

**DEVELOPMENT OF TECHNOLOGY FOR THE
PRODUCTION OF STABLE HIGH MOISTURE
DRIED FRUIT**

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DECLARATION

I, the undersigned hereby declare that the work contained in this thesis is my own original work and that I have not previously, in its entirety or in part, submitted it at any university for a degree.

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ABSTRACT

Dried fruit is a well-known food product that has been produced for many years. The product characteristics have remained constant throughout this time with a moisture content of *ca.* 18 - 26% (m/m). However, in recent times there has been a definite trend towards a final dried fruit product in the intermediate moisture range with a moisture content of *ca.* 36%. The high water activity (a_w) of the product (*ca.* 0.85) makes the product susceptible to microbiological spoilage and the product therefore requires a subsequent pasteurisation step to ensure a safe product. A further consequence of the increased moisture content, higher a_w and the temperature of the pasteurisation step, is the increased rate of non-enzymatic browning reactions. Currently the shelf life is only 15 weeks while a minimum shelf life of 30 weeks is required to enable product export.

Moisture sorption isotherms may be used to depict the relationship between moisture content and a_w . Moisture sorption isotherms were thus determined for Royal type apricots and nectarines at 25° and 40°C. Samples, equilibrated at relative humidities in the range of 11-97%, were obtained using saturated salt solutions and a static gravimetric method. Isotherms were found to be of type I, typical of dried fruit. Six mathematical models namely; BET, GAB, Iglesias and Chirife, Halsey, Henderson, and Chung and Pfost, were fitted to experimental data. The GAB model predicted the a_w of both apricots and nectarines the best at 25° and 40°C with the Henderson equation second best in all instances. The binding energy, as a function of moisture content, was calculated to determine energy requirements for drying. At low moisture contents (< 20%) an increase of energy was required for drying.

Discolouration of macerated dried Royal type apricots and nectarines during accelerated storage as affected by moisture (32, 36, and 40%, m/m) and sulphur dioxide (SO₂) content (2500, 3000 and 3300 mg.kg⁻¹ for apricots; 1800, 2200 and 2600 mg.kg⁻¹ for nectarines) was investigated. The macerated samples were stored at 30°, 40°, 50° and 60°C. Colour was quantified in terms of the L* value of the CIELab system (used throughout the study). Moisture and SO₂ contents affected both the initial fruit colour and the rate of discolouration. The highest L* values, i.e. lightest fruit colour, were obtained for fruit at 40% moisture content and the highest SO₂ levels. Increasing storage temperature accelerated the loss of moisture and SO₂.

The influence of a 10°C increase in storage temperature on the rate of browning and thus shelf life was described in terms of the Q_{10} value. Q_{10} and a_w values of apricots ranged from 1.96 - 2.47 and 0.833 - 0.890, respectively, while Q_{10} values of 1.50 - 4.61 and a_w values of 0.844 to 0.890 were obtained for nectarines.

Discolouration of dried nectarine halves during accelerated storage at 40°C as affected by rehydration method, moisture content, packaging atmosphere and pasteurisation method, was investigated. The fruit halves were rehydrated using three different methods to obtain moisture contents of 36 and 40%, respectively. Dry heat and steam pasteurisation techniques were used to render a microbiologically safe product. Commercial packaging material was used and the atmosphere was modified with CO₂ to lower the O₂ concentration in the headspace. A two-step rehydration at 45°C, steam pasteurisation at 90°C for 150 minutes and packaging under a high CO₂ atmosphere rendered a product with the best colour retention under accelerated storage conditions of 40°C for eight weeks.

To confirm the results obtained with accelerated storage at temperatures that the product would normally be retailed at, shelf life tests were also performed at 5° and 25°C. Discolouration of whole dried Royal type apricot and nectarine halves as affected by rehydration method, moisture content, packaging atmosphere and pasteurisation method was investigated. The methodology for rehydrating, pasteurising and packaging the high moisture dried fruit developed in this study was compared against the standard method used by the industry. The new processing method increased shelf life. Samples were stored for a period of 30 weeks and were tested every five weeks to determine CO₂ concentration in headspace, colour retention and SO₂ concentration of the fruit. Both apricots and nectarines achieved a shelf life of 30 weeks at both storage temperatures and an extrapolated shelf life of 89 weeks at 5°C, but only 32 weeks at 25°C.

