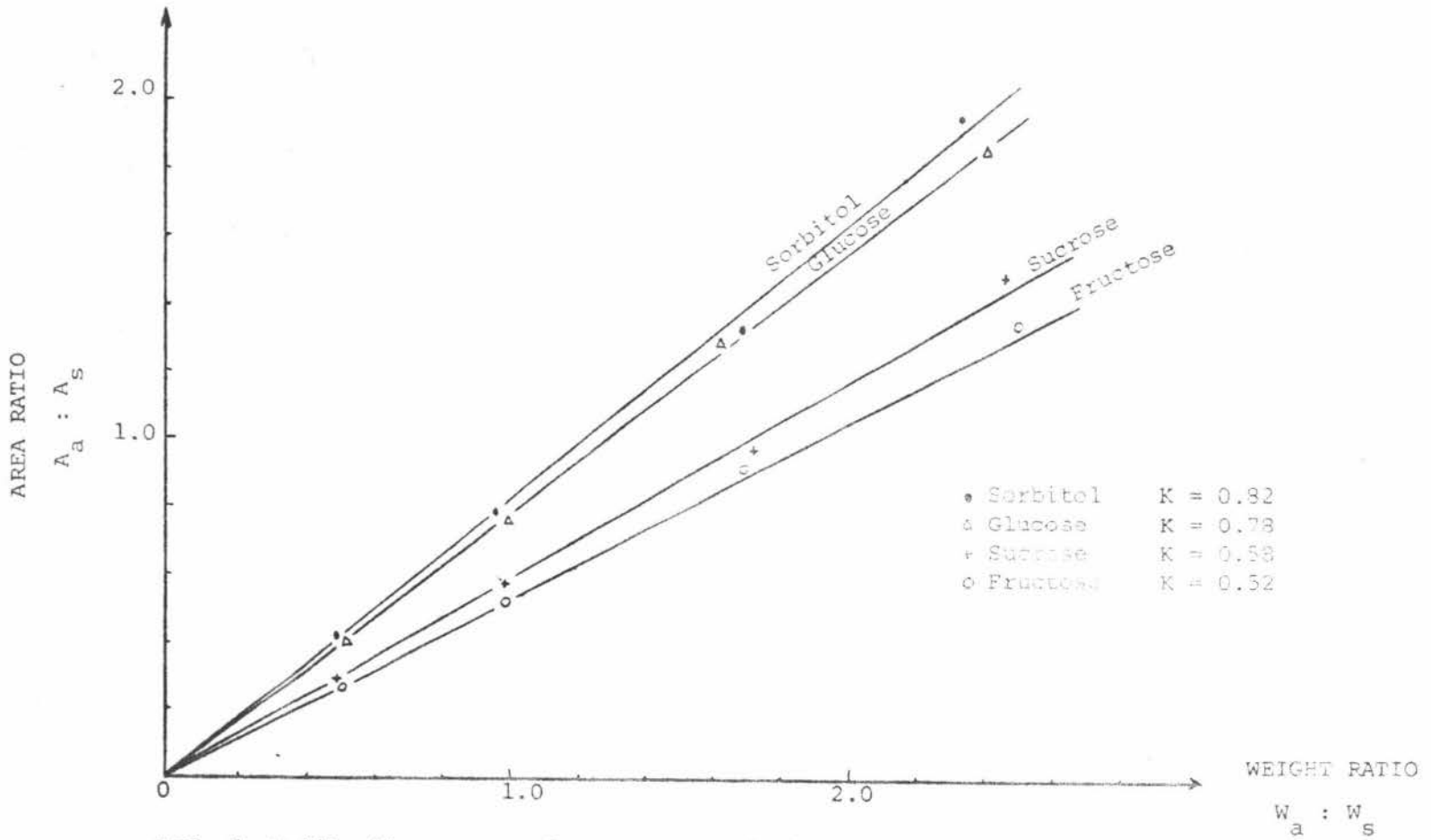


FIG. 7: Calibration curves for sugar standards;

Each point is the average of four determinations.

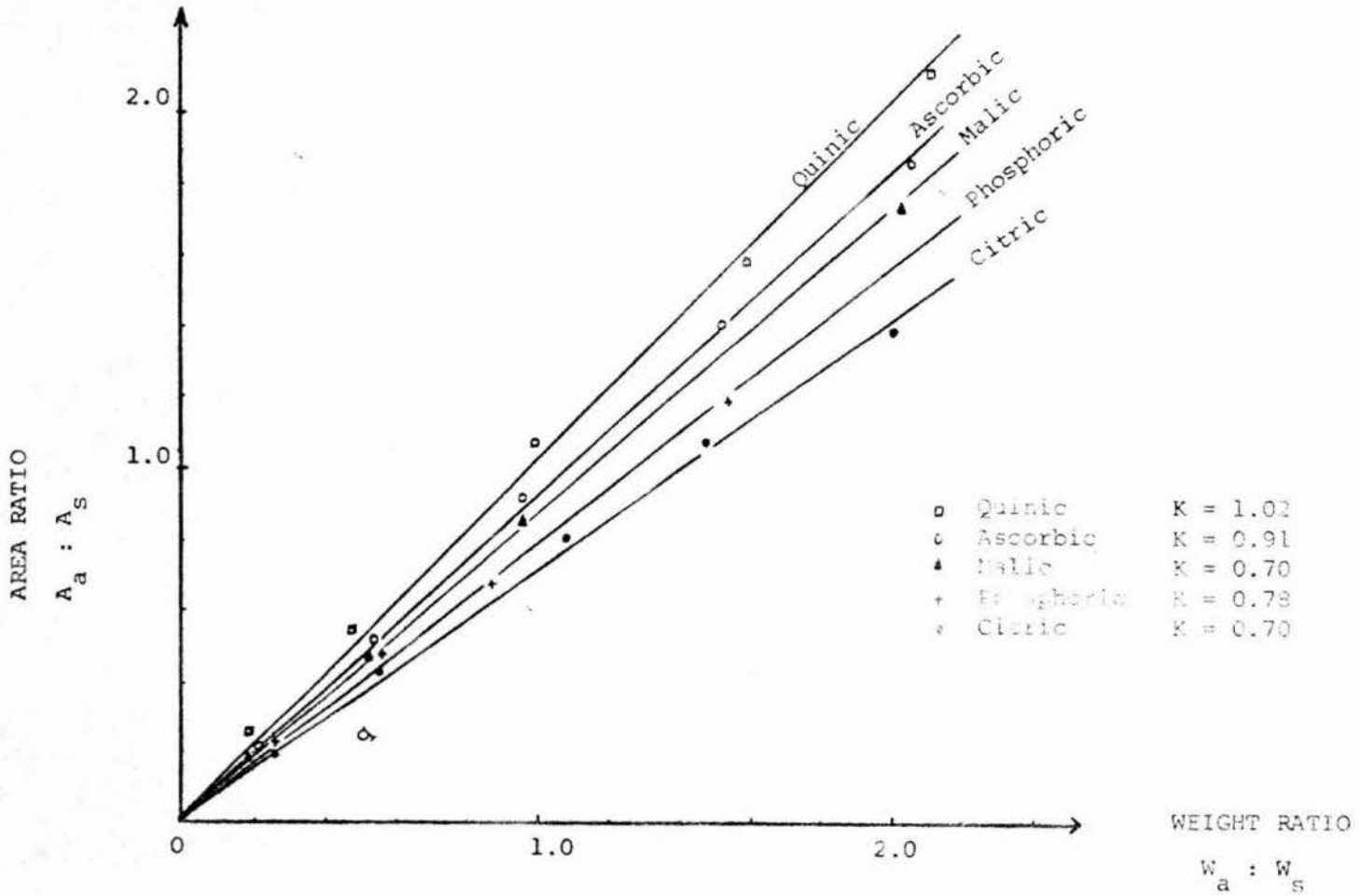


FIG. 8: Calibration curves of acid standards;

Each point is the average of four determinations.

results are presented in Table VI.

Figure 9 shows a typical g.l.c. pattern of sugar standards chromatographed on the SE-52 column.

Results from Table VII clearly established that complete recovery of sugars from a mixture of direct injection could be achieved under experimental conditions with an accuracy of ± 7% for the individual sugar and with an overall recovery of 99 ± 3%.

TABLE VII: Recovery of sugars by direct injection from various amounts input

Sugar	Input g	Recovery g	% Recovery	Average Recovery *
Sorbitol	200	200	100	102 ± 3%
	500	509	102	
	200	209	105	
Glucose	700	707	101	99 ± 6%
	500	459	92	
	500	518	104	
Fructose	500	433	87	94 ± 7%
	500	498	100	
	500	475	95	
Sucrose	500	505	101	99 ± 7%
	500	462	92	
	500	525	105	

* Average of three determinations

Overall Recovery	99 ± 3%

Direct injection of a synthetic mixture of TMS acids resulted in recoveries shown in Table VIII.

Figure 10 is a typical chromatogram of the acid standards eluted on the SE-52 column.

Results from Table VIII also showed that complete recovery of crystalline acids by direct injection could be

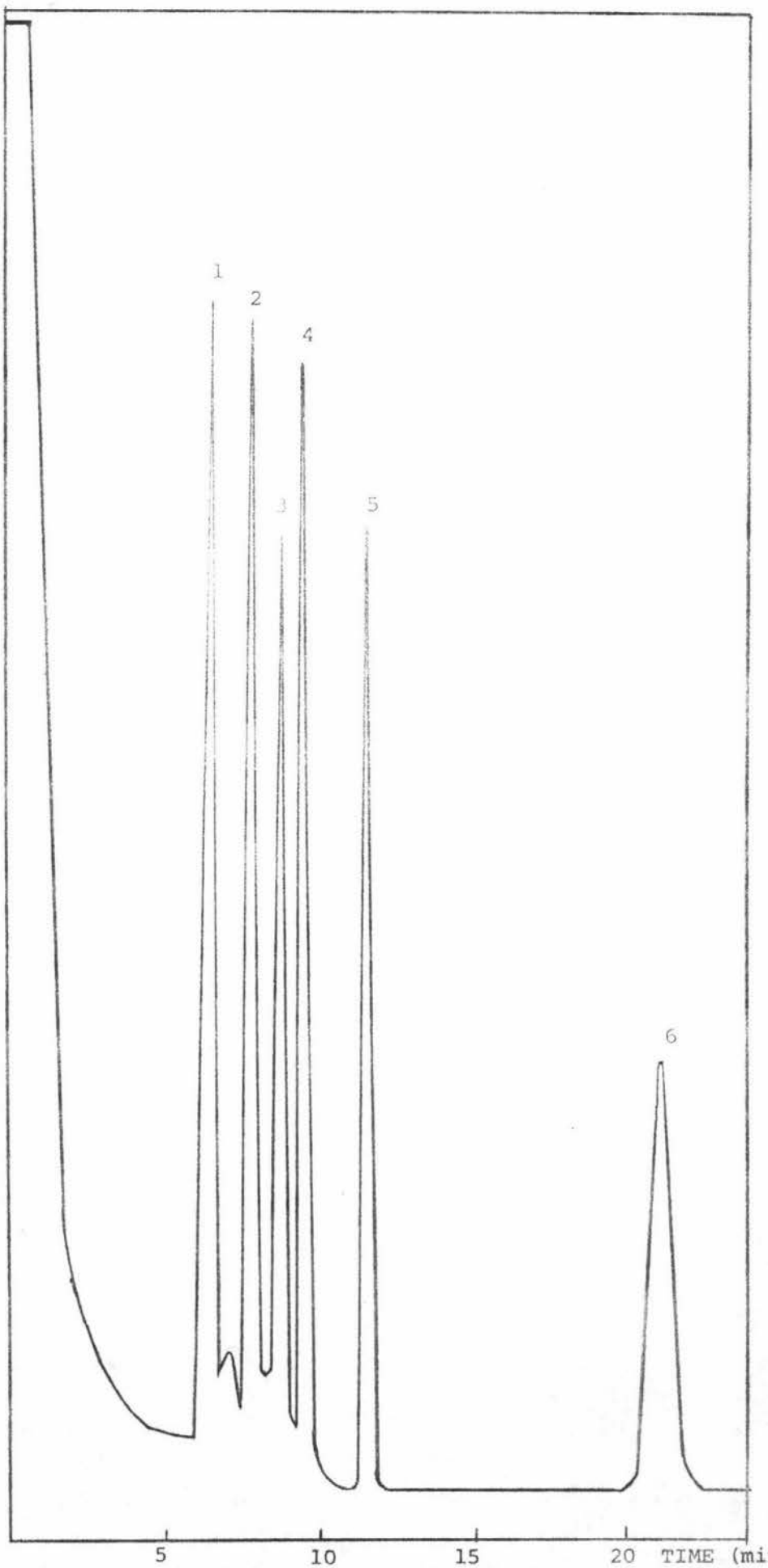


FIG. 9: GLC pattern of sugar standards: 1,α+β-D-Fructose; 2,α-D-Glucose; 3, D-Sorbitol; 4,β-D-Glucose; 5, Inositol (internal standard); 6, Sucrose.

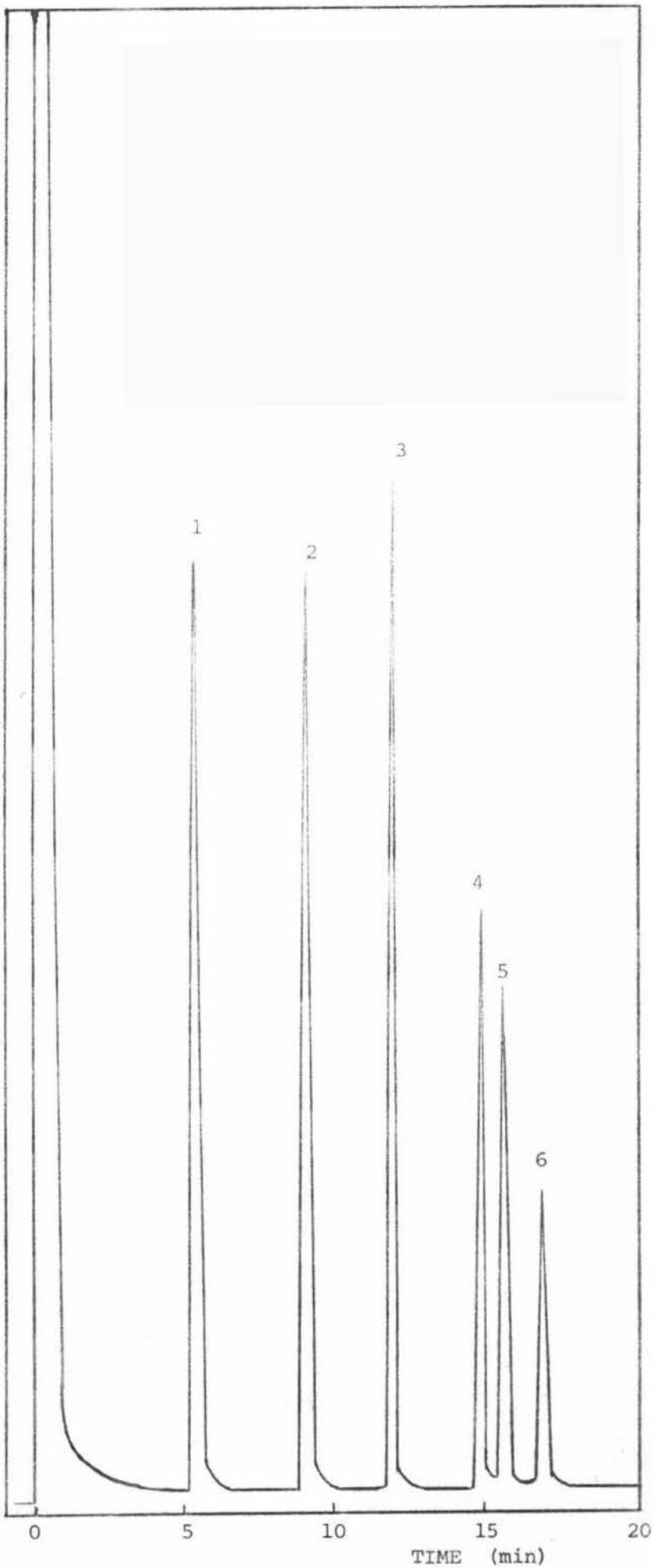


FIG. 10: GLC pattern of TMS derivatives of acid standards: 1, Phosphoric; 2, Malic; 3, Tartaric (internal standard); 4, Citric; 5, Quinic; 6, Ascorbic.

achieved with an accuracy of 4% for the individual sugar and with an overall recovery of 100 ± 4%.

TABLE VIII: Recovery of acids by direct injection

Acid	Input G	Recovery G	Average	Average % Recovery
Malic	4.5 ± 0.1	4.44 4.55	4.5 ± 0.1	100 ± 3%
Phosphoric	4.6 ± 0.1	4.39 4.72	4.6 ± 0.2	100 ± 4%
Citric	5.3 ± 0.2 (100 ± 0%)	4.89 5.08	5.0 ± 0.1	94 ± 2%
Quinic	5.0 ± 0.1	4.97 4.90	4.9 ± 0.1	98 ± 2%
Ascorbic	4.8 ± 0.1 (100 ± 2%)	5.20 5.09	5.1 ± 0.2	106 ± 4%
			Overall Recovery	100 ± 4%

3.4 Recovery of sugars and acids by analytical procedure

This section will provide information on the secondary response factor of the compounds which were analysed as any change in K value was reflected in the recovery of the compound analysed. The primary response factor was previously established by direct injection.

Synthetic mixtures of crystalline sugars and acids simulating a 1% w/w (W_1:Ws = 1.0) concentration of each acid and a 2% w/w (W_1:Ws = 1.0) concentration of each sugar in real fruit were prepared and taken through the entire procedure for recovery analyses.

Recovery of the individual sugar in 4 different mixtures of similar composition, average recovery of total

sugars and overall accuracy are listed in Tables IX and X.

Table IX: Individual recovery by analytical procedure from 4 synthetic mixtures at a W_1: Ws = 1.0

Mixture	Sugar	% Recovery	Average % Recovery *
A		108	
B	Fructose	100	101 ± 13%
C		83	
D		115	
A		110	
B	Glucose	103	104 ± 4%
C		100	
D		104	
A		100	
B	Sorbitol	92	97 ± 4%
C		94	
D		100	
A		91	
B	Sucrose	78	91 ± 14%
C		110	
D		80	

* Average of four determinations

Overall Recovery 98 ± 6%

TABLE X: Total sugar recovery by analytical procedure from mixtures A, B, C and D at a W_1:Ws = 1.0

Mixture	Sugar	% Recovery of each sugar	% Recovery total sugars
A	Fructose	108	102%
	Glucose	110	
	Sorbitol	100	
	Sucrose	91	
B	Fructose	100	93%
	Glucose	103	
	Sorbitol	92	
	Sucrose	78	

TABLE X (cont.)

Mixture	Sugar	% Recovery of each sugar	% Recovery total sugars
C	Fructose	83	97%
	Glucose	100	
	Sorbitol	94	
	Sucrose	110	
D	Fructose	113	100%
	Glucose	104	
	Sorbitol	100	
	Sucrose	84	
		Overall Recovery	98 ± 4%

Results from Table IX showed that variations in the recovery of the individual sugar in different mixtures could be as high as ± 13% and ± 14% for fructose and sucrose with glucose and sorbitol more accurately determined at ± 4%. However, if the recoveries of the individual sugars were pooled together, the overall accuracy was quite adequate at 98 ± 6%. On the other hand, if recovery of total sugars was considered, a higher overall accuracy of 98 ± 4% was achieved.

Similar results for acids are given in Table XI. Here only the recovery of the individual acid is considered because of the reported loss of ascorbic acid and the wide inaccuracy in quinic acid quantitation (Heatherbell, 1974).

TABLE XI: Recovery analysis of mixtures of acids at $W_1:Ws = 1.0$ by lead salt method

Acid	% Recovery	Average Recovery *
Phosphoric	99	102 ± 4%
	106	
	104	
	99	
Malic	92	96 ± 4%
	100	
	98	
	93	

TABLE XI (cont)

Acid	% Recovery	Average Recovery *
Citric	94 90 92 92	92 ± 2%
Quinic	44 57 53 50	51 ± 6%
Ascorbic	29 31 39 31	31 ± 7%

* Average of four determinations

Results from Table XI showed that good recoveries were obtained for the main three acids in GS apples, namely phosphoric, malic and citric, with an accuracy of ± 4%. However, the poor solubility of the lead salt of quinic acid (Heatherbell, 1974) resulted in very poor recovery with the loss amounting to about 50%. The loss of ascorbic (presumably due to oxidation during preparation and the drying method adopted) resulted in only one third of the original amount being recovered. Heatherbell (1974) earlier reported a 50% loss of ascorbic acid by the oven drying method.

Further investigations into the effect of lead salt drying conditions established that there was no significant difference between oven drying at 100 C for 1 hour and vacuum drying at 50 C overnight. Thus, the more convenient oven drying method was adopted in the analytical procedure. It is also important to bear in mind that although the loss of quinic and ascorbic acids may appear important, they only constituted about 2% of all the non-volatile acids present in GS apples, whereas the amount of phosphoric, malic and citric acids represented approximately 95% of the total acids. Since those three acids gave good recoveries, they

constituted the main non-volatile acids studied in later quantitative work.

3.5: Recovery of sugars and acids from apple extract

The extraction and separation procedure was evaluated by performing recovery experiments on the actual biological system. Samples of GS apple extract previously analysed for sugars and acids were fortified with known amounts of sugars (glucose, fructose, sorbitol and sucrose) and acids (phosphoric, malic, citric, quinic and ascorbic). Recovery in excess of 94% for the sugars and 96% for the acids was obtained. Thus, up to this point, the analytical procedure used in this work permitted the positive separation and identification combined with the rapid quantitation of a wide range of non-volatile organic acids and sugars commonly found in fruit. The applicability of this analytical method was investigated and is reported in the next section.

3.6: Application of method in determining sugars and acids in GS apples

Typical glc chromatograms of the sugars and non-volatile organic acids in GS apple extract were previously shown in Figures 3,4 and 5. The glc quantitative analysis of sugars in GS apples is reported in Table XII.

Results obtained indicated the predominance of fructose as the main sugar in GS apples, followed by glucose and sucrose and trace amounts of sorbitol. Total sugars established for GS apples were within the range encountered in tropical varieties such as mountain and rose apple (Chan et al., 1975). However, the result for total sugar appeared low compared to the figure for Canadian apple juice. This discrepancy can be accounted for because of the natural variation between areas, varieties, climate, etc., and also because the Canadian figure was taken as an average from 20 samples made from a blend of many different varieties.

TABLE XII: Quantitative determination of sugars in Granny Smith apples by glc

Sugar % Content	GS [a,b] apple	Mountain apple [b]	Rose apple [b]	Canadian apple juice [c]
Fructose	2.8	1.5	2.0	5.5
Glucose	1.0	2.1	3.0	2.5
Sorbitol	trace	-	-	1.0
Sucrose	0.4	-	1.8	1.8
Total Sugar (glc)	4.0	3.6	6.8	10.8
Source		(Chan et al., 1975)		(Ryan, 1972)

a. Average of 2 determinations

b. Expressed on a fresh weight basis as mg/100g fruit

c. Expressed on a fresh juice basis as mg/100ml juice

The quantitative analysis of the non-volatile acids in GS apples is reported in Table XIII. Total acids determined by glc was 0.66% as compared to 0.56% determined by titration and expressed as the major acid (malic). The discrepancy in correlating the two methods can be accounted for on the basis of the different molecular weights of malic (134.09) and citric (210.4). Excellent agreement resulted when results were expresed on a millicquivalent basis. This was obtained by dividing the mg acids/100g of fruit by the appropriate molecular weight.

TABLE XIII: Quantitative determination of organic acids[a] in Granny Smith apples

Acid	Molecular weight	mg/100g of fruit	meq/100g fruit
Phosphoric	98	trace	-
Malic	134.09	330	2.47
Citric	210.14	250	1.19
Quinic	192.2	40	0.21
Ascorbic	176.1	40	0.23
Total Acids (glc)		660	4.10
Total titratable acids[b] (as malic)		560	4.18

a. Average of two determinations

b. Determined by A.O.A.C. procedure

CHAPTER THREE

MEMBRANE CHARACTERISTICS AND

PREDICTION OF MEMBRANE PERFORMANCE

SECTION I

MEMBRANE CHARACTERISTICS

1. MECHANISM OF REVERSE OSMOSIS

The Gibbs equation relating the surface tension of a solution and the excess concentration of the solute at an interface predicts that for aqueous sodium chloride solutions, there is a negative adsorption of solute resulting in a multimolecular layer of pure water at the interface, the thickness of the layer being a function of the nature of the interface.

It was first suggested in 1956 that if the surface layer of pure water could be skimmed off, then solute could be separated from solvent. This suggestion was the starting point of investigations into the desalination of sea water by RO.

The mechanism of RO can be explained in terms of a conceptual model known as the preferential sorption-capillary flow mechanism (Sourirajan, 1970). Here the solution is in contact with a solid material in the form of a porous membrane. If the membrane has a preferential sorption for water (or a preferential repulsion for solute), a multimolecular layer of pure water could exist on the membrane surface. A continuous removal of this interfacial water can be effected by letting it flow under pressure through the membrane capillaries. This model also gives rise to the concept of a critical pore diameter for maximum separation and permeability. This is obviously twice the thickness of the interfacial pure water layer, for if the pore diameter is bigger, permeability will be higher but solute separation will be lower, since some of the feed solution will also flow through the pores. Smaller pores will increase separation but reduce permeability. An infinite variety of membrane solution combinations can give rise to different levels of solute separation.

In short, the indispensable twin requirement for the success of this separation process is an appropriate chemical nature of the film surface in contact with the solution, as

well as the existence of pores of appropriate size on the interfacial surface of the film.

For RO, the solvent and solute flux can be described simply by the following equations:

$$\text{Solvent Flux, } N_A = Ka\ (\Delta P - \Delta\pi) \qquad (1)$$

$$\text{Solute Flux, } N_B = Kb\ (\Delta C) \qquad (2)$$

The result of combining these two equations is that as the pressure is increased, water flux increases but salt flux does not. Thus at high pressures, the water flow predominates and pure water emerges from the membrane.

2. CONCENTRATION POLARISATION

As water transport proceeds through an RO membrane, there is a local concentration of solute at the site where water leaves the feed and passes through the membrane. This results in a subsequent local increase in osmotic pressure and decrease in water transport through this layer, a phenomenon termed concentration polarisation.

To overcome this reduction in water transport, the concentrated boundary layer must be displaced as it forms. This can be accomplished by ensuring turbulent flow conditions in the feed material over the membrane surface so that the concentrated layer is constantly replaced by a more dilute solution and water transport is facilitated.

