USE OF MEMBRANE TECHNIQUES TO PREPARE RASPBERRY JUICE CONCENTRATES

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BY

CONSTANCA MAGALHAES

A thesis submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements of the degree of

MASTER OF SCIENCE

To my Parents, my husband

and my daughters

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ABSTRACT

The consumption and production of fruit juice beverages in Canada has increased between two and three fold in the past thirty years. These juices are concentrated for reasons of economy. The industry initially used processes such as evaporation and freeze concentration, but these processes may produce juices with lower standards of colour, flavour and/or aroma. Juice was concentrated by reverse osmosis in this experimental work because it is a gentle alternative which does not involve a phase change, addition of chemicals and heat damaging effects.

Raspberry juices were produced and tested in the laboratory by two different concentration processes. Initially, the concentration of single strength raspberry juice (raspberry juice extract) was conducted using different concentration pressures and two types of reverse osmosis membranes, NF-40 and FT-30. This was followed by the concentration of second press juice using a FT-30 membrane to increase the yield of raspberry beverage concentrate. In the first experiment the pressure that proved to be more efficient for the equipment used was 2500 kPa. The use of the NF-40 membrane in the concentration of the raspberry juice extract removed more water from the feed juice than the FT-30 membrane, but the resulting concentrate had lower values of sugar, soluble solids and pigment content. In the second

experiment the FT-30 membrane proved to be effective in retaining sugars, soluble solids and pigments.

The final step of this project focused on the production of a beverage concentrate using juice extract and second press juice that could compete in quality and price with the ones already present in the raspberry juice market. The tests conducted in the laboratory demonstrated that the concentrate formula involving 93% raspberry juice extract and 7% second press juice compared well in quality with the commercial juices and was preferred by a majority of people in a preliminary test panel.

I. INTRODUCTION

In the past thirty years, there has been a tremendous increase in fruit juice products in the marketplace since they are seen as natural and healthy beverages. According to data from Agriculture Canada, Canadian juice production increased from 116.51 kilotons in 1960 to 304.86 kilotons in 1988, an increase of more than 100 %. Including imported juices such as citrus and tomato juices, the total supply of juice doubled from 328.45 kilotons in 1960 to 786.47 kilotons in 1988. Per capita consumption of equivalent fresh juice increased 100 % in the same period of time from 20.46 Kg to 40.87 Kg.

Existing processes often have drawbacks which may produce juices with poor colour or flavour, or lead to nutrient losses due to harsh processing methods. Vitamin C in particular may be lost using existing processes. The goal of this project was to study existing processes for the preparation of juice concentrates and to produce a fruit concentrate with a minimum deterioration of colour, flavour and nutrient composition; and, simultaneously to maximize extraction of juice from the raw material. The final objective was to produce a juice beverage using raspberry juice extract and second press raspberry juice.

II. LITERATURE REVIEW

A. RASPBERRIES

Raspberries are plants of the genus Rubus, which are native to most temperate regions of the world. Red raspberries are common in Manitoba. They are a hybrid between the American species Rubus strigosus and the European species Rubus idaeus, (Encyclopedia Americana, 1964). The plants produce many slender, upright, generally unbranched shoots and they spread rapidly by means of sucker plants. The fruit is a combination of drouplets, which separate freely from the receptacle when ripe.

The red raspberries processed in the present project were of the Boyne variety which originated in 1960 from a cross between the varieties Chief and Indian Summer at the Morden Research Station in Morden, Manitoba. It is a winterhardy, productive, biennial red raspberry with erect canes and good suckering habits. In Manitoba the yield varies between 2000 and 10000 kg/ha/year, depending on location and growing conditions (Anonymous, 1988).

In studies done previously in the Food Science Department at the University of Manitoba, Boyne variety raspberries were described as being of medium size with a dark colour, easy to pick and remaining intact after picking. A sensory panel rated Boyne raspberries as having a sweet flavour with some tartness (Lazzari, 1984). The average weight of ten berries is approximately 25 g.

1. Chemical Composition

According to Watt and Merril (1975) the composition of 100g of the edible portion of red, raw raspberries is:

Water.............	84.3 g
Protein...........	1.3 g
Fat...............	0.5 g
Carbohydrate......	10.2 g
Fiber.............	3.1 g
Ash...............	0.6 g

The food energy of 100g of berries is 57 calories. The mineral and vitamin content is:

Magnesium.........	20.00 mg
Calcium...........	22.00 mg
Phosphorus........	22.00 mg
Iron..............	0.90 mg
Sodium............	1.00 mg
Potassium.........	168.00 mg
Thiamin...........	0.03 mg
Riboflavin........	0.09 mg
Niacin............	0.90 mg
Ascorbic acid.....	25.00 mg
Vitamin A.........	130 I.U.

2. Physical Characteristics

When processing raspberries the colour, flavour and aroma are important aspects to take into consideration.

a. Colour. Anthocyanins are a group of reddish water soluble pigments that are very widespread in the plant kingdom. Many fruits, vegetables and flowers owe their attractive coloration to this group of compounds. In plant cells these pigments are located in the vacuole, and are suspended in an aqueous, and slightly acidic or neutral solution (Markakis, 1982). All of the anthocyanin pigments are derivatives of the basic flavylium cation structure (Figure 1). The three anthocyanins with red shades are: Pelargonin, Cyanin and Malvin. The respective anthocyanidins are represented in Figure 2.

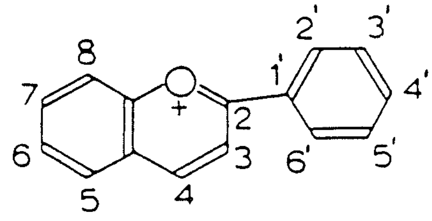
Anthocyanins are flavonoid pigments that occur in nature as glycosides in which the aglycone forms, or anthocyanidins, are substituted flavylium salts. These are less stable than the corresponding glycosides (Eskin, 1990), and esterified to one or more sugar residues or,occasionally, to various other organic acid residues. The sugar components which have been frequently found in natural anthocyanins and in order of relative abundance are: glucose, rhamnose, galactose, gentiobiose, xylose and arabinose. This group of pigments displays low stability both in the living tissue that hosts them and in products manufactured from them (Markakis, 1982). The flavylium nucleus of the pigment is deficient in electrons which makes it highly reactive. Such reactions usually result in decolouration of the pigments which is undesirable in the processing of fruits and vegetables (Geissman, 1962).

Many chemical and physical factors are involved in the degradation of anthocyanins. Included here are:

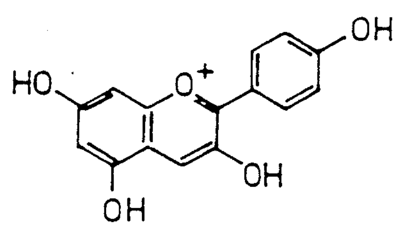
- Some enzymes will destroy the anthocyanin chemical structure by separating the pigment from its sugar moiety.
- As the processing temperature increases the anthocyanin degradation increases logarithmically.
- The presence of light favors anthocyanin biosynthesis and accelerates its degradation.

Figure 1. Flavylium Cation (Fennema, 1985)

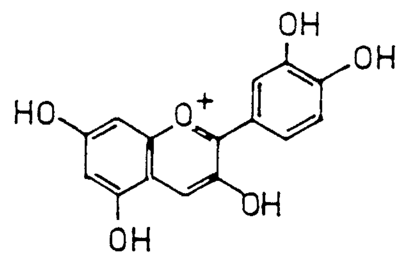
Figure 2. Anthocyanidins Chemical Structure (Fennema,1985)



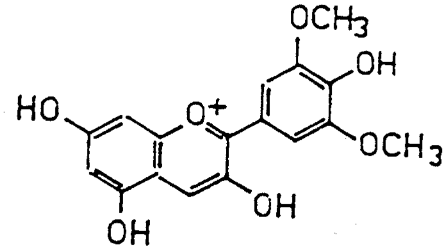
Flavylium cation (I)



pelargonidin



cyanidin



malvidin

- It is known that anthocyanins are more stable in acidic solutions than neutral or alkaline ones. The primary factor controlling the colour of anthocyanins resides in the hydroxyl groups attached to the flavylium nucleus. The deepening of visible colour is dependent on the number of hydroxyl groups (Geissman, 1962).
- It has been found that there is greater retention of anthocyanins in raspberries canned under nitrogen or vacuum than under atmospheres rich in oxygen.
- Ascorbic acid induces anthocyanin degradation. Because hydrogen peroxide is formed when ascorbic acid is oxidized in the presence of oxygen and copper, and hydrogen peroxide is known to decolourise anthocyanins.
- Several multivalent metal ions can interact with anthocyanins possessing vicinal phenolic hydroxyls and shift the colour of the pigment toward the blue end of the spectrum.
- The compound sulfur dioxide has the capability of bleaching anthocyanin pigments (Markakis, 1982).

The accelerated decolouration of anthocyanins in the presence of ascorbic acid, amino acids, phenols, sugar derivatives and others, may be caused by condensation reactions with these compounds. The polymers and degradation compounds produced are quite complex products (Markakis, 1982).

b. Flavour and Aroma. The flavour and aroma of fruit juices depends upon the presence of small amounts of volatile compounds which have a low molecular weight and include organic acids, alcohols and esters. They occur in fruit juices to the extent of about 1 % by weight.

During the process of evaporative concentration of fruit juices some of the aroma compounds are distilled off. The juice reconstituted from the concentrate alone therefore lacks the full aroma of the fresh juice. There are several technologies for recovering the essences. A detailed discussion on essence recovery will be presented in the next section.

3. Processing

There are a great variety of methods for processing raspberries. The picked berries can be canned, frozen or preserved in jam. They make excellent marmalades, jellies and syrups. Raspberries can be used to make fresh or concentrated juices. The acids and essence of the fruit are also extracted commercially. Any of the above products can be incorporated into ice-cream mixes, sherbets, yogurts, fruit flavoured milk-shakes, and other food products. Raspberry wine coolers (3.5 % alcohol) and liqueur (over 20 % alcohol) with raspberry flavour are also gaining popularity.

4. Raspberry Juices in the Market

Currently there are several commercial brands of raspberry juices on the market. The most common products are fruit drinks and fruit beverages from pure raspberry juice or mixtures with apple, cranberry and other fruit juices.

Fruit juice production and consumption have increased in the last ten years, as has the public demand for natural products and flavours. At present, food manufacturers in general, and fruit juice processors in particular, are focussing activities on the preparation of products which are as natural as possible, which necessitates a minimal use of processing, of additives and/or preservatives.

B. JUICE CONCENTRATION

In the processing of fruit juice concentrates, water is removed to provide a reduction in volume and weight, resulting in storage and transportation savings. An additional benefit is the microbiological stability and reduced chemical deterioration of the usually frozen or refrigerated stored concentrate. Water removal can be achieved by concentrating or drying the product. Natural fruit juices are commonly concentrated to a water content of about 30 % by weight, which is equivalent to 20 % total solids. The juices can also be dried and this type of processing reduces the water content to about 10 % by weight.

In an ideal concentration process, all components of the natural juice should be retained in the concentrate with the exception of water. For foods containing aromas this goal is extremely difficult to achieve because the aroma components are more volatile than water. The three main fruit juice concentration processes are described in detail in the following sections.

1. Evaporative Concentration

Evaporation is the best developed concentration technique and the one that will give the highest concentration rate for the product, usually with soluble solids in the range of 60-65° Brix.

Evaporators are specialized heat exchanger devices designed for specific applications (Joslyn and Heid, 1964). The exchanger working fluid is usually steam and transfers heat from the heating source to the solution to be concentrated. This raises the solution temperature to the boiling point, at the operating pressure, and provides the latent heat of vaporization. An evaporator system should also have a vapour and liquid separator, and a condenser to remove the resultant condensate. If the concentration is carried out under reduced pressure to allow the use of lower temperatures, a vacuum system is also required. The separator is usually a cyclone type which is designed to precipitate entrained droplets by centrifugal action. The concentrate and the condensate are then removed by pumps. The vacuum system consists either of a vacuum pump or of a steam ejector. Steam heated evaporators are the most common used by the food industry (Spicer, 1974).

The quality of fruit juices may be heat damaged by high temperatures, which produce undesirable chemical reactions which affect the flavour or the colour of the product. The deterioration of quality is a time-temperature process and, in this respect evaporators may be considered as chemical reactors in which operating temperatures and residence time are the most important parameters (Spicer, 1974).

Conventionally, fresh fruit juices are concentrated by high vacuum evaporation systems. During or after this operation the juice is vacuum deaerated (Torrey, 1974). Vacuum evaporators are used to remove water at a relatively low temperatures and minimize heat damage to the food product. In order to prevent chemical deterioration, some liquid foods have to be concentrated at temperatures below 50° C and at a very short residence time. A widely used evaporator is the multi-effect long tube falling film evaporator. The heat from the vapour of one stage is used in the next stage as a heating medium to evaporate water from juice under higher vacuum and therefore at necessarily lower temperature for each stage, as the thermal sensitivity of the product rises (Spicer, 1974).

Evaporation fulfills the economic goals of rapid water removal (high capacity), relatively simple equipment, no solids handling, continuous operation and low loss of product quality. Energy costs are relatively low, especially in view of the savings in energy consumption which are accomplished with multiple-effect evaporators.

a. Essence Removal. Heat damage to flavour and colour is a problem in the concentration of juices. Efficiency demands that heat be applied as intensely as possible without reaching the point of incipient damage to the product. Most berry and fruit juices can be concentrated in a falling film evaporator for two to three hours at a temperature below 55° C without detectable flavour change. Strawberry juice is more sensitive to heat than orange or apple juices and it can withstand a concentration temperature of only 40° C for a time of two and a half hours, without flavour and colour impairment (Van Arsdel, 1973).

The quality of any juice product deteriorates, however, with the evaporation of volatile flavour and aroma compounds that occurs along with the evaporation of water. Therefore, evaporation is frequently carried out in conjunction with some method to compensate for the loss of volatiles (Spicer, 1974). Attempts to restore the natural flavour of the juice have usually involved cutting back on the degree of juice concentration or the addition of essence concentrates. An ideal concentration process would eliminate the need for the use of flavour restoration techniques (Noyes, 1969).

The recovery of the natural flavour during the preparation and concentration of non-citrus juices is done by a procedure in which the juice is stripped of volatile flavours by vapourizing 10-30 % of the juice. The pre-evaporation of the juice under atmospheric conditions is followed by fractional distillation. This method for the recovery of water soluble essences of apples, pears and berry juices is widely used in the industry (Spicer, 1974). Continuous fractionation of the vapour at atmospheric pressure in a distillation column with a high reflux ratio is employed to concentrate the volatile materials. Some of the constituents are chemically unstable and under the distillation conditions may react with other chemicals, polymerize or change (Van Arsdel, 1973). Aromas with a volatility equal to or less than the volatility of water are lost in this process, and the aroma recovery is usually incomplete and not greater than 60 % (Spicer, 1974).

The recovered essence may be returned to the concentrated juice but the flavour imparted by the essence may be gradually lost due to hydrolysis caused by the natural acidity of the juice, or due to possible chemical changes. However, if the essence is stored separately from the concentrated juice at temperatures of 4.4° C, or less, its flavour is very stable and will not deteriorate for months or even more than a year (Torrey, 1974). Adequate levels of flavour concentrates are usually added back, near the end of processing of final products.

There are a number of problems which must be overcome in thermal concentration processes. These include: the formation of deposits on heat transfer surfaces, known as the burnt layer; the loss of volatile aromas; heat damage of sensitive products; and the browning of the product that occurs during evaporation or storage of the final products (Spicer, 1974).

Low temperature evaporators operate at temperatures that permit the growth of microorganisms. Rigid sanitation standards must be enforced in such operations and the design of equipment must avoid dead ends and stagnant areas (Joslyn, 1964).

The accumulation of a coat of cooked material on a metal surface, whether on the outside of the coil or in the inside of the tube, will decrease heat transfer, reduce production and adversely affect product quality. This accumulation is known as fouling or "burn on" and requires frequent cleaning of the equipment, and eventually the shut down of the operation. The fouling rate increases with continuous heat under medium temperatures, and with high pectin content and viscosity of the solution. Polished heating surfaces, high velocities and agitated films decrease the rate of fouling (Joslyn, 1964).

Fruit juices generally deteriorate in colour, flavour and nutritive value on exposure to air. The rate of deterioration is quite rapid during stages of processing methods that use high temperatures. It is difficult to extract the juice without any contact with air. Due to the presence of air in the intercellular spaces of the fruit, the juices extracted by commercial techniques contain appreciable quantities of oxygen. The oxygen should be eliminated immediately. Conventionally, it is removed from the juices by vacuum deaeration methods or by a stripping operation with nitrogen or other inert gases, such as argon, hydrogen or helium. Carbon dioxide can also be used in cases where a carbonated flavour is not objectionable.

2. Freeze Concentration

The process of freeze concentration is based on the general principle that when a solid or liquid food product freezes its components do not freeze at the same time. Water is the first compound to freeze in small ice crystals forming a slush inside the mixture. The solid concentration of the other ingredients of the food solution keeps rising as more water is frozen. Ultimately, the entire mixture freezes. It is possible, before this happens, to separate the initially formed ice crystals from the mixture. One way of doing this is to centrifuge or filter the partially frozen slush through a fine mesh screen. The concentrated unfrozen food solution passes through the screen while the frozen water crystals are retained and discarded. By repeating this process several times the final concentration of the unfrozen food solution can be increased several fold (Potter, 1980).

The freeze concentration process is particularly suited for heat labile liquid foods containing volatile aromas. Since the water is essentially removed from the solution after a change from the liquid to the solid phase, the aroma losses due to evaporation can be completely avoided. This low temperature process takes place at temperatures ranging from -3° C to -7° C, and fully eliminates thermal decomposition reactions (Spicer, 1974).