UITREKSEL

Droë vrugte is 'n welbekende voedselprodukt en word reeds vir baie jare vervaardig. Die produkeienskappe het konstant gebly gedurende hierdie tydperk met 'n produkvooghoud van *ca.* 18 - 26% (m/m). Daar is egter 'n tendens die afgelope tyd na 'n finale produk in die intermediêre voggebied met 'n voginhoud van *ca.* 36% en 'n water aktiwiteit (a_w) van *ca.* 0.85. Hierdie verandering in voginhoud en a_w maak die produk vatbaar vir mikrobiologiese bederf, en gevolglik word pasteurisasie benodig om dit te preserveer. 'n Verdere gevolg van die verhoogde voginhoud en a_w en die hoë temperatuur van pasteurisasie, is die verhoogde tempo van nie-ensiematiese verbruiningsreaksies. Huidig is die produk se rakleef tyd 15 weke terwyl 'n minimum van 30 weke benodig word om hierdie produk suksesvol uit te voer.

Vogsorpsie-isoterme kan gebruik word om die verwantskap tussen voginhoud en a_w uit te beeld. Vogsorpsie-isoterme van Royal tipe applekose en nektariens is gevolglik bepaal by 25° en 40°C. Monsters, geëkwilibreer by relatiewe humiditeite van 11 - 97%, is verkry deur gebruik te maak van versadigde soutoplossings en 'n statiese gravimetriese metode. Tipe I isoterme, wat tipies van droëvrugte is, is verkry. Ses wiskundige modelle naamlik; BET, GAB, Iglesias en Chirife, Halsey, Henderson, en Chung en Pfoest, is gepas op die data. Die GAB model het die a_w van beide applekose en nektariens by 25° en 40°C die beste voorspel en die Henderson model die tweede beste in al die gevalle. Die bindingsenergie as 'n funksie van voginhoud is bereken om die energie vereistes van droging te bepaal. By lae voginhoud ($< 20\%$) is 'n skerp styging in benodigde energie waargeneem.

Die verkleuring van gemaalde gedroogde Royal tipe applekose en nektariens gedurende versnelde opberging en die invloed van voginhoud (32, 36, en 40%, m/m) en swaweldioksied (SO_2) konsentrasie (2500, 3000 en 3300 mg.kg^{-1} vir applekose; 1800, 2200 en 2600 mg.kg^{-1} vir nektariens) is ondersoek. Die gemaalde monsters is gestoor by 30°, 40°, 50° en 60°C. Kleur is gekwantifiseer in terme van L^* waardes van die CIELab sisteem (ook gebruik vir daaropvolgende ondersoeke). Vog en SO_2 het albei die aanvanklike kleur asook die tempo van verbruining beïnvloed. Die hoogste L^* waardes, d.i. die ligste kleur, is verkry vir die monsters met 40% voginhoud en die hoogste SO_2 vlakke. Verhoogde temperatuur tydens opberging het aanleiding gegee tot verhoogde verliese van vog en SO_2 . Die invloed van 'n 10°C

verhoging in opbergingstemperatuur op die tempo van verbruining en dus rakleef tyd, word beskryf in terme van Q_{10} waardes. Q_{10} en a_w waardes van die appelkose het gestrek van 1.96 – 2.47 en 0.833 – 0.890, onderskeidelik, terwyl Q_{10} waardes van 1.50 – 4.61 en a_w waardes van 0.844 tot 0.890 verkry is vir die nektariens.

Verkleuring van gedroogde nektarien halwes gedurende versnelde opberging by 40°C en die invloed van rehidrasie metode, voginhoud, verpakkingsatmosfeer en pasteurisasie metode is ondersoek. Die vrughalwes is gerehidreer deur middel van drie metodes om die voginhoud te verhoog tot 36 en 40%, onderskeidelik. Droë hitte en stoompasteurisasie metodes is gebruik om 'n mikrobiologiese veilige produk daar te stel. Kommersiële verpakkingsmateriaal is gebruik en die CO_2 konsentrasie van die atmosfeer in die verpakking is verhoog om die invloed daarvan te bepaal. 'n Twee-stap-rehidrasie by 45°C, stoompasteurisasie by 90°C vir 150 minute en 'n hoë CO_2 atmosfeer het aanleiding gegee tot die monster met die beste kleurbehoud tydens versnelde opberging by 40°C vir agt weke.