3. DESCRIPTION AND OPERATION OF THE TM5-14 MODULE

A flow diagram of the RO pilot plant used in this study is presented in Fig. 11. The AS-197 membrane was seamless, 1.27 mm in inside diameter and 1.52 m long (Abcor, 1971). They were inserted into porous fibreglass epoxy-impregnated support tubes, fourteen of which were arranged in a circular pattern and connected by stainless steel headers in each TM5-14 module. A clear plastic shroud encased each module for collection of permeate.

The module which was freighted from America, contained 0.89 m^2 of membrane surface with a tubeside hold-up volume of 2.83 litres and could produce up to 757 litres of permeate per day, depending on operating conditions (Abcor, 1976).

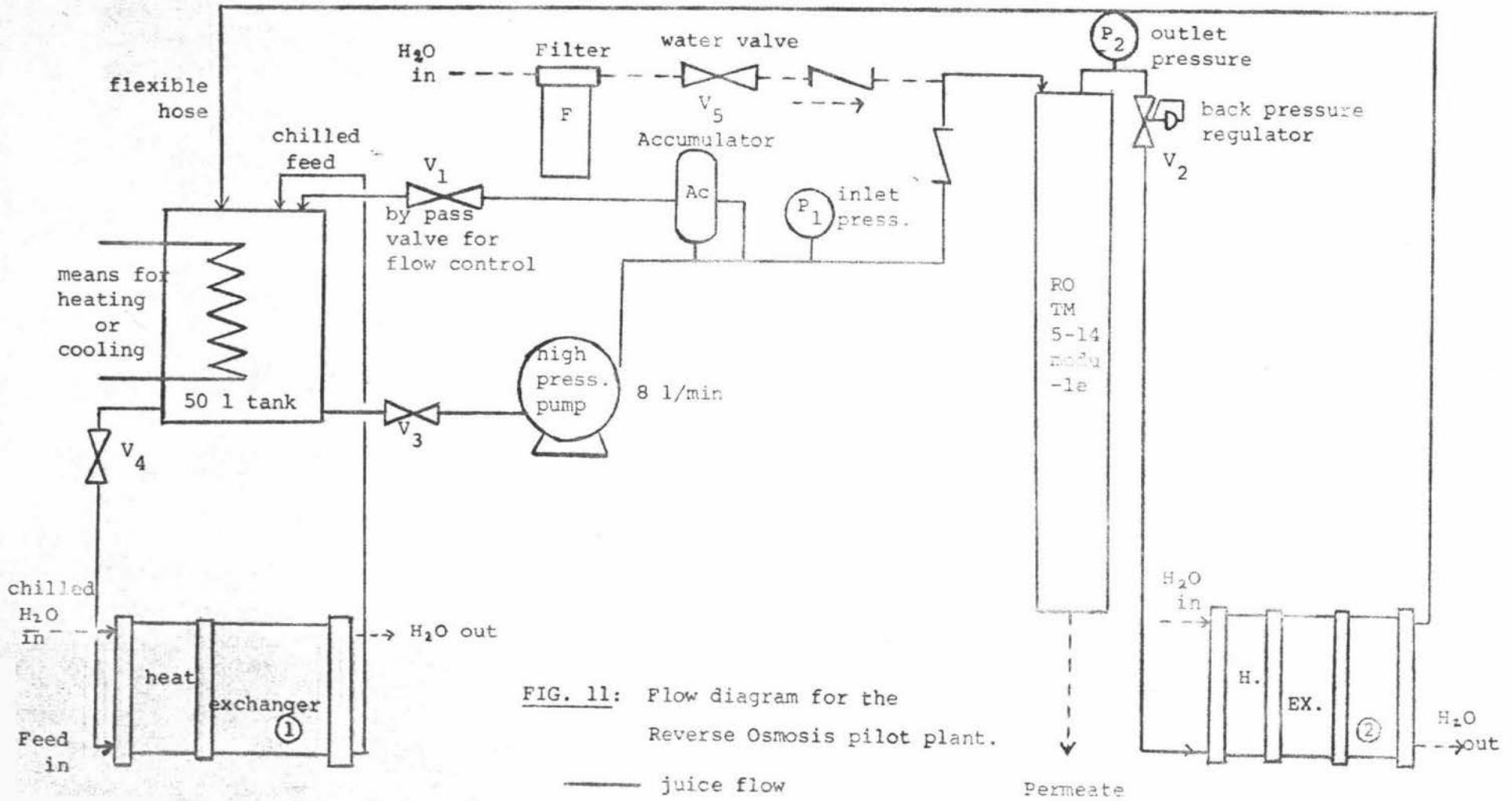


FIG. 11: Flow diagram for the Reverse Osmosis pilot plant.

The high pressure Triplex pump (model 520 Cat pump 2.5 H.P.) was operated at a fixed speed (355 rpm) and could pump up to 102 atmospheres. The tubes were fitted with turbulence promoters in the form of small spherical plastic beads inside the tubes.

A Greer-Olear high pressure accumulator (maximum working pressure = 204 atm) was incorporated into the system to dampen the surge produced by the pump.

A by-pass valve provided means of controlling the feed flow rate delivered by the pump, and a back pressure regulator was used to adjust the pressure in the system.

During standby periods, the module was kept wet since drying out tightens the structure of the membrane making it impermeable. A Teel 1P635 filter and water valve were added to the system to properly store the membrane; this was done by circulating filtered water at a small flow rate (200 - 400 mℓ/min).

Sanitation of the module was done after each run by dissolving commercial hypochlorite (0.75 g) in freshly filtered water (50 ℓ) and running the solution thus made (10 ppm Cl_2) under pressure for about 15 min. The module was then rinsed with pure water and the membranes kept wet as previously described.

Because of the high pressures involved, all components downstream of the high pressure pump were able to withstand pressures of at least 102 atm back pressure. Non-return valves V_1, V_2 and V_5 were used to ensure unidirectional feed flow and to withstand high back pressure build-up.

The feed tank, high pressure pump, accumulator, filter, module and all the interconnecting fittings and tubing, pipes and valves were built as a compact unit using commercially-available quick-assembly stainless steel.

Operating the system required some care. Before starting the pump, valve V-5 must be closed and valves V_1,

V_2 and V_3 must all be open. Initially, the pump was started and the pressure delivered was increased slowly by using the back pressure regulator V-2 to set the back pressure indicated at P2 (Fig.3). The inlet pressure was slowly increased by slowly closing the by-pass valve V-1. The operating pressure across the length of the membrane was taken as the arithmetic mean of the inlet and outlet back-pressure i.e. $P = \frac{P1 + P2}{2}$

The feed temperature was controlled mainly through the use of two Alfa-Laval plate heat exchangers. The small heat exchanger marked (1) in Fig.3 had 41 standard plates and the bigger P20-HB heat exchanger (2) had 63 plates. Running cool tap water through heat exchanger (1) and/or (2) was sufficient to maintain the feed temperature at 25 C.

Running at the lower temperature however, was more difficult due to the rapid heating of the pump at the high pressures and also to the warm ambient temperature (experiments were performed during summer). In this case both heat exchangers were used with chilled water at 1 C pumped from a large nearby cooling vat. Heat exchanger (2) was used to cool the concentrate and heat exchanger (1) the feed solution via a small recirculating pump. The feed tank was further insulated by circulating the outlet chilled water from the small heat exchanger inside thick plastic hose (1 cm inside diameter) wrapped along its length. The outlet chilled water from both exchangers was returned to the vat for cooling. The feed solution was either kept under refrigeration (2 C) before starting the experiment or cooled overnight in the feed tank using heat exchanger (1). The lowest temperature achieved by this system under steady state was 5-6 C but 7 C was chosen as a more practical figure. The concentrate and permeate were returned to the feed tank to complete a close loop system. Steady-state operating conditions were achieved after recirculating the feed for about 20-30 min.

The main details of the pilot RO plant are summarised in Table XIV below.

TABLE XIV: CHARACTERISTICS OF THE TM5-14 MODULE

Membrane Area	0.69 m^2
Maximum pressure	102 atm (1500 psig)
Maximum flow rate	8 litres/min
Temperature range	5 - 40 C
pH range	2.5 - 7.0
Concentration range	up to about 40° Brix

Source: Abcor (1972)

Typical performance for the cellulose acetate membrane used in this study is given in the table below.

TABLE XV: TYPICAL [illegible] C. [illegible] AS-197 MEMBRANE

Membrane Type	System	Rejection Range	Maximum Operating Pressure	
AS-197	NaCl: [illegible]	90-95%	102 atm	Rejection readings made at T=25 C at 41 atm after 30 min, 0.5% NaCl solution, 2.8 ℓ/min brine feed

Source: Abcor (1971)

4. EXPERIMENTS WITH DILUTE SALT SOLUTIONS

To ensure that the membrane was performing satisfactorily, and also to be able to monitor any changes in the operating characteristics of the membrane under actual experimental conditions, it was necessary to first establish the performance of the module on dilute sodium chloride solutions, since these data provide the common means for comparing different systems.

4.1 EXPERIMENTAL

4.1.1 Test Solution

In every case, this was an aqueous solution (0.5% w/v) made up of salt (food grade, 150 g) in fresh filtered water (50 ℓ).

4.1.2 Measurement of salt concentration

The salt concentrations in the permeate and feed samples were measured using a Philips Conductivity meter type PW 9501. The conductivity readings K (ohm^{-1} cm^{-1}) were converted to actual salt concentration (% w/v) using standard conversion graphs. The accuracy of the meter was assessed at $\pm$ 4%.

4.1.3 Permeate Flow (PF) and Rejection (R%)

All readings were taken when the experimental operating conditions reached steady state. The permeate flow (PF) was measured using a beaker and stopwatch. The permeate was collected at the outlet of the module and expressed in litres/min.

Rejection of solute expressed as a percentage was calculated according to the formula:

$$R\% = \frac{C_F - C_P}{C_F}$$, where

C_F = solute concentration in the feed (% NaCl)

C_P = solute concentration in the permeate (% NaCl)

PF and R% are commonly used as criteria for monitoring membrane performance (Morley, 1970).

4.1.4 Running-in procedure

The TMS-14 module was first subjected to a running-in period which consisted of operating the membrane continuously under pressure using the test salt solution (0.5% NaCl) until the separation efficiency and the permeate flow dropped to a steady value. The reduction in performance was rapid initially but after the initial period, the performance became virtually constant.

4.1.5 Material balance

A run was made to ensure that nothing was lost from the system. Pure water was used, with pressure being varied from 14 atm to 100 atm (200 - 1500 psi), while the permeate flow was collected at different feed flow rates to permit material balances to be drawn up. Results are presented in Table XVI.

4.1.6. Effect of Operating Pressure

The effect of operating pressure on the performance of the membrane (PF and R%) was assessed by running the test salt solution (0.5% NaCl) through the module at a constant recirculation rate (5.0 ± 0.2 ℓ/min) and temperature (25 ± 1 C). Results are listed in Table XVII and illustrated in Fig.12.

4.1.7 Effect of Concentration

This was assessed by running the module at a constant pressure of 75 atm and constant temperature of 25 C at the maximum recirulation rate of 5.0 ± .2 ℓ/min, while the concentration of the salt solution was varied from 0.5 to 1.5%. Results are listed in Table XVIII and illustrated in Fig. 13.

4.1.8 Effect of Recirculation Rate (RR)

The effect of recirculation rate on the PF and R% was assessed by running the test solution at a constant pressure of 60 atm, temperature of 25 C and altering the recirculation rate. Results are listed in Table XIX and illustrated in Fig. 14.

4.1.9 Effect of Operating Time

The effect of compaction on membrane performance was carried out over a period of six months of intermittent operation. Conditions chosen for PF and R% were near the optimum for the membrane and were as follows:

Temperature	24 ± 1 C
Pressure	77 atm (1130 psi)
Recirculation Rate	5.0 ± 0.2 ℓ/min
Concentration	0.5% NaCl

4.1.10 Effect of Temperature

This effect was tested at constant operating pressure (77 atm), feed concentration (0.5% NaCl) and recirculation rate (5.0 ± 0.2 ℓ/min). Results are listed in Table XXI and illustrated in Fig. 16.

5. RESULTS

TABLE XVI: Material balance for the RO Module run with fresh water. T = 25 C

Pressure atm	Recirculation ℓ/min	Retentate ℓ/min	Permeate ℓ/min
13.6	2.9	2.5	negl
27.2	3.2	3.2	negl
40.8	4.0	3.9	0.1
54.4	4.8	4.7	0.1
68.7	5.5	5.1	0.4
81.6	6.1	5.6	0.5
95.2	6.8	6.1	0.7
102	8.0	6.3	1.7
102	5.7	4.7	1.0

TABLE XVII: Effect of concentration pressure on membrane performance. RR = 8 ℓ/min ; T = 25 C

Pressure atm	Feed % NaCl	Permeate % NaCl	R %	PF ℓ/min
27.2	0.44	0.025	94.9	0.21
43.5	0.45	0.021	95.5	0.30
57.5	0.45	0.013	97.1	0.39
71.4	0.45	0.010	97.8	0.48
76.9	0.47	0.012	97.5	0.51

TABLE XVIII: Effect of concentration on membrane performance. RR = 8 ℓ/min - P = 75 atm ; T = 25 C

Feed % NaCl	Permeate % NaCl	R %	PF ℓ/min
0.53	0.019	96.4	0.48
0.96	0.043	95.5	0.46
1.50	0.072	95.2	0.43

TABLE XIX: Effect of Recirculation Rate on membrane performance. P = 60 atm - T = 25 C

RR ℓ/min	Feed % NaCl	Permeate % NaCl	R %	PF %
3.5	0.47	0.016	96.6	0.40
4.0	0.48	0.012	97.5	0.40
5.1	0.48	0.015	96.9	0.40
6.3	0.50	0.013	97.4	0.41

TABLE XX: Effect of operating time on membrane performance - RR = 5 ℓ/min; C = 0.5% NaCl; P = 77 atm; T = 25 C

Cumulated time (hours)	PF ℓ/min	R %
2	0.49	97.5
91	0.47	97
107	0.48	97
124	0.48	97
149	0.48	96
161	0.44	95

TABLE XXI: Effect of feed temperature on membrane performance. RR = 5 ℓ/min; P = 77 atm

Temp C	Feed % NaCl	Permeate % NaCl	R %	PF ℓ/min
23	0.47	0.010	98	0.47
25	0.47	0.012	97	0.51
27	0.47	0.012	97	0.54
31	0.47	0.013	97	0.59

Fig. 12: Effect of operating pressure (atm) on membrane performance (PF and R%)

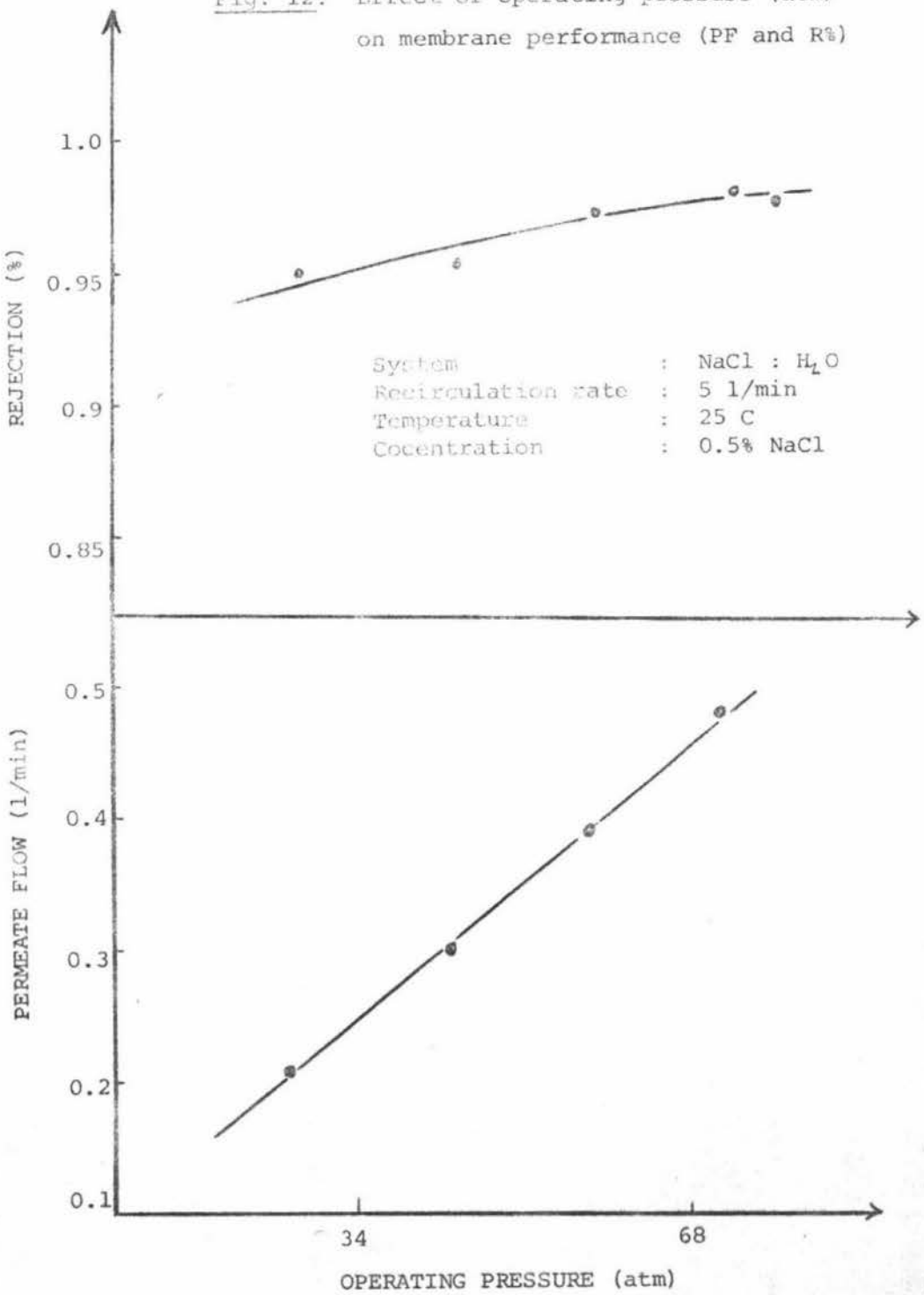


Fig. 13 : Effect of concentration (% NaCl) on Membrane performance (PF and R%)

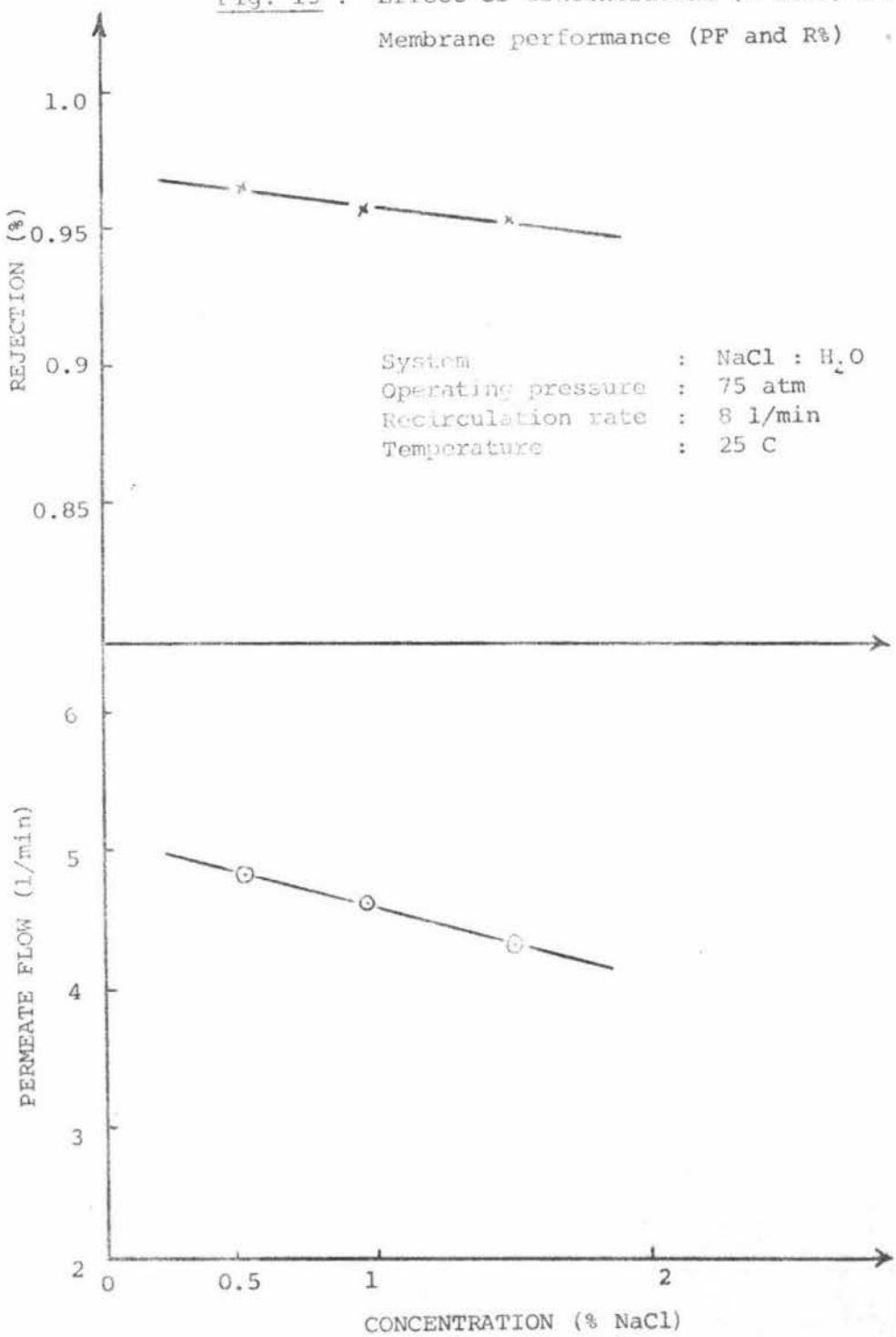


Fig. 14: Effect of recirculation rate (l/min) on membrane performance (PF and R%)

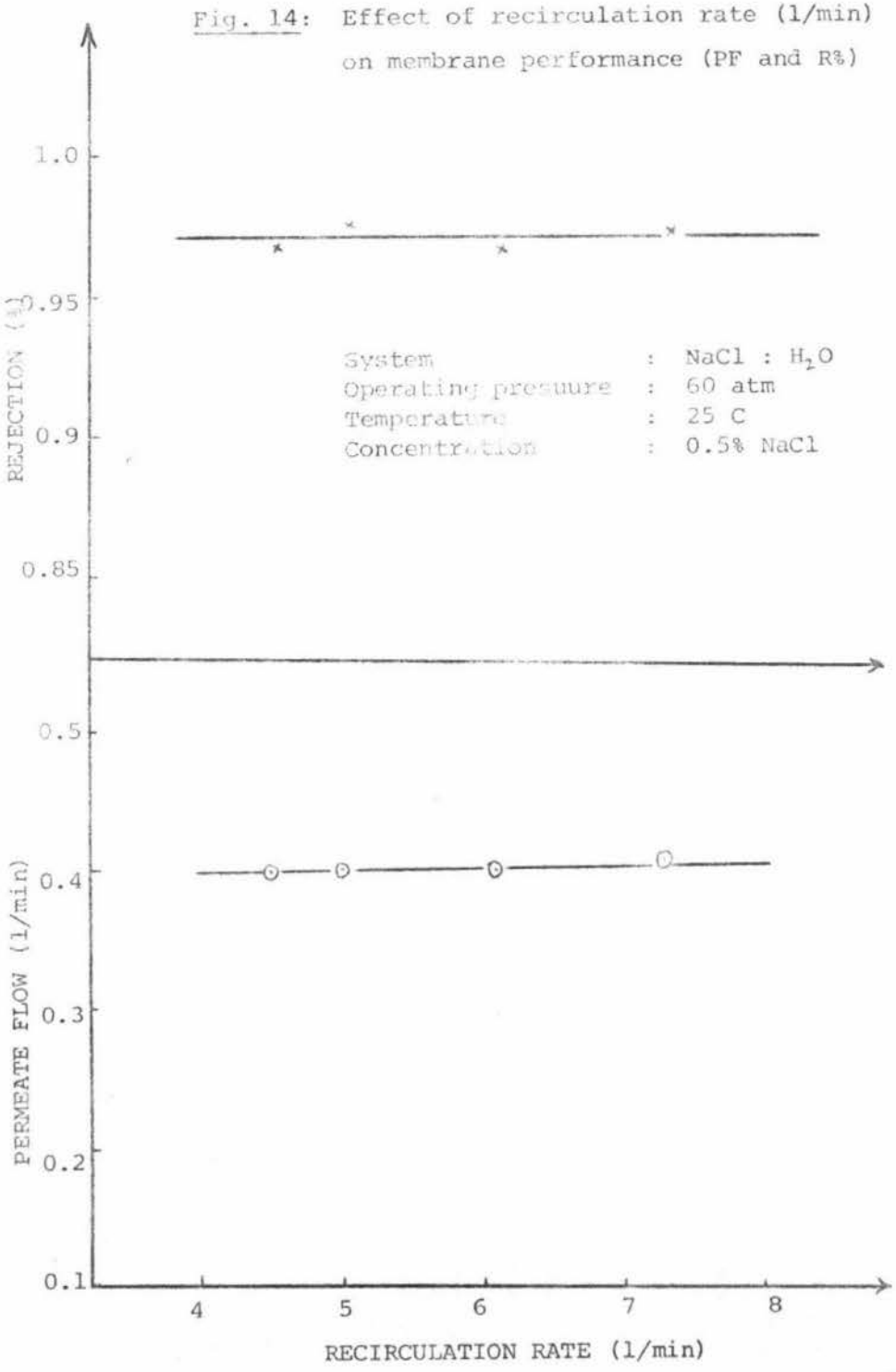


Fig. 15: Effect of operating time (hours) on membrane performance (PF and R%)