The maximum concentration obtained by using this process with fruit juices is in the range of 35-55 % by weight. In terms of the equilibrium separation factor, the freeze concentration process produces the best selective water removal results. A continuous operation of the process is possible. Since freeze concentration involves the formation of solids, it therefore incurs a penalty of equipment complexity to handle the solid phase effectively (Spicer, 1974).

Three main disadvantages of this technique prevented it from being competitive in the past. These are the loss of dissolved solids with the ice, approximately 1 %, partial loss of aromas during the ice-liquid separation and, typically, the higher processing costs involved relative to evaporators with aroma recovery techniques. However, heat labile and aromatic liquid foods can be concentrated without any loss in quality if the separation of the concentrated liquid from the ice is performed in a closed apparatus without a gas head space, such as a press or wash column (Spicer, 1974).

As there are solids remaining in the ice phase a second refinement of this phase may be necessary. The concentrate contains a substantial amount of sugars and practically all of the volatile flavour constituents that were present in the fresh juice. These flavour constituents are concentrated in the initial flow from the centrifuge and are completely recovered. However, substantial amounts of sugars and pulp remain in the residue ice which is thawed to release all of the occluded sugars and pulp into a liquid solution. Since sugars and pulp are not heat labile, this liquor is concentrated by evaporation, preferably under vacuum at low temperatures, without deterioration of taste. After most of the water has been removed, the concentrated liquor is returned and mixed with the centrifuged concentrate so that the mixture contains practically all of the valuable constituents of the fresh juice without loss of quality or deterioration of flavour. This method is often used in the citrus juice industry (Gutterson, 1970).

If high local supercooling during crystallization is prevented, ice crystals of a very high purity are produced. The loss of solute is then completely controlled by the degree of perfection of the ice-liquid separation. It is Spicer's opinion (1974) that the freeze concentration process is superior to the evaporation process in the concentration of liquid foods containing volatile aromas.

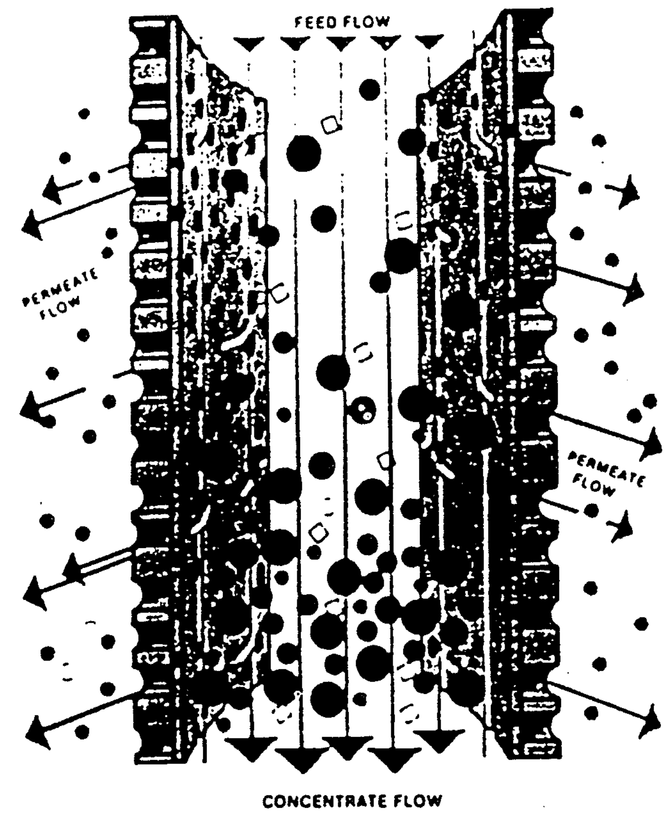
The amount of specific energy required to freeze water is 335 J/kg and to evaporate water is 2325 J/kg. In spite of the larger amounts of heat energy required in the evaporation process and the use of three or more cycles of evaporation the total cost of energy required in the evaporation process is considerably less than the cost of the electrical energy required to drive compressors and other equipment in the freeze-concentration process. The freeze concentration technique can only be justified on the basis of improved quality of the product, so the product must be of high commercial value.

3. Reverse Osmosis

Although the possibility of using a membrane system has been known for more than one hundred years, its use in research projects and commercial application grew only in the last two decades. The general trend of increasing energy costs supports a rapid increase of membrane systems in the immediate future, especially for commercial applications (Hendrick, 1984).

Membrane filtration is the separation of the components of a pressurized fluid performed by polymeric membranes. In this filtration the influent stream, or feed flow, is separated into two effluent streams (Figure 3), known as permeate and concentrate. Permeate is that fraction which has passed through the semi-permeable membrane. The concentrate, also known as retentate, is that stream enriched in the solutes or suspended

Figure 3. Schematic Representation of a Cross flow Membrane Filtration (Paulson _et.al.,_ 1984)



FEED FLOW
PERMEATE FLOW
PERMEATE FLOW
CONCENTRATE FLOW

solids which have not passed through the membrane.

There are several types of membrane processes. For juice processing the main types are: reverse osmosis and ultrafiltration. Both types retain small molecules and fractionate components in the liquid form on the basis of molecular size. They differ in the range of molecular selection.

By definition, reverse osmosis is a pressure driven membrane separation process performed on aqueous solutions which involves the selective removal of water or other hydrogen bonding solvents but impedes the passage of salts and small molecules. The molecular size cut-off range is between 0.0001 and 0.001 μm. In general the membrane rejects organic molecules with molecular weights greater than 150 daltons (1 dalton = the weight of one hydrogen atom) but has a lower weight limit for inorganic salts (Paulson et al., 1984).

Ultrafiltration is also a separation process that involves a pressure driven membrane but separates only larger molecules and colloids from the solution. The range of molecular size cut-off values of these membranes is between 0.001 and 0.1 μm (Spicer, 1974). In the present laboratory study a reverse osmosis separation process was used, therefore it will be discussed in more detail in the next section.

These membranes exist in several configurations. The most commonly used by the food industry are: the hollow fiber, tubular, spiral wound, and plate-and-frame membranes (Paulson et al.,1984).

a. Reverse Osmosis Membranes. The first commercially used reverse osmosis membranes were made of cellulose acetate and were used in the purification of sea water (Hendrick, 1984). Nowadays, applications for reverse osmosis include water purification, waste water treatment, food processing, and medical and pharmaceutical techniques. In food processing the main applications are: water removal, selective salt removal, protein enrichment, and in the concentration of products such as milk and whey, maple sap, juice, beer, wine and coffee.

The membranes have an anisotropic morphology due to a dense layer on the surface of the membrane and a spongy support layer underneath. The dense surface layer controls the degree of separation to be obtained. Reverse osmosis polymers currently available include asymmetric membranes of cellulose acetate, aromatic polyamide, and thin film composite membranes. The type of membrane is selected on the basis of its compatibility with the chemistry and pH of the liquid, operating pressure and/or temperature conditions.

During the concentration of a solution, pressure is applied in excess of the solution osmotic pressure. The solvent, which is usually water, flows through the membrane in the opposite direction of the osmotic flow. Water flows through the homogeneous polymer phase barrier by a process of dissolution and molecular diffusion. The force that drives the water results from the excess of the hydrostatic pressure over the osmotic pressure at the membrane surface (Spicer, 1974). The rate per unit area at which the water passes through the membrane surface is defined as the flux or permeation rate of the membrane, and is usually expressed in L/m^2/hr.

Reverse osmosis is potentially a very gentle process since it involves no phase change, no addition of chemicals or adsorbants, and occurs entirely at ambient temperature. Thermal degradation should not occur in this process because the only energy consumption is used to drive a pump. The volume of concentrate produced per unit of time is controlled by the discharge of permeate, which permits the monitoring of the ratio of concentration.

A significant advantage of the reverse osmosis process is the low energy requirement compared to conventional systems. This method uses from one percent to ten percent of the energy required for heat evaporation. There is little or no detrimental change in the sensory, nutritional value or functional qualities of the food products during reverse osmosis processing. The resulting water permeate may be of acceptable quality to be reused in the plant, producing additional savings.

Compared to the evaporation method, reverse osmosis has lower operating costs, simpler installation and lower labour needs due to automatic controls, lower operating time, and increased product yield. The major disadvantage of reverse osmosis is the higher capital cost of the equipment and the high cost of membrane replacement (Blanck and Eykamp, 1985).

b. Considerations for Juice Concentration. The success of the reverse osmosis process for juice concentration depends upon the selectivity of the membrane and the rate of water removal. Selectivity is the ability of the membrane to pass water but reject dissolved solutes and suspended solids. Selectivity is primarily determined by the chemical composition of the juice and of the membrane. The permeation rate depends upon the operating pressure, temperature, membrane porosity and juice viscosity. Both permeation rate and selectivity are influenced by the juice concentration at the surface of the membrane and are therefore affected by elevated solute concentration in this region as a result of water removal (Merson and Morgan, 1968).

A fruit juice is a complex aqueous solution containing a suspension of sugars, acids, flavouring components, pigments, pectic substances and other compounds. The major water soluble components in fruit juices are sugars (up to 20 %), much smaller quantities of organic acids and inorganic salts (0.1 to 1 %), and still smaller quantities (in ppm range) of many organic volatile flavour components including alcohols, aldehydes, ketones and esters. The sugars and organic acids are the major contributors to the osmotic pressure of the juice. However, the minor constituents of the juice determine the relative success of the process by impacting the overall juice quality. The ability of the membrane to retain these molecules is the single most important factor in determining the quality of the concentrate produced. The flavour varies from juice to juice and some molecules, such as the oil-soluble aroma molecules in orange juice are retained better than the water soluble esters, alcohols and aldehydes in apple juice (Merson and Morgan, 1968). Reverse osmosis membranes are not totally selective to water as they are also permeable to low molecular weight oxygenated organic compounds. The retention of these compounds depends upon the tightness of the membrane and the permeation rate of the juice (Spicer, 1974).

Pectins are large molecules that increase the viscosity of the juice. Viscosity of the fluid is important in determining the power requirements of the pump, as well as in facilitating the circulation of the feed. Increased viscosity may lead to fouling, which is an accumulation of solids on the surface of the membrane (Merson and Morgan, 1968). High viscosities result in low diffusion of food concentrates which tends to cause severe concentration polarization adjacent to the membrane surface. This effect lowers the water flux and raises the amount by which the feed must be pressurized to overcome the osmotic pressure at the feed/membrane interface.

Some fruit and vegetable juices that may be concentrated industrially by reverse osmosis processes and they include: apples, cranberries, cherries, grapes, pineapples, oranges and tomatoes, among others. However, none is known to be available in the Canadian marketplace at this time. The concentration limits of commercial membranes for reverse osmosis processes on liquid food range from about 20-35° Brix (Sheu and Riley, 1983). One of the difficulties in achieving a higher concentration is related to equipment limitations and membrane compaction, at the higher pressures required.

Reverse osmosis can be used as a pre-concentration step to provide a feed juice for evaporation, storage, further processing. Another efficient use of the reverse osmosis technique is to concentrate fruit or vegetable juices two or three fold, followed by aseptic packaging. The resulting product may be marketed for shelf-stable consumer type concentrated juices. (Sheu and Riley, 1983).

Merson and Morgan (1968), studied the concentration of orange and apple juices by reverse osmosis using modified cellulose acetate membranes. It was concluded that the aroma retention depended upon the chemical nature of the aroma molecules: the oil soluble flavour molecules were easily retained in the concentrate, as well as at least 25 % of the water soluble flavour molecules. The apple juice concentrate was a flavourful product obtained in a single operation. It seemed that the flavour compounds present in apple and orange juice concentrates might be more stable during storage because they had never been separated from the juice and had not been subjected to rigorous thermal processing.

C. RECOVERY AND CONCENTRATION OF SECOND PRESS JUICE

During the pressing of many fruits for the production of juice, considerable quantities of sugar and other soluble solids are lost as waste in the press cake.

A counter current diffusion-extraction involving diffusion of soluble material within the cell under the influence of concentration gradient is widely applied in the fruit juice industry. The concentration gradient causes the cells to lose their organized structure, thus making the cell walls permeable to the cell contents. Disorganization of cell structure is most readily achieved by application of heat (Gunasekaran et al., 1989). This process involves the use of heat that is detrimental to the quality of a raspberry juice product, as discussed before.

A possible way of recovering at least a portion of the soluble solids left in the press cake that does not require a heat treatment is to add water to the press cake, and then repress it (Timbers, 1973).

One of the problems with the second press juice is the low concentration of soluble solids. Concentrating the second press juice is the best way of increasing its soluble solids. Reverse osmosis can be used to concentrate the second press juice. This product can then be incorporated in beverage formulation instead of water, decreasing the percentage of single strength juice used and producing a yield increase of the initial juice. Timbers (1973) developed a process for concentration and recovery of second press apple juice using a reverse osmosis concentration process. A "good quality juice was obtained with 12 % soluble solids and with a relatively small amount of darkening" of its colour.

III. METHODS AND MATERIALS

A. SOURCE OF RASPBERRIES

Raspberries from the cultivar Boyne were handpicked at their proper maturity at Richer, Manitoba. They were kept in covered 11.4 L plastic pails which held approximately 10 Kg and placed in a field cold-storage trailer at -10° C. The raspberries were fully frozen in one to three days. Subsequently, they were transported to the frozen storage room at the Department of Food Science, University of Manitoba, where they were stored at a temperature of -20° C to be processed at a later date.

B. RASPBERRY JUICES

As described below, two different products were processed and investigated in the present project: the juice resulting from the first press of the raspberries, labelled raspberry juice extract; and the juice resulting from washing the press cake with water and repressing it, which was identified as second press raspberry juice.

The choice of reverse osmosis membranes used in both processes described below was determined by its availability in the Food Science Department.

1. **Concentration of Raspberry Juice Extract**

At the time of processing the necessary number of pails were removed from the frozen storage and the berries were allowed to thaw overnight. They were then treated with Pectinex ultra SP-L, a commercially available enzyme formulation from Novo Enzymes which consists of a mixture of polygalacturonase, pectin-esterase, pectin-transeliminase and hemicellulase. The enzyme treatment was for 16 to 22 hours as the raspberry mash warmed to the ambient temperature of 16° C (Rigby, 1990). After the enzyme treatment, the raspberries were pressed with a Willmes press. An ultrafiltration process was followed, recycling the crude juice through a "PM 50" hollowfiber membrane with a molecular weight cut-off of 50,000 daltons (Rigby, 1990). The product collected was the permeate, which was a polished clear juice which will be called raspberry juice extract throughout this project. This juice extract was kept in 11.4 L pails and stored in frozen storage at a temperature of -40° C until needed for analysis and/or beverage formulation. The press cake left in the Wilmes press was also kept in 11.4 L pails and stored under the same conditions until second extraction work was done.

Raspberry juice extract was concentrated by reverse osmosis with the objective of reducing its volume and producing a concentrate that would retain the maximum amount of juice flavour and aroma compounds, as well as most of the sugars and acids present in the original fruit. It was desirable that the concentrate would have little or no deterioration in colour.

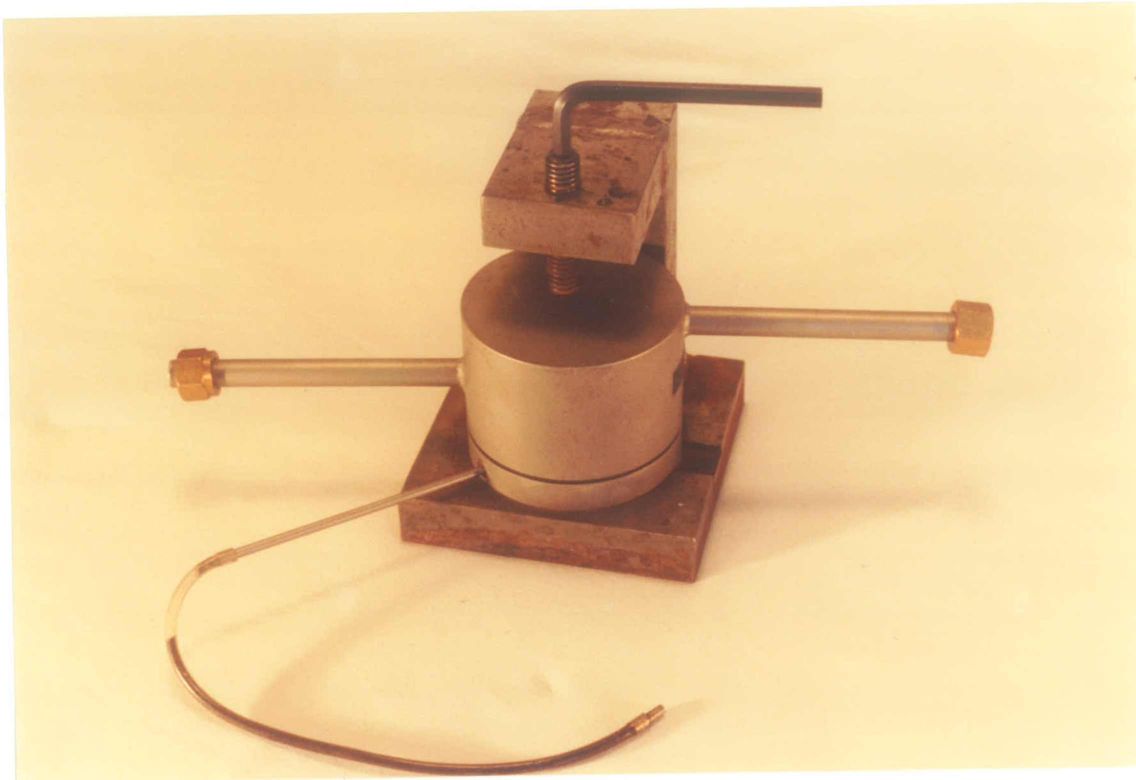
a. Apparatus. A stainless steel cross-flow cell supplied by Export Packers, Winnipeg, Manitoba, as pictured in Figures 4 and 5, was fitted with a Filmtec NF-40 reverse osmosis membrane (described below), a CAT electrical pump and several pressure gauges and control valves were the basic equipment components used for this investigation (Figure 6).