Om die resultate, verkry met die versnelde rakleef tyd studie, te bevestig by temperature waarby die produk normaalweg blootgestel sal word tydens kleinhandel, is 'n rakleef tyd studie uitgevoer by 5° en 25°C. Verkleuring van heel gedroogde Royal tipe appelkoos en nektarien halwes, die invloed van rehidrasie metode, voginhoud, verpakkingsatmosfeer en pasteurisasie metode is ondersoek. Die metodiek vir die rehidrasie, pasteurisasie en verpakking van hoë vog droëvrugte ontwikkel in hierdie studie, is getoets teen die standaardmetode wat deur die industrie gebruik word. Die nuwe prosesseringsmetode het aanleiding gegee tot 'n langer rakleef tyd. Monsters is opgeberg vir 'n tydperk van 30 weke om die rakleef tyd te bepaal. Die CO_2 konsentrasie in die pakkie, kleurbehoud en SO_2 konsentrasie van die vrugte is elke vyf weke getoets. Beide appelkose en nektariens het 'n rakleef tyd van 30 weke by albei opbergingstemperature behaal, terwyl 'n ekstra-gepoleerde rakleef tyd van 89 weke by 5°C en 32 weke by 25°C behaal is.

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The language and style used in this thesis are in accordance with the requirements of the *International Journal of Food Science and Technology*. This thesis represents a compilation of manuscripts where each chapter is an individual entity and some repetition between chapters has, therefore, been unavoidable.

Chapter 1

Introduction

The South African dried fruit industry produces raisins, prunes and dried apricots, pears, peaches and apples, as well as other processed products like fruit candies and high moisture dried fruit. With annual sales of up to 1 billion Rand (40 000 tons) of which 70% of the Rand value is returned to the industry, the dried fruit industry plays a major role in die local economy by creating revenue and jobs in rural areas (D. Smit, 2000, Dried Fruit Technical Services, personal communication). South African Dried Fruit (SAD) processes about 75% of the total annual production and can be considered to be the major processor of dried fruit in South Africa.

In the past only the traditional dried fruit with moisture contents of 19-22% were available to the South African and international consumer, but over the last few years there has been a trend to a softer, more palatable product with a relatively high moisture content. In developed countries, this is the only sector of the dried fruit market that is growing. Therefore, it became necessary for the South African dried fruit industry to develop and implement this technology (J. Schoeman, 1999, SAD, personal communication). Consequently, a high moisture “ready-to-eat” product, packed in attractive laminated aluminum stand-up pouches, was introduced to the South African market at the end of 1998. These so-called “ready-to-eat” products with a relative high moisture content of 36% and high water activity in the range of 0.83-0.89, can be classified as intermediate moisture foods (El-Halouat *et al.*, 1998). These high levels of moisture and subsequent water activity (a_w) presented major problems, in the form of non-enzymatic browning, for the processor of some products, e.g. nectarines. Non-enzymatic browning reaction (Maillard reaction) caused excessive browning. South African produced apricots also have a high tendency to undergo browning (Joubert *et al.*, 1999). To overcome the browning problem, Malatya apricots were imported from Turkey. These apricots do not undergo browning as easily than the local Royal type apricot (J. Schoeman, 1999, SAD, personal communication). Unfortunately the costs of importing these Malatya apricots make the final product too expensive compared to the local product. Present

processing techniques should, therefore, be adapted to allow the successful processing of South African apricots and nectarines.

Production of these high moisture dried fruit consists of rehydrating, resulphuring, packaging and pasteurisation (J. Schoeman, 2000, SAD, personal communication). Very little (McBean & Wallace, 1967) has been reported on rehydration or pasteurisation of dried fruit. McBean & Wallace (1967) rehydrated apricots with 12-16% moisture content to 22% by subjecting the dried fruit to an aqueous dipping or spraying treatment. Such a process can, if metabisulphate is added to the water, also be used to increase the sulphurdioxide (SO₂) content of the dried fruit, but locally produced fruit are resulphured after dipping by means of fumigation.

Packaging needs to be attractive, but strong enough to withstand pasteurisation, which is currently being done in a warm air tunnel. Pasteurisation is necessitated by the high water content and subsequent high a_w that gives rise to a microbiologically unstable product. However, this heat treatment accelerates unacceptable non-enzymatic browning and thus shortens the shelf life of the product. High moisture dried fruit products prepared from nectarines are exceptionally sensitive to excessive heat treatment. An effective pasteurisation technique or combination treatment is needed to obtain a microbiologically stable product that also has good retention of colour for an extended period (i.e. 9 months) to allow marketing overseas, for instance Europe.