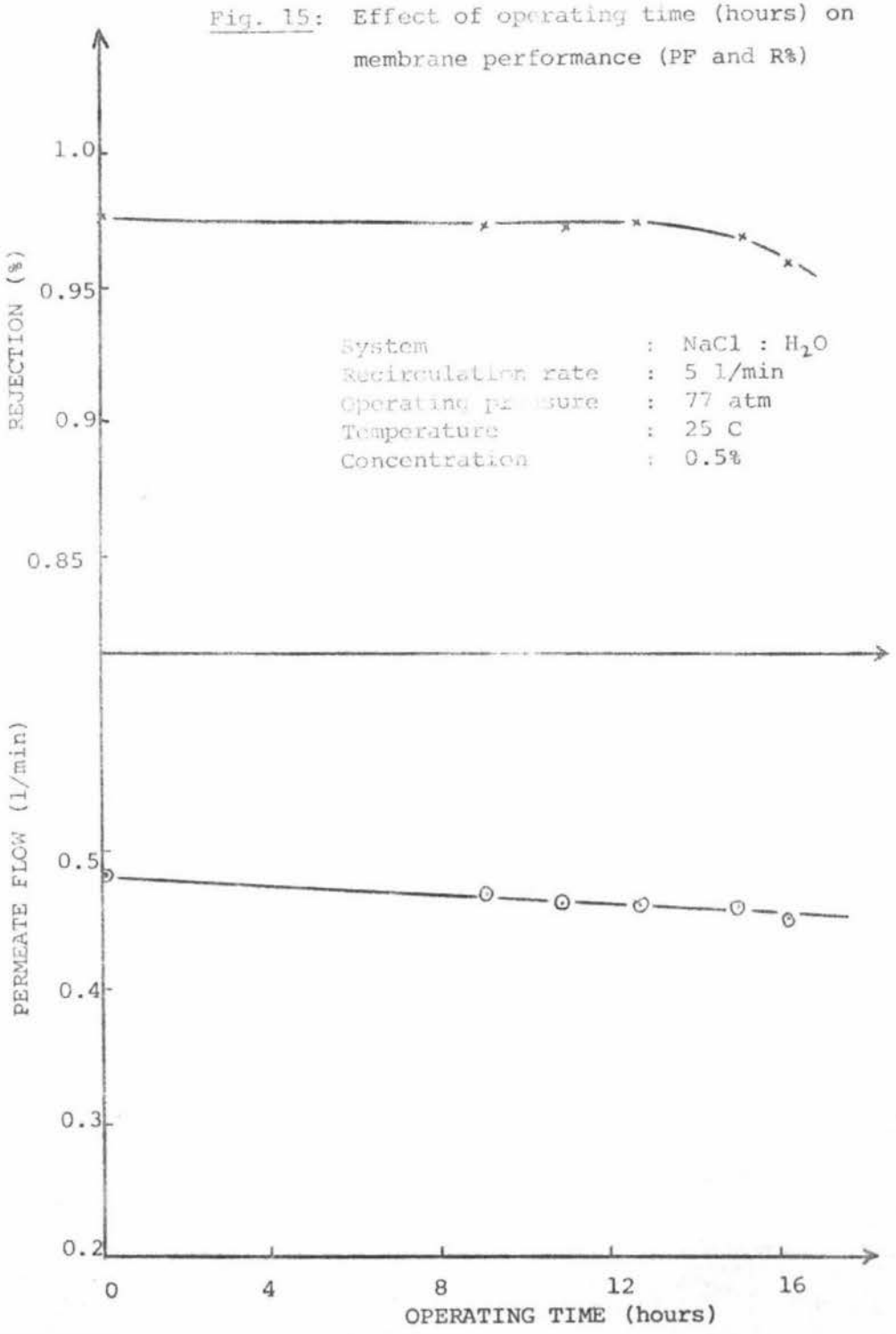
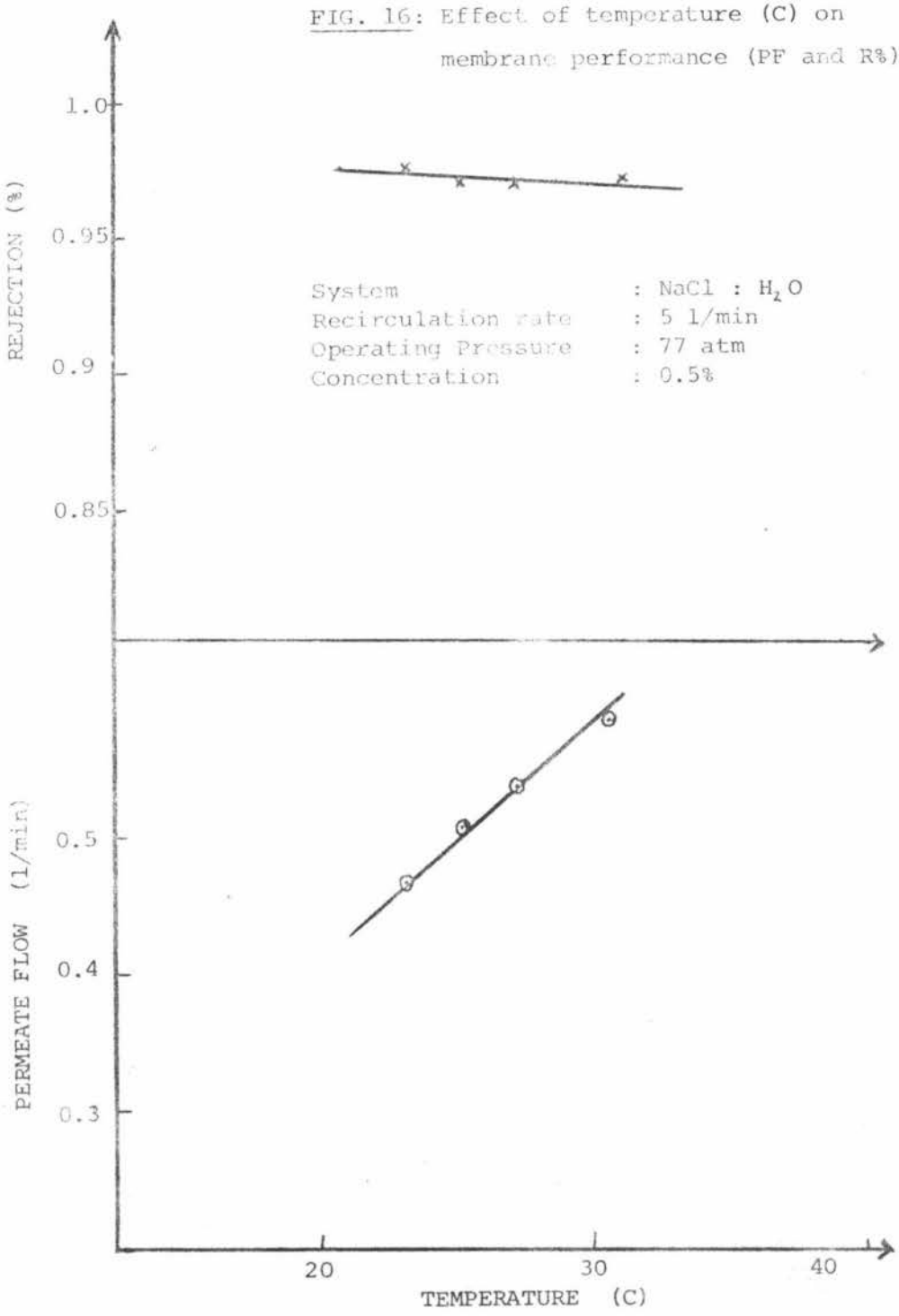


FIG. 16: Effect of temperature (C) on membrane performance (PF and R%).



6. DISCUSSION

On the basis of equation (1) described earlier, the module appears to perform satisfactorily when run with pure water (Table XVI). At the lower pressures (13 - 27 atm) and lower recirculation rates (2.3 - 3.2 ℓ/min), the PF was neglible but gradually increased with feed rate and operating pressures, as expected (Worley, 1970).

The maximum PF for pure water at maximum pressure (102 atm) and maximum recirculation rate (8 ℓ/min) was 1.7 ℓ/min. It dropped quickly to 1 ℓ/min at the same pressure (102 atm) when the by-pass was slightly opened, reducing the recirculation rate to 5.7 ℓ/min.

When run with dilute salt solutions (0.5% NaCl) the membrane also performed according to equations (1) and (2). Table XVII and Fig. 12 show the effect of the operating pressure on the membrane performance (PF and R%). The PF increased linearly with pressure, while the R% increased exponentially to a limiting level of about 97 - 98%. This value agrees with the membrane characteristics presented in Table IV. From Table XVII, the PF shows a 2.4 fold increase for a 2.8 fold increase in operating pressure, while the R% only increased 3% for nearly a 3 fold increase in pressure. Worley (ibid.) obtained similar variations with high rejecting CA membranes.

Concentration, on the other hand, has a negative effect on PF and R%, as shown in Table XVIII and Fig.13. This can be due to the effect of concentration polarisation described earlier and is shown by a 10% decrease in PF and R% for a 3 fold increase in concentration at 75 atm within the range 0.5 to 1.5% NaCl (0.1 - 0.3 M NaCl). Worley (ibid.) similarly obtained a 6% decrease in R% and a 30% decrease in PF for a 3 fold increase in concentration at 102 atm within the range 0.5 to 1.5 M NaCl. Thus concentration has an important effect on rejection, mainly due to the effect of concentration polarisation. Although PF decreased with increasing concentration, the relative decrease (10%) was not as marked as the relative increase in PF with pressure

(85% i.e. for a 100% increase in P, the PF increased correspondingly by 85%). Thus operating pressure appears to be relatively more important than concentration in its effect on the membrane performance.

In contrast to pressure and concentration, feed recirculation rate had relatively little effect on PF and R% as shown in Table XIX and Fig.14. Worley (ibid.) showed that this was the case with high rejecting RO membranes.

The results from Table XX and Fig. 15 have to be taken into the context of the conditions of the membrane treated over a period of six months when this study was done. Over the first three quarters of this period, the membrane showed little decrease in R% and a 4% decrease in PF. The last part of this period was spent experimenting with model solutions of sugars, acids, and real apple juice; the compaction effect was marked, as shown by a 2% drop in R% and a 4% drop in PF. The overall figure, however, was a 10% drop in PF for the whole period as well as a 2.5% drop in overall rejection of salt. Judging from Fig.15, the membrane performance was not drastically changed over the period tested. Thus, for the purpose of this study, it could be assumed that the membrane characteristics remained relatively constant over the length of the experimental work.

Finally, as expected (Worley, ibid.) an increase in temperature of the solution generally improved membrane performance, as shown in Fig. 16 and Table XXI. R% remained virtually constant at about 97% while PF increased 26% for a 35% increase in temperature 23 to 31 C. This represented a relative increase in PF of 74% with respect to temperature compared to 85% for pressure.

7. CONCLUSION

The TM5-14 module (AS-197 membrane) performed as expected when a standard aqueous salt solution was used to check its characteristics.

From the five process variables investigated, the effect of operating pressure is the most important factor affecting membrane performance; next is temperature, then concentration and operating time. Recirculation rate had little effect on PF and R%.

SECTION II

PREDICTION OF MEMBRANE PERFORMANCE USING THE KIMURA-SOURIRAJAN ANALYSIS

1. INTRODUCTION

Kimura and Sourirajan (Sourirajan, 1970) based their analysis of RO experimental data on the isothermal separation of binary aqueous solutions, using Loeb-Sourirajan porous CA membranes. Their analysis led to the development of a set of basic transport equations which, together with the correlations of the RO experimental data, enabled the practical prediction of membrane performance from a minimum of experimental data. This approach was based on a generalised capillary diffusion model for the transport of solute through the membrane, and was applicable to the entire range of solute separations in the RO process. In their analysis, the transport of solvent water through the porous membrane was proportional to the effective pressure, while that of the solute was due to pore diffusion, and hence proportional to the difference in solute concentration across the membrane. (See Section I, p.51).

The object of this study was to extend the Kimura-Sourirajan analysis to the pilot plant RO module under study, using the system sodium chloride-water to predict membrane performance. If the analysis was successful, the prediction of membrane performance would be extended to aqueous model solutions of sugars and acids, and ultimately to apple juice.

2. EXPERIMENTAL PROCEDURE

Following is a theoretical treatment of the Kimura-Sourirajan analysis and the application of this method to the prediction of membrane performance related to the RO module under study.

2.1. Kimura-Sourirajan analysis of Reverse Osmosis Experimental Data

Figure 17 shows an RO process under continuous operation. The existence and the continuous withdrawal of the preferentially sorbed interfacial layer along with the

bulk feed solution through the porous membrane gives rise to a product solution which is less concentrated than the feed solution. Thus, a concentration gradient arises between the boundary solution and the bulk feed solution; this effect is called concentration polarisation .

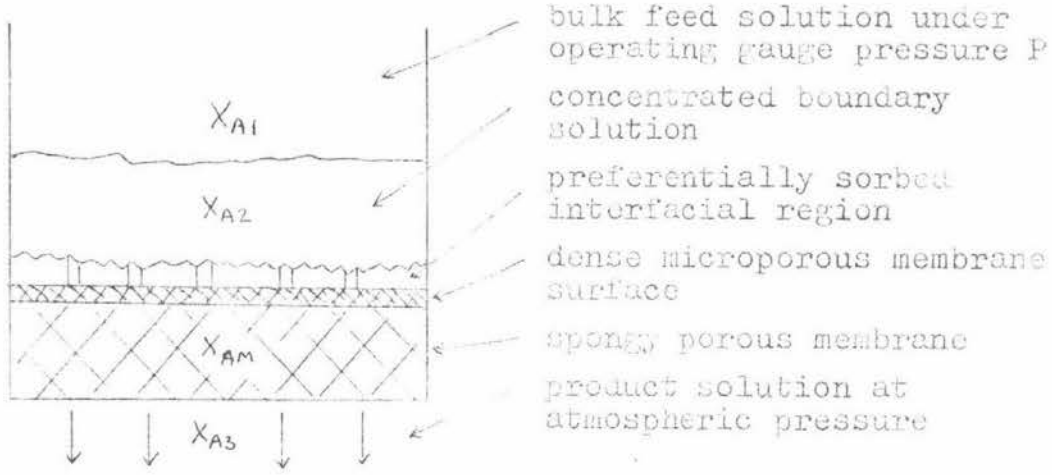


Fig. 17: RO process under steady state conditions

Let X and N represent the mole fraction of the solute and solvent flux through the membrane (in g.mole/cm^2/sec), and c the molar density of solution (in g.mole/cm^3), and let the subscripts A, B, M, 1, 2 and 3 represent solute, solvent-water, membrane phase, bulk feed solution, concentrated boundary solution, and the membrane permeated product solution respectively.

Then X_{AM}, X_{A1}, X_{A2}, and X_{A3} are the mole fractions of solute in the membrane phase, bulk feed solution and the concentrated boundary solution on the high pressure side of the membrane, and the membrane permeated product solution on the atmospheric side of the membrane respectively; the symbols for the molar densities c_M, c_1, c_2, and c_3 have similar meanings. N_A and N_B are the solute and solvent flux through the membrane.

2.1.1 Pure Water Permeability Constant (A)

For a given area of membrane surface (S cm^2), the pure water permeability rate, PWP in g/hr is proportional to the operating pressure (P atm), and the proportionality constant (given as g.mole H_2O/cm^2. sec. atm) is represented

by the symbol A defined as follows:

$$A = \frac{PWP}{M_B \cdot S \cdot 3600 \cdot P} \qquad (3)$$

where M_B is the molecular weight of water.

In this analysis, A is a fundamental quantity. It is a measure of the overall porosity of the film, given in terms of the permeation rate of pure water for which the membrane material has a preferential sorption from the aqueous solution in the RO process. A corresponds to conditions of zero concentration polarisation and is independent of any solute under consideration.

2.1.2 Transport of solvent water through the porous membrane

The solvent-water flux (N_B) through the membrane is proportional to the effective pressure (P) where the proportionality constant is A. Thus

$$N_B = A \Delta P = A \left[P - \left\{ \pi(X_{A2}) - \pi(X_{A3}) \right\} \right] \qquad (4)$$

$$N_B = A \left[P - \pi(X_{A2}) + \pi(X_{A3}) \right] \qquad (5)$$

where

(X_{A2}) = osmotic pressure π due to solute mole fraction X_{A2}

(X_{A3}) = osmotic pressure π due to solute mole fraction X_{A3}

Equation (5) is applicable to systems where the kinematic viscosity of the product solution is not too different from that of pure water. This condition is reasonably satisfied in most cases of practical interest such as the system sodium chloride-water.

The quantities N_B, A, P and X_{A3} can be obtained from the experimental data on PWP , PR , solute separation, operating pressure, and the membrane area. Using the above data, $\pi(X_{A2})$ can be calculated and hence (X_{A2}) from equation (5). Since the value of A must be known to obtain (X_{A2}), it

is a fundamental quantity with respect to the membrane and to the RO process.

At a given operating pressure, A is a constant, and is independent of any solution under consideration, while N_B and X_{A3} are functions of feed concentration and feed flow rate at the membrane interface.

By itself, equation (5) does not suggest the existence or otherwise of any unique relationship, independent of feed concentration and feed flow rate, between X_{A2} and X_{A3}.

2.1.3 Transport of solute through the membrane phase

During the RO process under continuous steady-state operation, a concentration difference exists on either side of the porous membrane. The transport of solute through the membrane is then treated as being due to pore diffusion. Consequently, the solute flux through the membrane is proportional to the concentration difference on either side of the membrane phase. Thus:

$$N_A = (D_{AM}/\delta).(c_{M2} \cdot X_{AM2} - c_{M3} \cdot X_{AM3}) \qquad (6)$$

where X_{AM2} and X_{AM3} are mole fractions of solute in the membrane phase in equilibrium with X_{A2} and X_{A3} in the solution phases respectively; c_{M2} and c_{M3} are the molar densities corresponding to X_{AM2} and X_{AM3} in the membrane phase, while D_{AM} is the diffusivity of the solute in the membrane phase and δ is the effective thickness of the membrane.

None of the quantities on the right hand side of equation (6) are known or easily measurable, and the dividing line in the membrane phase between the regions corresponding to X_{AM2} and X_{AM3} is only conceptual.

Equation (6) can be transformed into one containing measurable quantities and a group of unknown quantities, by assuming a simple linear relationship between X_A

(concentration in the solution phase) and X_{AM} (concentration in the membrane phase). Thus let:

$$c.X_A = K \cdot c_M \cdot X_{AM} \qquad (7)$$

where K is a constant. Rewriting equation (7) for equilibrium conditions on either side of the membrane:

$$c_2 \cdot X_{A2} = K \cdot c_{M2} \cdot X_{AM2} \qquad (8)$$

$$c_3 \cdot X_{A3} = K \cdot c_{M3} \cdot X_{AM3} \qquad (9)$$

Equation (6) can now be rewritten as:

$$N_A = (D_{AM}/K\delta) \cdot (c_2 \cdot X_{A2} - c_3 \cdot X_{A3}) \qquad (10)$$

Since N_A, c_2, c_3, and X_{A3} are measurable quantities and X_{A2} can be obtained from equation (3), the quantity $(D_{AM}/K\delta)$ (known as the solute transport parameter) can be calculated from equation (10). Now:

$$\frac{N_A}{N_A + N_B} = X_{A3} \qquad (11)$$

$$\therefore \quad N_A = \frac{X_{A3}}{(1 - X_{A3})} \cdot N_B \qquad (12)$$

Substituting equation (12) into equation (10):

$$N_B = (D_{AM}/K\delta) \cdot \frac{(1 - X_{A3})}{X_{A3}} \left(c_2 \cdot X_{A2} - c_3 \cdot X_{A3}\right) \qquad (13)$$

The parameter $(D_{AM}/K\delta)$ plays the role of a mass transfer coefficient with respect to the solute transport through the membrane. Hence, it is treated as a single quantity for the purposes of analysis. It must, however, be remembered that $(D_{AM}/K\delta)$ is not a single factor, but a combination of several inter-related factors, none of which are, or need to be known precisely for the purposes of these calculations.

In the original derivation, equation (7), and hence equation (8) and (9), were assumptions. Since X_{A2} and X_{A3} are bound to the membrane phase concentrations by the same relation (7), equations (8) and (9) imply that with respect to any membrane, the values of X_{A2} and X_{A3} must be uniquely related, and this relationship must be independent of feed concentrations and feed flow rate past the surface of the membrane.

This was verified experimentally for the systems sodium-chloride-water, glycerol-water and urea-water (Sourirajan, 1970). Consequently, equation (7) is no longer an assumption but rests on the basis of firm experimental evidence.

2.1.4 Mass transfer on the high pressure side of the membrane

Since the solute in the concentrated boundary solution also diffuses back to the less concentrated feed solution on the high pressure side of the membrane, a mass transfer coefficient k, characteristic of the experimental conditions on the high pressure side of the membrane can be calculated on the basis of the simple 'film theory'. The solute transfer from the concentrated boundary condition can be represented by the relation (Bird et al., 1960):

$$N_A = X_A \cdot (N_A + N_B) - D_{AB} \cdot c_1 \cdot \frac{dX_A}{dz} \qquad (14)$$

where D_{AB} is the diffusivity of the solute in the aqueous feed solution, and z is the thickness of the concentrated boundary layer. Using equation (11), equation (14) can be written as:

$$\frac{dX_A}{dz} - \frac{(N_A + N_B)}{c_1 \cdot D_{AB}} \cdot X_A = - \frac{(N_A + N_B)}{c_1 \cdot D_{AB}} \cdot X_{A3} \qquad (15)$$

The boundary conditions for equation (15) are:
when $z = 0$, $X_A = X_{A1}$, and
when $z = l$, $X_A = X_{A2}$ (l = thickness in cm)

On solving the simple differential equation (14) with the above boundary conditions:

$$X_{A2} = X_{A3} + (X_{A1} - X_{A3}) \exp.\left[\frac{(N_A + N_B)}{c_1} \cdot \frac{1}{D_{AB}}\right] \quad (16)$$

or: $$\ln\left(\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right) = \frac{(N_A + N_B)}{c_1} \cdot \frac{1}{D_{AB}} \quad (17)$$

Defining the mass transfer coefficient, k, on the high pressure side of the membrane in the conventional manner of the film theory (Sherwood, 1959; Sherwood and Pigford, 1952; Treybal, 1955):

$$k = \frac{D_{AM}}{l} \quad (18)$$

Equation (17) can be written as:

$$\ln\left(\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right) = \frac{(N_A + N_B)}{k\, c_1} \quad (19)$$

From Equation (12):

$$N_A + N_B = \frac{N_B}{(1 - X_{A3})} \quad (20)$$

Substituting equation (20) into equation (19):

$$\ln\left(\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right) = \frac{N_B}{k.c_1.(1 - X_{A3})} \quad (21)$$

or: $$N_B = k.c_1 \cdot (1 - X_{A3}) \cdot \ln\left(\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right) \quad (22)$$

2.1.5 Basic transport equations

From the foregoing analysis, the relationships:

$$A = \frac{PWP}{M_B \cdot S \cdot 3600 \cdot P} \quad (3)$$

$$N_B = A\left[P - \pi(X_{A2}) + \pi(X_{A3})\right] \quad (5)$$

$$= (D_{AM}/K\delta) \cdot \left(\frac{1 - X_{A3}}{X_{A3}}\right) \cdot (c_2 X_{A2} - c_3 X_{A3}) \quad (13)$$

$$= k.c_1 . (1 - X_{A3}) . \ln \left(\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}} \right) \qquad (22)$$

emerge as a set of basic equations describing the solute and solvent transport in an RO process involving binary aqueous solutions and membranes having a preferential sorption for water from such aqueous solutions.

In many aqueous solutions (such as sodium chloride-water) and in concentration ranges of practical interest (0 - 1.0 M NaCl), the molar densities c_1, c_2 and c_3 may essentially be the same (see Appendix I). In such cases, an average value can be used to represent the molar density (c) of the solution and it may be assumed that:

$$c = c_1 = c_2 = c_3 \qquad (23)$$

The set of basic transport equations (5), (13) and (22) for the system sodium chloride-water can then be written as:

$$N_B = A \left[P - \pi(X_{A2}) + \pi(X_{A3}) \right] \qquad (5)$$

$$= c (D_{AM}/K\delta) . \left(\frac{1 - X_{A3}}{X_{A3}} \right) . (X_{A2} - X_{A3}) \qquad (24)$$

$$= k.c (1 - X_{A3}) . \ln \left(\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}} \right) \qquad (25)$$

2.1.6 Solute separation in terms of mole fraction

Let W_A and W_B represent respectively the weight in grams of solute and solvent in an aqueous solution, and let M_A be the molecular weight of the solute. Solute separation (R) can then be expressed in terms of mole fractions (X_A) as follows:

$$R = \frac{(m_1 - m_3)}{m_1} = 1 - \frac{m_3}{m_1} \qquad (26)$$

$$m = \frac{W_A}{M_A} . \frac{1000}{W_B} \qquad (27)$$

$$X_A = \frac{W_A / M_A}{\frac{W_A}{M_A} + \frac{W_B}{M_B}} \qquad (28)$$

$$1 - X_A = \frac{W_B/M_B}{\frac{W_A}{M_A} + \frac{W_B}{M_B}} \quad (29)$$

$$\frac{X_A}{1 - X_A} = \frac{W_A/M_A}{\frac{W_B}{M_B}} \quad (30)$$

Therefore $$m = \frac{X_A}{1 - X_A} \cdot \frac{W_B}{M_B} \cdot \frac{1000}{W_B}$$

$$= \frac{X_A}{1 - X_A} \cdot \frac{1000}{M_B} \quad (31)$$

Therefore $$m_1 = \frac{X_{A1}}{1 - X_{A1}} \cdot \frac{1000}{M_B} \quad (32)$$

and $$m_3 = \frac{X_{A3}}{1 - X_{A3}} \cdot \frac{1000}{M_B} \quad (33)$$

Therefore $$R = 1 - \left(\frac{X_{A3}}{1 - X_{A3}}\right) \cdot \left(\frac{1 - X_{A1}}{X_{A1}}\right) \quad (34)$$

2.1.7 Permeate Flow

Let (PF) represent permeate flow in grams per hour per S cm^2 of film surface, and Q' the product rate in grams per second per cm^2 of film area. Also, let w_A and w_B be the grams of solute and solvent respectively in Q' grams of product solution. Then:

$$Q' = w_A + w_B \quad g/sec.cm^2 \quad (35)$$

$$(PF) = Q' \cdot S \cdot 3600 \quad g/hr \quad (36)$$

From equation (26):

$$m_3 = m_1 \cdot (1 - R) \quad (37)$$

Since: $$m_3 = \frac{w_A}{M_A} \cdot \frac{1000}{w_B} \quad (38)$$

Then: $$\frac{w_B}{w_A} = \frac{1000}{m_1 \cdot (1 - R) \cdot M_A} \quad (39)$$

and: $$Q' = w_A \cdot \left[1 + w_B/w_A\right] \quad (40)$$

$$= w_A \cdot \left[1 + \frac{1000}{m_1 \cdot (1-R) \cdot M_A}\right] \quad (41)$$

Therefore $$w_A = \frac{Q'}{1 + \frac{1000}{m_1 \cdot (1-R) \cdot M_A}} \quad (42)$$

Since $$\frac{w_B}{M_B} = N_B \quad ,$$

$$w_B = N_B \cdot M_B \quad (43)$$

Also $$w_B = Q' - w_A$$

$$= Q' \left[1 - \frac{w_A}{Q'}\right] \quad (44)$$

$$= Q' \left[1 - \frac{1}{1 + \frac{1000}{m_1 \cdot (1-R) \cdot M_A}}\right] \quad (45)$$

Therefore $$Q' = \frac{N_B \cdot M_B}{\left[1 - \frac{1}{1 + \frac{1000}{m_1 (1-R) M_A}}\right]} \quad (46)$$

Therefore $$PF = \frac{N_B \cdot M_B \cdot S \cdot 3600}{\left[1 - \frac{1}{1 + \frac{1000}{m_1 \cdot (1-R) \cdot M_A}}\right]} \quad (47)$$

2.1.8 Correlations of RO experimental data

The correlations of the quantities A, $(D_{AM}/K\delta)$, and k with operating pressure, temperature, feed concentration, feed flow rate and the nature of solute are of practical interest from the point of view of predicting membrane performance under different operating conditions. Such correlations have to be established experimentally for every specific membrane-solution-operating system. The basic transport equations(3), (5), (13) and (22), by themselves are independent of such correlations. On the basis of extensive experimental studies (Sourirajan, 1970), significant experimental correlations have been established for a number of solution systems, of which sodium chloride-water

is a typical example. Briefly, the experimental conditions were as follows. Membranes shrunk at different temperatures were used to give different levels of solute separation under various operating conditions. The experiments were of the short run type (each lasting 2 hours) and were carried out at the laboratory temperature (25 C). The effective area of the film used was 7.6 cm^2, and the reported product rates were those corrected to 25 C using the relative viscosity and density data for pure water.