The Filmtec Nanofilm NF-40 nanofiltration membrane, supplied by Filmtech Corporation, Minneapolis, MN, possesses performance characteristics between reverse osmosis and ultrafiltration. It exhibits a high rejection of divalent ions and of organic compounds having molecular weight above 300 daltons. Monovalent ion rejections are in the 0-20 % range at high concentrations. The membrane type is a Thin-Film composite (Figure 7) which consists of three layers: a polyester support web, a microporous polysulfone interlayer, and an ultrathin barrier coating on the top surface. It has a maximum operating pressure of 4.1 MPa, a maximum operating temperature of 45° C and a pH range of 2-11.

The permeate flow rate ranged from 40 to 150 mL/h and averaged 95 mL/h. The equipment hold up volume was approximately 300 mL. Three operating pressures were tested; 2000 kPa, 2500 kPa and 2800 kPa. The equipment was sanitized with chlorine at a 300 ppm concentration for 30 minutes after

Figure 4. The Stainless Steel Crossflow Cell Used in the Concentration of Raspberry Juice Extract

Figure 5. The Different Parts of the Stainless Steel Crossflow Cell Pictured Above



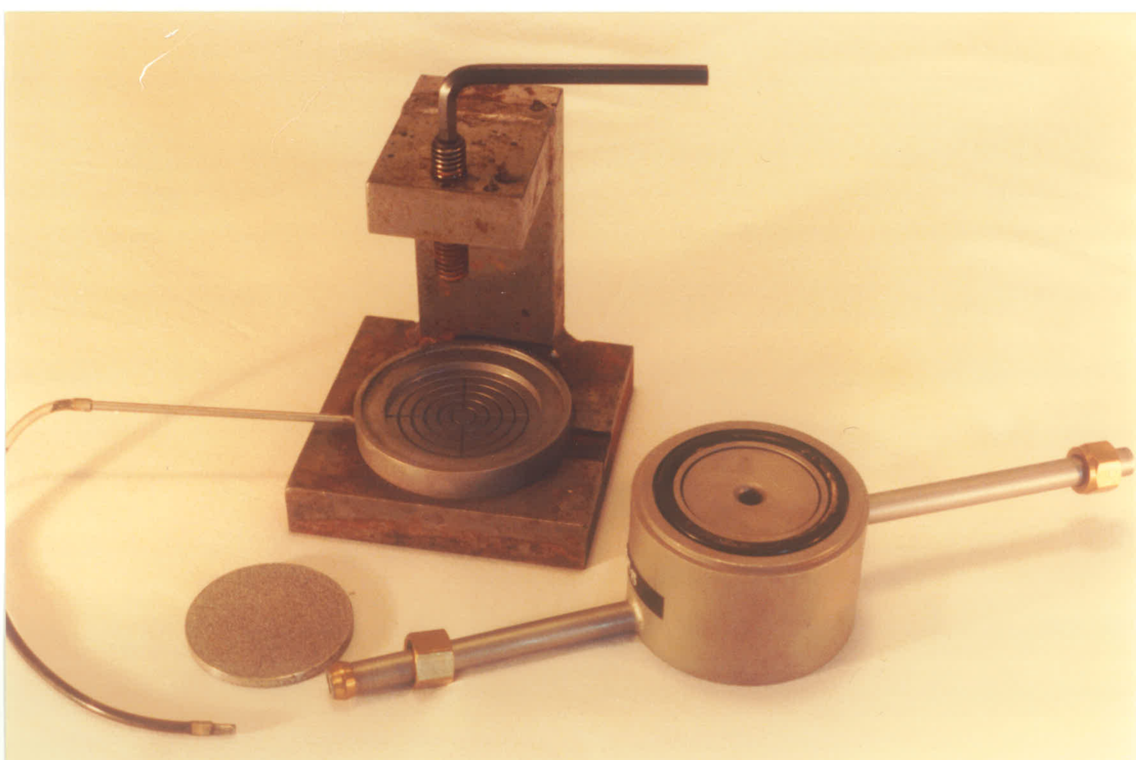
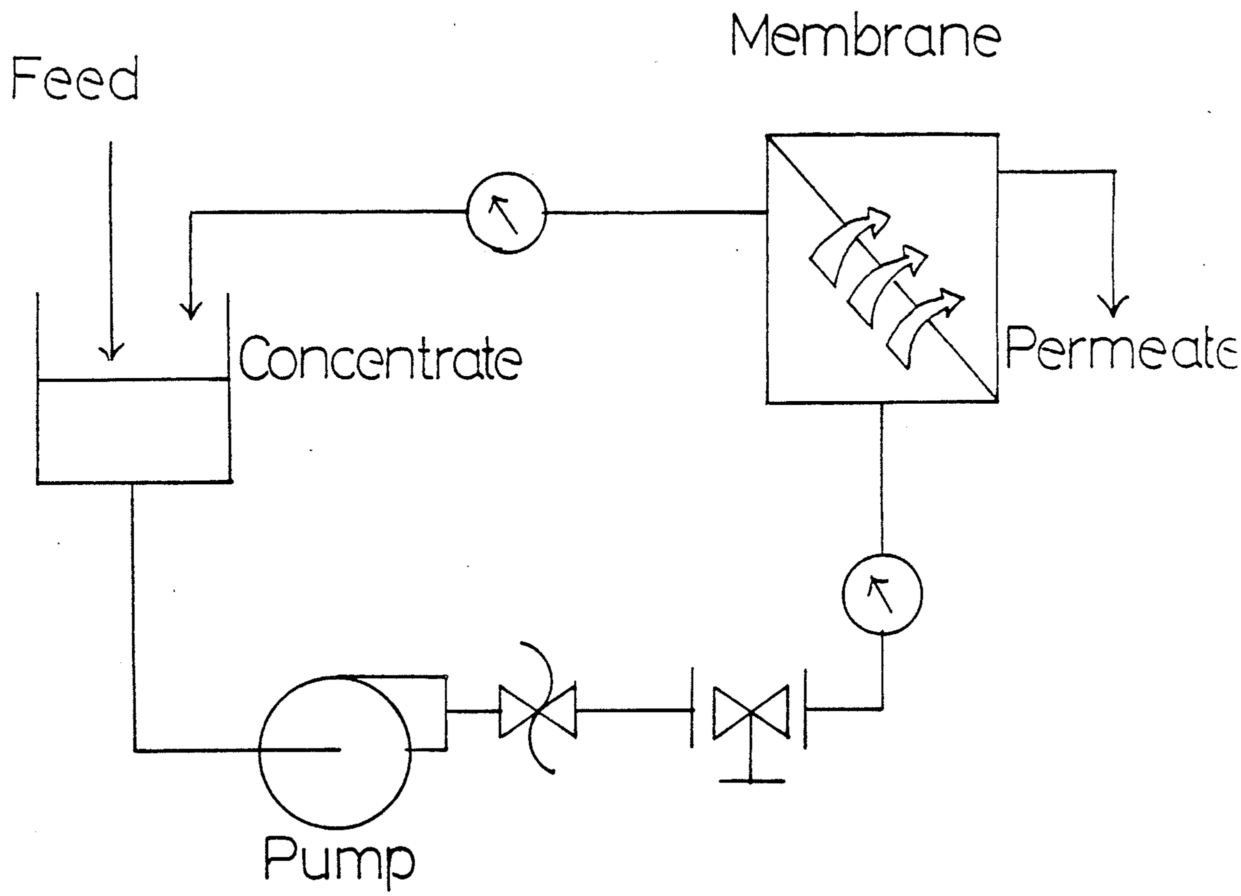


Figure 6. Flow Chart of the Raspberry Juice Extract Concentration Process and a Schematic Representation of the Crossflow Cell


Membrane
Feed
Concentrate
Permeate
Pump

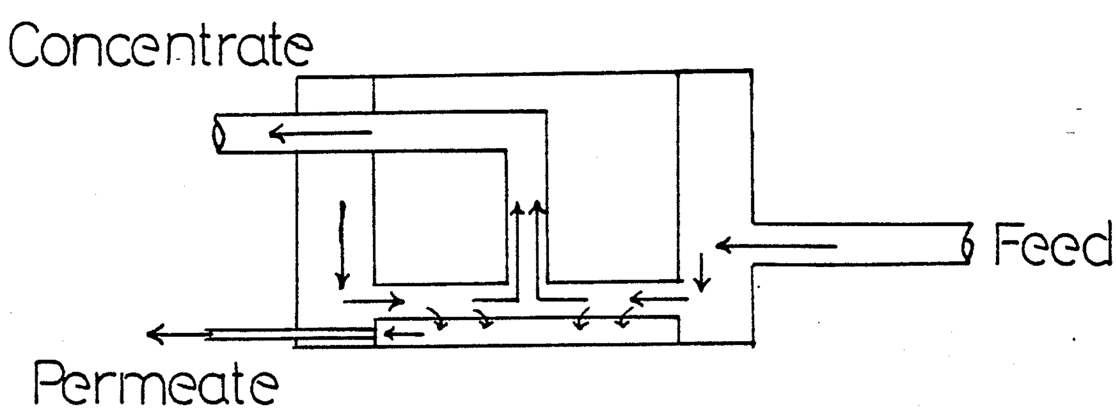
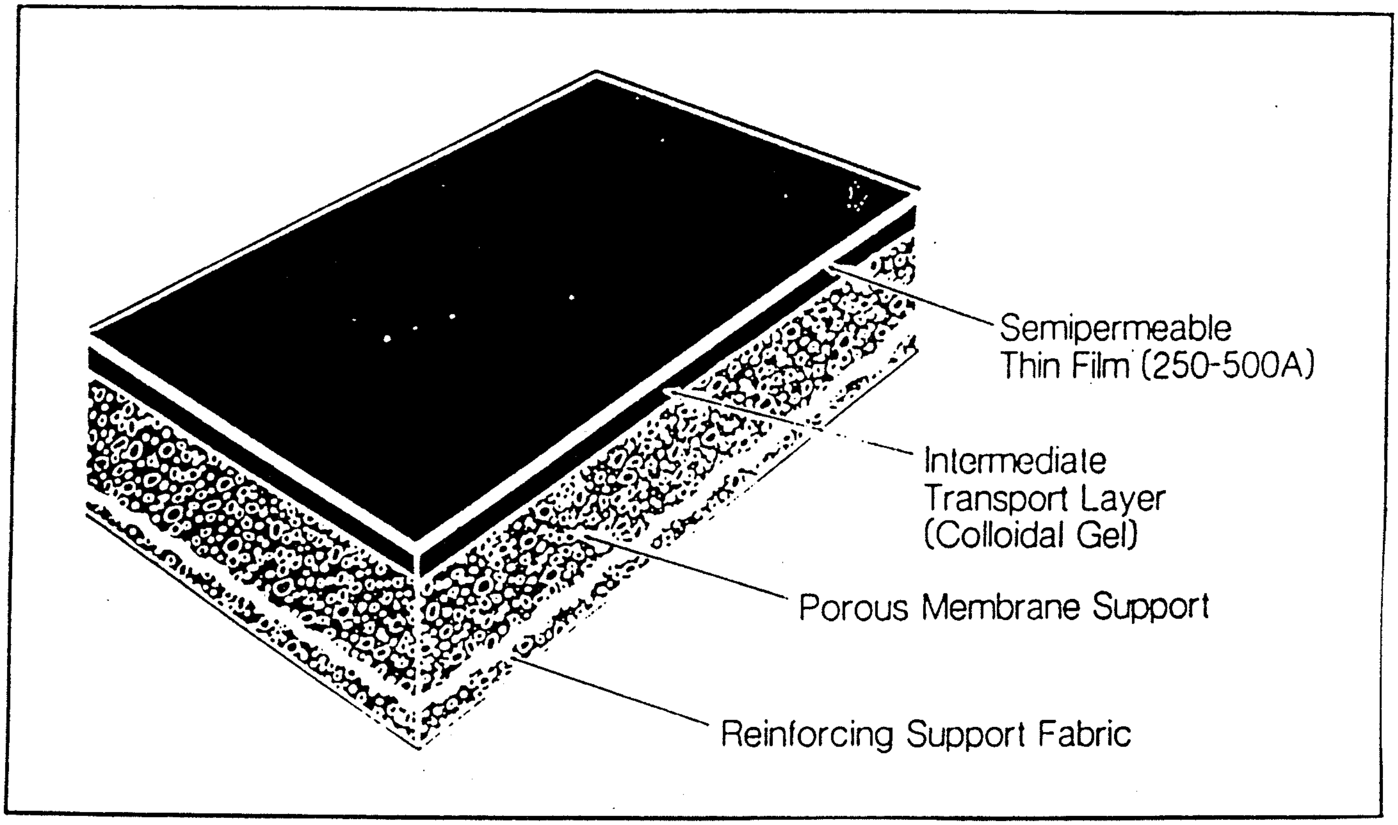

Concentrate
Feed
Permeate

Figure 7. Thin Film Composite Membrane (Paulson et.al.,1984)


Semipermeable
Thin Film (250-500A)
Intermediate
Transport Layer
(Colloidal Gel)
Porous Membrane Support
Reinforcing Support Fabric

each use, and stored with the same solution. The apparatus was flushed with distilled water prior to use.

b. Operating Conditions. Raspberry juice extract was recycled through the apparatus for one hour. Samples of feed juice were taken at the start of the process, and samples of permeate and approximately 50 mL of concentrate were taken every thirty minutes. The rate of water removal was measured and tests were performed on the feed juice, concentrate and permeate samples. These tests consisted of refractive index, absorbance reading at 515 nm (samples were diluted 1/25 for this analysis), pH, and total soluble solids. A 20 mL aliquot of each sample was stored in glass flasks at -40° C for further chromatographic analysis. The performance of the FT-30 reverse osmosis membrane was also tested and compared against the performance of the NF-40 membrane, at the 2500 kPa pressure.

2. **Concentration of Second Press Juice**

During the first press of the raspberries some sugars, pigments and soluble solids were retained in the press cake. Washing this press cake, filtering and re-pressing it recovered those raspberry juice components and increased the juice yield.

To prepare the second press raspberry juice, the press cake was mixed with twice its weight of water. The mixture was stirred, filtered through a Whatman #4 filter paper and stored at -40° C until needed for concentration or use in beverage formulation.

Second press raspberry juice was concentrated through a FT-30 spiral wound reverse osmosis membrane for two hours to generate a product with a greater concentration of sugars, soluble solids and pigments. The membrane unit used was a Aqua-cleer reverse osmosis module no. 4428-45, supplied by Culligan Water Conditioning (Figure 8).

a. Apparatus. The equipment used consisted of a Culligan spiral wound FT-30 reverse osmosis membrane a CAT pump driven by an electrical motor and several pressure gauges and valves (Figures 9 and 10).

The FT-30 membrane is a Filmtec reverse osmosis membrane which exhibits high rejection at low pressures with very stable long term operation. It is a Thin-Film Composite Polyamide membrane with a maximum operating pressure of 6.8 MPa, a maximum operating temperature of 45° C and a pH range of 2-11. Although the membrane could operate at higher pressures, the maximum pressure recommended for the spiral wound configuration of this membrane is 530 kPa.