(i) Correlations of A

At a given temperature:

$$A = A_o \exp (-\alpha P) \qquad (48)$$

where A_o, the value of A obtained by extrapolation when $P = 0$, is a constant; α is a function of the overall porosity of the membrane, and its value has to be determined experimentally for each film. Equation (48) expresses the fact that the value of A tends to decrease with increase in operating pressure.

(ii) Correlations of $(D_{AM}/K\delta)$

At a given temperature (Sourirajan, 1970):

$$(D_{AM}/K\delta) \propto P^{-\beta} \qquad (49)$$

and, at a given pressure (Sourirajan, 1977):

$$(D_{AM}/K\delta)_{NaCl} \propto \exp (0.005\ T) \qquad (50)$$

Equation (49) expresses the fact that $(D_{AM}/K\delta)$ tends to decrease with increasing operating pressure; β is a function of the overall porosity of the membrane, and its value has to be determined experimentally for each film. The effect of temperature on $(D_{AM}/K\delta)$ for sodium chloride is expressed by equation (50) for the temperature range 5 to 36 C. At a given temperature and pressure the solute transport parameter for many inorganic and organic solutes was shown by Sourirajan (1970) to be independent of feed

concentration and feed flow rate.

(iii) Correlations of k

At a given temperature, k is a function of nature of solute, feed concentration, feed flow rate, and the geometry of the apparatus or membrane configuration. (Sourirajan, ibid.) Sourirajan (1971) considered k independent of operating pressure, and the effect of feed flow rate Q on k may be expressed by the relation:

$$k \propto Q^n \qquad (54)$$

where n is a constant characteristic of the nature of the solute.

2.1.9 Predictability of membrane performance

A single set of experimental pure water permeability PWF , permeate flow Pf and solute separation (R) data at any operating pressure was shown by Sourirajan (1970) to enable the prediction of both R and (Pf) at that pressure, for all feed concentrations and feed flow rates for which $(D_{AM}/K\delta)$ remains constant. Such prediction involves the following steps:

(i) From the experimental data, the values of A and $(D_{AM}/K\delta)$ are calculated using equations (3), (5) and (13). These values were shown by Sourirajan (1970) to remain constant for all feed concentrations and feed flow rates.

(ii) The value of k can be obtained from predetermined experimental data (Sourirajan, ibid.). Combining equations (24) and (25) for the system sodium chloride-water:

$$c\,(D_{AM}/K\delta).\left(\frac{1 - X_{A3}}{X_{A3}}\right).(X_{A2} - X_{A3}) = k.c\,.\,(1 - X_{A3})\,.\,\ln\left(\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right)$$

or

$$(D_{AM}/K\delta)\left(\frac{X_{A2} - X_{A3}}{X_{A3}}\right) = k \cdot \ln\left(\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right) \quad (52)$$

or

$$\left(\frac{X_{A2} - X_{A3}}{X_{A3}}\right) = \frac{k}{(D_{AM}/K\delta)} \cdot \ln\left(\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right) \quad (53)$$

(iii) By trial and error, the combinations of X_{A2} and X_{A3} satisfying equation (53) are first found - there are several.

(iv) Finally, that particular combination of X_{A2} and X_{A3} which satisfies the equality of equations (5) and (24) is determined - this determines the value of N_B.

(v) Using the values of X_{A3} and N_B determined above, and the known value of X_{A1}, corresponding to the preset operating conditions, the values of solute separation R, and permeate flow (PWP) are determined using equations (34) and (47).

The foregoing prediction procedure points out that, with reference to a given solute and operating pressure and temperature, while data on A and $(D_{AM}/K\delta)$ are enough to specify the membrane (Sourirajan, 1977) they are not enough to predict solute separation and permeate flow obtainable with the membrane for any feed concentration and any feed flow rate. For such prediction, the applicable value of k is needed in addition to the data on A and $(D_{AM}/K\delta)$.

2.2 Application of the Kimura-Sourirajan analysis to this study.

In an attempt to predict the performance of the RO membrane used in this study, experimental data were derived and subjected to the Kimura-Sourirajan analysis previously described.

2.2.1 Effect of operating pressure on the Pure Water Permeability constant A

Fresh filtered water was used for tests at various pressures. The Pure Water Permeability rate (PWP) was measured using a beaker and stopwatch, and the Pure Water

Permeability constant (A) calculated according to equation (3).

2.2.2 Effect of feed flow rate and feed concentration on the solute transport parameter ($D_{AM}/K\delta$)

Tests were carried out at two different pressures (54.4 and 92.5 atm) representing the low and high operating range of the TM5-14 RO module used. The feed flow rates were changed over the range possible with the pump (4.0 - 6.9 ℓ/min), and the feed concentrations were varied from 0.5 to 7% NaCl (w/v).

2.2.3 Effect of feed flow rate and feed concentration on the average mass transfer coefficient k

The experimental results obtained in 2.2.2 were used to assess the effect of feed flow rates and feed concentrations on the k values at 54.4 and 92.5 atm.

2.2.4 Prediction of membrane performance

With respect to the experimental data obtained in 2.2.2 and 2.2.3, membrane performance prediction could not be carried out (See subsection 4)

3. RESULTS

3.1 Effect of operating pressure on the Pure Water Permeability Constant A

This effect is given in Table XXII below and illustrated in Fig. 18 (p.88).

TABLE XXII: Effect of pressure on the Pure Water Permeability Constant A

Pressure atm	(PWP)* ml/min	g/hr	A
54.4	357.5 ± 2.5	21,450 ± 150	6.8×10^{-7} (± 0.7%)
68.0	437.5 ± 2.5	26,250 ± 150	6.7×10^{-7} (± 0.6%)
81.6	515 ± 2.5	30,900 ± 150	6.6×10^{-7} (± 0.5%)
92.5	575 ± 2.5	34,500 ± 150	6.5×10^{-7} (± 0.4%)

* Average of four determinations
(Sample calculation in Appendix I)

3.2 Effect of feed flow rate and feed concentration on the solute transport parameter ($D_{AM}/K\delta$)

Results are given in Tables XXIII, XXIV, XXV and XVI and illustrated in Fig.19 (p.89) A sample calculation of ($D_{AM}/K\delta$) is presented in Appendix III (p.144).

3.3 Effect of feed flow rate and feed concentration on the average mass transfer coefficient k

The effect is presented in Tables XXVII and XXVIII and illustrated in Fig.20 (p.90). A sample calculation of k is presented in Appendix IV (p.147).

TABLE XXIII: Effect of changing feed flow rates (FR, ℓ/min) and feed concentrations (S, % NaCl, (w/v)) on Permeate Flow (PF, mℓ/min) and permeate concentration (Cp, % NaCl, (w/v)). P = 54.4 atm

S* % NaCl	FR * ℓ/min	PF* mℓ/min	P* % NaCl
0.52 ± 0.02	4.2 ± 0.2 5.0 ± 0.25 5.0 ± 0.3 6.7 ± 0.3	357.5 ± 2.5	0.0165 ± 0.0035
1.09 ± 0.04	4.6 ± 0.2 5.0 ± 0.25 6.3 ± 0.3	3[illegible] ± 2.5	0.045 ± 0.001
1.85 ± 0.07	4.0 ± 0.2 5.6 ± 0.3	2[illegible] ± 3.5	0.121 ± 0.005
4.0 ± 0.2	4.1 ± 0.2 5.2 ± 0.3	145 ± 2.5	0.533 ± 0.050
7.15 ± 0.3	4.9 ± 0.25	39 ± 0.5	3.38 ± 0.05

* Average of four determinations

TABLE XXIV: **Effect of changing feed flow rates (FR) and feed concentrations (S) on Permeate Flow (PF) and permeate concentration (Cp). P = 92.5 atm)**

S* % NaCl	FR* ℓ/min	PF* ml/min	P* % NaCl
0.513 ± 0.02	4.2 ± 0.2 5.7 ± 0.3 6.9 ± 0.3	550 ± 2.5	0.01125 ± 0.00002
1.13 ± 0.05	4.3 ± 0.2 6.5 ± 0.3	512 ± 2.5	0.035 ± 0.001
1.93 ± 0.08	4.0 ± 0.2 6.3 ± 0.3	457.5 ± 2.5	0.078 ± 0.002
4.07 ± 0.16	5.8 ± 0.3	345 ± 2.5	0.293 ± 0.005
7.15 ± 0.3	5.0 ± 0.25	132.5 ± 2.5	1.45 ± 0.01

*Average of four determinations

TABLE XXV: Effect of feed concentration (S, %NaCl) on the solute transport parameter ($D_{AM}/K\delta$)
P = 34.4 atm

S* % NaCl	(D_{AM}/K) * cm/sec	Standard Error ± %
0.52	$(29.1 \pm 9.1) \times 10^{-6}$	± 31.1
1.09	$(26.8 \pm 3.8) \times 10^{-6}$	± 14.2
1.85	$(29.6 \pm 3.3) \times 10^{-6}$	± 11.1
4.0	$(29.8 \pm 2.2) \times 10^{-6}$	± 7.5
7.15	$(37.8 \pm 3.2) \times 10^{-6}$	± 8.5

* Average of four determinations - $A = 6.8 \times 10^{-7}$ g-mole H_2O/cm^2.sec.atm (Sample calculation in Appendix III)

TABLE XXVI: Effect of feed concentration on $(D_{AM}/K\delta)$
P = 92.5 atm

S* % NaCl	(D_{AM}/K) * cm/sec	Standard error ± %
0.51	$(20.2 \pm 3.9) \times 10^{-6}$	± 19.1
1.13	$(24.7 \pm 2.8) \times 10^{-6}$	± 11.2
1.93	$(25.8 \pm 2.0) \times 10^{-5}$	± 7.9
4.07	$(38.7 \pm 1.9) \times 10^{-6}$	± 4.9
7.15	$(38.9 \pm 1.8) \times 10^{-6}$	± 4.5

* Average of four determinations - $A = 6.5 \times 10^{-7}$ g.mole H_2O/cm^2.sec.atm (Sample calculation in Appendix III)

TABLE XXVII: Effect of feed concentration (S, % NaCl or mole fraction X_{A1}) on the mass transfer coefficient k.
P = 54.4 atm (Flow Rate = 4.0 - 6.9 ℓ/min)

% NaCl S	X_{A1}	g.mole/cm² sec atm N_B	X_{A3}	$(1-X_{A3})$	X_{A2}	$\ln \frac{X_{A2}-X_{A3}}{X_{A1}-X_{A3}}$	k	Standard Error (%)
0.52	0.001609	35.1×10^{-6}	0.[illegible]051	1	[illegible]	0	k undefined	± 37[illegible]
1.09	0.003369	32.0×10^{-6}	0.000139	1	0.003136	0	k undefined	± 21%
1.85	0.005775	26.7×10^{-6}	0.000374	1	0.006479	0.123	$(5.9 \pm 0.4) \times 10^{-3}$	± 11%
4.0	0.012670	14.9×10^{-6}	0.001649	0.9[illegible]	0.018575	[illegible]	$([illegible].89 \pm 0.09) \times 10^{[illegible]}$	± 1[illegible]
7.15	0.024764	37.7×10^{-6}	0.010480	0.98952	0.029844	0.2939	$(0.25 \pm 0.[illegible]) \times 10^{[illegible]}$	± 15%

(Sample calculation in Appendix IV)

TABLE XXVIII: Effect of feed concentration (S, % NaCl or mole fraction X_{A1}) on the mass transfer coefficient k.
P = 92.5 atm (Flow Rate = 4.0 - 6.9 ℓ/min.)

% NaCl S	X_{A1}	g.mole/cm² sec atm N_B	X_{A3}	$(1-X_{A3})$	X_{A2}	$\ln \frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}$	k	Standard error %
0.513	0.001587	57.2×10^{-6}	0.000035	1	0.001858	0.140	$(7.4 \pm 1.7) \times 10^{-3}$	± 23%
1.13	0.003511	53.3×10^{-6}	0.000108	1	0.004316	0.212	$(4.5 \pm 0.6) \times 10^{-3}$	± 13%
1.93	0.006028	47.6×10^{-6}	0.000241	1	0.008261	0.329	$(2.6 \pm 0.3) \times 10^{-3}$	± 10%
4.07	0.012826	35.7×10^{-6}	0.000907	1	[illegible]	0.255	$(2.7 \pm 0.2) \times 10^{-3}$	± 8%
7.15	0.023131	13.4×10^{-6}	0.004482	0.990	0.032485	0.407	$(0.6 \pm 0.1) \times 10^{-3}$	± 9%

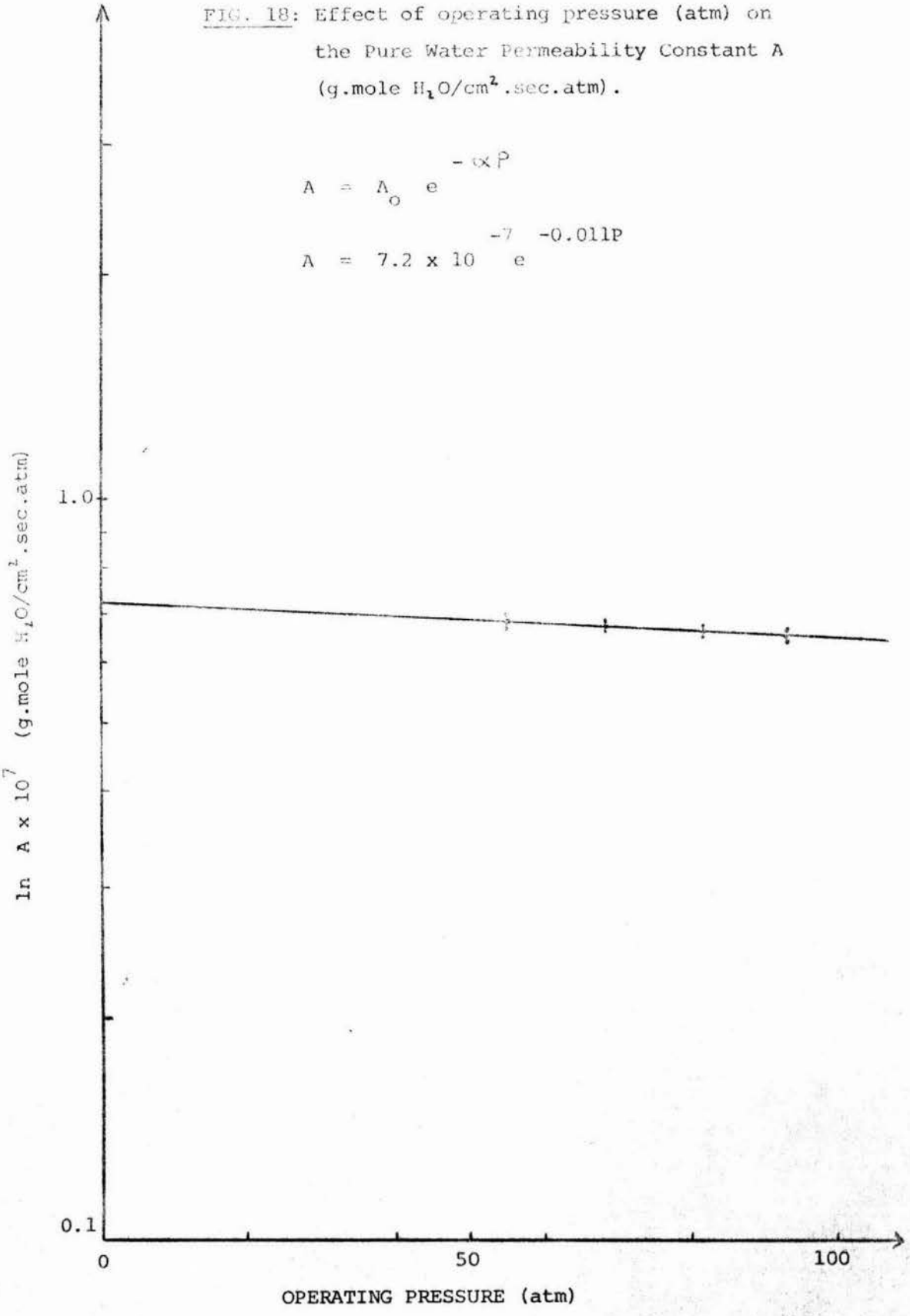
$$* N_B = \frac{PF \times 60}{18 \times 3600 \times 8900 \times P \text{ atm}}$$; PF ml/min) at P (atm) taken from Table

(Sample calculation in Appendix IV)

FIG. 18: Effect of operating pressure (atm) on the Pure Water Permeability Constant A (g.mole H_2O/cm^2.sec.atm).

$$A = A_o e^{-\alpha P}$$

$$A = 7.2 \times 10^{-7} e^{-0.011P}$$



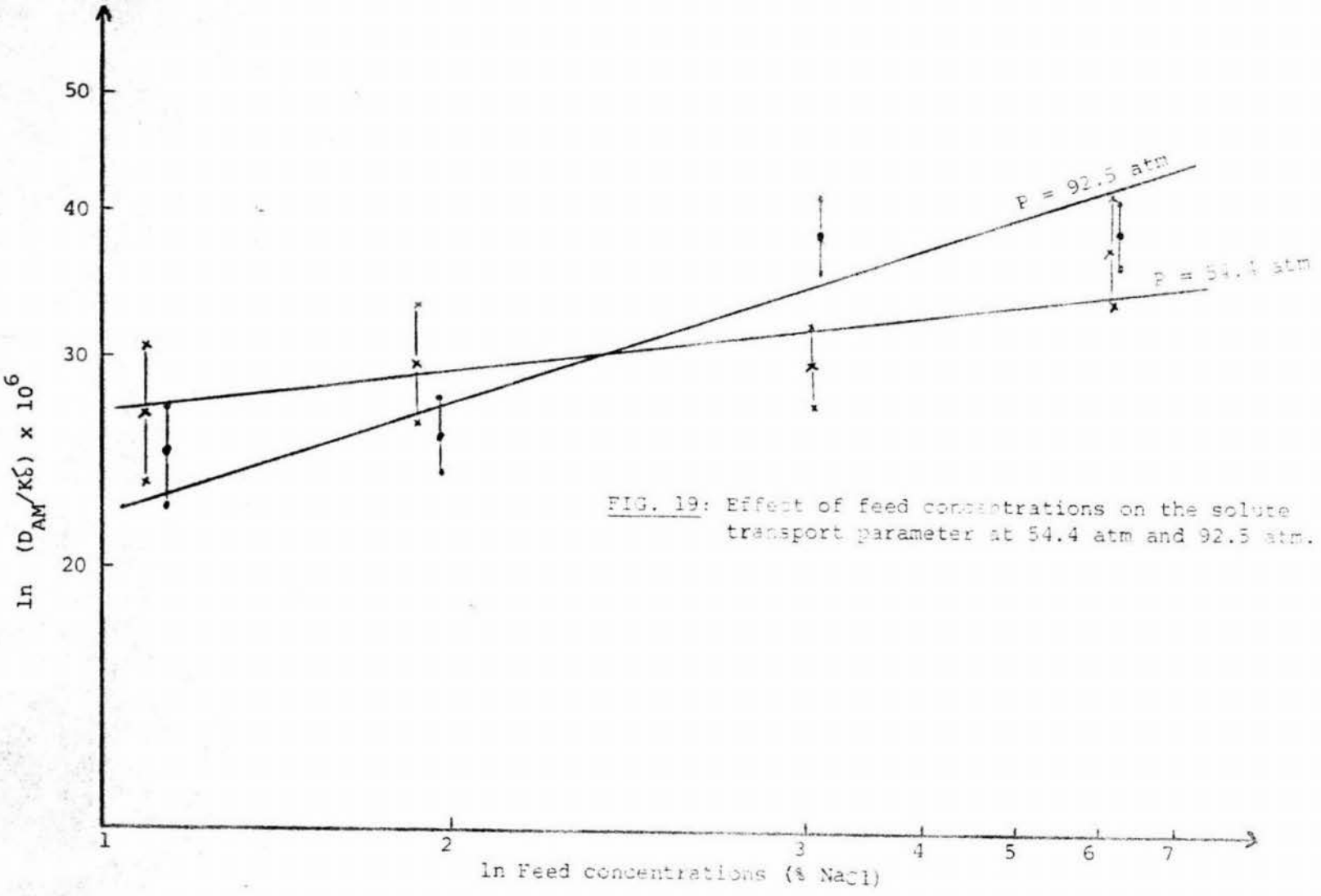


FIG. 19: Effect of feed concentrations on the solute transport parameter at 54.4 atm and 92.5 atm.

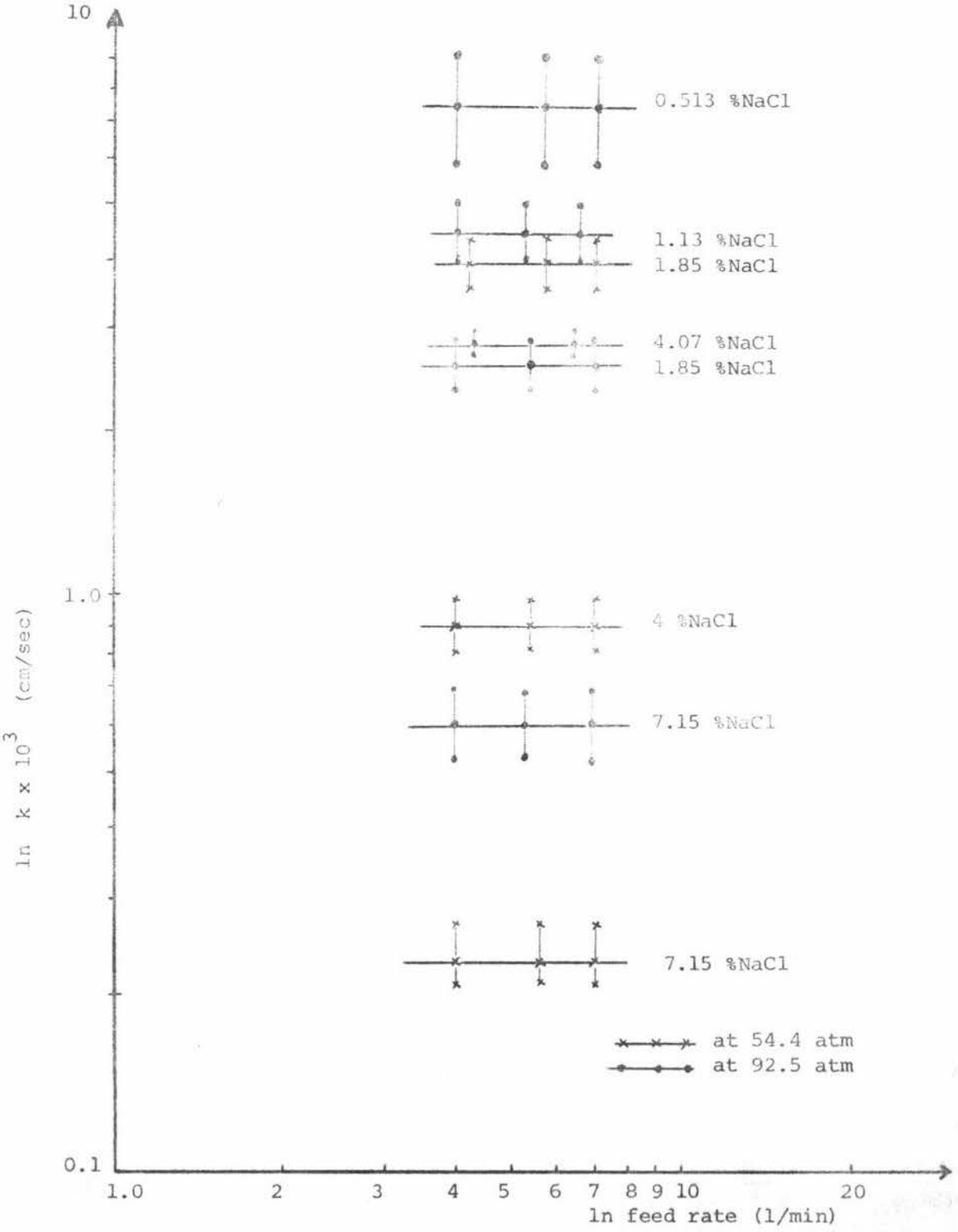


FIG. 20: Effect of feed flow rate and feed concentration on the average mass transfer coefficient for the system Sodium Chloride-Water.

4. DISCUSSION

4.1 Effect of operating pressure on the Pure Water Permeability constant

The Pure Water Permeability Constant A decreased exponentially with operating pressure, as expected (Sourirajan, 1970). The results from Table XXII and Fig.18 could be correlated as follows:

$$A = Ao \cdot e^{-\alpha P} \qquad \text{(equation 48)}$$

$$A = (7.2 \times 10^{-7}) \cdot e^{-0.011P}$$

4.2 Effect of feed flow rate and feed concentration on the solute transport parameter

Sourirajan (ibid.) found that $(D_{AM}/K\delta)$ was independent of feed concentration and feed flow rate at a given operating pressure. Results presented in Tables XXIII and XXIV showed that $(D_{AM}/K\delta)$ was essentially constant with feed flow rate within the narrow range of flow rate used in this study (4.0 - 6.9 ℓ/min). This narrow range severely restricted the prediction of membrane performance to an average flow rate (5.0 ℓ/min).

More significant was the fact that the values of $(D_{AM}/K\delta)$ were not independent of feed concentrations as expected. Results from Tables XXV and XXVI and Fig.19 showed that there was in fact an increase in $(D_{AM}/K\delta)$ with feed concentrations (within experimental errors). It must be noted that the standard error in $(D_{AM}/K\delta)$ was very large at the lower concentrations (e.g. $\pm$ 30% at 0.5% NaCl). Equation (49) expresses the fact that the solute transport parameter tends to decrease with an increase in operating pressure, as was established by Sourirajan (ibid.). Results from Tables XXV and XXVI did not establish any significant relationship between operating pressure and the values of $(D_{AM}/K\delta)$ since half of these values at the higher pressure were above those at the lower pressure at the corresponding concentrations, and half were below. This effect was shown in Fig.19 by the straight line relationship of $(D_{AM}/K\delta)$ at the higher pressure intersecting with the line at the lower pressure.

4.3 Effect of feed flow rate and feed concentration on the average mass transfer coefficient k

The correlation of the mass transfer coefficients k with feed concentrations (Tables XXVII, XXVIII and Fig. 20) showed that k varied with changing concentrations and that k could not be accurately determined at the lower concentrations.

At the lower salt concentration (e.g. 0.5% NaCl) the calculation of k depended on how accurately X_{A2} could be determined which, in turn, depended on measurements of X_{A3}, the mole fraction of solute in the permeate. Since X_{A3} was very small at the lower feed concentrations, any error in X_{A3} brought about a much larger error in X_{A2} through equations (4) and (5). Moreover, as readings were indirect i.e. conductivity values were first converted into % NaCl (w/v) using calibrating graphs and then to mole fraction values using published data (Appendix II), there was an inherent limitation in accuracy at the lower concentrations, and this led to values of X_{A2} fluctuating around $\pm$ 20% error (e.g. at 0.5% NaCl/54.4 atm). Errors of about $\pm$ 40% in k were not uncommon at the lower concentrations and higher pressure (Table XXVII) and k values could not be determined under such conditions.

The relation $k \propto Q^n$ from equation (51) expresses the fact that k tends to increase with an increase in flow rate (Sourirajan, ibid.). The experimental results obtained (Tables XXVII and XXVIII) showed that k was essentially constant with flow rate within the narrow range of flow rate possible with the pump.

Furthermore, k was not found independent of operating pressure, which disproved recent consideration (Sourirajan, 1977). Fig.20 showed that the k values at the higher pressure were different to the k values at the lower pressure at similar concentrations.

Thus, although Sourirajan (1970) expressed k as a function mainly of flow rate, the experimental results obtained would suggest a more complex relationship.

5. CONCLUSION

The experimental RO data obtained did not establish any significant correlation between ($D_{AM}/K\delta$) with feed concentration and operating pressure; neither were the k values significantly correlated with feed flow rate. The relatively narrow range of feed flow rates under which the RO system was able to be operated meant that the Kimura-Sourirajan analysis was of little use for predicting membrane performance.

On the basis of the experimental results obtained, the Kimura-Sourirajan analysis could not be used to meaningfully predict the performance of the RO membrane under study.

SECTION III

USE OF TAFT NUMBERS TO PREDICT MEMBRANE PERFORMANCE

1. INTRODUCTION

Early publications on the mechanism of membrane transport in RO pointed to the fact that permeation through a membrane was not completely defined in terms of the molecular and configurational size of the dissolved solute and its concentration, the pore size of the membrane, and the pressure applied. Adsorption by the membrane, both of water and of dissolved solute, viscosity of the solution and other factors also seemed to be involved (Goodall, 1972; Agrawal and Sourirajan, 1970; Banks and Sharples, 1966; Carter, 1968; Harrison, 1970a; Lonsdale et al., 1965; Harrison, 1970b; Merson et al., 1968; Peri, 1971; Sammon, 1969; Sharples, 1970).

Extensive studies on solute separation by CA membranes have been carried out by Sourirajan (1970) and Matsuura and Sourirajan (1971a, 1971b, 1972a, 1972b). These authors developed a popular concept to explain the mechanism of RO. This concept, called 'the preferential sorption-capillary flow mechanism', recognizes the fact that RO separation is governed not only by the chemical nature of the membrane, but also by the existence of pores of appropriate size on the surface of the membrane (see Section I, p.50-51). The solute separation occurs only if, under the conditions of the experiment, the membrane surface material has a preferential sorption for water rather than for solute and thus water passes through the membrane pores. For a given pore size on the membrane surface, and constant operating conditions, a high solute separation means that the membrane has a preferential sorption for water with respect to the solute. Where the membrane surface has a preferential sorption for solute instead of water, then solute passes through the membrane pores, resulting in negative solute separation or enrichment of solute in the permeate.

The surface layer of an RO membrane is microporous at all levels of solute separation, and if the membrane surface material has a preferential sorption for water, practically any degree of solute separation can be obtained by changing the pore size on the membrane surface. Thus, when considering a feed solution containing several solutes applied to a membrane surface, separation or concentration of solutes can occur, depending on whether the surface has a preferential sorption for water with respect to each solute. With a constant pore structure, this depends on the permeation rate and solute separation with respect to each solute, i.e. the preferential sorption of one solute over another.

Therefore, the performance of the membrane in RO (i.e. solute separation and permeation rate) depends on three main factors:

(i) the number, size and size distribution of the pores on the membrane interface;
(ii) the chemical nature of the membrane material and the feed solution;
(iii) the operating conditions of the experiment.

Assuming (i) and (iii) can be held constant for a given membrane and under a particular set of experimental conditions, then (ii) will dictate how well the solute under consideration will be separated by the membrane. The physico-chemical criteria for preferential sorption of water with respect to different solutes is governed by the Taft number of the organic solute under study, as outlined below.

1.1 Taft Number - a criterium for the Reverse Osmosis separation of solutes

In this approach, solute separation in RO is thought of as a function of the extent of preferential sorption of water by the membrane material and the porous structure of the membrane surface. With reference to a given membrane material, preferential sorption of water is a function of the chemical nature of the organic solute. Both the functional group (-OH, -COOH, etc..) and the substituent group in the organic molecule affect preferential sorption of water, and

hence solute separation.

One of the physico-chemical criteria governing RO separation of organic solutes in aqueous solution is the polar effect of the solute molecule, which includes the effect of both the functional group and the substituent. For the separation of organic solutes such as alcohols, phenols, and monocarboxylic acids, acidity is considered to be the relevant expression of the polar effect of the molecule (Matsuura and Sourirajan, 1971b). A measure of acidity is given by the ease of hydrogen bond formation and/or the degree of dissociation of the molecule in solution. These parameters are related to Taft and Hammet numbers which give a quantitative measure of the influence of the substituent group on the polar effect of the molecules (Taft, 1956).

1.2 Significance of Taft and Hammet numbers

Hammet (1940) established that within a reaction series of the meta- and para-substituted derivatives of benzene, the effect of structure on rates or equilibria is nearly always determined by the polar effect of the substituent. This is expressed as the Hammet equation:

$$\log (k/k_o) = \sigma\rho \qquad (1)$$

where k and k_o are rate or equilibrium constants for a given reaction and a standard reaction, respectively; σ is the substituent constant which depends solely on the nature of the reaction and the reaction conditions. The validity of the Hammet equation is restricted to substituents in the meta- and para- positions of the benzene ring where interference from primary steric effects is negligible.

Taft extended the Hammet equation to cover a wider range of reactions including aromatic orthocompounds, phenols and aliphatic compounds where the substituent group is closed to the reaction centre. Taft (ibid.) defined:

$$\sigma^* = \frac{1}{2.48}\left[\log\left(\frac{k}{k_o}\right)_B - \log\left(\frac{k}{k_o}\right)_A\right] \qquad (2)$$

where σ^* is a polar substituent constant called the Taft

number and k and k_0 are the rate constants for the hydrolyses of RCOOR' and CH_3COOR' respectively. The subscripts $_B$ and $_A$ refer respectively to alkaline and acid hydrolyses carried out for the same R' under identical experimental conditions. The constant 2.48 adjusts σ^* to the same scale as σ. The assumption here is that the mechanisms for acidic and alkaline hydrolyses are similar, and hence resonance and steric effects essentially cancel out. Thus σ^* gives a measure entirely of the polar effect of the substituent. From this work, the Taft equation analogous to the Hammet equation is:

$$\log\left(\frac{k}{k_0}\right) = \sigma^* \rho^* \qquad (3)$$

where the Taft number σ^* is entirely analogous to the Hammet number, but of different origin.

The significant points about the Taft and Hammet numbers are:

(i) both σ and σ^* quantitatively express the influence of the substituent group on the polar effect of the organic molecule;

(ii) both σ and σ^* are independent of the nature of the reaction considered and hence have wide general applicability;

(iii) with reference to a given functional group, a lower value of σ or σ^* indicates lower acidity for the molecule (Matsuura and Sourirajan, 1971b).

These inherent characteristics of σ and σ^* offer a basis for the application of these parameters in RO to explicitly differentiate each substituent group, within each functional group, in the organic molecule. Extensive data of σ and σ^* are available in the literature (Taft, ibid.).

1.3 Separation of organic components (alcohols, aldehydes, ketones and esters)

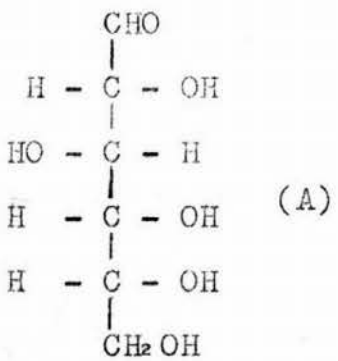
In solution, these compounds are present essentially as undissociated molecules, and solute separation in RO is governed by the polar effect of the molecule. This, as mentioned earlier, can be represented by the hydrogen bonding ability (acidity) or by the Taft number σ of the substituent

group in the solute with respect to each functional group. The Taft number gives a measure of the electron-withdrawing power of the substituent group in a polar molecule. Since polar effects are additive for polysubstituted derivatives, the total polar effect of the substituent groups is given by the sum of their respective Taft numbers; this sum is represented by σ^*. Matsuura and Sourirajan (1971b; 1972a and b; 1973) have shown that, with respect to a large number of alcohols, aldehydes, ketones and esters, the solute separation increases with a decrease in acidity or an increase in basicity of the molecule. Since a decrease in Taft number is equivalent to a decrease in acidity or an increase in basicity, an increase in solute separation can be expected with a decrease in Taft number for those compounds.

The total polar effect of the solute molecule is due to the substituent and functional groups in the molecule and, since the Taft number is a measure of the polar effect of the substituent groups only, the total polar effect of the molecule is different for different functional groups at a given Taft number. Similarly, the effect of a change in Taft number on the change in total polar effect of the molecule is different for different functional groups, and it is these differences that affect solute separation (Kearsley, 1974).

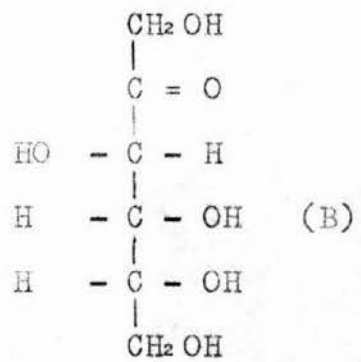
1.4 Separation of sugars

The structures of the four sugars of interest in apple juice are depicted below:



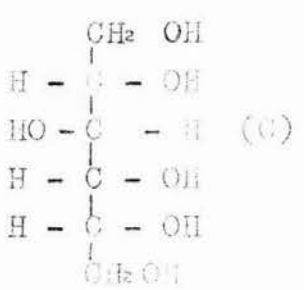
(A)

D-glucose

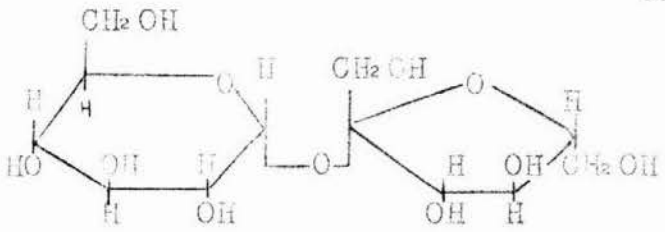


(B)

D-fructose



Sorbitol



Sucrose - (A) + (B)

Glucose has a Taft number of -0.951 with respect to -OH, and -0.[illegible] with respect to -CHO. No estimates of Taft numbers for fructose, sorbitol or sucrose are available. However, due to the close proximity of their structure to glucose, fructose and sorbitol are believed to have a Taft number approximately equal to the Taft number ($\Sigma\sigma^*$) of glucose. On the other hand, sucrose, which is made up of a molecule each of glucose and fructose, is thought to have a Taft number of twice the value of the glucose Taft number (Kearsley, 1974).

In general, it can be said that sugars have very high negative Taft numbers, and are relatively far more separated from water than other solutes in RO. Separation of the order of 99.5% has been achieved under actual experimental conditions (Pereira et al., 1976) for glucose, fructose and sucrose.

1.5 Separation of organic acids

The acids may be present as dissociated or undissociated species. Solute separation for the dissociated acid is due to electrostatic repulsion of the ions, and that for the undissociated acid is due to the acidity (hydrogen bonding ability and hence Taft number) of the molecule (Matsuura et al., 1973). While repulsion of ions always results in preferential sorption for water at the membrane-water interface, and hence positive solute separation in RO, either water or undissociated acid may be preferentially sorbed at the interface, depending on the relative acidities of the respective molecules. This is quantitatively expressed as pK_a, where K_a is the dissociation constant for the acid.

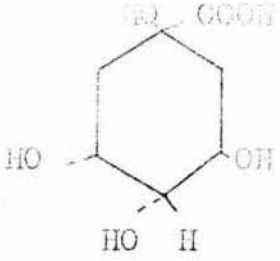
A decrease in pK_a represents an increase in acidity, which tends to increase the hydrogen bonding ability and hence the Taft number of the acid, resulting in a decrease in solute separation. On the other hand, when the acidity of the molecule is high enough to stretch the -OH bond to the point of rupture, the molecule dissociates and exists in solution as ions. These are subject to electrostatic repulsion at the membrane interface, which results in a decrease in solute separation. For monocarboxylic acids in aqueous solution, a pK_a range of 4 to 4.6 is particularly significant with respect to solute separation. When pK_a is greater than 4.6, the acidity (hydrogen bonding ability and thus Taft number) is low enough to result in preferential sorption for water, and hence positive solute separation. When pK_a is less than 4, the dissociation of the acid is high enough to again result in net positive solute separation. With respect to the undissociated species, a transition from repulsion for solute to attraction for solute at the membrane-solution interface occurs in the pK_a region 4 to 4.6. Thus the degree of dissociation of the acids present, and the Taft number of the undissociated acids, constitute the governing physico-chemical criteria for the RO separation of organic acids.

The major acids present in Granny Smith apple juice are malic and citric, with lesser amounts of phosphoric, quinic and ascorbic acid (Chapter Two, p.35). In correlating solute separation data as a function of the Taft number of the acid, Matsuura et al.(ibid.) established that solute separation is generally in the order monohydroxy-tricarboxylic acid (citric) > dihydroxy-dicarboxylic acid (tartaric) > monohydroxy-dicarboxylic acid (malic) > monohydroxy-monocarboxylic acid > monocarboxylic acid (quinic and ascorbic).

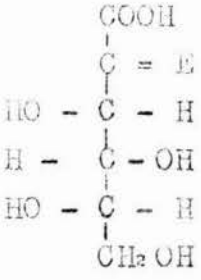
The above order indicates that an increase in the number of polar functional groups in the solute molecule results in higher solute separation. Further, when the degree of dissociation of the acid molecule is increased, its separation is also increased in all cases.

While each monocarboxylic acid has a single Taft number, each hydroxy-carboxylic acid has two Taft numbers - one for each functional group. The Taft number for each hydroxy-carboxylic acid is arbitrarily expressed as the sum of its Taft number for each functional group (σ^* COOH + σ^* OH). (Matsuura et al., ibid.). However, such simple summation is not really valid because Taft numbers for different functional groups are not generally on the same scale with respect to their effect on solute separation. No technique has yet been developed to express the effective Taft number for substituent groups in molecules containing different functional groups.

For entirely undissociated species, citric ($\Sigma\sigma^*$ = -0.61) and tartaric acid ($\Sigma\sigma^*$ = -0.40) showed almost complete separation. Malic acid ($\Sigma\sigma^*$ = -0.30) was not retained as much as the former two, while benzoic acid ($\Sigma\sigma^*$ = 0.60) was negatively separated and hence preferentially sorbed at the interface (Matsuura et al.,ibid.). This suggests that quinic acid (a tetrahydroxy-benzoic acid) would also be preferentially sorbed at the membrane interface. On the other hand, ascorbic acid (a trihydroxy keto-monocarboxylic acid) would be expected to have a similar degree of separation as quinic acid, due to its double functional group:



Quinic



Ascorbic

Finally, phosphoric acid (H_3PO_4) though not an organic acid, has a strong tribasic character and hence would be expected to have a low Taft number (to a decrease in Taft number an increase in basicity is equivalent). Therefore it would be expected to be better separated than the monocarboxylic acids considered.

1.6 Conclusion

On the basis of the above discussion, it can be concluded that, in the case of Granny Smith apple juice,

the following general order of solute separation by RO would be expected:

sucrose, fructose, glucose and sorbitol
greater than
citric acid
greater than
malic acid
greater than
phosphoric acid
greater than
ascorbic acid, quinic acid

2. EXPERIMENTAL

Experiments were carried out with simple solutions containing one or more sugars or acids, to confirm whether or not the general order of solute separation mentioned earlier was observed, and to reveal whether or not there were any interactions between these components.

2.1 Preliminary analysis of sugars and acids (food grade) with glc

On the basis of the earlier analysis of Granny Smith apple juice (Tables XII and XIII, p.48) it was decided to work with malic and citric (as the main acids) and glucose, fructose, sucrose (as the main sugars).

Since analytical grades of these components could not be used in this study because of the cost of the reagents and the amounts required, the use of food grade sugars and acids necessitated a reassessment of the retention times and K values by glc for subsequent identification purposes.

2.2 Reverse Osmosis experiments

2.2.1 With model solutions of sugars

Model solutions of sugars were prepared to within the approximate concentration found in GS apple juice (6% w/w). Typically, the food grade sugar (1.5 kg) was weighed into a container and the solution (2.5 kg) made up with fresh filtered water.

Due to limitations in the amount of fructose available (only 5 kg of fructose could be obtained), the simple solution of sugars were kept under refrigeration for subsequent reuse. The model solution of mixed sugars was made up by adding the simple solutions of sugars together in the correct proportions. Although this had a diluting effect on the individual sugar, the total percentage of sugar in all model solutions made remained the same (about 6% w/v).

The soluble solid contents (°Brix) of the sugar solutions were monitored by an Abbe refractometer and this provided a quick way of checking the concentrations of sugars in the feed and permeate. However, due to the lack of precision of this method, the absolute concentrations of sugar in the feed and permeate are reported only on the basis of glc analysis.

The model solutions (simple or mixed) were passed through the RO module at two different temperatures (7 °C and 25 °C), constant operating pressure (77 atm), and constant feed flow rate (5 ℓ/min). The permeate and concentrate were returned to the feed tank to make a close circuit system. The performance of the membrane was assessed by measuring the permeate flow (PF, mℓ/min) and rejection (R %) from samples simultaneously collected from the feed solution and the permeate once operating conditions remained constant.

2.2.2 With model solution of acids

The preparation of model solution of acids and RO experiments with these were carried out using the same procedure as described above for sugars. The concentrations used were malic (0.4% w/v), and citric (0.3% w/v), both being made up with fresh filtered water (50 kg). The mixture of malic and citric acids was made from fresh reagents, due to the low concentrations involved and availability of the acids.

The concentration of acid was monitored by titrating the acid sample (25 mℓs) with standard NaOH solution (0.1 N) using Cresol Red as indicator (six drops). This provided a

quick way of checking the concentration of acid in the feed and permeate. The absolute concentrations of acid in the feed and permeate, however, are reported only on the basis of glc analysis.

2.2.3 With model solutions of sugars and acids

The model solution of sugars and acids was made in the following way. The above mixture of acids was concentrated to half of its original volume; the same was done with the mixture of sugars from 2.2.1. The two concentrated solutions were then mixed together to give a solution of sugars and acids of the desired composition.

The first run was made at 25 C and P (mℓ/min) and R % calculated as before. The mixed solution was then cooled down to 7 C and experiments repeated at that temperature.

2.2.4. Experimental design

Because it was thought that there could be interactions between the sugars and acids mixed together, an experimental design was made so that the nature of any such interactions could be determined.

The process variables involved in the design were:

Process Variables	-1	cp	+1
A (Sucrose %)	2	4	6
B (Fructose - Glucose %)	2	4	6
C (Malic %)	0.1	0.4	0.7
D (Citric %)	0.1	0.3	0.5
E (Temperature C)	7	16	25
F (Pressure atm)	54.4	73.5	92.5

The symbols -1, cp and +1 represent the low, high and 'centre' level of the variables considered, in the units mentioned.

The experimental design chosen was a Box and Hunter fold-over design for eight factors in 16 runs, and can be represented diagrammatically as follows:

CODE	RUN	A)$_1$	B)$_2$	C)$_3$	D)$_4$	E)$_5$	F)$_6$	G)$_7$	H)$_8$
1	1	-1	-1	-1	-1	-1	-1	-1	-1
AEFH	2	+1	-1	-1	-1	+1	+1	-1	+1
BEGH	3	-1	+1	-1	-1	+1	-1	+1	+1
ABFG	4	+1	+1	-1	-1	-1	+1	+1	-1
CFGH	5	-1	-1	+1	-1	-1	+1	+1	+1
ACEG	6	+1	-1	+1	-1	+1	-1	+1	-1
BCEF	7	-1	+1	+1	-1	+1	+1	-1	-1
ABCH	8	+1	+1	+1	-1	-1	-1	-1	+1
DEFG	9	-1	-1	-1	+1	+1	+1	+1	-1
ADGH	10	+1	-1	-1	+1	-1	-1	+1	+1
BDFH	11	-1	+1	-1	+1	-1	+1	-1	+1
ABDE	12	+1	+1	-1	+1	+1	-1	-1	-1
CDEH	13	-1	-1	+1	+1	+1	-1	-1	+1
ACDF	14	+1	-1	-1	+1	-1	+1	-1	-1
BCDG	15	-1	+1	+1	+1	-1	-1	+1	-1
ABCD EFGH	16	+1	+1	+1	+1	+1	+1	+1	+1

Source: Boag, (1977)

The first column (code) refers to the combinations of variables having a high level (+1). Columns 7 and 8 are not considered as process variables but the corresponding values of G and H are used for grouping the experimental runs into four blocks of four runs each according to the following code:

		Runs
BLOCK I	G = -1 H = -1	1, 7, 12, 14, cp, cp
BLOCK II	G = -1 H = +1	2, 8, 11, 13, cp, cp
BLOCK III	G = +1 H = -1	4, 6, 9, 15, cp, cp
BLOCK IV	G = +1 H = +1	3, 5, 10, 16, cp, cp

The 'runs' on the right hand side of the table refer to the case where G and H obey the levels specified in the middle section. Within each block, the runs were randomised (using a table of random numbers) to eliminate any trend effect. The purpose of having two extra centre points "cp" within each block was to have a measure of the curvilinearity of the response to change in the process variables. However, the design is only suitable for first order models where the relationship between response variables and process variables is essentially linear. This "blocking" also has the effect of minimising the time trend effect of the membrane due to compaction.

A run is an experiment performed at the different levels of process variables specified across the design table.

3. RESULTS

TABLE XXIX: Relative Retention time and K factors of TMS derivatives of sugars and acids (food grade) on SE-52 column

Compound	Retention Time	K^c factors
Fructose	0.57[a]	0.69
α-Glucose	0.68[a]	0.74
β-Glucose	0.83[a]	
Sucrose	1.81[a]	0.46
Malic	0.77[b]	0.89
Citric	1.25[b]	0.65

[a]Relative to inositol (internal standard)

[b]Relative to tartaric acid (internal standard)

[c]Average of three determinations

TABLE XXX: Reverse osmosis of glucose, FR = 5 ℓ/min P = 77 atm

	T = 25 C	T = 7 C
[a]PF (mℓ/min)	427.5	247.5
[a]CF (% w/v)	3.7	4.9
[a]CP (% w/v)	0.09	0.13

TABLE XXX: (cont)

	T = 25 C	T = 7 C
^{b}R %	98 ± 1%	97 ± 1%

[a] All results are the average of two determinations.

[b] $R\ \% = \frac{CF - CP}{CF} \times \frac{100}{1}$ %, calculated to the nearest %

TABLE XXXI: Reverse osmosis of fructose; FR = 5 ℓ/min P = 77 atm

	T = 25 C	T = 7 C
PF (mℓ/min)	410	245
CF (% w/v)	6.6	5.61
CP (% w/v)	0.06	0.06
R %	99 ± 1%	99 ± 1%

All results are the average of two determinations.

TABLE XXXII: Reverse osmosis of sucrose; FR = 5 ℓ/min P = 77 atm

	T = 25 C	T = 7 C
PF (mℓ/min)	437.5	257.5
CF (% w/v)	6.1	5.7
CP (% w/v)	- trace -	- trace -
R %	~ 100%	~ 100%

All results are the average of two determinations.

TABLE XXXIII: Reverse osmosis of mixture of sugars (glucose = G; fructose = F; sucrose = S) FR = 5 ℓ/min; P = 77 atm

	T = 25 C	T = 7 C
PF (mℓ/min)	437.5	250
CF (% w/v)	F 1.5 G 1.7 S 2.2	F 1.7 G 1.8 S 1.9

TABLE XXXIII:(cont)

	T = 25 C	T = 7 C
CP (% w/v)	F 0.03 C 0.04 S 0.03	F 0.04 C 0.05 S 0.02
R %	F 97 ± 2% C 98 ± 2% S 98 ± 2%	F 98 ± 2% C 98 ± 2% S 99 ± 2%

All results are the average of two determinations.

TABLE XXXIV: Reverse osmosis of malic acid
Q = 5 ℓ/min; P = 77 atm

	T = 25 C	T = 7 C
PF (mℓ/min)	480	270
CF (% w/v)	0.45	0.45
CP (% w/v)	0.05	0.04
R %	89 ± 1%	91 ± 1%

All results are the average of two determinations.