The flow rate of the permeate ranged from 100-270 mL/h, and averaged 185 mL/h. The hold up volume of the equipment was approximately 350 mL. The equipment was sanitized as in the previous experiments.

b. Operating Conditions. Press cake wash was recycled for two hours with a sample of feed juice taken at zero time, and samples of permeate and 50 mL (approximately) of

Figure 8. The Spiral Wound Membrane Used in the Concentration of Second Press Raspberry Juice

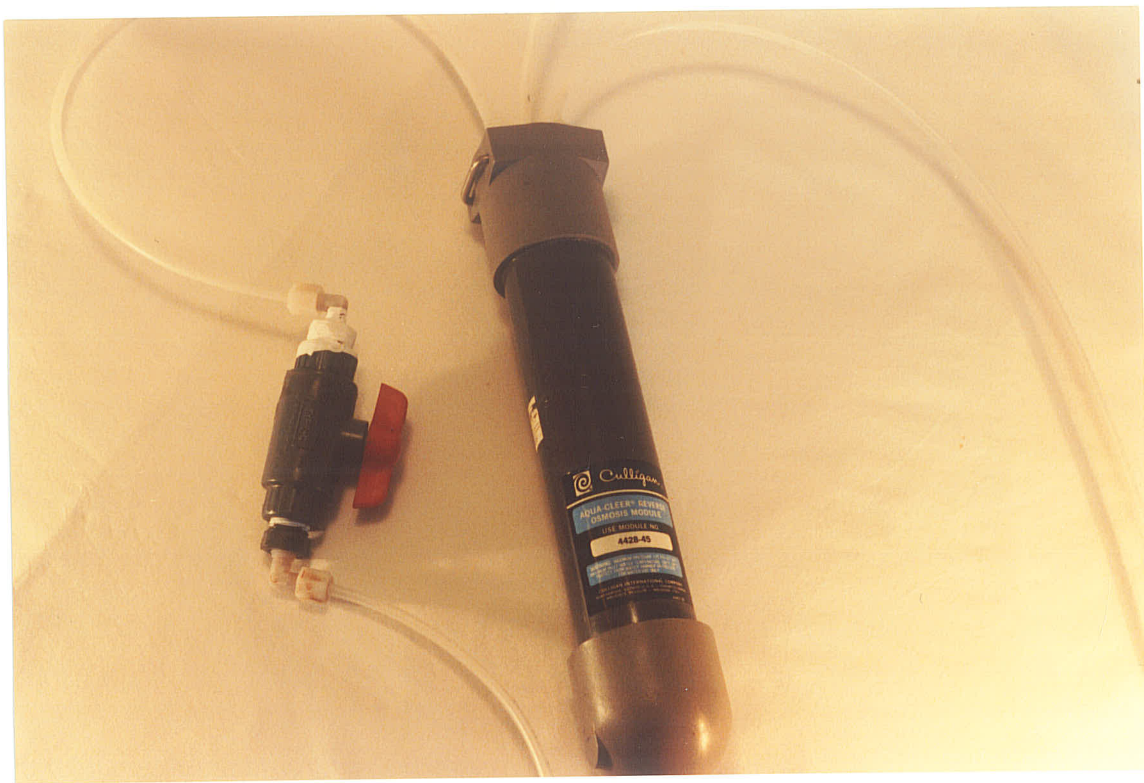
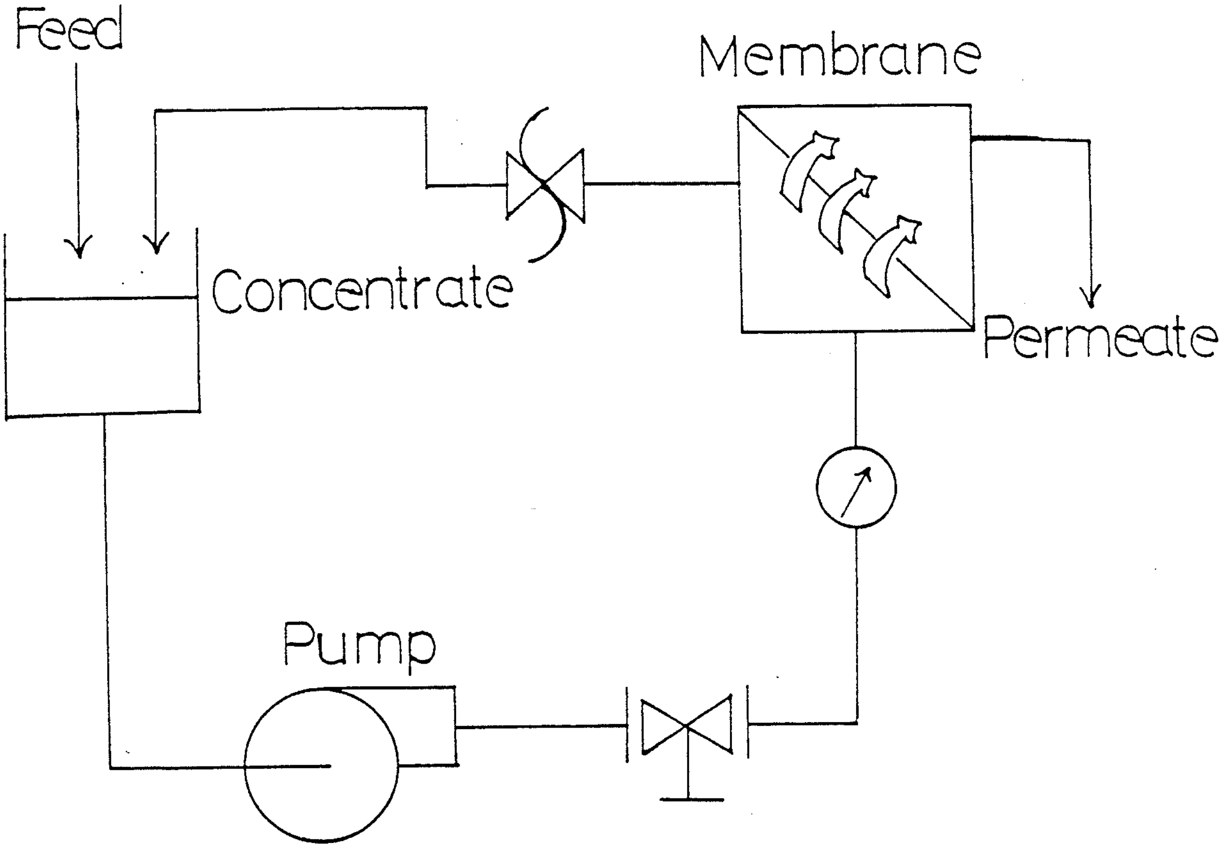

Culligan
AQUA-CLEER® REVERSE
OSMOSIS MODULE
USE MODULE NO.
4428-45

Figure 9. Flow Chart of the Second Press Raspberry Juice Concentration Process and a Schematic Representation of the Spiral Wound Membrane Unit


Feed
Membrane
Concentrate
Permeate
Pump

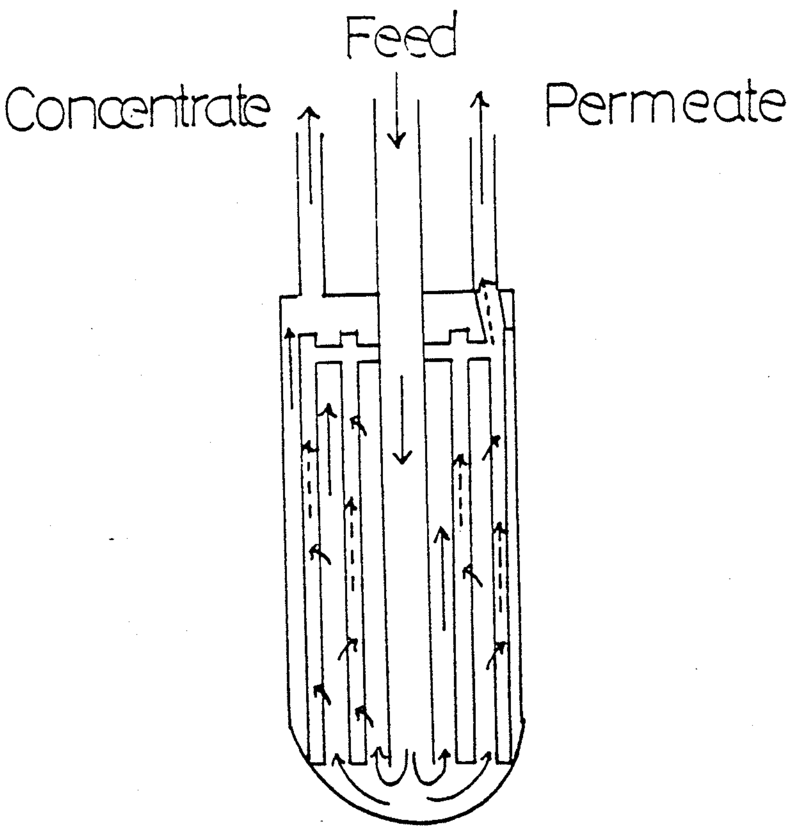
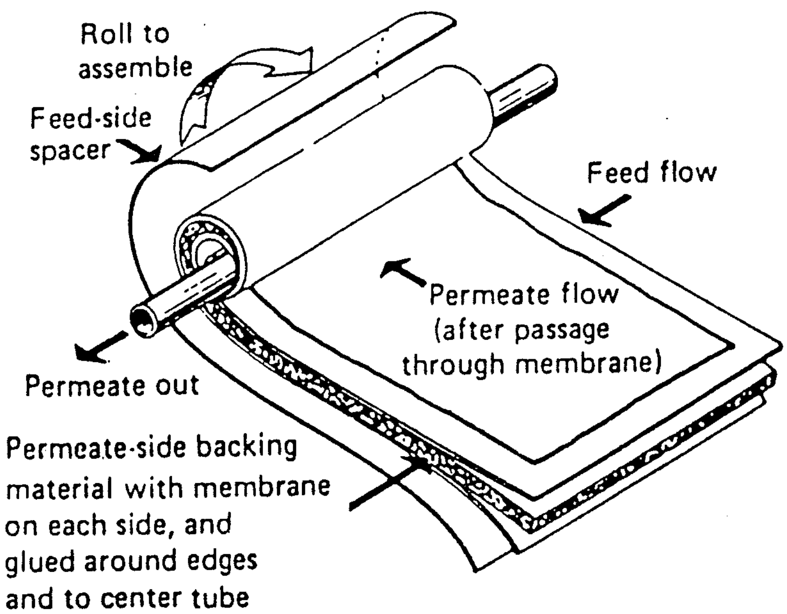

Feed
Concentrate
Permeate

Figure 10. Schematic Representation of a Spiral Wound Membrane Module (Paulson _et.al._, 1984)



spiral-wound module

concentrate taken every half hour. The rate of water removal was monitored and the following analysis were performed on the feed, permeate and concentrate samples: pH, total acidity, total soluble solids, refractive index and absorbance reading at 515 nm. Feed and concentrate samples were diluted 1/25 for the absorbance reading analysis. A 20 mL aliquot of each sample was stored in glass flasks at -40° C for further chromatographic analysis.

C. LABORATORY ANALYTICAL METHODS

Both raspberry juice extract and second press raspberry juice were subjected to concentration processes through reverse osmosis membranes. The following laboratory tests were performed on the feed materials, permeate and concentrate samples collected during the processing of the juices as well as on the beverage concentrates described in chapter E:

a) Measurement of pH values.

b) Refractive index values were determined using an Abbe Table Refractometer. These values measured primarily the amount of total sugars present in the sample and were expressed in g/L of sucrose, following A.O.A.C. method # 31.011 or # 22.024 (1984).

c) Titratable acidity of samples which was expressed as the percentage of citric acid present in the sample and was determined according to A.O.A.C. method # 22.061 (1984).

d) Absorbance readings using a Bausch and Lomb Spectronic

20 Spectrophotometer:

- at 430 nm wavelength: this analysis was performed on 1/25 diluted samples of beverage concentrate formulations and on 1/25 diluted samples of their respective dilutions to assess browning. (These formulations will be described in detail in chapter E.).

- at 515 nm wavelength: samples were diluted 1/25 prior to analysis and red colour was assessed. The 515 nm wavelength is the wavelength of maximum absorbance of the raspberry juice extract as determined by the Hewlett Packard Diode Array Spectrophotometer.

e) Total soluble solids were determined by the forced draft oven procedure following A.O.A.C. method # 22.018 (1984).

f) Determination of λ max

The wavelength of maximum absorbance determined for the raspberry juice extract was the one used for red colour determination in all the tests throughout this project. This wavelength was later compared against the commercial "Westvale" frozen concentrate, produced by Abbotsford Coop B.C., and its recommended dilution ratio, the University of Manitoba raspberry juice beverage and the "Westvale" commercial boxed drink.

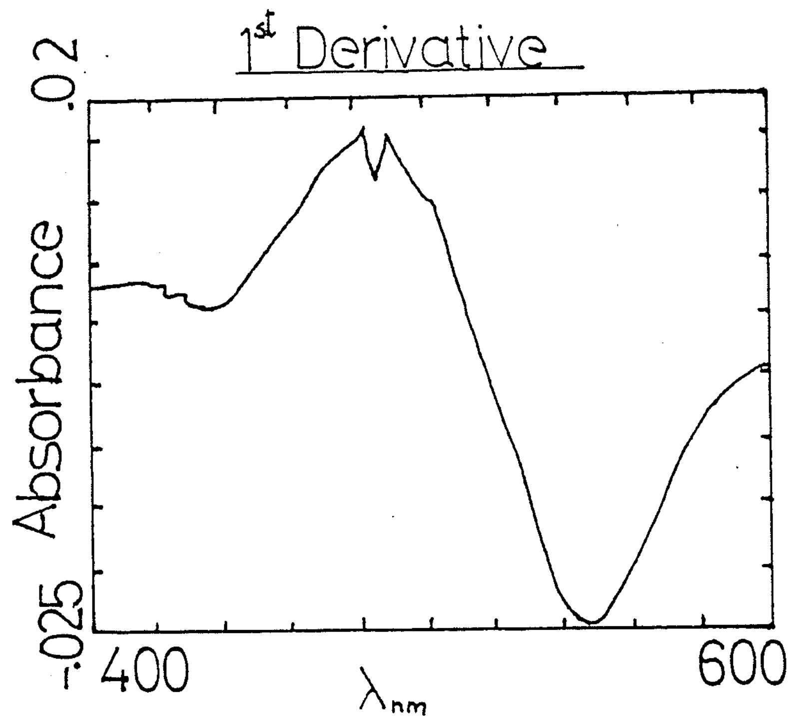
a. Apparatus. A Hewlett Packard 8451 Diode Array Spectrophotometer was used. This is a single beam, microprocessor-controlled, ultraviolet-visible spectrophotometer that operates at high speed. Absorbance spectra over the full 190-820 nm wavelength range can be obtained in 0.1 second with a 0.7 second repetition rate. The HP 8451 includes the operating system of the HP 85A Personal Computer with a built-in CRT and printer/plotter. The wavelength range used in this project was between 400-700 nm, requiring the use of good quality glass cells.

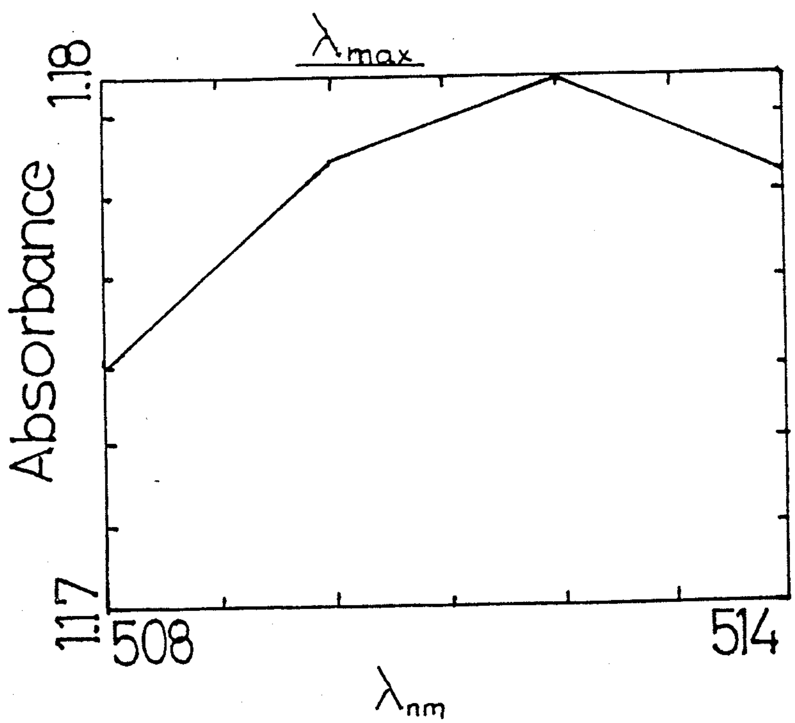
The first derivative of the absorbance was determined. (Figure 11-1st derivative). This value can be used to confirm the λ max value and has the additional advantage of eliminating spectral variations due to baseline drifts caused by factors such as turbidity.

b. Sample Preparation. The "Westvale" frozen concentrate sample was allowed to thaw overnight in the refrigerator and the sample was mixed with water just prior to analysis. Its respective dilution was done following the manufacturer's instructions: one part of concentrate to three parts of water. For the other commercial products, no sample preparation was required.

c. Operating Conditions. Approximately 2.5 mL of sample were placed in a glass cuvette and a scanning was done between 400-700 nm wavelengths. A wavelength peak for the raspberry juice extract was identified between 508 nm and 514 nm (Figure 11- λ max), precisely at 512 nm. This is the wavelength of maximum absorbance. Since it is difficult to set the spectrophotometer used during the absorbance reading tests to

Figure 11. Determination of λ max and 1st Derivative





Peak Find

512 = 1.1827

the measured peak of 512 nm, an operating wavelength of 515 nm was chosen. Once the wavelength of maximum absorbance was found, the first derivative was determined. The zero crossing on the first derivative graph coincides with the λ max on the absorbance curve, thus confirming its value.

D. CHROMATOGRAPHIC ANALYSIS

The chromatographic analyses done in this experiment was the determination of sugar content by high performance liquid chromatography.

Sugar Analysis by HPLC

Samples of raspberry juice extract, second press raspberry juice feed samples plus the samples of concentrates and permeates resulting from the respective reverse osmosis processes were analyzed by high performance liquid chromatography (HPLC). These samples were kept frozen in 20 mL glass flasks at -40° C, and were thawed just prior to sample preparation. The thawed samples were filtered through a 0.45μm nylon filter, supplied by Micron Separations Inc. (Honeoye Falls, N.Y.) to ensure removal of any particulate impurities that might be present. Since pigments in the juice can severely hinder the life of the analytical column, Sep-Pak C18 cartridges (Waters Associates Inc.) were used to retain these coloured pigments. The Sep-Pak was placed at the end of a 10 mL graduated syringe. The C18 cartridge was first pre-wet with 2 mL of methanol and then flushed with 5 mL of distilled water. After this, a 3 mL sample was poured into the graduated syringe. The first 2 mL of the sample were discarded, and the remaining 1 mL was used for HPLC analysis.

a. Apparatus. A carbohydrate column (Aminex HP-87P Heavy Metal) was placed in a temperature controlled oven and attached to a Waters Associates HPLC assembly. The HPLC consisted of a solvent delivery system (model 6000A), sample injector (model U6K), an ultraviolet absorbance detector (model 440) with extended wavelength (214 nm) module and a differential refractometer (model R401).

b. Eluent Preparation. Water was the eluent used. The mobile phase was filtered through a 0.45 μm filter and degassed under vacuum prior to use. The mobile phase was held in a reservoir and kept warm by placing the reservoir on a hot plate.

c. Operating Conditions. Sugar analyses were performed at a flow rate of 0.60 mL/min at 85° C. Recording and analysis of detector responses were conducted on a Vista 401 (Varian Instrument Group).

E. PREPARATION OF BEVERAGE CONCENTRATE

Raspberry juice extract is a naturally concentrated product, high in both acids and sugar, and quantities of water have to be added to it in order to produce a drinkable beverage. The next step of this project focused on the production of a beverage concentrate that could be competitive with the ones already present in the raspberry juice market.

1. Using Raspberry Juice Extract

A beverage concentrate was prepared mixing raspberry juice extract with appropriate amounts of granulated sugar and food grade citric acid. This beverage concentrate was then tested simultaneously with the commercial "Westvale" frozen raspberry beverage concentrate, and the results were compared. The analyses performed on these concentrates were pH, total acidity, refractive index, absorbance at 515 nm and at 430 nm and total soluble solids.

One part of each beverage concentrate was diluted with three parts of water. These 1:3 diluted beverages were analyzed and the results compared with each other and with the "Westvale" raspberry boxed drink beverage, which is thermally processed, and with the U.of M. raspberry juice beverage, which is processed using an ultrafiltration membrane.

2. Using Juice Extract and Second Press Juice

The juice extract and the second press juice were mixed in different proportions with the objective of increasing the yield of the raspberry beverage concentrate. Appropriate amounts of granulated sugar and food grade citric acid were added to these mixtures. The analyses performed on these concentrates were: pH, total acidity, refractive index, absorbance readings at 515 nm and at 430 nm, and total soluble solids. The "Westvale" commercial frozen concentrate was analyzed at the same time and all the analytical results were compared.

Dilutions of each beverage concentrate were prepared and analyzed as described above. The analysis performed on these diluted samples were: pH, total acidity,refractive index, absorbance readings at 515 nm and at 430 nm and total solids.

F. STATISTICAL ANALYSIS

Each experiment was repeated three times and three measurements were done on each sample. Therefore, a total of nine observations were obtained. The means and standard deviations for each test were calculated. Analysis of variance of the data from each experiment was also done to assess the differences within each series of experiments and between each series. Duncan's multiple range test was used to compare the means from the experiments.

IV. RESULTS AND DISCUSSION

A. CONCENTRATION OF RASPBERRY JUICE EXTRACT

The performance of a NF-40 membrane was tested at different operating pressures to determine the pressure that would produce a concentrate with maximum percentages of sugars, total soluble solids and pigments. Subsequently, the performances of NF-40 and FT-30 membranes were tested and compared during the concentration of raspberry juice extract.

1. Membrane performance for varying pressure conditions.

Tests using the NF-40 membrane were performed on the three types of samples: feed juice, permeate and concentrate samples collected after half an hour and one hour of experiment. The membrane was subjected to operating pressures of 2000 kPa, 2500 KPa and 2800 kPa to study the effects of pressure on the concentration of raspberry juice extract. For each test the refractive index, absorbance reading and total soluble solids were measured.

The results of the measurements are shown in Table 1 and indicate that:

a) The best average permeate flow rate of 124 mL/h was obtained using a pressure of 2500 kPa. At 2800 kPa the flow rate dropped to 99 mL/h and at 2000 kPa the average permeate flow rate was only 40 mL/h. This result could be due to two reasons. First, the lower pressure of 2000 kPa may not have

TABLE 1. Concentration of Raspberry Juice Extract Using a NF-40 Membrane Subjected to Different Operating Pressures.

Operating Pressure (kPa)		2000	2500	2800
Time (h)			Feed and Concentrate Samples:	
	pH	2.90 ± 0.00*[a1]	2.99 ± 0.11	2.97 ± 0.10
0	RI	7.1 ± 1.1	7.1 ± 1.5	7.2 ± 0.3
	TS	7.35 ± 0.93	7.44 ± 0.81	7.59 ± 0.18
	pH	2.94 ± 0.01	2.99 ± 0.03	2.92 ± 0.99
0.5	RI	7.3 ± 1.1	7.3 ± 1.3	7.5 ± 0.8
	TS	7.46 ± 0.94	7.66 ± 0.76	7.64 ± 0.75
	pH	2.93 ± 0.01	2.99 ± 0.05	2.95 ± 0.09
1.0	RI	7.3 ± 1.1	7.3 ± 1.2	7.2 ± 0.6
	TS	7.65 ± 0.98	7.89 ± 0.76	7.71 ± 1.73
Time (h)			Permeate Samples:	
	pH	2.77 ± 0.07	2.73 ± 0.17	2.54 ± 0.15
0.5	RI	0.5 ± 1.1	0.4 ± 0.1	0.2 ± 0.1
	ABS	0.084 ± 0.015	0.007 ± 0.006	0.081 ± 0.063
	pH	2.98 ± 0.01	2.68 ± 0.07	2.46 ± 0.01
1.0	RI	0.7 ± 0.2	0.3 ± 0.0	0.3 ± 0.1
	ABS	0.009 ± 0.011	0.019 ± 0.027	0.031 ± 0.063
Permeate Flow Rate (mL/h)		40	124	90

Concentration effect with time: letters in columns; concentration effect with pressure: numerals in rows.
* Mean ± Standard Deviation (n=9); $p \leq 0.01$.
RI - Refractive Index in g/L of Sucrose.
ABS- Absorbance Reading at 515 nm.
TS - Total Soluble Solids in % (w/w).

been efficient in driving the permeate through the membrane. Second, at higher pressures the phenomenon of concentration polarization or the process of membrane compaction may be occurring. Both of these high pressure phenomena have been previously observed (Paulson et al., 1984) and result in the accumulation of solids in front of the membrane and the compaction of the membrane which restricts the flow of permeate.

b) The average refractive index value of the permeate samples was 0.2 g/L (sucrose standardization) for the experiment conducted at a pressure of 2800 kPa. The refractive index values using processing pressures of 2500 kPa and 2000 kPa were 0.4 g/L and 0.6 g/L respectively. The results show that lower operating pressures increase the passage of sugar to the permeate. The same results could be explained on the basis of the membrane compaction or concentration polarization processes, which will make the passage of sugar molecules through the membrane more difficult with higher operating pressures.

c) For the permeate samples, the average absorbance readings at a wavelength of 515 nm was in the order of 0.013 unit, for the experiment run at a pressure of 2500 kPa. The same experiment performed at a pressure of 2000 kPa had an average reading of 0.047 unit, and the one using an experimental pressure of 2800 kPa gave an average absorbance reading of 0.056 unit. The molecular weight of the anthocyanin pigments is approximately 300 daltons. The molecular weight cut-off point of the NF-40 membrane is also 300 daltons. It is possible that a lower pressure will permit a longer contact of the juice with the membrane, thus allowing more pigments to pass through it. The higher result obtained with the working pressure of 2800 kPa may be explained by the pigments being forced to penetrate the membrane, at a higher pressure.

d) In every experiment there were no significant changes in the acidity (pH) of the different samples. There was a slight increase in the refractive index and in the total soluble solids values with increasing operating pressure. However a statistical analysis of the data showed that these increases were not significant. Comparing the percentage total soluble solids of the raspberry juice extract feed sample with the same value of the concentrate sample collected at the end of the experiment, a 0.45 % increase in total solids was measured for the experiment run at 2500 kPa. At a 2000 kPa experimental pressure the increase was 0.30 %, and at 2800 kPa it was only 0.12 %. These results also confirm that the most efficient pressure for the operation of the process is 2500 kPa.

2. Performance of NF-40 and FT-30 Membranes at Constant Pressure

By recirculating the raspberry juice extract through NF-40 and FT-30 membranes at an operating pressure of 2500 kPa during a period of one hour, the performance of the two types of reverse osmosis membranes for juice concentration was compared. Feed juice, permeate, and concentrate samples collected after half an hour and one hour of passage through the membranes were tested in the laboratory. The results of the tests are shown in Table 2.

a) The FT-30 membrane did not allow the passage of significant amounts of sugars through it. The sugar concentration was measured by the average refractive index value of the permeate samples, and was 0.0 g/L for the FT-30 membrane. The NF-40 membrane allowed the passage of trace amounts of sugars; the refractive index value of the permeate samples was 0.4 g/L.

b) There was more coloration in the permeate collected from the FT-30 membrane than from the NF-40 membrane. The average absorbance reading at a wavelength of 515 nm was 0.046 unit for the FT-30 tests and 0.013 unit for the NF-40 membrane tests.

c) The percentage of total soluble solids of the last concentrate sample as compared to the feed sample increased by 0.45 % in the experiment using the NF-40 membrane and 0.56 % in the experiment using the FT-30 membrane. Although these differences between experiments are not statistically significant, the results suggest that the FT-30 membrane has a higher capacity for retaining solids than the NF-40 membrane.

TABLE 2. Performance of the NF-40 and FT-30 Membranes at Constant Operating pressure of 2500 kPa.

Time (h)		Feed and Concentrate Samples:	
		NF-40	FT-30
0	pH	2.99 ± 0.11*^{a1}	3.07 ± 0.06
	RI	7.1 ± 1.5^{a1}	6.6 ± 0.5
	TS	7.44 ± 0.81^{a1}	6.47 ± 0.41
0.5	pH	2.99 ± 0.03	3.06 ± 0.04
	RI	7.3 ± 1.3	6.9 ± 0.7
	TS	7.66 ± 0.76	6.83 ± 0.38
1.0	pH	2.99 ± 0.05	3.03 ± 0.07
	RI	7.3 ± 1.2	7.1 ± 0.7
	TS	7.89 ± 0.76	7.03 ± 0.30
Time (h)		**Permeate Samples:**	
0.5	pH	2.73 ± 0.07^{a1}	3.17 ± 0.41
	RI	0.4 ± 0.1^{a1}	0.0 ± 0.0
	ABS	0.007 ± 0.006^{a1}	0.055 ± 0.035
1.0	pH	2.68 ± 0.07	3.06 ± 0.31
	RI	0.3 ± 0.0	0.0 ± 0.0
	ABS	0.019 ± 0.027	0.036 ± 0.026
Permeate Flow Rate (mL/h)		124	54

Membrane effect: numerals in rows; concentration effect with time: letters in columns.
* Mean ± Standard Deviation (n=9); p 0.01.
RI - Refractive Index in g/L of Sucrose.
ABS- Absorbance Reading at 515 nm.
TS - Total Soluble Solids in % g/L of Sucrose.

d) The average permeate flow rate was 124 mL/h for the experiment conducted with the NF-40 membrane and 54 mL/h for the experiment using the FT-30 membrane. The flow rate more than doubled when the NF-40 membrane was used.

e) The results of the HPLC analysis performed on the feed and permeate samples of the experiment run at 2500 kPa using the NF-40 membrane are summarized in Table 3 and Figure 12. Glucose and fructose were present in the feed juice at an average concentration of 4.03 mg/mL and 5.55 mg/mL, respectively. Only 0.03 mg/mL of glucose and 0.09 mg/mL of fructose passed through the membrane to be present in the permeate. This is respectively equivalent to 0.74 % and 1.62 % of the glucose and fructose concentrations initially present in the feed juice.

The above results indicate that the use of a NF-40 membrane will speed up the concentration process at the cost of the quality of the concentrate. The concentrate generated by the FT-30 membrane has a higher concentration of soluble solids and of sugars.

B. SECOND PRESS RASPBERRY JUICE

Several experiments were conducted to determine the best way of recovering sugars, soluble solids and pigments from the press cake. A second press raspberry juice was obtained from the press cake by washing it with distilled water and adding food grade citric acid and dextrose or fructose to maximize

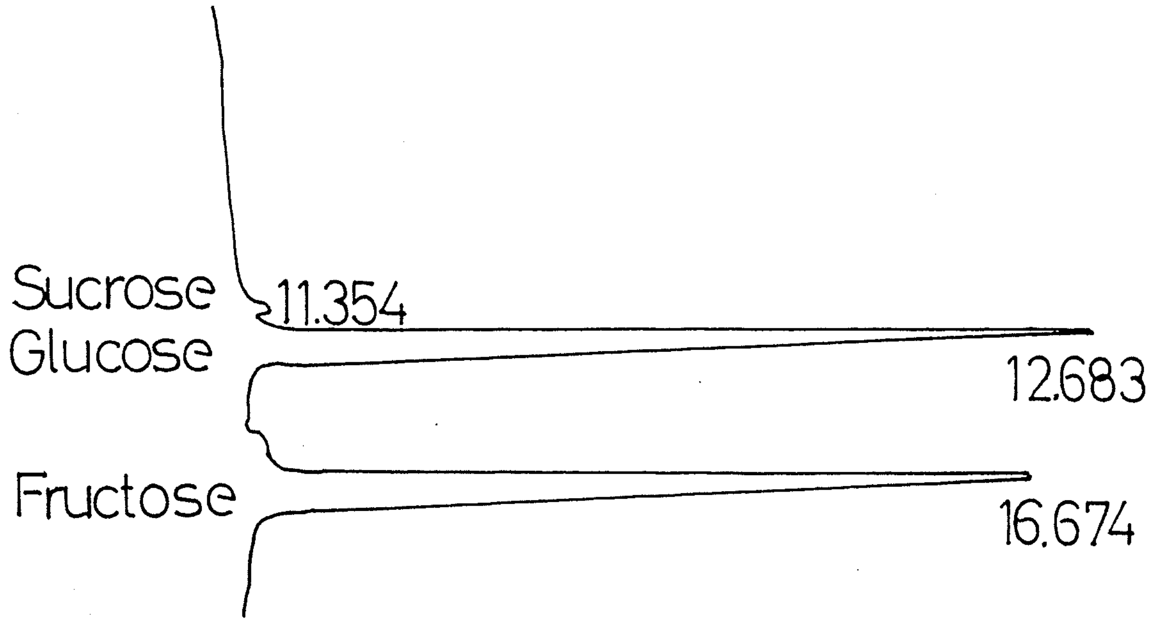
TABLE 3. HPLC Sugar Analysis on Samples Collected During Concentration Through a NF-40 Membrane.

	Glucose (mg/mL)	Fructose (mg/mL)	Total (mg/mL)
Feed	4.03 ± 0.15*	5.55 ± 0.23	9.58
Permeate	0.03 ± 0.03	0.09 ± 0.06	0.12

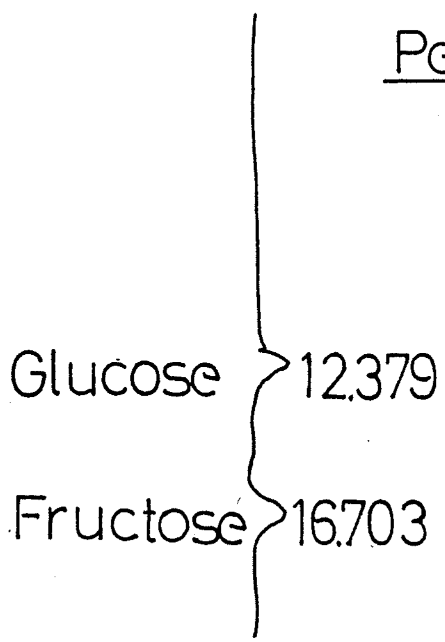
* Mean ± Standard Deviation.

Figure 12. HPLC Chromatograms of Raspberry Juice Extract and Permeate Sample Collected During its Concentration through a NF-40 Membrane

RJE



Permeate



the solubility of press cake components. For each experiment the control sample contained only the given amounts of water and citric acid for that experiment - no sugar was added to it. The refractive index and total soluble solids values for each addition of dextrose or fructose were subtracted from their respective standard solution values (Appendices I-III).

1. **Addition of Different Amounts of Water**

Comparing the two control samples in the experiments reported in Table 4, the effect on the extraction of sugars, soluble solids and pigments due to different amounts of water and dextrose added to the press cake was investigated. A volume of 150 mL of distilled water was added to 50 g of press cake and 0.2 g of citric acid. In a second experiment 100 mL of distilled water were added to the same quantities of press cake and citric acid. Samples from both experiments were analysed and compared. Within the same treatment there were no significant differences between the analysis of the samples that contained different added amounts of dextrose. Between experiments, the only differences assessed were those for the absorbance readings amongst the samples that contained the same amount of dextrose, which were significant. The more diluted juice had an average refractive index value of 0.1 g/L lower, an average absorbance reading 0.061 unit lower, and an average percentage total soluble solids 0.41 % lower, than in the second experiment.

TABLE 4. The Effect of Dilution and Addition of Dextrose on the Recovery of Second Press Raspberry Juice.

Dextrose (g/L)	150 mL H_2O				100 mL H_2O			
	pH	RI	ABS	TS	pH	RI	ABS	TS
0.0	3.16 ± 0.01*[a1]	1.6 ± 0.1[a1]	0.164 ± 0.017[a1]	1.60 ± 0.07[a1]	3.08 ± 0.18[a]	2.3 ± 0.3[a1]	0.225 ± 0.043[a2]	2.31 ± 0.07[a1]
2.5	3.07 ± 0.01	0.5 ± 0.1	0.173 ± 0.046	0.96 ± 0.03	3.08 ± 0.09	1.4 ± 0.2	0.233 ± 0.039[b2]	1.58 ± 0.06
3.5	3.22 ± 0.02	0.5 ± 0.0	0.162 ± 0.017	0.78 ± 0.05	3.22 ± 0.01	1.1 ± 0.2	0.245 ± 0.061[a2]	1.07 ± 0.16
5.5	3.27 ± 0.05	0.4 ± 0.1	0.153 ± 0.019	0.66 ± 0.30	3.18 ± 0.09	0.5 ± 0.2	0.225 ± 0.018[a2]	0.87 ± 0.80
7.5	3.31 ± 0.07	0.2 ± 0.0	0.144 ± 0.032	0.52 ± 0.00	3.21 ± 0.05	0.3 ± 0.1	0.235 ± 0.036[a2]	0.73 ± 0.74

Dilution effect: numerals in rows; sugar concentration effect: letters in columns.
* Mean ± Standard Deviation (n=9); $p \leq 0.01$.
RI - Refractive Index in g/L of Sucrose.
ABS- Absorbance Reading at 515nm.
TS - Total Soluble Solids in % (w/w).