TABLE XXXV: Reverse osmosis of citric acid
Q = 5 ℓ/min; P = 77 atm

	T = 25 C	T = 7 C
PF (mℓ/min)	485	272
CF (% w/v)	0.39	0.40
CP (% w/v)	0.02	0.02
R %	95 ± 1%	95 ± 1%

All results are the average of two determinations.

TABLE XXXVI: Reverse osmosis of mixture of acids (malic = M; citric = C)
FR = 5 ℓ/min; P = 77 atm

		T = 25 C	T = 7 C
PF mℓ/min)		480	270
CF (% w/v)	M	0.43	M 0.42
	C	0.36	C 0.33
CP (% w/v)	M	0.05	M 0.04
	C	0.02	C 0.013
R %	M	88 ± 1%	M 91 ± 1%
	C	94 ± 1%	C 96 ± 1%

All results are the average of two determinations.

TABLE XXXVII: Reverse osmosis of mixture of sugars and acids (glucose = G; fructose = F; sucrose = S; malic = M; citric = C)
FR = 5 ℓ/min; P = 77 atm

	T = 25 C		T = 7 C	
	Sugars	Acids	Sugars	Acids
PF (mℓ/min)	415		240	
CF (% w/v)	F 1.7	M 0.39	F 1.6	M 0.37
	G 1.6	C 0.29	G 1.5	C 0.31
	S 2.1		S 2.2	
CP (% w/v)	F 0.05	M 0.03	F 0.02	M 0.03
	G 0.07	C 0.004	G 0.03	C 0.003
	S 0.05		S -trace-	
R %	F 97 ± 2%	M 92 ± 2%	F 98 ± 2%	M 92 ± 2%
	G 96 ± 2%	C 99 ± 2%	G 98 ± 2%	C 99 ± 2%
	S 98 ± 2%		S ~100%	

All results are the average of two determinations.

4. DISCUSSION

The results for the rejection of sugars and acids singly or in mixtures were as expected from a knowledge of the Taft numbers and the molecular weights.

As regards the sugars studied, sucrose (MW = 342.3) had the highest rejection (close to 100%, Table XXXII), with fructose next (MW = 180.2; R = 99%, Table XXXI), and then glucose (MW = 180.2, R = 98%, Table XXX). However, the experimental errors involved in the measurements of CF and CP (and thus in the computation of R ,%) was such ($\pm$ 2%) that no significant differences can be said to exist between the rejections of the sugars. Overall, the rejection of sugars was very high (98 - 100%).

With respect to the organic acids under study, malic showed a rejection of about 90% (Table XXXIV), while that of citric was about 9 % (Table XXXV). This was as expected, since citric has a higher molecular weight (210.1) than malic (134.1) as well as having a greater number of functional group, resulting in a lower Taft number (p 99).

Mixing the sugars together did not significantly alter the rejections of the individual sugars (Table XXXIII). The same was true for the acids (Table XXXVI).

Temperature had a considerable effect on the permeate flux of both sugars and acids. This was not expected from earlier results (Chapter Three, Section I). A temperature of 7 C almost halved the PF of the sugars and acids (Tables XXX to XXXVII), compared to runs at 25 C. Decreasing the feed temperature increased the rejection of both sugars and acids (Tables XXXIII, XXXIV and XXXVII), but in most cases this was not significant because of the experimental errors.

Mixing sugars and acids together increased the rejection of malic and citric acids (Table XXXVII), while the rejection of sugars remained high (97 - 100%). The 99% rejection of citric acid (Table XXXVII) represents a steep increase over the earlier results (about 95%, Tables XXXV and XXXVI). However, the citric acid concentration in the mixture was low, resulting in large errors when the permeate was analysed, since glc response was very low for citric as compared to malic. (Table XXIX). The standard error involved was $\pm$ 2%, and thus 95 and 99% rejection cannot be said to be

significantly different. The apparent increase in rejection of malic and citric acids in the presence of sugars could be possibly due to sugars blocking the majority of the active sites available for pore diffusion on the membrane interface, with the result that the lower molecular weight acids would have less chance to pass through with the permeate.

On the basis of the above results, it was concluded that there was not any significant interaction between the components studied. Therefore, the experimental design described in subsection 2.4 was not followed.

Any suspicions that membrane compaction could have influenced the results obtained were allayed when the RO module was checked after the sugar and acid runs with standard 0.5% NaCl. Permeate flow and rejection values for the system sodium chloride-water tested under standard RO conditions were not significantly different from values found earlier (F_v = 0.46 ℓ/min and R = 96% at 149 hr after the experiments were completed, compared to 0.46 ℓ/min and 96.7% at 107 hr, before the experiments started.).

5. CONCLUSION

The above results from model solutions of sugars and acids present as single components or as complex mixtures confirmed the use of Taft numbers to predict membrane performance. The use of molecular weight as an indicator of solute rejection was also confirmed, higher molecular weights giving greater rejections. These results confirm earlier reports (Matsuura and Sourirajan 1971a, 1971b, 1972a and 1972b) that the mechanism of solute rejections by RO cellulose acetate membranes involves both preferential sorption and capillary flow of the solute through the membrane.

CHAPTER FOUR

[illegible] ANALYSIS OF APPLE JUICE

1. INTRODUCTION

On the basis of the results obtained in Chapter Three, section III, a high retention of sugars with some loss of acids was expected when apple juice was concentrated. Some loss of sugars (mainly sucrose) at higher concentrations was also expected (Gherardi et al., (1972); Schobinger et al., (1974).

In this section of the investigation, apple juice was concentrated by RO to see if it behaved as predicted from the work on model solutions.

2. EXPERIMENTALS

Single strength Granny Smith apple juice (50 ℓ) and 72° Brix concentrate (5 ℓ) were obtained from the Apple and Pear Board juice factory at Hastings. The single strength (s/s) juice was prepared as follows. After extraction in continuous, horizontal Bucher-Guyer hydraulic presses, enzyme (Ultrazyme 100 Special, Ciba Geigy Ltd., Switzerland) containing pectinases and amylase was added. The juice was held for 16 hours, before being passed through a diatomaceous earth filter to produce a sparkling clear juice. On receipt at Massey, it was pasteurised by heating to 85 C for 30 seconds. The pasteurised juice was immediately cooled to room temperature (10 C) using a plate heat exchanger, then passed through a PF-30 filter press (British Filters Ltd.) to give a brilliantly clear juice. The pasteurised and clarified s/s juice was kept at chill temperatures (2 C) until used.

The concentrate was prepared as follows: clarified s/s juice was passed trough an aroma recovery unit where the volatile components were flashed off and recovered separately. The juice was then concentrated to 72° Brix using a triple effect APV plate evaporator. The concentrate was stored at Massey at 2 C until required. The concentrate was reconstituted to single strength juice by diluting it with fresh filtered water until its total soluble solids content (as measured on an Abbe refractometer) was the same as the s/s juice. The characteristics of the different juices are presented in Table XXXVIII.

2.1 Reverse Osmosis experiments with single strength juice

The s/s juice was concentrated at a pressure of 77 atm, a flow rate of 5 ℓ/min and a temperature of 25 C. When these conditions were reached, duplicate samples of feed and permeate were collected and the permeate flux recorded. The samples were analysed by glc, and rejection of the sugars and acids calculated. The same juice was cooled down to 7 C and the experiment repeated at this temperature.

With the aim of comparing whether or not there were any significant differences in behaviour between the single strength juice and the diluted concentrate, the latter was also run at 25 C and 7 C. The RO conditions were the same as described above.

2.2 Reverse Osmosis concentration of applejuice

(i) Clarified s/s juice was concentrated by running it at the highest practical pressure (99 atm) and at 7 C. The total soluble solids content (using an Abbe refractometer) of the feed and the permeate flux of the RO module were recorded at regular intervals throughout the process. The concentration was continued until the level in the feed tank was insufficient to provide flooded suction to the pump. The sugar and acid contents of both the concentrate and permeate were determined.

(ii) Diluted concentrate was similarly concentrated at 7 C at the highest practical pressure (99 atm), with the aim to achieve a high flux rate, which would be desirable for economical reasons. The total solids content and the flux rate were measured as before. The process was stopped when there was insufficient feed to provide flooded suction to the pump. Sugars and acids in the concentrate and permeate were determined, and the process compared to the run at 7 C.

(iii) Since cooling of the juice during its concentration by RO has a large bearing on the manufacturing cost

of the concentrate - especially on an industrial scale - it was decided to assess the effect of concentrating the juice at the lowest temperature that could be achieved when fresh tap water was used to cool the feed. The temperature achieved by this means, with RO conditions as before, was 20 C. The higher cooling temperature would be expected to substantially increase the permeate flux, without significantly increasing the sugar and acid retentions of the concentrate (see Chapter Three, section I, p.66). A higher permeate flux would also be highly desirable from an economical point of view.

3. RESULTS

TABLE XXXVII: Characteristics of the apple juice studied

	s/s juice on receipt from Hastings	s/s juice after pasteurisation and clarification	Concentrate	Diluted concentrate
pH	3.2	3.2	3.1	3.2
°Brix (at 20 C)	10.5	10.5	72	12
% Total Acids	0.94[a]	0.94[a]	5.03[b]	0.98[a]

[a] by glc

[b] by titration with 0.1 N NaOH, expressed as malic acid

TABLE IXL: Permeate Flow and rejection characteristics of single strength apple juice; P = 17 atm

	T = 25 C		T = 7 C	
	sugars	acids	sugars	acids
PF (mℓ/min)	330		185	
CF (%)	F 5.1 G 2.1 S 3.5	M 0.90 C -trace-	F 5.3 G 2.2 S 3.6	M 0.90 C -trace-

TABLE IXL: (cont)

	T = 25 C		T = 7 C	
	sugars	acids	sugars	acids
CP (%)	F 0.10 G 0.04 S 0.03	M 0.04 C -	F 0.17 G 0.09 S 0.10	M 0.04 C -
R %	F 98 ± 2% G 98 ± 2% S 98 ± 2%	M 96 ± 2% C -	F 97 ± 2% G 96 ± 2% S 97 ± 2%	M 96 ± 2% C -

All results are the average of two determinations

TABLE XL : Permeate Flow and rejection characteristics of diluted apple juice concentrate; P = 77 atm

	T = 25 C		T = 7 C	
	sugars	acids	sugars	acids
	330		185	
CP (%)	F 5.1 G 2.2 S 3.6	M 0.94 C -trace-	F 5.0 G 2.0 S 3.4	M 0.94 C-trace-
CP (%)	F trace G trace S trace	M 0.04 C -	F trace G trace S trace	M 0.04 C -
R %	F, G, S 100%	M 96 ± 2% C -	F, G, S 100%	M 96 ± 2% C -

All results are the average of two determinations

TABLE XLI : Sugars and acids of permeate and concentrate obtained from concentrating single strength apple juice

	°Brix	pH	* glc sugars	* acids
Concentrate	34.5	3.1	F 16.5 G 7.7 S 12.7	M 3.1 C 0.13

TABLE XLI : (cont)

	°Brix	pH	Glc *sugars	*acids
Permeate	0.3	3.0	F-trace- G-trace- S 0.14	M 0.13 C -trace-
Rejection %			F 100% G 100% S 99 ± 2%	M 96% C ~ 100%

* Average of two determinations

TABLE XLII : Sugars and acids of permeate and concentrate obtained from concentrating diluted apple juice concentrate

	°Brix	pH	Glc *sugars	*acids
Concentrate	58	3.1	F 17.7 G 8.4 S 13.8	M 3.2 C 0.16
Permeate	1.0	2.9	F 0.23 G 0.18 S 0.15	M 0.60 C-trace-
Rejection %			F 98 ± 2% G 98 ± 2% S 99 ± 2%	M 81 ± 2% C ~ 100%

*Average of two determinations

TABLE XLIII: Concentration of single strength apple juice P = 99 atm

time (min)	° Brix	PF (mℓ/min)	Flux (ℓ/m²/hr)
0	10.5	260	17.5
30	11.2	250	16.9
60	14	205	13.8
90	18	190	12.8

TABLE XLIII: (cont)

time (min)	° Brix	PF (mℓ/min)	Flux (ℓ/m²/hr)
120	22.5	155	10.4
150	29.5	95	6.4
180	32.5	80	5.4
195	34.5	60	4.0

TABLE XLIV: Concentration of diluted apple juice concentrate; P = 99 atm

time (min)	° Brix	PF (mℓ/min)	Flux (ℓ/m²/hr)
0	12	225	15.2
30	14.5	220	14.8
60	18	185	12.5
90	23.5	150	10.1
120	29.5	100	6.7
135	32.5	85	5.7
150	35	60	4.0
165	37.5	45	3.0
180	38	40	2.7

TABLE XLV : Effect of cooling temperature on concentration of single strength apple juice; P = 99 atm

time (min)	T = 7 C ° Brix	T = 7 C End-to-end flux (ℓ/m²/hr)	T = 20 C ° Brix	T = 20 C End-to-end flux (ℓ/m²/hr)
5-15	10.5	17.5	11	-
30	11.2	17.1	15	21.9
60	14	15.7	19.5	21.5
90	18	14.8	27	18.9
120	22.5	13.9	35.5	16.4
150	29.5	12.5		
170	32.2	11.7		

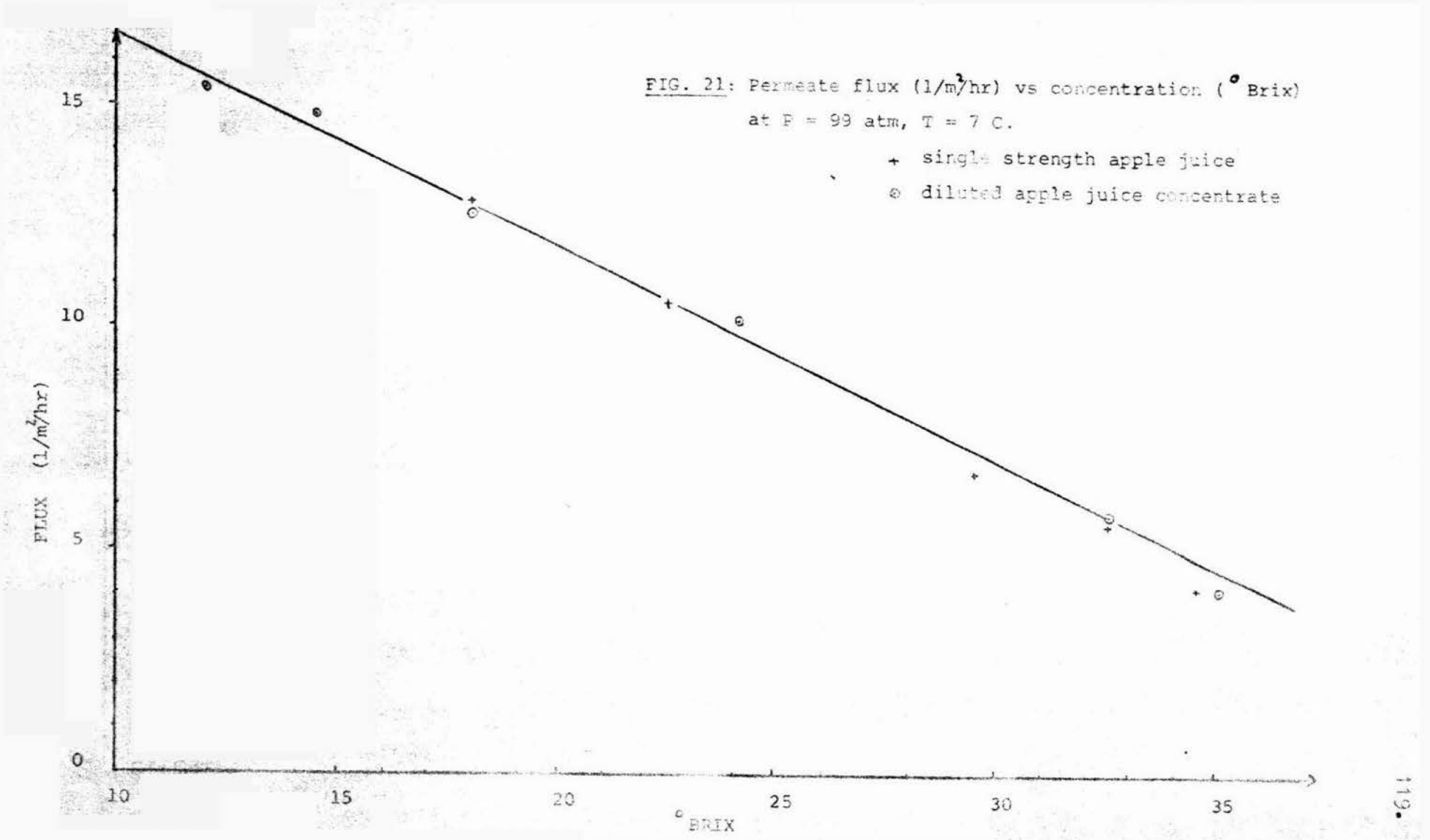


FIG. 21: Permeate flux (l/m²/hr) vs concentration (° Brix) at P = 99 atm, T = 7 C.

+ single strength apple juice

⊙ diluted apple juice concentrate

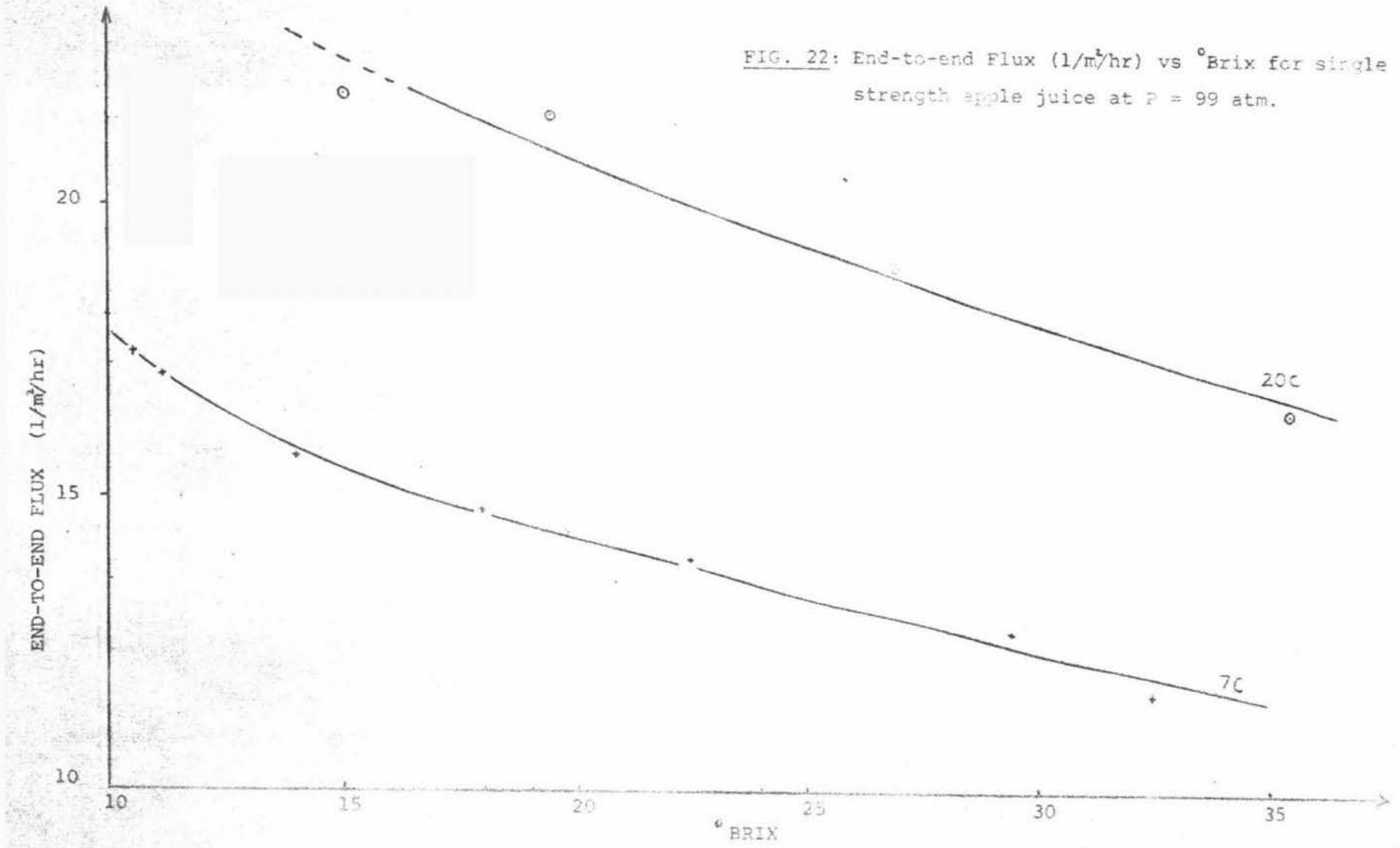


FIG. 22: End-to-end Flux (l/m²/hr) vs °Brix for single strength apple juice at P = 99 atm.

4. DISCUSSION

The results in Table XL confirm the results found previously with model solutions of sugars and acids. The three main sugars were almost totally retained while the extent of loss of malic acid (96%), although higher than that found using model solutions (92%), was not outside experimental error ($\pm$ 2%).

There was no significant differences in the rejection characteristics of the single strength and diluted concentrate under the same experimental conditions (Tables XL and XL).

Comparison of the 34.5 °Brix concentrate with the corresponding permeate (Table XLI) shows that, with respect to sugars and acids, the quality of the concentrate is not significantly different to single strength juice. Sugars were nearly totally retained (99 - 100%) while malic acid was partially lost (R = 96%). There was not detectable loss of citric acid.

On comparing the 38 °Brix concentrate with the permeate (Table XLII), it is seen that the sugars are well retained (98-99%), while the malic acid has started to leak out to a large extent (R = 81%). Citric, on the other hand, seems to be totally retained (Tables XLI and XLII), but as this acid exists in the juice in very small amounts, its retention or loss does not significantly affect the overall quality of the juice.

There was not any significant differences between the single strength and the diluted apple juice concentrate when concentrated at the high pressure. Results from Tables XLIII and XLIV and Fig.21 show that the instantaneous permeate flux of the two juices followed a linear decrease with concentration (°Brix); a lower flux was obtained at the higher °Brix, as expected from concentration polarisation effect (Chapter Three, section I).

An improved performance of the RO module was obtained at the higher cooling temperature (20 C) using fresh running water, as shown by results from Table XLV and Fig. 22. On comparing the end-to-end flux (defined as the total permeate accumulated over the length of the concentration, in litres, divided by the product of the time required for the concentration, in hours, and the membrane area, in square meters) versus the °Brix of the feed, it is seen (Fig.22) that the curves at 20 C and 7 C ran parallel to one another as expected, and that there was a significant increase (40%) in permeate flux throughout the concentration process when the higher cooling temperature was used.

The use of fresh running water instead of chilled water to cool the feed would mean an increase in efficiency of the RO module (i.e. increase in flux) as well as a reduction in cooling costs, which would result in a substantial economy of the process on an industrial scale, provided that there were no detrimental organoleptic changes in the juice at the higher temperature.

5. CONCLUSION

There was no significant difference between the single strength and the diluted juice concentrate when concentrated at 7 C by the RO module in use. The apple juice can be concentrated at 99 atm to 35 °Brix (7 C) without any significant loss in sugars and organic acids.

A 40% increase in end-to-end flux was achieved when fresh running water was used to cool the feed (20 C). This would result in substantial savings in cooling costs from a commercial point of view, provided that there were no detrimental organoleptic changes in the juice at the higher temperature.

CHAPTER FIVE

ECONOMIC EVALUATION OF REVERSE OSMOSIS

1. INTRODUCTION

The experimental concentration of apple juice using the TM5-14 RO module under study was shown in the previous chapter to be feasible up to a concentration of 35^{o} Brix. Since apple juice can be concentrated up to 72^{o} Brix using traditional evaporation methods, RO appeals as a preconcentration step prior to evaporation to increase the output of concentrate from the evaporator.

The object of this chapter is to consider the industrial application of RO, based on the earlier experimental data. In particular, the incorporation of RO into a commercial plant that currently uses evaporation to concentrate apple juice will be considered, and the proposed system subjected to an economic evaluation.

2. CURRENT EVAPORATION SYSTEM

The basis of the evaluation relies on data from an actual commercial plant. The Apple and Pear Board juice factory located at Hastings, New Zealand, currently concentrates apple juice for export using locally grown apples, mostly of the Granny Smith variety.

The apples are received at the factory in large wooden crates which hold approximately 1000 kg of apples each. After washing, the apples are crushed in a hammer mill and fed to Bucher-Guyer high pressure horizontal presses where the juice is extracted. Following extraction the juice is pasteurised at 85^{o}C for 30 seconds using an APV plate heat exchanger. The pasteurised juice is then treated with enzymes (Ultrazym 100 Special which contains pectinases and an amylase) and held in

large stainless steel tanks for 16 hours, when all the cloud particles in the juice form a sediment on the bottom of the tank. The supernatant juice is then passed through a diatomaceous earth filter to produce a clear juice which is fed, via a valance tank, to the first effect of an APV plate evaporator. The vapour from the first effect is passed into an aroma recovery unit, to yield apple essence of approximately 200 times concentration. The juice leaves the first effect at 23° Brix, the second effect at 35° Brix, and the third effect at 72° Brix (Gyde, 1977).

The Apple and Pear Board juice factory processes on average 68,000 litres of juice per 8 hour day. The season lasts 120 days. In 1976, the factory processed 20,000 tonnes of fruit. Seasonal throughput is expected to remain almost constant until 1979, but by 1985 it is projected that throughput will double to almost 40,000 tonnes per year (Gyde, ibid).

3. PROPOSED REVERSE OSMOSIS SYSTEM

For a commercial plant, it is usual to design an RO system on a "once-through" principle i.e. the feed passes through the high pressure pump and the modules only once, the concentrate leaving downstream from the modules and flowing to the concentrate tank. In the work reported in earlier chapters, a large membrane assembly was not used, necessitating a batchwise operation with recirculation of the retentate until the desired concentration was reached.

In commercial plants, pressure drop becomes an important design parameter. Harris et al. (1976) have discussed this in detail. Briefly, allowance needs to be made in any design for the drop in pressure and the increase in concentration of the juice along the flow path. If the flow rate is very high, the pressure drop will also be high, permitting the use of only a few modules in series. It is important that a particular combination of design parameters does not result in an "infeasible" case, e.g. when the pressure drop necessary to drive the juice through the module would be excessive; or the available pressure is too low to achieve satisfactory flux in the right direction.

Two types of flow configurations are outlined by Harris et al. (ibid). One is known as a "straight-through flow", where the number of modules in parallel remains constant throughout the axial flow path of the juice, resulting in a steady decline in juice velocity as water is removed. The other type of flow configuration is known as a "tapered-flow cross-section" where the number of parallel modules decreases from section to section (or stage to stage). The flow cross-section is thus reduced in steps to restore the retentate velocity to that at the inlet to the first modules. As a consequence, the linear velocity of the feed remains reasonably uniform in spite of the progressive decrease in feed volume due to hyperfiltration.