These results confirm the anticipated assumption that the greater the amount of water added to the press cake, the smaller the concentration of soluble solids and pigments in the second press juice.

2.Addition of Citric Acid

Results of tests conducted with varying amounts of citric acid and dextrose are shown in Table 5 and Figure 13. In all tests, the juice recovered was from 50 g of press cake which had been washed with 100 mL of distilled water and mixed with the citric acid and dextrose. Citric acid amounts ranged from 0.2 to 1.0 g, and dextrose amounts ranged from 0.0 to 7.5 g.

Comparing the results of the tests conducted in the three control samples the following results were observed:

a) There were no significant differences on the average refractive indices of the recovered juice when the amount of citric acid increased from 0.2 to 1.0 g.

b) The average absorbance reading value increased progressively from 0.225 unit in the experiment using 0.2 g of citric acid to 0.281 unit in the experiment using 1.0 g of citric acid. Therefore, there was a significant increase in coloration of the juice, indicating enhanced anthocyanin coloration, with the addition of citric acid.

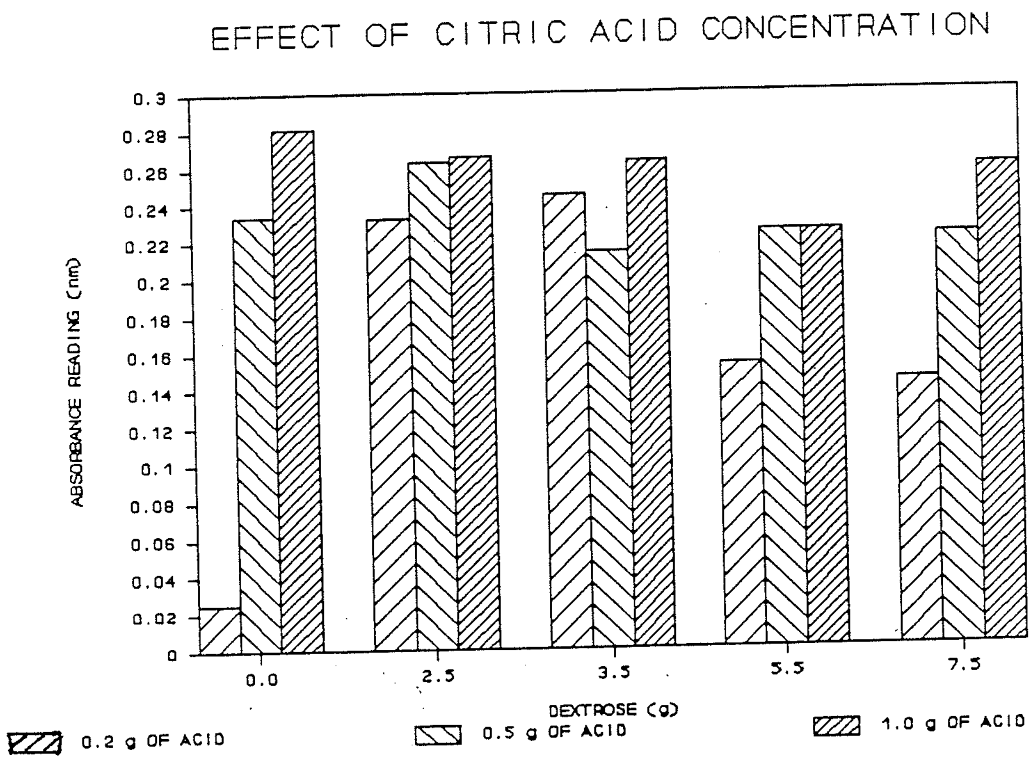
c) The measurements of pH in the range of 2.8-3.0 were not conclusive. However, the absorbance reading values increased with the amount of acid added to the sample, as proven by an increase in red colour.

TABLE 5. The Effect of Citric Acid Concentration on the Recovery of Second Press Raspberry Juice.

Dextrose (g)		Citric Acid (g)		
		0.2	0.5	1.0
	pH	3.08 ± 0.18[*a]	2.82 ± 0.12	2.98 ± 0.09
0.0	RI	2.3 ± 0.3[a1]	2.2 ± 0.1	1.8 ± 0.3
	ABS	0.025 ± 0.043[a1]	0.234 ± 0.060	0.281 ± 0.039[2]
	TS	2.31 ± 0.07[a1]	2.25 ± 0.25	2.10 ± 0.15
	pH	3.08 ± 0.09	3.04 ± 0.16	2.95 ± 0.03
2.5	RI	1.4 ± 0.2	1.0 ± 0.4	0.7 ± 0.2
	ABS	0.233 ± 0.039[b]	0.263 ± 0.053	0.266 ± 0.021
	TS	1.58 ± 0.06	1.62 ± 0.10	1.33 ± 0.03
3.5	pH	3.22 ± 0.01	2.95 ± 0.11	2.94 ± 0.04
	RI	1.1 ± 0.2	0.8 ± 0.4	0.2 ± 0.4
	ABS	0.245 ± 0.061	0.214 ± 0.012	0.263 ± 0.039
	TS	1.07 ± 0.16	1.18 ± 0.19	1.23 ± 0.04
	pH	3.18 ± 0.09	3.18 ± 0.09	2.97 ± 0.04
5.5	RI	0.5 ± 0.2	0.0 ± 0.2	0.2 ± 0.3
	ABS	0.155 ± 0.018	0.225 ± 0.018	0.225 ± 0.006
	TS	0.87 ± 0.80	0.84 ± 0.80	0.60 ± 0.38
	pH	3.21 ± 0.05	3.08 ± 0.09	2.96 ± 0.06
7.5	RI	0.3 ± 0.1	0.2 ± 0.1	0.6 ± 0.1
	ABS	0.235 ± 0.036	0.222 ± 0.019	0.260 ± 0.016[2]
	TS	0.73 ± 0.74	0.05 ± 0.16	0.11 ± 0.131

Effect of citric acid concentration: numerals in rows; effect of sugar concentration: letters in columns.
* Mean ± Standard Deviation (n=9); $p \leq 0.01$
RI - Refractive Index in g/L of Sucrose;
ABS- Absorbance Reading at 515 nm;
TS - Total Soluble Solids in % (w/w).

Figure 13. The Effect of Citric Acid Concentration on the Absorbance Reading (Anthocyanin Content) of the Recovered Second Press Raspberry Juice


EFFECT OF CITRIC ACID CONCENTRATION
ABSORBANCE READING (nm)
0.3
0.28
0.26
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0.0
2.5
3.5
5.5
7.5
DEXTROSE (g)
0.2 g OF ACID
0.5 g OF ACID
1.0 g OF ACID

d) With a 0.8 g/100 mL increase in citric acid added, the average increase in total soluble solids was not statistically significant, and it was only 0.68 %. This may signify that with an increase in acidity it will be more difficult to release additional soluble solids from the press cake mass.

The pattern observed with the control samples for the three experiments was generally repeated with the samples containing the same amount of dextrose, as this addition was not statistically different.

3. **Addition of Dextrose**

Different amounts of dextrose were added to the mixture of press cake, water and citric acid with the objective of studying the effect of dextrose addition on the removal of sugars, pigments and soluble solids from the press cake. Tables 4 and 5 show the effect of increasing amounts of dextrose on these characteristics, subtracted from the respective standard values. A better extraction of sugars, pigments and total solids was achieved using a smaller amount of diluting water (which may also be a dilution effect). The addition of increasing quantities of dextrose to 50 g of press cake, 100 mL of distilled water, and citric acid, Table 5, revealed no significant differences within the refractive index and total soluble solids values of the samples of the same experiment. They also show that:

a) There was no proportional increase in the average refractive index values of the recovered juice with the addition of dextrose, after allowing for the effects of its addition.

b) With respect to pigment recovery, a statistical analysis revealed no significant differences within the same experiment. The general trend in the three experiments was a reduction in the average absorbance reading values of the recovered juice with an increasing addition of dextrose to the press cake and water. However, the best overall average absorbance readings were obtained in the experiment that used 1 g of citric acid. Since the pH is essentially constant, this probably indicates an increased pigment release from the press cake with an increasing acid content.

The overall conclusion is that the addition of dextrose did not improve the extraction of sugars, soluble solids and pigments from the press cake, while the addition of citric acid did, up to the 1 % level.

4. **Addition of Fructose**

A set of experiments was carried out using fructose instead of dextrose, to study the possibility of increasing recovery of sugars, pigments and soluble solids from the press cake using a different type of sugar. Based on the results of the previous experiments, 100 mL of distilled water and 1.0 g of citric acid were added to 50 g of press cake. Amounts of fructose varying from 0.0 to 7.5 g were added to the cake. The results of the tests on the recovered juice are summarized in

Table 6, and compared with the results of the same experiment when dextrose was used. No significant differences among the results of the two experiments using the same amount of sugar were observed. This suggests that the recovery of sugars, pigments and soluble solids is not dependent of the type of sugar added to the press cake.

C. CONCENTRATION OF THE SECOND PRESS RASPBERRY JUICE

The juice obtained by washing 50 g of press cake with twice its weight of distilled water was concentrated by recirculating it through a FT-30 reverse osmosis spiral wound membrane. Tests were performed on the juice at zero time, i.e. the feed juice, and on four 50 mL samples of the concentrate collected every half hour during a test period of two hours. Samples of the permeate were also collected at the same times and tested. The samples were analysed for pH, titratable acidity, refractive index, absorbance reading at 515 nm and percentage total soluble solids. The permeate flow rate was also measured to determine the rate of water removal. Although there were very few significant differences between the analysis of the feed and concentrate samples, the data in Table 7 and Figure 14 indicates that:

a) The pH values remained constant for the feed juice and the different concentrate samples.

b) The average titratable acidity, measured as percentage citric acid, was 0.38 % for the juice as it was fed to the

TABLE 6. The Effect of the Type of Sugar Used
on the Recovery of Second Press Raspberry Juice.

Sugar (g)	Dextrose				Fructose			
	pH	RI	ABS	TS	pH	RI	ABS	TS
0.0	2.98 ± 0.09[*a]	1.8 ± 0.3[a1]	0.281 ± 0.039[a1]	2.10 ± 0.15[a1]	2.97 ± 0.05[a]	1.9 ± 0.5[a1]	0.294 ± 0.067[a1]	2.30 ± 0.19[a1]
2.5	2.95 ± 0.03	0.7 ± 0.2	0.266 ± 0.021	1.33 ± 0.03	2.98 ± 0.09	1.2 ± 0.3	0.283 ± 0.055	1.77 ± 0.30
3.5	2.94 ± 0.04	0.2 ± 0.4	0.263 ± 0.039	1.12 ± 0.04	2.98 ± 0.09	0.1 ± 0.4	0.268 ± 0.038	1.31 ± 0.22
5.5	2.97 ± 0.04	0.2 ± 0.3	0.225 ± 0.006	0.60 ± 0.38	3.05 ± 0.09	0.1 ± 0.2	0.274 ± 0.051	0.45 ± 0.25
7.5	2.96 ± 0.06	0.1 ± 0.1	0.260 ± 0.016	0.16 ± 0.13	2.94 ± 0.00	0.1 ± 0.1	0.242 ± 0.020	0.03 ± 0.02

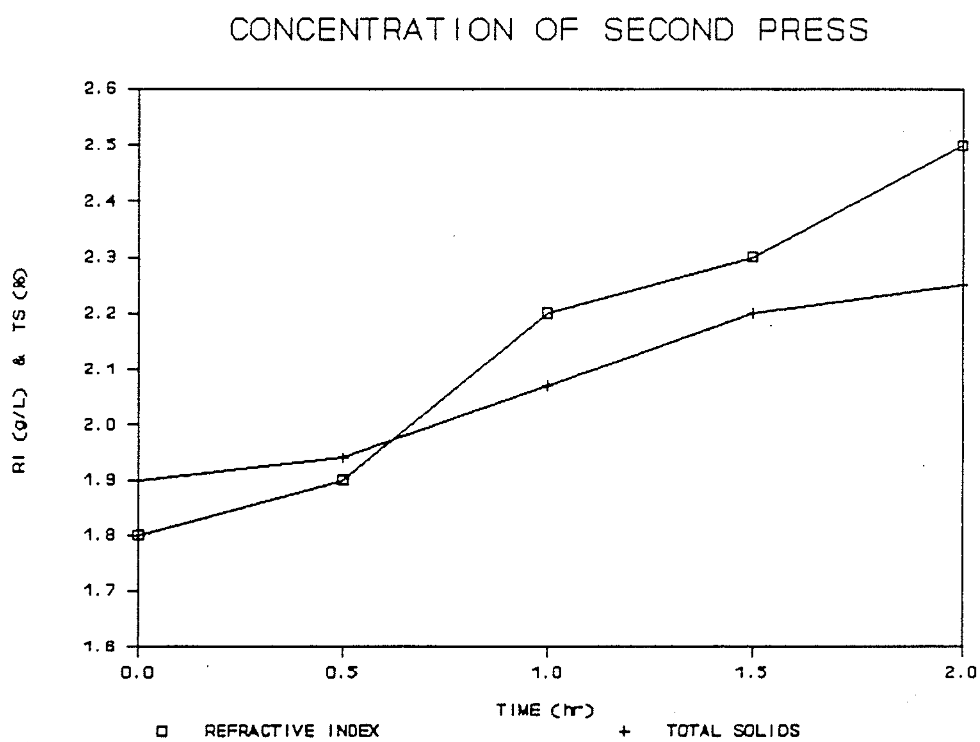
Sugar concentration effect: letters in columns; Sugar effect: numerals in rows.
* Mean ± Standard Deviation (n=9); $p \leq 0.01$.
RI - Refractive Index in g/L of Sucrose.
ABS- Absorbance Reading at 515 nm.
TS - Total Soluble Solids in % (w/w).

TABLE 7. Concentration of Second Press Raspberry Juice Using a FT-30 Spiral Wound Membrane.

Time (h)	pH	TA	RI	ABS	TS	PFR
				Feed and Concentrate Samples:		
0	3.06 ± 0.06*^{a}	0.38 ± 0.00^{a}	1.8 ± 0.0^{a}	3.82 ± 0.57^{a}	1.90 ± 0.21^{a}	-
0.5	3.06 ± 0.05	0.43 ± 0.04^{a}	1.9 ± 0.0^{a}	4.09 ± 0.74	1.94 ± 0.39	-
1.0	3.07 ± 0.05	0.45 ± 0.04^{ac}	2.2 ± 0.0^{ac}	4.33 ± 0.50	2.07 ± 0.35	-
1.5	3.06 ± 0.06	0.47 ± 0.04^{bc}	2.3 ± 0.2^{ac}	4.50 ± 0.78	2.20 ± 0.39	-
2.0	3.05 ±0.07	0.45 ±0.00^{ac}	2.5 ± 0.1^{bc}	4.77 ± 1.39	2.25 ± 0.63	-
				Permeate Samples:		
0.5	3.04 ± 0.07^{a}	0.06 ± 0.04^{a}	0.0 ± 0.0^{a}	0.034 ± 0.020^{a}	0.09 ± 0.05^{a}	91.7 ± 14.5^{b}
1.0	3.04 ± 0.07	0.09 ± 0.04	0.1 ± 0.1	0.098 ± 0.090	0.21 ± 0.14	100.0 ±50.0^{b}
1.5	3.02 ± 0.07	0.10 ± 0.06	0.1 ± 0.1	0.179 ± 0.160	0.32 ± 0.03	58.3 ± 14.4^{a}
2.0	3.08 ± 0.12	0.10 ± 0.00	0.1 ± 0.1	0.139 ± 0.030	0.27 ± 0.03	52.5 ± 31.8^{a}

Concentration effect: letters in columns.
* Mean ± Standard Deviation (n=9); p 0.01.
RI - Refractive Index in g/L of Sucrose.
TA - Titratable Acidity in % Citric Acid.
ABS- Absorbance Reading at 515 nm.
TS - Total Soluble Solids in % (w/w).
PFR- Permeate Flow Rate in mL/h.

Figure 14. The Rate of Increase of the Refractive Index and Total Soluble Solids During the Concentration of Second Press Raspberry Juice


CONCENTRATION OF SECOND PRESS
RI (g/L) & TS (%)
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
0.0
0.5
1.0
1.5
2.0
TIME (hr)
REFRACTIVE INDEX
TOTAL SOLIDS

membrane, and increased to 0.47 % after 1.5 hours of recirculation through the membrane.

c) The refractive index increased progressively from 1.8 g/L in the feed juice to 2.5 g/L after two hours of recirculation through the membrane.

d) The absorbance readings at a wavelength of 515 nm increased steadily from 3.8 units in the feed juice to 4.8 units in the concentrate sample collected after two hours.

e) The percentage of total soluble solids increased from 1.90 % in the feed sample to 2.25 % in the concentrate sample collected at the end of the experiment.

f) The average permeate flow rate decreased during the experiment, due to fouling of the membrane, also described by Paulson et al., 1984. In general, there was an increase in most of the parameters with the duration of the concentration process, which indicates the viability of this process in concentrating second press raspberry juice.