At the same inlet velocity, a tapered-flow path gives a higher average feed velocity than the corresponding straight-through flow case. Therefore, inlet velocities which are infeasible because of a high pressure drop in a straight-through arrangement would be even less feasible in the corresponding tapered cases.

On the other hand, at lower inlet velocities, where a low Reynolds number is likely to be limiting, use of a tapered-flow cross-section arrangement improves feasibility because a higher average feed velocity is being maintained.

For food applications, Abcor almost always uses TM 5-20 modules. These are bigger versions of the TM 5-14 module used in this study, containing 20 instead of 14 RO membranes and support tubes per module. The membrane surface area in the TM 5-20 module is 1.25 m^2 compared to 0.89 m^2 in the TM 5-14. The tubes in both modules are identical in size, and area, but have different headers which results in the modules having different flow arrangements. With series headers the TM 5-20 gives 2 tubes in parallel and 10 tubes in series per module, compared to the TM5-14 where series headers give 1 tube in parallel and 14 tubes in series per module. This results in different pressure drops for a given flow rate in the two types of modules (see Figure 23 for pressure drop data as supplied by Abcor).

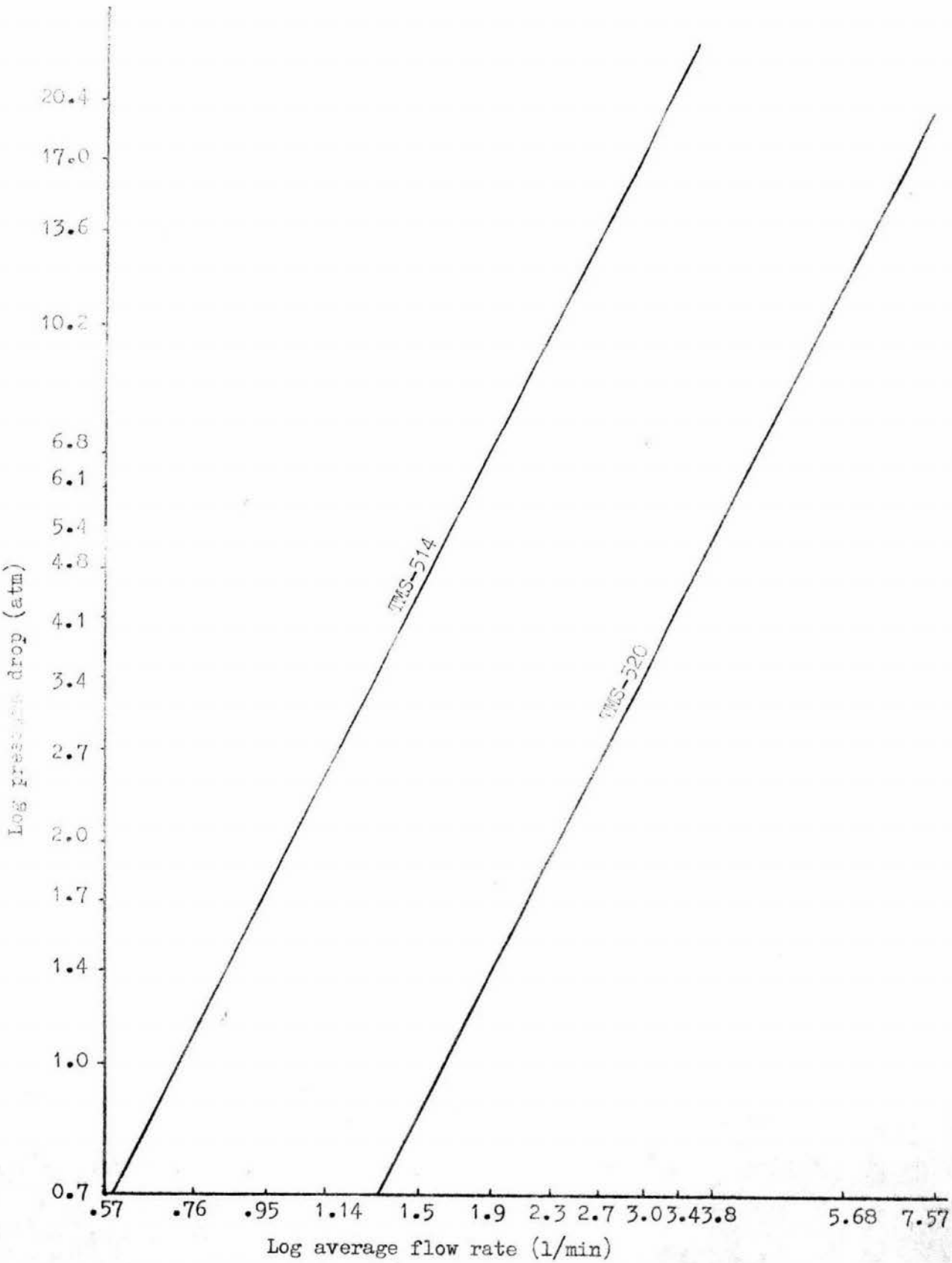


FIG.23: Flow rate versus pressure drop for TM 5-14 and TM 5-20 tubular RO modules series heads

Adapted from data supplied by Abcor (1977)

The advantage of the TM 5-20 module is its ability to be connected in sets by using a header to bridge between two modules. The module set is connected by tubular headers which perform the function of narrowing the flow path and thus restoring the retentate velocity to near its original value, resulting in a "tapered-flow cross-section" type of flow configuration as discussed above.

4. SIZE OF RO PLANT REQUIRED

The APV evaporator at the Apple and Pear Board factory in Hastings presently concentrates 68,000 litres of juice from 11°B to 72°B in 8 hours. By 1985 it will be required to concentrate twice this quantity of juice per day. This could be done simply by operating the evaporator for 16 instead of 8 hours per day. However, to enable an economic evaluation of RO to be done, the above scenario will not be considered further in this study. Instead, an RO plant will be selected to preconcentrate the juice to such an extent that the existing evaporator will be able to, in conjunction with the RO plant, concentrate 136,000 litres of juice from 11°B to 72°B in 8 hours.

To simplify the calculations detailed below, it has been assumed that degrees Brix is equivalent to percent total soluble solids. The basic material balance for the existing evaporator is as follows:

IN	OUT
68,000 l juice at 11°B per 8 hours	10,400 l concentrate at 72°B per 8 hours
≡ 8,500 l/h	57,600 l water evaporated per 8 hours
≡ 142 l/min juice at 11°B	≡ 7,200 l/h
	≡ 120 l/min water evaporated

If the juice is preconcentrated by RO to various levels, the water required to be removed by the evaporator, as well as other relevant

flow rates, together with the membrane area required and the number of modules can be calculated and are summarised in Table XLVI.

At this stage, a decision must be made as to the temperature at which the system will operate. A search of the published literature has failed to reveal any reports of detrimental effects on juice quality likely to arise from processing the juice at 20 C rather than 7 C. In fact, early in the juice processing season (March), the ambient air temperature at the factory can exceed 20 C on occasions, causing the juice to approach this temperature. However, no adverse effects have been noted on juice quality. Consequently, the plant will operate at a juice temperature of 20 C. This results in an increase in flux of approximately 40% compared to that at 7 C, and a considerable saving in the number of modules required.

The next decision to be made concerns the level to which the juice is to be concentrated by RO. As results in the previous chapter indicated, the flux rate declines quite rapidly as the concentration of the feed increases, resulting in a large increase in the number of modules required when high concentrations of juice are desired. The magnitude of such an increase is shown in Figure 24 where a straight line results from plotting the log of the final juice concentration against the number of modules.

As well as the additional modules which are required at higher final juice concentrations, the time required for the existing evaporator to concentrate the juice leaving the RO system to 72°B must also be considered. Reference to Table XLVI indicates that if the juice is concentrated by RO to 20°B, the evaporator would require 7.50 hours to concentrate this juice to 72°B. This time, together with a safety margin of 0.50 hours, means that the existing evaporator could handle the projected 1985 throughput by

TABLE XLVI: Material balances for preconcentration by RO from 11°Brix to various concentrations in 8 hours
(Apple juice feed = 136,000 l)

Final concentration	18°B	20°B	24°B	30°B	35°B
Concentrate, l	83,100	74,800	62,300	49,900	42,700
Permeate, l	52,900	61,200	73,700	86,100	93,300
H_2O to be removed by evaporator to reach 72°B, l	62,300	54,000	41,500	29,100	21,900
Evaporator time to remove this H_2O, h	8.65	7.50	5.76	4.04	3.04
Permeate Flux at 7°C, l/m^2hr	14.8	14.4	13.6	12.3	11.8
l/m^2 8 hr	118.4	115.2	108.8	98.4	94.4
Area required, m^2	447	531	677	875	988
Number of modules	358	425	542	700	791
Permeate Flux at 20 C, l/m^2hr	21.5	20.7	19.5	18.0	17.3
l/m^2 8 hr	172.0	165.6	156.0	144.0	138.4
Area required, m^2	308	370	472	598	674
Number of modules	247	296	378	479	540

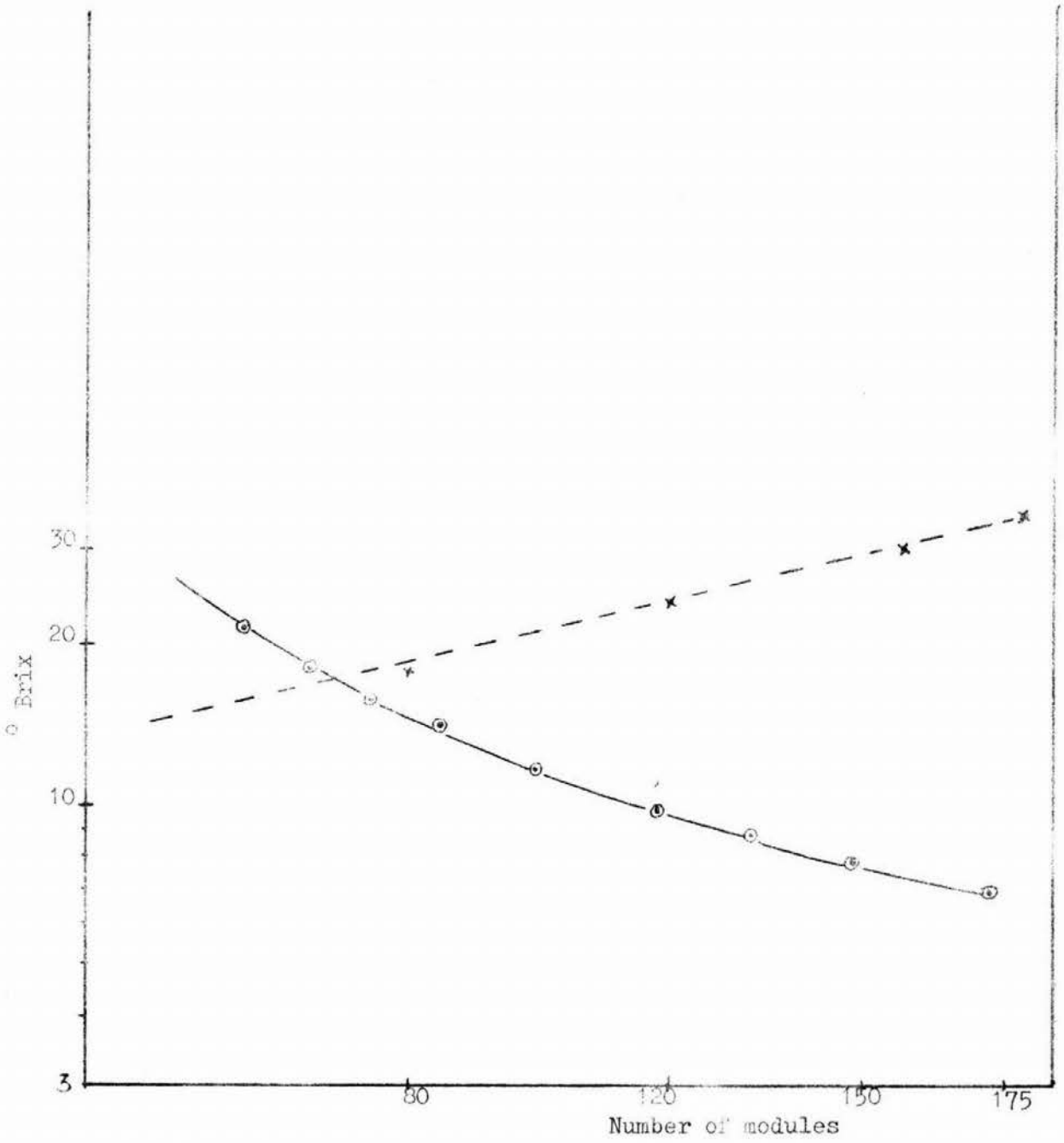


FIG.24: Number of modules required as a function of final juice concentration (—— x —— x ——) and hours of operation (— ⊙ — ⊙ —).

operating 8 hours per day, provided that the juice was preconcentrated by RO to 20°B. This will require an RO plant consisting of 296 modules to operate for 8 hours per day.

5. DESIGN OF MODULE CONFIGURATION

The first step in the design of a suitable module configuration is to calculate the acceptable pressure drop across the system. It is assumed that the inlet pressure will be 100 atm. (1500 psi). The osmotic pressure of apple juice at 20°B is 29.7 atm (430 psi), according to Morgan et al. (1965). Therefore, a maximum acceptable pressure drop to ensure that there is still sufficient driving force across the membrane in the final modules would be 30 atm (450 psi), giving a minimum driving force of 41.3 atm (620 psi).

The apple juice feed rate will be 136,000 l over 8 hours or 284 l/min. The number of modules required is 296. Based on information supplied by Abcor (Ryan, 1977) it was decided to divide the modules over 5 cabinets, each containing 60 modules. These 5 cabinets would be set up to operate in parallel. The problem then becomes one of selecting the module configuration within each cabinet so as to get an average flow rate sufficiently low to give an acceptable pressure drop. The procedure to be followed in such calculations is shown below.

284 l/min Feedrate to total RO plant

56.8 l/min Feedrate to each cabinet

5.16 l/min feed to first module | 11 modules in parallel; 3 modules in series | 3.87 l/min flow out of last module

42.6 l/min Flowrate from above group of modules

4.73 l/min feed to first module | 9 modules in parallel; 3 modules in series | 3.44 l/min flow out of last module

30.9 l/min Final concentrate flow out of cabinet

25.9 l/min Total permeate flow out of cabinet

$$\text{Average module flowrate} = \frac{11\left(\frac{5.16+3.87}{2}\right) + 9\left(\frac{4.73+3.44}{2}\right)}{20}$$

$$= 4.32 \text{ l/min}$$

From Figure 23, the pressure drop in a TM 5-20 module at this flow rate = 6.67 atmos (100 psi).

Therefore total pressure drop = 6.67 X 6

= 40 atmos (600 psi).

This exceeds the acceptable pressure drop calculated earlier of 30 atmos, and therefore the above configuration must be rejected, on the grounds that the average module flow rate resulted in an excessively high pressure drop.

An alternative configuration can be derived still utilising 5 cabinets in parallel each containing 60 modules, but this time, in an attempt to reduce the pressure drop, only 5 modules will be connected in series.

4.37 l/min feed to first module | 13 modules in parallel; 3 modules in series | 3.07 l/min flow out of last module

40.0 l/min Flowrate from above group of modules

4.00 l/min feed to first module | 10 modules in parallel; 2 modules in series | 3.14 l/min flow out of last module

31.4 l/min Final concentrate flow out of cabinet

25.4 l/min Total permeate flow out of cabinet

$$\text{Average module flowrate} = \frac{13\left(\frac{4.37+3.07}{2}\right) + 10\left(\frac{4.00+3.14}{2}\right)}{23}$$

$$= 3.65 \text{ l/min}$$

From Figure 23, the pressure drop in a TM 5-20 module at this flow rate = 5 atmos (75 psi).

Therefore total pressure drop = 5 X 5

= 25 atmos (375 psi)

This figure is inside the allowable pressure drop set earlier of 30 atmos, and therefore the above module configuration is feasible. The actual flow path through the above module design is shown in Figure 25, where the feed is introduced to 13 modules in parallel, 3 modules in series (a, b, c), then into a header and back into 10 modules in parallel, 2 modules in series (a, b), and then out into a header to exit as final concentrate of 20°B.

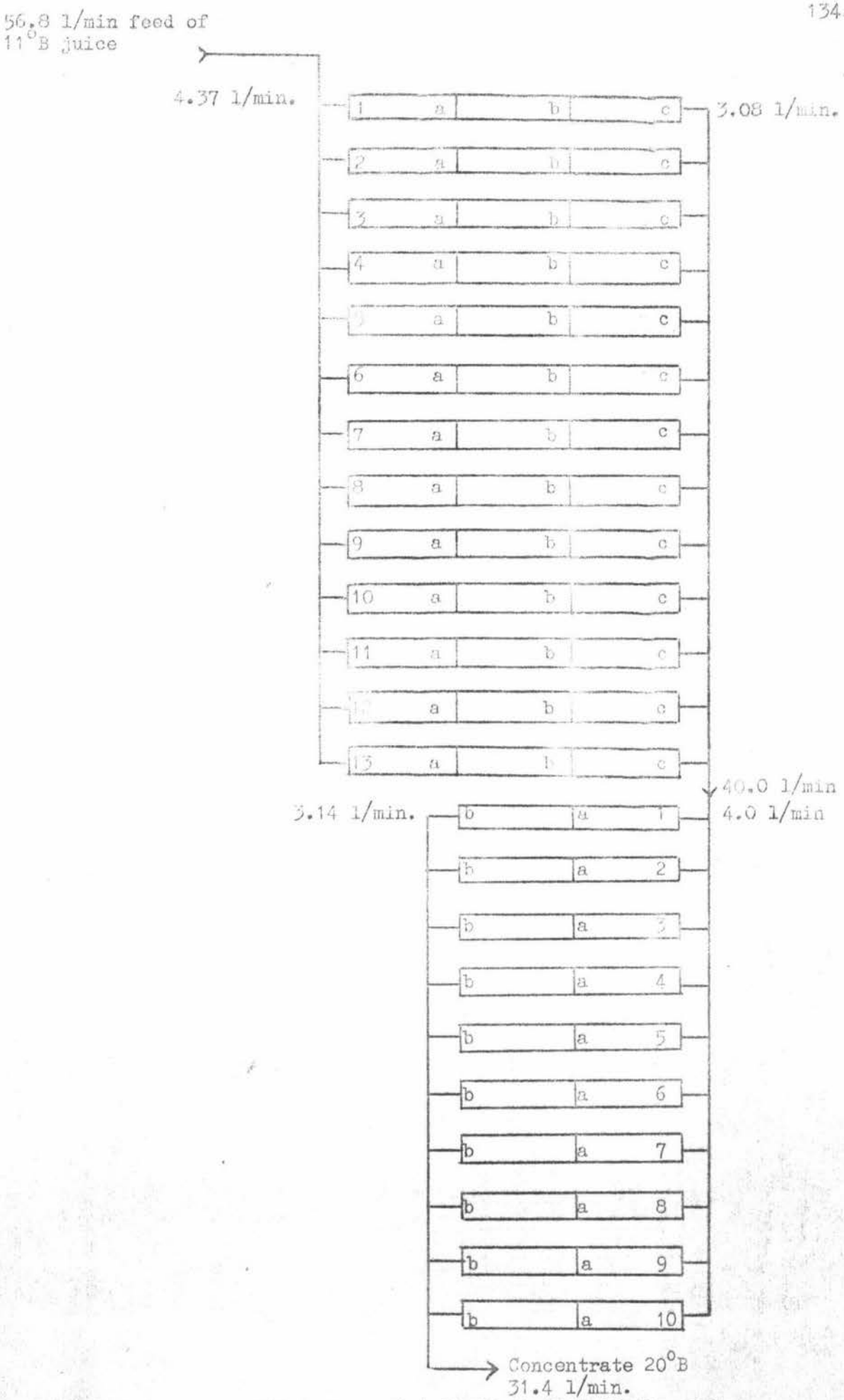


FIG.25: Flow path through one of 5 identical cabinets required for feasible RO module configuration design.

6. COSTING OF FEASIBLE MODULE CONFIGURATION

The above module configuration was presented to Abcor Inc., Massachussetts, U.S.A., with the request that they verify the feasibility of such a configuration and supply the installed cost of such a plant at the Hastings Apple and Pear Board factory. The configuration was approved by Abcor (Tutunjian, 1978) who supplied the information on which the following cost calculations are based. (NOTE - all costs are in $NZ, assuming that $US = $NZ).

(a) the power requirements of such a plant consist of one large pump with one booster pump to feed all five cabinets; another pump is needed for spraying and cleaning purposes. The normal operating horsepower for an RO plant with a capacity of 68,000 l of juice per day is 30 HP, assuming an efficiency factor of not less than 73% (Ryan, 1977). Thus the power consumption of this RO plant is taken as 60 HP based on a direct capacity ratio.

(b) the estimated capital cost for this plant is $600,000 C.I.F. New Zealand. This does not include tanks for processing for which $10,000 has been allowed. Installation costs are generally 15% of the initial capital costs, and fabrication usually takes about 6-8 months.

(c) a complete replacement of membranes is envisaged every two seasons (Ryan, ibid). Membrane replacement is budgeted at $140 per TM 5-20 module. It is estimated to take an average of 60 minutes to reline each module, making a total of 300 hours to reline all the modules. In addition a machine costing $2,000 is needed to perform the relining.

(d) the cleaning time is 4 hours a day, while the total cost for chemicals is $40 a day.

(e) maintenance costs for membrane concentration is commonly 5% of capital cost (Thijssen and Van Oyen, 1977).

(f) one man is able to operate the complete RO plant.

(g) the area of such a plant would occupy 80-100 m^2, such room currently being available in the existing factory.

Table XLVII summarises the costing of the proposed RO plant.

TABLE XLVII: Cost estimates for the reverse osmosis concentration of 136,000 l of apple juice from 11°Brix to 20°Brix in 7.5 hours

RO PLANT	
Concentration factor	= 1.8 : 1
Membrane type	= AS-197
Membrane area	= 308 m^2
Number of modules	= 296
Water removed/hr	= 7,659 kg
Operating hours	= 7.5 hrs a day, plus 4 hrs for cleaning
Operating days/year	= 120 days

CAPITAL COST	= $610,000
Installation cost (15%)	90,000
TOTAL	= $700,000

System includes clean-in-place facilities, controls, all pumps, tanks, etc.

ANNUAL OPERATING COSTS =		
Depreciation of plant at 10%	=	$ 70,000
Membrane replacement	=	22,000
Labour, one man at $5 per hour	=	7,200
Power at 5.0 cents/Kwhr, 60 HP	=	3,200
Cleaning chemicals and water	=	4,800
Maintenance (5% of capital cost)	=	35,000
TOTAL	=	$142,200

OPERATING COST/1000 KG WATER REMOVED

$$\frac{142,200}{7,659 \times 7.5 \times 120} \times 1000 = \$21$$

FIXED COST AS PERCENTAGE OF TOTAL

$$\frac{700,000}{842,000} = 83\%$$

CONCENTRATION COST/1000 KG WATER REMOVED

$$\frac{842,000}{7,659 \times 7.5 \times 120} \times 1000 = \$122$$

7. COST OF EQUIVALENT EVAPORATOR

As discussed earlier, for the purposes of economic evaluation, the cost of an RO plant capable of concentrating, in conjunction with the existing APV plate evaporator, 136,000 litres of apple juice from 11°Brix to 72°Brix in 8 hours, is to be compared with the cost of purchasing and operating another APV plate evaporator identical to the existing one. Therefore, the New Zealand agents for APV (Bell, Bryant (N.Z.) Ltd.) were requested to supply the relevant cost details and these are summarised below.

TABLE XLVIII: Cost estimates for the evaporating concentration of 68,000 l of apple juice from 11°Brix to 72°Brix in 8 hours

Evaporator = one APV series III triple effect plate evaporator complete with thermocompressor spray condenser and preheater

Performance = Feed 9,090 kg/hr apple juice at 11% T.S.
Product 1,388 kg/hr concentrate at 72% T.S.
Evaporation 7,702 kg/hr water

Operating hours = 7.5 hours per day with 1.5 hours clean up

CAPITAL COST[1]	=	$222,000
Installation cost (15%)	=	33,000
Boiler[2]	=	27,000
TOTAL:	=	$282,300

ANNUAL OPERATING COSTS

Depreciation of plant at 10%	=	$28,230
Labour, one man at $5 per hour[3]	=	5,400
Operating supplies[3]	=	2,400
Power, including cooling costs[4], 55 HP	=	2,200
Steam generation cost[4]	=	27,600
Maintenance (2% of capital cost)	=	5,646
TOTAL:	=	$71,500

OPERATING COST/1000 KG WATER REMOVED

$$\frac{71,500}{7,702 \times 7.5 \times 120} \times 1000 = \$10$$

FIXED COST AS PERCENTAGE OF TOTAL

$$\frac{282,300}{353,800} = 80\%$$

CONCENTRATION COST/1000 KG WATER REMOVED

$$\frac{353,800}{7,702 \times 7.5 \times 120} \times 1000 = \$51$$

Basis for cost calculations:

(1) Evaporator cost and details supplied by Bell Bryant (N.Z.) Ltd. (Kelly, 1978).

(2) The existing boiler at Hastings is currently operated at full capacity. Therefore, there is no alternative but to install a new boiler of similar capacity. The present steam demand was based on the following requirements:

Steam at 150 psi		
Evaporator	=	1909 kg/hr
Preheater	=	182 kg/hr
TOTAL	=	2091 kg/hr steam

Source: Kelly (1978)

Given a thermal efficiency of 80%, a light oil-fired boiler with a capacity of at least 2,600 kg/hr steam at 150 psi g is needed. Mason Anderson Ltd. (1978) gave the cost of a 2900 kg/hr oil-fired boiler as $27,000 (installed). The fuel cost for light oil is $230 per day, since oil costs $0.107 per l.

(3) One man is able to operate the evaporator. Cleaning time is estimated at 1.5 hours and the cost of cleaning materials at $20 per day.

(4) Cooling water is drawn from a bore so the only cost is the power required to draw the amount needed. A 10 HP pump is allowed for in the calculations. The evaporator draws 45 HP and power costs 5.0 cents/Kwhr.

(5) Source: Thijssen and Van Oyen (1977).