Monitoring the permeate samples was important, as the objective was to maximize the membrane retention of sugars, soluble solids and pigments. It was verified that:

a) The permeate samples collected throughout the experiment did not show any significant differences in pH values.

b) The titratable acidity of the permeate increased from 0.06 % citric acid after the first half an hour of experiment to 0.10 % citric acid at the end of the experiment.

c) In the same period of time the absorbance readings of the permeate samples increased from 0.034 unit to 0.139 unit, showing a slightly pink coloration, which signifies a loss in pigments.

d) The percentage of the total soluble solids of the permeate samples increased from 0.09 % after the first half hour of experiment to 0.27 % at the end of the experiment.

e) The average refractive index value was 0.0 g/L of sucrose after the first half hour, then remaining constant at 0.1 g/L until the end of the experiment. The previous results suggest a good retention of sugars, soluble solids and pigments by the FT-30 membrane.

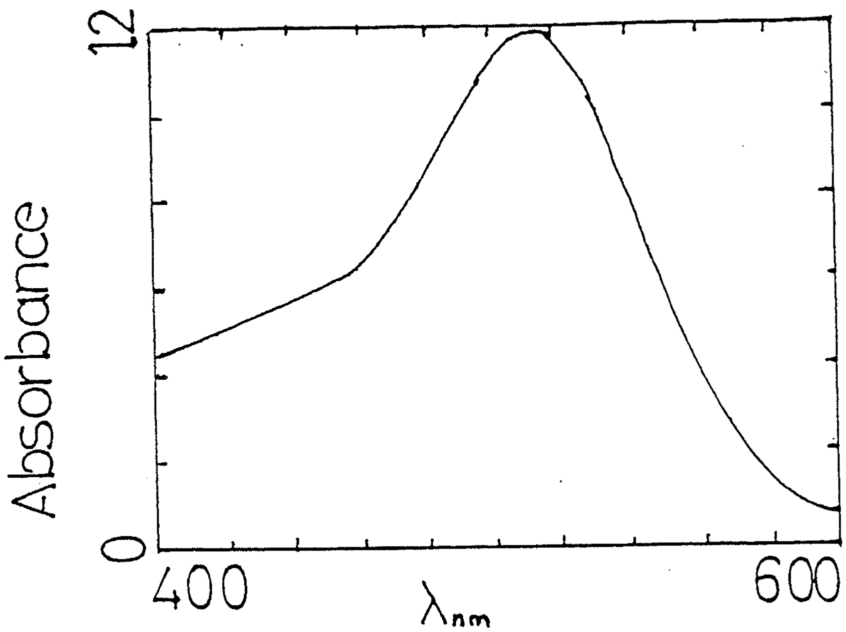
D. DETERMINATION OF WAVELENGTH OF MAXIMUM ABSORBANCE

The wavelength of maximum absorbance (λ max) of the fresh raspberry juice extract (Figure 15-RJE) was determined innitially with the objective of assessing the wavelength that should be used during the experiments with raspberry juice products, and also as an indicator of quality.

The commercial products were poured into glass flasks and visually compared for colour. The differences in shades of red were noticeable, and the λ max of these products was evaluated, as indicated in Figure 15 (West Con) and 16 (West Bev and West Rec). The wavelengths of maximum absorbance varied from 512 nm for both the raspberry juice extract and the raspberry beverage sold at the University of Manitoba, to

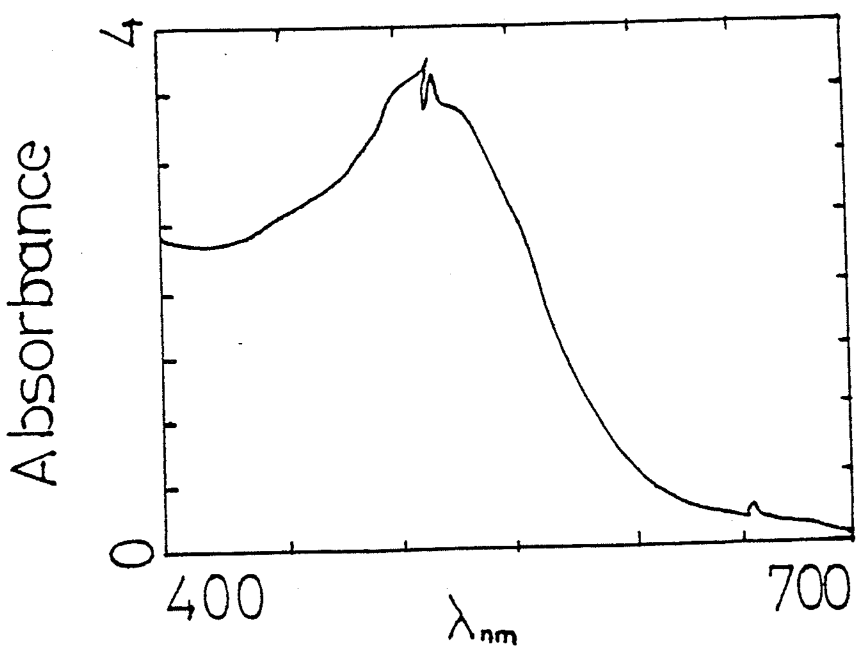
Figure 15. Maximum Absorbance Readings of Fresh Raspberry Juice Extract and "Westvale" Raspberry Frozen Concentrate Using a Hewlett Packard Diode Array Spectrophotometer

RJE



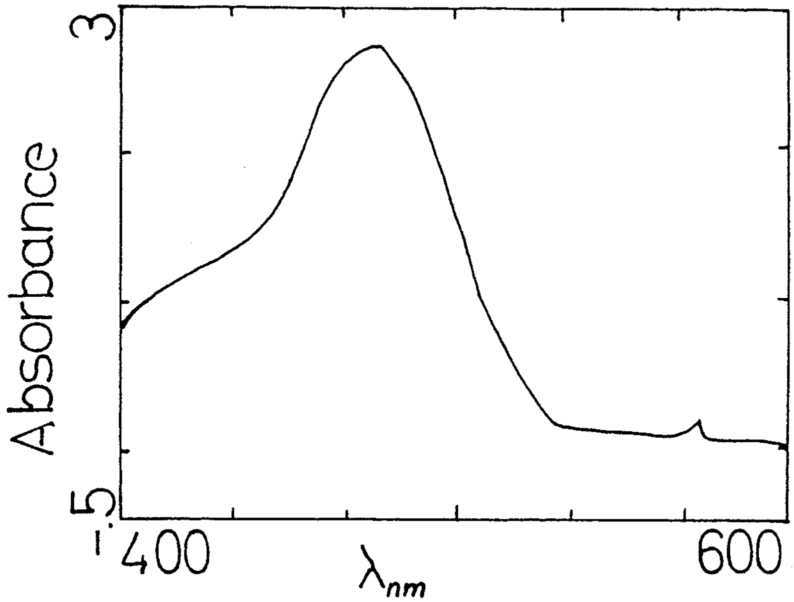
Peak Find
512=1.1827

West Conc

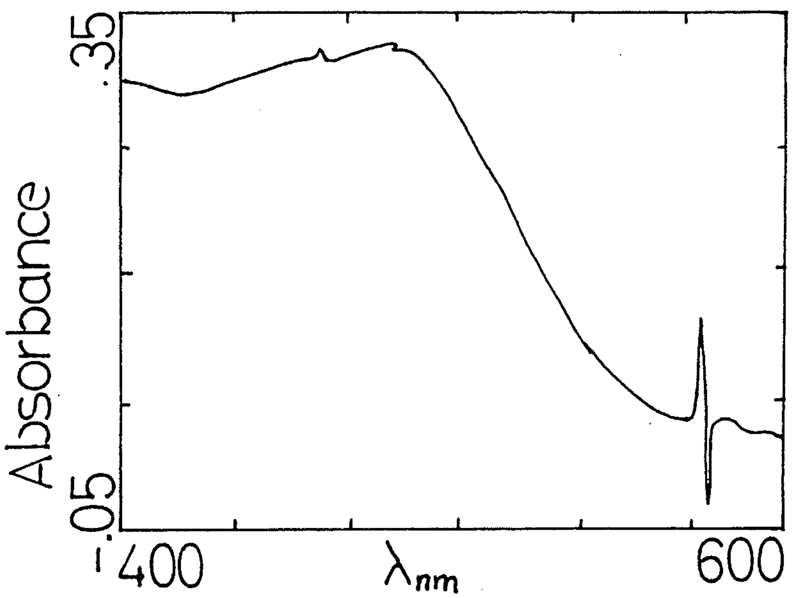


Peak Find
516=3.71501
520=3.57727

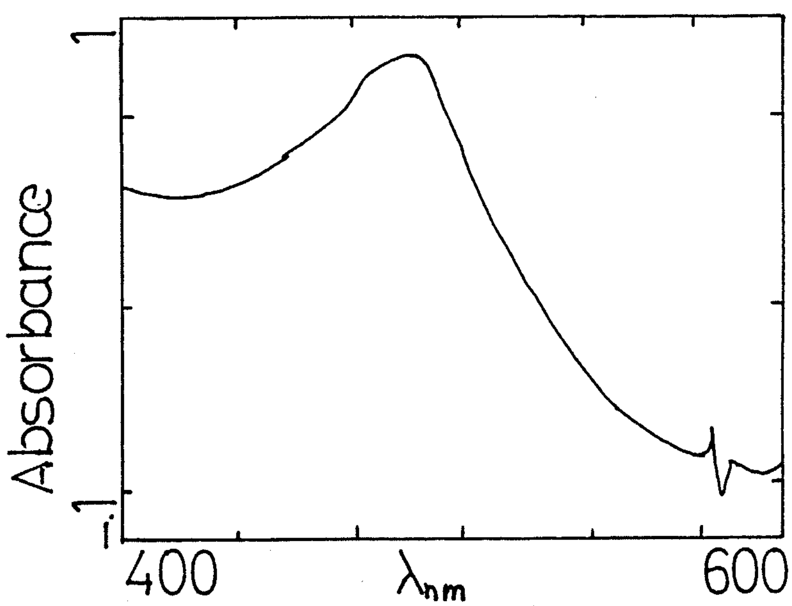
Figure 16. Maximum Absorbance Readings of Raspberry Beverages Existing in the Market Using a Hewlett Packard Diode Array Spectrophotometer



U of M
Peak Find
512 = 2.665



West Bev
Peak Find
514 = .3268



West Rec
Peak Find
518 = .9091

518 nm for the "Westvale" raspberry frozen concentrate reconstituted juice. The operating wavelength of 515 nm chosen for the laboratory absorbance readings was an average of the two previous values and appropriate for the four products compared.

E. SUGAR ANALYSIS BY HPLC

A study was conducted to separate and identify the sugars in raspberry juice extract and second press juice. Typical chromatograms for both products are shown in Figures 12 and 17 and the respective concentrations are summarized in Tables 3 and 8. Fructose was the major sugar component in both samples, with smaller amounts of glucose being identified. Sucrose was only identified in the second press juice sample.

The results of the HPLC analysis of the raspberry juice extract and the permeate from a NF-40 membrane at a pressure of 2500 kPa were previously discussed. An FT-30 membrane was used during the concentration of the second press juice. The data in Table 8 show that of the total amount of sugar present in the second press juice, 0.53 mg/mL (13.3 %) of sucrose, 0.06 mg/mL (1.6 %) of glucose and 0.17 mg/mL (3.3 %) of fructose passed through the membrane into the permeate. Compared with the feed juice the concentrate sample had a glucose concentration of 4.62 mg/mL (23 % increase), and a fructose concentration of 7.1 mg/mL (38 % increase). The amount of sucrose dropped to 3.12 mg/mL (21 % decrease).

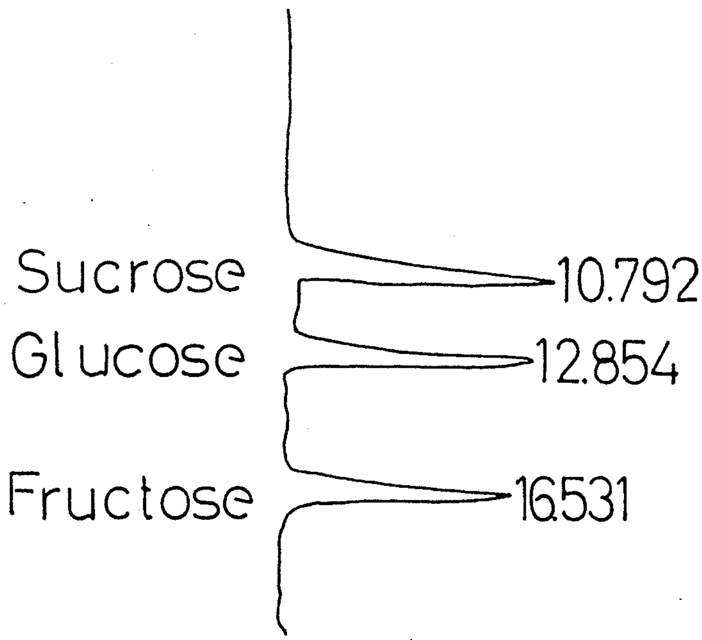
TABLE 8. HPLC Sugar Analysis on Samples Collected During the Concentration of Second Press Juice.

	Sucrose (mg/mL)	Glucose (mg/mL)	Fructose (mg/mL)	Total (mg/mL)
Feed	3.98 ± 1.85*	3.77 ± 1.83	5.16 ± 2.53	12.91
Permeate	0.53 ± 0.57	0.06 ± 0.02	0.17 ± 0.00	0.76
Final Concentrate	3.12 ± 0.22	4.62 ± 0.68	7.12 ± 1.10	14.87

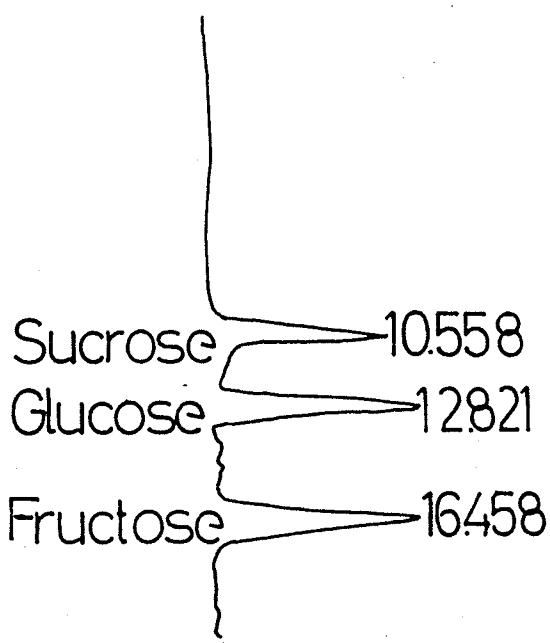
* Mean ± Standard Deviation (n=9).

Figure 17. HPLC Chromatograms of Second Press Raspberry Juice, Permeate and Concentrate Samples After its Concentration through a FT-30 Membrane

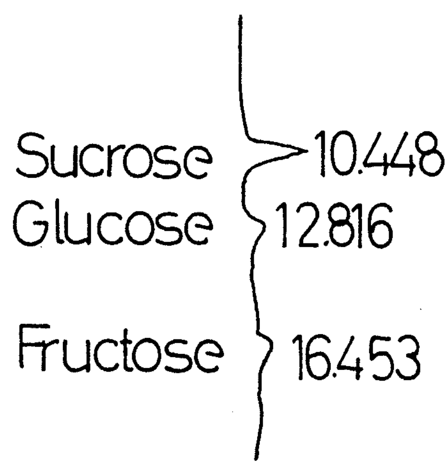
Feed



Concentrate



Permeate



Despite the apparent sucrose inversion, there was a 15 % overall increase in the concentration of total sugars, from 12.91 mg/mL to 14.87 mg/mL, during the concentration process.

F. BEVERAGE CONCENTRATES

Nature produces a naturally concentrated raspberry juice. When the juices are produced industrially, the concentration of the product is important to reduce the costs of storage of the products and/or the associated transportation costs. The raspberry juice extract was used to produce a beverage concentrate. Some experiments were carried out with the objective of preparing concentrated samples that could be frozen. The concentrate was diluted with three parts of water to produce a beverage similar to the commercially available raspberry juices.

No specific freezing studies were done, but the beverage concentrates were processed, diluted and compared with the "Westvale" raspberry diluted frozen concentrate, the "Westvale" raspberry boxed drink beverage and the U.of M. raspberry juice beverage.

1. Raspberry Juice Concentrate

Concentration tests were conducted using 55.5 % (w/w) raspberry juice extract as the source material with sugar and food grade citric acid in percentages of 43 % and 1.5 % respectively, of total weight. The results were compared against corresponding tests on samples of commercially available "Westvale" raspberry juice frozen concentrate.

These results are summarized in Table 9 and indicate that the experimental concentrate presents significantly higher results for most of the tests performed, which is an indication of a better quality product.

In comparing the diluted samples with each other, with the raspberry juice beverage and with the "Westvale" raspberry boxed drink, the same pattern of results occurred. As can be observed in the data on Table 10, the experimental dilution presented higher refractive index and total soluble solids values. If the quality of the concentrated juice produced in the laboratory was better than the equivalent products available in the market, it is expected that the same pattern of results would occur for the diluted samples.

2. Juice Extract and Second Press Juice Mixtures

Several mixtures of the juice extract and second press juice were prepared. The samples had a volume of 60 mL; the quantity of raspberry juice extract in the mixture ranged from 30 to 60 mL, and the quantity of second press juice ranged from 30 to 0 mL (representing 55.5 % of the total weight). The amounts of sugar and citric acid added were 43 % and 1.5 % respectively, of total weight. The tests performed on these mixtures are summarized on Table 11 and Figure 18, and compared with the "Westvale" raspberry frozen concentrate juice. In general, a slight increase in pH values, refractive indices, titratable acidity, total solids and absorbance

TABLE 9. Laboratory Analysis of Raspberry Beverage Concentrates.