8. DISCUSSION

Bomben et al. (1973) carried out a comparison of evaporation, freeze concentration and RO, and reported that RO became competitive with both freeze concentration and evaporation at small capacities. For nearly year-round operation (7,500 hours/year), RO was cheaper at capacities below about 400 kg of water removal per hour. They also found that at 2,000 operating hours a year, RO became cheaper for capacities smaller than 200 kg of water removal per hour.

Thijssen and Van Oyen (1977) carried out an economic evaluation of concentration by evaporation and RO. The approximate costs of concentration were given for dewatering capacities in the range of 1 to 50,000 kg per hour and 1,800 and 6,300 productive hours per year (see Figures 26 and 27). For capacities similar to the evaporator and RO proposed in this study, their results and results found in Tables XLVII and XLVIII are summarised below.

TABLE XLIX: Summary of concentration costs ($/tonne water removed) of RO and plate evaporator at a capacity of 7,700 kg/hr removed

Operational hours/year		900	1800	6300
REVERSE OSMOSIS	A	122		
	B		17	5
PLATE EVAPORATOR	A	51		
	B		7.4	2

A 20.7 l/m^2hr, 10-20% T.S.

B(1) 13.5 l/m^2hr, 10-30% T.S., labour costs not included

(1) Source: Thijssen and Van Oyen (1977)

From Table XLIX, it can be seen that both RO and evaporation is very expensive for short seasonal operation, due to the high capital investment ($700,000 for RO and $282,300 for the evaporator). For 900 operational hours per year, the concentration cost ($/tonne water removed). For RO is more than twice as expensive than evaporation ($122 compared to $51), thus making RO very unattractive for short term operation. Results from Thijssen and Van Oyen (ibid.) also indicate a concentration cost for RO of more than double that of plate evaporation, even at 1800 hours operation a year.

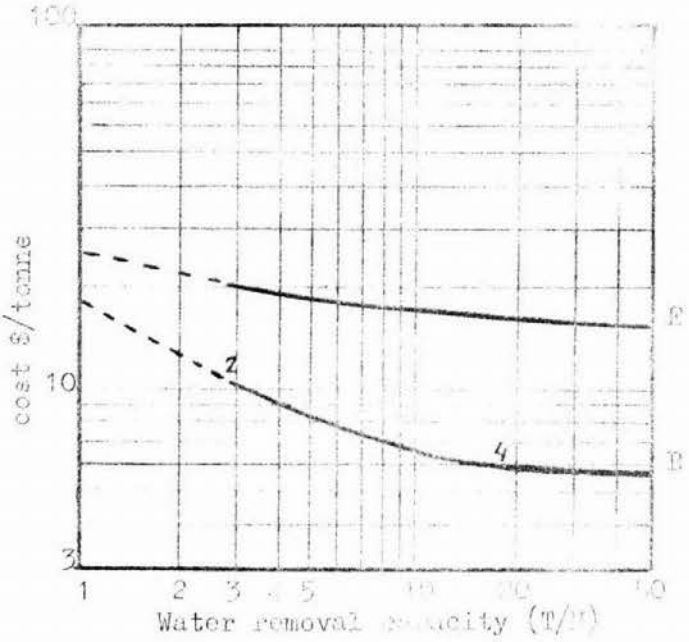


FIG.26: Dewatering costs in dollars per tonne water removal without aroma retention or recovery. For plate evaporation and reverse osmosis at 1800 productive hours per year.

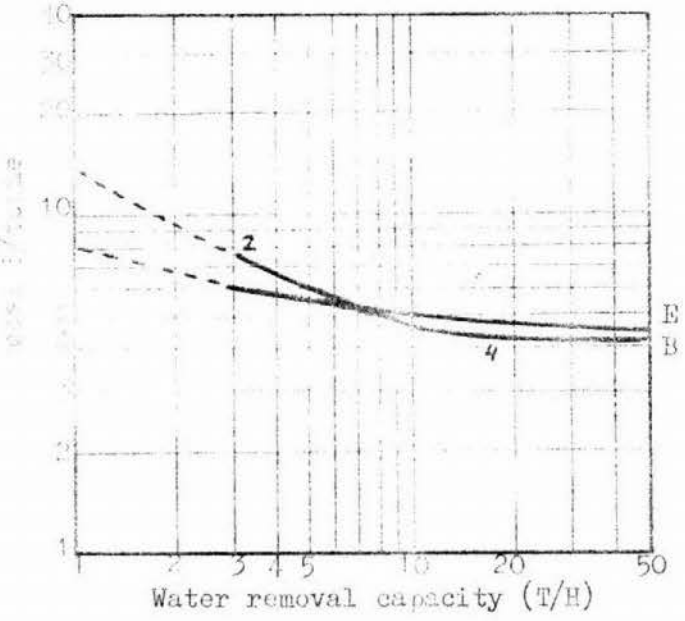


FIG.27: Dewatering costs in dollars per tonne water removal without aroma retention or recovery. For plate evaporation and reverse osmosis at 6,300 productive hours per year.

Labour costs and costs due to possible product losses are not included. The figures along the curves indicate the economic optimum number of effects.

B. multi-effect plate type evaporators with vapour compression for fruit juices 10-70%.

E. reverse osmosis flux 13.5 $l/m^2/hr$, 10-30% for fruit juices.

Adapted from Thijssen and Van Oyen (1977).

Their results and those found in this study suggest that doubling the operational hours per year from 900 to 1,800 will reduce the concentration costs for both processes by a factor of about seven. On the other hand, a 7 X increase in operational hours per year from 900 to 6,300 will reduce RO concentration costs 24 times while for the evaporator, concentration costs are only reduced 10 times. At 6,300 hours per year both concentration costs are equal. Thus, it seems that the cost of RO is competitive with plate evaporation only when used year round (6,300 hours a year). This confirms an earlier report (Thijssen, 1970) which arrived at a similar conclusion, even although it used much more approximate costing figures than were used in the later study (Thijssen and Van Oyen, ibid.).

The results found in this study indicate that the annual operating costs for RO ($142,200) is substantially higher than the equivalent for plate evaporation ($71,500), pointing to the fact that the use of the RO plant at this high capacity is not as economical as the use of a plate evaporator. Thus it seems that the use of RO as a preconcentration technique in apple juice processing will never be realised unless capital costs are reduced considerably and operating hours are increased significantly. On the basis of this study, it would not be financially prudent for the Apple and Pear Board in Hastings to consider RO for the preconcentration of apple juice when the capacity of their present evaporator is no longer adequate.

APPENDIX I

SAMPLE CALCULATION OF 'A'

FROM TABLE XVII

$$P = 54.4 \text{ atm}$$

$$PWP = (357.5 \pm 2.5) \text{ mℓ/min}$$

$$= (357.5 \pm 2.5) \frac{\text{mℓ}}{\text{min}} \times 1 \frac{\text{g}}{\text{mℓ}} \times 60 \frac{\text{min}}{\text{hr}}$$

$$= (21,450 \pm 150) \text{ g/hr}$$

$$A = \frac{(PWP)}{18 \times 8900 \times 3600 \times P \text{ atm}} \qquad \text{Eqn. A}$$

Thus

$$A = \frac{(21,450 \pm 150)}{18 \times 8900 \times 3600 \times (54.4 \pm 1)}$$

$$= (6.3 \pm 0.2) \times 10^{-7}$$

APPENDIX II

DATA FOR THE SYSTEM [NaCl - H_2O] at 25 C

[a]Weight % (w/v) solute	Molarity	Mole Fraction x 10^3	Weight % (w/v) solute	Osmotic pressure (psi)	Density (g/cm^3)	Molar density (mole/cm^3 x10^2)
0.	0.	0.	0	0	0.9971	5.535
0.5817	0.1	1.798	0.5811	67	1.0011	5.535
1.1615	0.2	3.590	1.1555	133	1.0052	5.535
1.7390	0.3	5.375	1.7283	199	1.0091	5.535
2.3143	0.4	7.154	2.2986	264	1.0130	5.534
2.8875	0.5	8.927	2.8695	331	1.0169	5.534
3.4587	0.6	10.693	3.4382	398	1.0208	5.534
4.0282	0.7	12.453	3.9307	466	1.0248	5.534
4.5949	0.8	14.207	4.4671	534	1.0286	5.533
5.1589	0.9	15.955	4.9976	603	1.0322	5.532
5.7199	1.0	17.696	5.5222	673	1.0357	5.530
6.8342	1.2	21.160	6.5543	814	1.0427	5.526
7.9460	1.4	24.601	7.5640	959	1.0505	5.526
9.0491	1.6	28.016	8.5522	1109	1.0581	5.525
10.1450	1.8	31.408	9.5194	1262	1.0653	5.524
11.2222	2.0	34.777	10.4665	1419	1.0722	5.521

[a] obtained by multiplying weight % solute (w/w) to density of solution (g/cm^3)

Source: Sourirajan (1970), p.563

APPENDIX III

SAMPLE CALCULATION OF $(D_{AB}/\Delta x)$

(i) Data:

A = [illegible] $\times 10^{-7}$ ($\pm$ 0.4%) (Table XXII)

S = [illegible] NaCl (w/v) ($\pm$ [illegible]) (Table XXIV)

PF = [illegible] mℓ/min ($\pm$ 0.5%) (Table XXIV)

= [illegible] x 60

= [illegible] ℓ/hr ($\pm$ 0.5%)

C_B = 0.01125 % NaCl ($\pm$ 0.2%) (Table XXIV)

P = [illegible] atm (1300 psi)

(ii) Solvent Flux:

$$N_B = \frac{[illegible] (\pm 0.5\%)}{[illegible] \cdot 3600 \cdot 8900}$$

= [illegible] $\times 10^{-6}$ ($\pm$ 0.5%) g.mole/cm^2 sec

(iii) $$X_{A3} = \frac{1.7[illegible] \times 10^{-3} \times 0.01125 (\pm 0.2\%)}{0.5811}$$

= [illegible] $\times 10^{-3}$ ($\pm$ 0.2%) mole fraction

by interpolation from columns (1) and (3) from Appendix II

(iv) $$X_{A3} = \frac{57 \times 0.01125 (\pm 0.2\%)}{0.5817 \times 14.7}$$

= 0.09 atm ($\pm$ 0.2%)

by interpolation from columns (1) and (5) from Appendix II and taking 1 atm = 14.7 psi

(v) $$N_B = A \left[P - \pi(X_{A2}) + \pi (X_{A3}) \right]$$ Eq. (5)

$$\therefore \underset{(\pm 0.5\%)}{57.2 \times 10^{-6}} = 6.5 \times 10^{-7} (\pm 0.4\%) \left[92.52 + 0.09 (\pm 0.2\%) - \pi(X_{A2}) \right]$$

$$\text{i.e. } 572 (\pm 0.5\%) = 6.5 (\pm 0.4\%) \left[92.61 - \pi(X_{A2}) \right]$$

or $(P_{A2}) = \frac{[\text{illegible}]}{[\text{illegible}]}$

$= \frac{[\text{illegible}]}{[\text{illegible}]}$

$=$ [illegible] atm ($\pm$ [illegible])

$=$ [illegible] psi ($\pm$ [illegible])

$(X_{A2}) = \frac{[\text{illegible}] \times 1.7[\text{illegible}] \times 10^{-3}}{67}$

$=$ 1.[illegible] $\times 10^{-3}$ mole fraction (w/v) ($\pm$ [illegible])

by interpolation from columns (3) and (5), Appendix II

Thus $(X_{A2}) =$ [illegible] $\times 10^{-3} \times 1.0011$

$=$ 1.[illegible] $\times 10^{-3}$ mole fraction (w/v) ($\pm$ 18%)

using density values from column (6), Appendix II

(vi) [illegible] $= c.(D_{AM}/K\delta).\left(\frac{1 - X_{A3}}{X_{A3}}\right).(X_{A2} - X_{A3})$ [illegible] (24)

[illegible]

[illegible] $\times 10^{-6}$

($\pm$ 0.5%) $= 553.5 \times 10^{-4}\ (D_{AM}/K\delta)$

$= \left(\frac{1 - 0.000035}{0.000035}\right)\left(0.001821 - 0.000035\right)$

Thus

$(D_{AM}/K\delta) = \frac{572 \times 10^{-3}\ (\pm 0.5\%)}{553.5 \times 28570.4\ (\pm 2\%) \times 0.001786\ (\pm 18.4\%)}$

$= (20.2 \pm 3.9) \times 10^{-6}$ cm/sec ($\pm$ 19.1%)

APPENDIX IV

CASE 2: CALCULATION OF 'k'

(i) Data:

S	=	0.513 % NaCl (w/v) (± 4%)	(Table XXIV)
N_B	=	57.2 x 10^{-6} g.mole/cm².sec.atm (± 0.5%)	(Appendix III)
X_{A3}	=	0.000035 mole fraction (± 0.2%)	(Appendix III)
X_{A2}	=	1.821 x 10^{-3} mole fraction (± 18%)	(Appendix III)
c	=	553.5 x 10^{-4} mole/cm³	(Appendix II)

(ii) $X_{A1} = \frac{1.798 \times 10^{-3} \times 0.513}{0.9847}$

$= 1.587 \times 10^{-3}$ mole fraction (± 4%)

by interpolation from columns (1) and (3), Appendix I.

(iii) Equation (4.2) gives

$$N_B = k\,c\,.\,(1 - X_{A3})\,.\,\ln\left(\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right)$$

57.2×10^{-6} (± 0.5%) $= k\,.\,(553.5 \times 10^{-4})\,.\,(1 - 0.000035\ (\pm\ 0.2\%))$

$$= \ln\left(\frac{0.001821\ (\pm\ 18\%) - 0.000035\ (\pm\ 0.2\%)}{0.001587\ (\pm\ 4\%) - 0.000035\ (\pm\ 0.2\%)}\right)$$

Thus $$k = \frac{57.2 \times 10^{-6}\ (\pm\ 0.5\%)}{(553.5 \times 10^{-4}).(0.999965).(0.140\ (\pm\ 22\%))}$$

$$k = (7.4 \pm 1.7) \times 10^{-3}\ \text{cm/sec}\ (\pm\ 23\%)$$

BIBLIOGRAPHY

Abcor

1971 Instruction sheet, MS-71-21; Abcor, Inc., U.S.A.

Abcor

1972 Instruction sheet, PIB 217; Abcor, Inc., U.S.A.

Abcor

1976 Product bulletin, MA-76-10; Abcor, Inc., U.S.A.

Agrawal, J.P., and Sourirajan, S.

1969 "Reverse osmosis".
Industrial Engineering Chemistry, 61, (11), 62-89.

Agrawal, J.P., and Sourirajan, S.

1970 "Reverse osmosis separation of some inorganic salts in aqueous solution containing mixed solutes with a common ion".
Industrial Engineering Chemistry - Product Research Development - 9, (1), 12-18.

Association of the Official Analytical Chemists

1975 A.O.A.C. - "Methods of analysis" - Washington, 12th edition, Chapter 22, 401-409.

Banks, W., and Sharples, A.

1966 "Mechanism of solute rejection"
Journal of Applied Chemistry, 16, (5), 153.

Boag, I.F.

1977 Lecturer, Department of Industrial Management and Engineering, Massey University, Palmerston North. Personal communication.

Bird, R.B., Stewart, W.E. and Lightfoot, E.N.

1960 "Transport phenomena", p.520. John Wiley, New York.

Bomben, J.L., Bruin, S., Thijssen, H.A.C. and Merson, L.

1973 "Aroma recovery and retention in concentration and drying of foods". In Advances in Food Research, Ed. C.O. Chichester, Vol.20, pp.2-152. Academic Press, New York and London.

Carter, J.W.

1968 "Developments in membrane processes". British Chemical Engineering, 13, (4), 533-536

Chan, H.T. and Kwok, S.C.M.

1975a "Identification and determination of sugars in some tropical fruit products". Journal of Food Science, 40, 419-420.

Chan, H.T. and Lee, C.W.Q.

1975b "Identification and determination of sugars in soursop, rose apple, mountain apple and surinam cherry". Journal of Food Science, 40, 89[illegible]-393.

Clamp, J.R.

1974 "Gas-liquid chromatography of TMS-derivatives of sugars and related substances". Journal of the American Chemical Society, 52, 2497-2507.

Dal Nogare, S., and Juvet, R.S.

1962 "Gas-liquid chromatography. Theory and practice". Interscience, New York and London. p.256.

Florez, E.F., Kline, D.A. and Johnson, A.R.

1970 "Glc determination of organic acids in fruits as their TMS-derivatives". Journal of the Association of Official Analytical Chemists. 53, (1), 17-20.

Feberwee, A., and Evers, G.H.

1970 "Reverse osmosis of aqueous solutions of organic solutes - Influence of the molecular weight of organic solutes in aqueous solution on their retention during reverse osmosis". Lebensmittel - Wissenchaft - Technologie, 3.

Gherardi, S., Porretto, A. and Dall Aglio, G.

1972 "The use of reverse osmosis in the concentration of fruit juices".
Industria Conserve (Parma), 47, 16.

Goodall, H.

1972 "Reverse osmosis and ultrafiltration and their practical applications".
The British Food Manufacturing Industries Research Association - Scientific and Technical Surveys - 5, (77), 1-21.

Gyde, M.

1977 Production supervisor, Apple and Pear Board Factory, Hastings.
Personal communication.

Hammett, L.P.

1940 "Physical organic chemistry"
McGraw-Hill Book Co., New York, 184.

Harris, F.L., Humphries, G.B. and Spiegler, K.S.

1976 "Reverse osmosis (Hyperfiltration) in water desalination".
Chapter in "Membrane Separation Processes" pp.121-186.
Ed. by P. Meares, Elsevier Scientific Pub. Co. Amsterdam - Oxford - New York.

Harrison, P.S.

1970a "Some applications of reverse osmosis under consideration for industrial use".
Chemistry and Industry, (3), 325-328.

Harrison, P.S.

1970b "Reverse osmosis and its application in the food industry".
Food Trade Review, 40, (11), 33-37.

Heatherbell, D.A.

1974 "Rapid concurrent analysis of fruit sugars and acids by glc".
Journal of the Science of Food and Agriculture, 25, 1095-1107.

Heatherbell, D.A.

1975a "Identification and quantitative analysis of sugars and non-volatile organic acids in Chinese gooseberry fruit". Journal of the Science of Food and Agriculture, 25, 1095-1107.

Heatherbell, D.A.

1975b "Identification and quantitative analysis of sugars and non-volatile acids in Tamarillo fruit". Confructa, 20, (1), 17-22.

Hulme, A.C.

1970 "Biochemistry of apple and pear fruits" In: The Biochemistry of fruits and their products, chapter 10, 2, 322 (Hulme ed.) London, Academic Press.

Kavanagh, J.A.

1971 "Introduction to reverse osmosis". Technical presentation 750-3706, Appendix I-1. Aqua-Chem, Inc., U.S.A.

Kearsley, M.W.

1974 "Concentration of sugars by reverse osmosis". Food Trade Review, (6), 9-11.

Kelly, J.C.

1978 Engineering Manager, Bell Bryant (N.Z.) Ltd., Penrose, Auckland. Personal communication.

Leightell, B.

1972 "Reverse osmosis in the concentration of food". Process Biochemistry, 7, (3), 40-42.

Lonsdale, H.K., Merten, U., and Kiley, R.L.

1965 "Transport properties of cellulose acetate membranes". Journal of Applied Polymer Science, 9, (4), 1341-1362.

Lowe, E., Durkee, E.L., Merson, R.L., Ijichi, K. and Cimino, S.L.

1969 "Egg white - concentrated by reverse osmosis". Food Technology, 23, (6), 45.

Manjikian, S.

1967 "Desalination membranes from organic casting solutions". Industrial Engineering Chemistry - Product Research Development, 6, 23-32.

Marshall, P.G., Dunkley, W.L., and Lowe, E.

1968 "Fractionation and concentration of whey by reverse osmosis". Food Technology, 22, (8), 37.

Mason Anderson Ltd.

1978 Boilermakers, Palmerston North.

Matsuura, T., and Sourirajan, S.

1971a "Reverse osmosis separation of some organic solutes in aqueous solutions using porous cellulose acetate membranes". Industrial and Engineering Chemistry - Process Design and Development, 10, (1), 102-107.

Matsuura, T., and Sourirajan, S.

1971b "Physico-chemical criteria for reverse osmosis separation of alcohols, phenols and monocarboxylic acids in aqueous solutions using cellulose acetate membranes". Journal of Applied Polymer Science, 15, 2905-2927

Matsuura, T. and Sourirajan, S.

1972a "Physico-chemical criteria for reverse osmosis separation of aldehydes, ketones, ethers, esters and amines in aqueous solutions using cellulose acetate membranes". Journal of Applied Polymer Science, 16, 1663-1686.

Matsuura, T. and Sourirajan, S.

1972b "Reverse osmosis separation of phenols in aqueous solutions using cellulose acetate membranes". Journal of Applied Polymer Science, 16, 2531-2554.

Matsuura, T., Baxter, A.G. and Sourirajan, S.
1973 "Concentration of fruit juices by reverse osmosis using porous cellulose acetate membranes".
Acta Alimentaria, 2, (2), 109-150.

Matsuura, T., Baxter, A.G., and Sourirajan, S.
1974a "Studies on reverse osmosis for concentration of fruit juices".
Journal of Food Science, 39, 704-711.

Matsuura, T., Blais, P., Dikson, J.M. and Sourirajan, S.
1974b "Reverse osmosis separations for some alcohols and phenols in aqueous solutions using aromatic polyamide membranes".
Journal of Applied Polymer Science, 18, 3671.

Matsuura, T., Baxter, A.G., and Sourirajan, S.
1975 "Reverse osmosis recovery of flavor components from apple juice waters".
Journal of Food Science, 40, 1039-1046.

McNair, H.M., and Bonelli, E.J.
1968 "Basic gas-chromatography".
Varian Aerograph, Walnut Creek, California.

Merck
1960 "The Merckx Index of chemicals and drugs".
Merckx and Co. Inc., New Jersey, U.S.A.; 7th edition, p.604.

Merson, R.L., Ginette, L.F., and Morgan, A.I., Jr.
1968 "Reverse osmosis for food processing".
Dechema Monographien, 63, 179-201.

Merson, R.L., and Morgan, A.I. Jr.
1968 "Juice concentration by reverse osmosis".
Food Technology, 22, (5), 97-100.

Morgan, A.J., Jr., Lowe, E., Merson, R.L., and Durkee, E.L.
1965 "Reverse osmosis"
Food Technology, 19, 1990-92.

Pereira, E.B., Matsuura, T., and Sourirajan, S.
1976 "Reverse osmosis separations and concentrations of food sugars".
Journal of Food Science, 41, 672-680.

Peri, C.
1971 "L'osmose inverse; principes fondamenteaux".
Industries Alimentaires Agricoles, 88, (9-10), 1323-1328.

Peri, C., Pompei, C., and Berardi, A.
1973 Concentration of orange juice by reverse osmosis.
I - Retention and permeation rate .
Scienza e Tecnologia degli Alimenti, 3, (6), 329-336.

Peri, C.
1973 Concentration of orange juice by reverse osmosis.
II - Cost analysis and optimisation .
Scienza e Tecnologia degli Alimenti, 4, (1), 43-47.

P[illegible], and Pompei, C.
197[illegible] "Concentration of grape juice by reverse osmosis".
Vini d'Italia, [illegible], 179-185.

Pierce Chemical Company
1972 "Handbook of silylation".
Rockford, Illinois, U.S.A.

Podall, H.E.
1972 "Reverse osmosis", in: "Recent developments in separation science", 2, 171-172.
CRC press, U.S.A.

Pompei, C., and Rho, G.
1974 "Passion flower juice concentration by reverse osmosis".
Lebensmittel-Widdenchaft-Technologie, 7, (3), 167-172.

Potter, C.L.
1972 "A development in reverse osmosis".
Process Biochemistry, 7, (6), 25-26.

Roosmani, A.B., Saroja, A. and Manjundaswamy, A.M.
1974 "Reverse osmosis and its possible application in the food industries".
Indian Food Packer, 28, (1), 49-63.

Ryan, J.J.
1972 "Chemical composition of Canadian apple juice".
Journal of the Association of Official Analytical Chemists, 55, (5), 1104-1108.

Ryan, J.M.
1977 Director of Technology, membrane equipment group, Abcor Inc., U.S.A.
Personal communication.

Sammon, D.C.
1969 "Reverse osmosis for the processing of foods".
Food Processing Marketing, 38, 219-221.

Schobinger, V., Kaufmann, K., and Grab, W.
1974 "Studies on the behaviour of the aroma of cider during concentration by reverse osmosis".
Lebensmittel-Wissenschaft-Technologie, 7, (1), 29-37.

Sheppler, J.
1970 "An introduction to reverse osmosis".
Chemistry and Industry, (10), 323-324.

Sherwood, T.K.
1952 "Absorption and extraction", p.53.
McGraw-Hill, New York.

Sherwood, T.K.
1959 "Mass transfer between phases".
33rd Annual Priestley Lecture, p.38,
Pensylvania State University.

Sourirajan, S.
1970 "Reverse osmosis".
Logos Press Limited, London.

Sourirajan, S.

1977 "Reverse osmosis and synthetic membranes. Theory - Technology - Engineering", pp.45-49. National Research Council, Canada.

Smith, B.R.

1974 "Reverse osmosis and ultrafiltration for food processing". National Chemical Engineering Conference, Surfers Paradise. - Process Industries in Australia - Impact and Growth pp.461-467.

Sweeley, C.C., Bentley, R., Makita, M., and Wells, W.W.

1963 "Gas-liquid chromatography of TMS-derivatives of sugars and related substances". Journal of the American Chemical Society, 85, 2497-2507.

Taft, R.W. Jr.

1956 "Separation of polar, steric and resonance effects in reactivity". In: "Steric effects in organic chemistry". M.S. Newman editor, Wiley, New York, pp.556-675.

Thijssen, H.A.C.

1970 "Concentration processes for liquid foods containing volatile flavours and aromas". Journal of Food Technology 5, 211.

Thijssen, H.A.C. and Van Oyen, M.J.M.

1977 "Analysis and economic evaluation of concentration alternatives for liquid foods - Quality aspects and costs of concentration". Journal of Food Process Engineering 1, 215-240.

Treybal, R.E.

1955 "Mass transfer operations", p.38. McGraw-Hill, New York.

Tutunjian, R.S.

1978 Market Manager, Food/Pharmaceutical Abcor Inc., U.S.A. Personal communication.

Underwood, J.C. and Willits, C.O.

1969 "Operation of a reverse osmosis plant for the partial concentration of maple sap".
Food Technology 23. (6), 79-82.

Urlich, R.

1970 "Constituents of fruits: organic acids", In: "The biochemistry of fruits and their products", 1, 97; A.C. Hulme editor.

Worley, A.

1970 "Reverse osmosis plant".
Chemistry and Industry, (3), 354-357.