	Experimental Concentrate	"Westvale" Frozen Concentrate
pH	2.78 ± 0.01*[a]	2.77 ± 0.02[a]
RI	47.4 ± 0.4[b]	41.6 ± 1.56[a]
TA	2.82 ± 0.00[a]	2.09 ± 0.09[a]
ABS @ 515 nm	0.623 ± 0.003[b]	0.349 ± 0.002[a]
ABS @ 430 nm	0.263 ± 0.062[b]	0.169 ± 0.002[a]
TS	51.02 ± 0.00[b]	39.43 ± 2.04[a]

Effect of type of concentrate: letters in rows.
* Mean ± Standard Deviation (n=9); $p \leq 0.01$.
RI - Refractive Index in g/L of Sucrose.
TA - Titratable Acidity in % Citric Acid.
ABS- Absorbance Reading @ respective Wavelength.
TS - Total Soluble Solids in % (w/w).

TABLE 10. Laboratory Analysis of Raspberry Juice Beverages.

	Experimental Dilution	"Westvale" Reconstituted	U. of M. Beverage	"Westvale Boxed Drink
pH	2.69 ± 0.01*[a]	2.77 ± 0.01[a]	2.64 ± 0.01[a]	2.72 ± 0.04[a]
RI	14.3 ± 0.3[c]	12.6 ± 0.4[b]	12.4 ± 0.1[b]	11.3 ± 0.4[a]
TA	0.76 ± 0.00[b]	0.58 ± 0.04[a]	0.79 ± 0.01[b]	0.41 ± 0.01[a]
ABS @ 515 nm	0.117 ± 0.003[a]	0.067 ± 0.000[a]	0.122 ± 0.007[a]	0.010 ± 0.000[a]
ABS @ 430 nm	0.050 ± 0.001[a]	0.031 ± 0.000[a]	0.088 ± 0.010[a]	0.009 ± 0.000[a]
TS	14.20 ± 0.10[c]	11.56 ± 0.75[a]	13.12 ± 0.08[b]	10.85 ± 0.27[a]

Differences between beverages: letters in rows.
* Mean ± Standard Deviation (n=9); $p \leq 0.01$.
RI - Refractive Index in g/L of Sucrose.
TA - Titratable Acidity in % Citric Acid.
ABS- Absorbance Readings @ Respective Wavelengths.
TS - Total Soluble Solids in % (w/w).

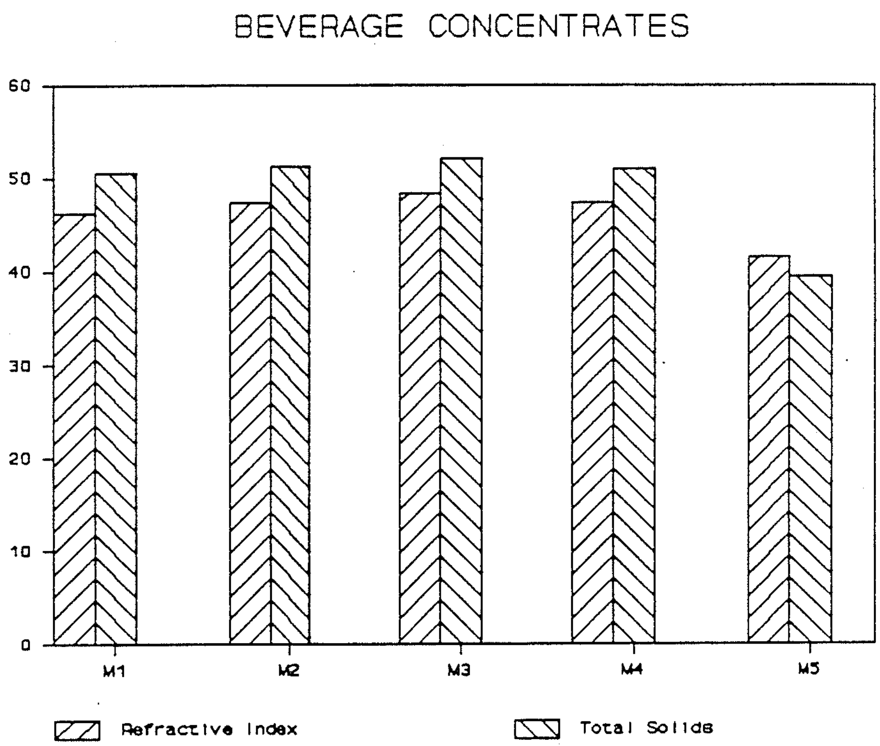
TABLE 11. Analysis of Beverage Concentrates with Mixtures of Raspberry Juice Extract (RJE) and Second Press Raspberry Juice (SPJ).

M_1 - 30 mL RJE + 30 mL SPJ
M_2 - 45 mL RJE + 15 mL SPJ
M_3 - 55 mL RJE + 5 mL SPJ
M_4 - 60 mL RJE + 0 mL SPJ
M_5 - "Westvale" Frozen Concentrate

	M_1	M_2	M_3	M_4	M_5
pH	$2.61 \pm 0.01^{*a}$	2.70 ± 0.02^{a}	2.75 ± 0.00^{a}	2.78 ± 0.01^{a}	2.77 ± 0.02^{a}
RI	46.3 ± 0.2^{b}	47.4 ± 0.1^{bc}	48.4 ± 0.4^{c}	47.4 ± 0.4^{bc}	41.6 ± 1.56^{a}
TA	2.28 ± 0.00^{a}	2.55 ± 0.02^{a}	2.70 ± 0.00^{a}	2.82 ± 0.01^{a}	2.09 ± 0.09^{a}
ABS @ 515 nm	0.408 ± 0.003^{a}	0.570 ± 0.010^{b}	0.580 ± 0.007^{b}	0.623 ± 0.003^{b}	0.349 ± 0.002^{a}
ABS @ 430 nm	0.171 ± 0.008^{a}	0.235 ± 0.008^{a}	0.239 ± 0.021^{a}	0.263 ± 0.062^{a}	0.169 ± 0.002^{a}
TS	50.52 ± 0.00^{b}	51.22 ± 0.01^{b}	52.05 ± 0.00^{b}	51.02 ± 0.02^{b}	39.43 ± 2.04^{a}

Effect of Type of Mixture: letters in rows.
* Mean ± Standard Deviation (n=9); $p \leq 0.01$.
RI - Refractive Index in g/L of Sucrose.
TA - Titratable Acidity in % Citric Acid.
ABS- Absorbance Readings at Respective Wavelengths.
TS - Total Soluble Solids.

Figure 18. Refractive Index and Total Soluble Solids of the Mixtures Listed in Table 11


BEVERAGE CONCENTRATES
60
50
40
30
20
10
0
M1
M2
M3
M4
M5
Refractive Index
Total Solids

readings was observed with the increase of raspberry juice extract in the mixture. Mixture M_3 (55 mL of raspberry juice extract and 5 mL of second press juice) was the beverage with the higher refractive index value (48.4 g/L of sucrose) and total soluble solids (52.1 %). When compared with "Westvale" raspberry frozen concentrate the tests were always more favorable.

As indicated in Table 12 and Figures 19 and 20, the tests in the diluted samples, prepared by adding three parts of water to one part of the respective mixture, showed the same pattern as the tests of the concentrated ones. The same occurred for the reconstituted "Westvale" raspberry frozen concentrate and the U. of M. beverage. Comparing the laboratory results with the U. of M. beverage it can be observed that the mixtures developed performed better than the regular juices in terms of refractive index and amounts of total soluble solids. The U. of M. juice had a stronger colour and higher acidity.

It will be possible, therefore to prepare a commercial concentrate product or a juice beverage incorporating second press juice in its formulation and increasing the juice yield. This product will have properties similar to the commercial products available in the market.

Data indicated that the laboratory produced concentrate after a 3:1 dilution produced a juice beverage which performed very well in preliminary sensory tests. This initial

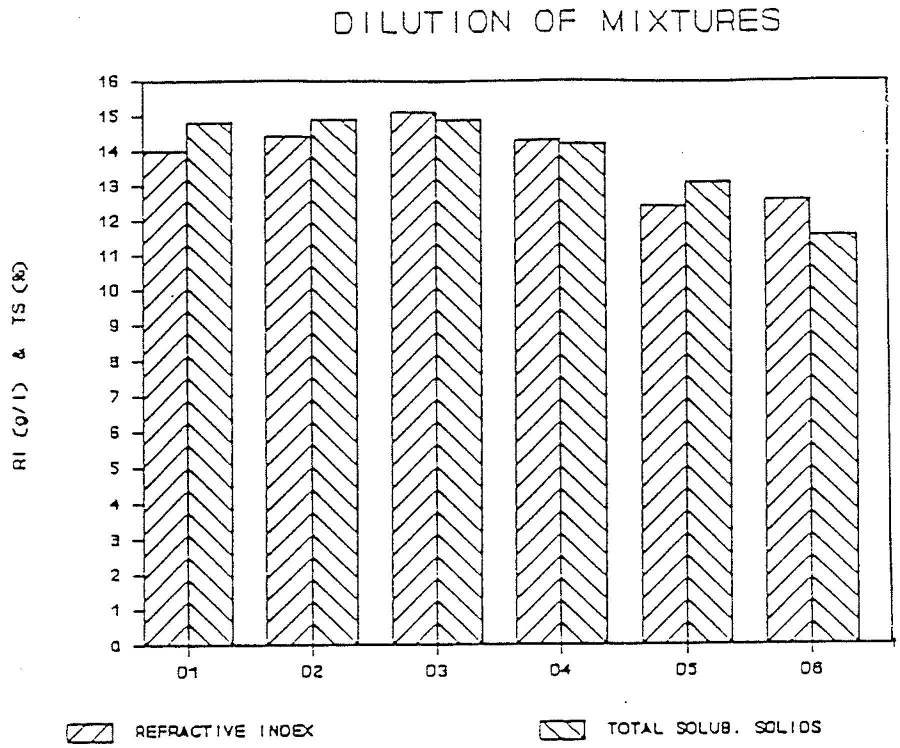
TABLE 12. Dilutions (1:3) of the Mixtures Listed in Table 11 (M_i = D_i).
D_5 - U. of M. Raspberry Beverage
D_6 - "Westvale" Raspberry Frozen Concentrate Reconstituted

	D_1	D_2	D_3	D_4	D_5	D_6
pH	2.56 ± 0.01*[a]	2.63 ± 0.01[a]	2.66 ± 0.02[a]	2.69 ± 0.01[a]	2.64 ± 0.01[a]	2.77 ± 0.02[a]
RI	14.0 ± 0.1[b]	14.4 ± 0.2[b]	15.1 ± 0.5[b]	14.3 ± 0.3[b]	12.4 ± 0.1[a]	12.6 ± 0.4[a]
TA	0.35 ± 0.00[a]	0.40 ± 0.01[ab]	0.47 ± 0.00[ab]	0.43 ± 0.02[ab]	0.79 ± 0.01[c]	0.58 ± 0.04[bc]
ABS @ 515nm	0.090 ± 0.007[a]	0.093 ± 0.002[ab]	0.097 ± 0.003[b]	0.101 ± 0.003[ab]	0.122 ± 0.007[bc]	0.067 ± 0.000[a]
ABS @ 430 nm	0.042 ± 0.008[a]	0.063 ± 0.002[a]	0.059 ± 0.003[a]	0.050 ± 0.001[a]	0.088 ± 0.010[a]	0.031 ± 0.000[a]
TS	14.83 ± 0.00[c]	14.89 ± 0.00[c]	14.88 ± 0.01[c]	14.20 ± 0.00[c]	13.12 ± 0.08[b]	11.56 ± 0.75[a]

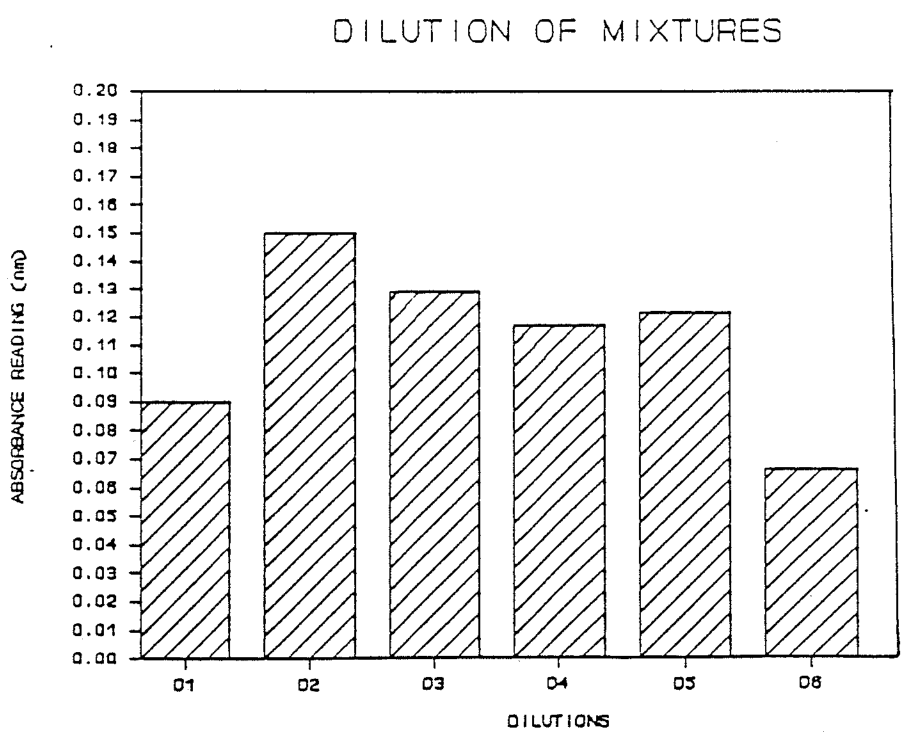
Effect of Type of Beverage: letters in rows.
* Mean ± Standard Deviation (n=9); $p \leq 0.01$.
RI - Refractive Index in g/L of Sucrose.
TA - Titratable Acidity in % Citric Acid.
ABS- Absorbance Readings at Respective Wavelengths.
TS - Total Soluble Solids.

Figure 19 Refractive Index and Total Soluble Solids of the Dilutions Listed in Table 12

Figure 20 Absorbance Readings of the Dilutions Listed in Table 12



DILUTION OF MIXTURES
RI (g/l) & TS (%)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
D1
D2
D3
D4
D5
D6
REFRACTIVE INDEX
TOTAL SOLUB. SOLIDS



DILUTION OF MIXTURES
ABSORBANCE READING (nm)
0.20
0.19
0.18
0.17
0.16
0.15
0.14
0.13
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
D1
D2
D3
D4
D5
D6
DILUTIONS

observation should be confirmed and optimized with extensive sensory work.

V. CONCLUSIONS

The use of a NF-40 membrane in the concentration of raspberry juice extract was more efficient in removing water from the feed juice than the FT-30 membrane, but the resulting concentrate was poorer in sugar and soluble solids content. Further experimentation should be done using a larger membrane area and more powerful equipment to allow for a wider range of operating pressures.

The tests done with the second press raspberry juice to assess the most efficient way of recovering sugars, soluble solids and pigments from the press cake, showed that the cake should be washed with twice its weight of water before the concentration process. The addition of food grade citric acid to the press cake in the ratio of 2 % of the initial press cake weight will improve pigment recovery and will thus enhance the coloration of the recovered juice. The FT-30 membrane used in the concentration of second press juice proved to be effective in retaining sugars, soluble solids, and pigments.

Finally, the incorporation of second press juice in the formulation of raspberry juice concentrate seems feasible. The tests conducted in the laboratory demonstrated that a formula involving 93 % raspberry juice extract and 7 % second press juice is quite satisfactory. More extensive studies should be done in this area. Frozen storage testing of the concentrate and more extensive sensory testing of the resulting beverage should be undertaken.

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Appendix I. Refractive Index and Total Soluble Solids for the Standard Solutions Of the Dilution Effect Experiment.

Dextrose (g)	150 mL H_2O + 0.2g Ac.		100 mL H_2O + 0.2g Ac.	
	RI	TS	RI	TS
0.0	0.0	0.06	0.0	0.09
2.5	2.0	1.87	2.5	2.72
3.5	3.0	1.87	3.5	3.69
5.5	4.0	2.47	5.5	5.72
7.5	5.5	5.18	7.0	7.71

RI - Refractive Index in g/L of sucrose.
TS - Total Soluble Solids in % (w/w).
Ac.- Citric Acid Added.

Appendix II. Refractive Index and Total Soluble Solids Values of the Standard Solutions for the Effect of Citric Acid Addition Experiment.

Dextrose (g)	0.2g		0.5g		1.0g	
	RI	TS	RI	TS	RI	TS
0.0	0.0	0.09	0.0	0.41	0.5	0.97
2.5	2.5	2.72	3.0	2.85	3.5	3.35
3.5	3.5	3.69	4.0	3.86	4.5	4.27
5.5	5.5	5.72	6.0	5.75	6.0	6.23
7.5	7.0	7.71	7.5	7.68	8.0	8.22

RI - Refractive Index in g/L of Sucrose.
TS - Total Soluble Solids in % (w/w).

Appendix III. Refractive Index and Total Soluble Solids for the Type of Sugar Used Experiment.

Sugar (g)	Dextrose		Fructose	
	RI	TS	RI	TS
0.0	0.5	0.97	0.5	0.94
2.5	3.5	3.35	3.0	3.22
3.5	4.5	4.27	4.5	4.14
5.5	6.0	6.23	6.0	5.92
7.5	8.0	8.22	8.0	7.71

RI - Refractive Index in g/L of Sucrose.
TS - Total Soluble Solids in % (w/w).