With the development of a high moisture content dried fruit product the water activity is arguably the most important factor in controlling shelf life. It is generally accepted that a_w is more closely related to the physical, chemical and biological properties of foods than its total moisture content. Specific changes in colour, aroma, flavour, texture stability and acceptability of processed dried fruit has been associated with relatively narrow a_w changes (Rockland & Nishi, 1980). Product a_w and storage temperature generally can be used to control non-enzymatic browning (Labuza & Saltmarch, 1981), which is largely responsible for colour deterioration of dried fruit (Ames, 1990).

The main objectives of this study were to develop a production process for high moisture dried nectarines and Royal apricots that would lead to a stable product with an extended shelf life of at least 6 months. This were done by determining the relationship between water activity and moisture content of dried nectarines and

apricots in the form of moisture sorption isotherms. Accelerated storage trails were used to study the effect of moisture content, water activity, SO₂ content and storage temperature on the shelf life of the product in terms of colour retention. Different rehydration and pasteurisation techniques and modification of the atmosphere inside the packaging were evaluated to determine the effect on colour retention through the use of accelerated storage studies. These studies were concluded with an extended storage period at normal storage temperatures to verify the changes introduced to the current process used by the industry.

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Chapter 2

Literature review

Introduction

The processing, preservation and analysis of intermediate moisture foods in specific relation to high moisture dried fruits will be discussed in this review. The importance of water activity (a_w) for product stability and prevention of non-enzymatic browning and their role in dried fruit quality will also be discussed. Lastly, the literature review will cover the physical properties of the final product, i.e. texture and colour as factors that will influence the choice of the consumer. Since this study did not primarily concern itself with the microbiological aspects of the product, there will be no discussion on this issue. Microbiological stability of high moisture content dried fruit is the subject of a parallel study (S. Engelbrecht, Department of Food Science, University of Stellenbosch, personal communication) being undertaken in conjunction with the study described in this thesis.

Dried fruit

Traditional dried fruit are produced in South Africa by sun drying to a final moisture content (wet basis) of less than 20% (m/m), but preferably to 18% or even less. The fruit are sold to the market at moisture contents of 20% - 28%. This translates to an a_w of between 0.56 and 0.68. Table 1 gives a summary of moisture contents of different dried fruit with their corresponding a_w 's. The SO_2 content of this traditional dried fruit should range between 1200 – 2500 ppm (Anonymous, 1996). A demand for softer and less tough dried fruit paved the way for intermediate moisture dried fruit that has a moisture content of about 36% (wet basis) and an a_w of between 0.82 and 0.86 (J. Schoeman, SAD, personal communication). This form of dried fruit will from now on be referred to as intermediate moisture dried fruit or soft-eating dried fruit.

In South Africa the market opportunity for a soft, moist dried fruit product was realised by SAD and a product range was launched in 1998. Although this product

range is fairly successful on the South African market, certain products need further research. The nectarines have a shelf life of three months, or less, in contrast with the six months of the rest of the product range. The apricots currently being used are imported from Turkey, because of its superior colour stability and texture. However, rising import costs are forcing SAD to switch to the local Royal apricot cultivar. This cultivar is not as resistant to colour degradation and adaptation of technology currently being used, is needed (J. Schoeman, SAD, personal communication).

Table 1. Moisture content and water activity of traditional South African dried fruits.

Fruit	Moisture content (%) (Range)	a_w (Range)
Apricots (Royal type)	17.34-18.99	0.54-0.64
Peaches (Elberta)	16-18	0.64-0.66
Pears (Bon Cheretin)	16-20	0.57-0.63
Sultanas (OR)	9.95-18.05	0.53-0.71

Joubert, E. (1997)

Development of intermediate moisture foods (IMF)

The development of intermediate moisture foods requires a pragmatic approach. In the last three to four decades a great deal of time and money has been invested in the development of technology to produce such foods. Despite all this attention IMF have not lived up to its expectations. Examples of IMF products in use are restricted to defence and space programs and pet foods. The reason for this slow development of new products is blamed on a lack of strategic planning (Brimelow, 1985).

With the development of a new IMF product the following questions should be asked (Brimelow, 1985):

- How feasible is the product idea?

- **What is the a_w range of the product?**
- What is the proposed packaging system?
- How will it be manufactured?
- **How will quality be assured?**

When these questions are considered, in relation to the intermediate moisture dried fruit product currently produced in South Africa, two aspects stand out, namely the a_w of the product and quality assurance. In the first instance, the a_w of the product makes it susceptible to quality deterioration due to browning and microbial spoilage amongst others. Secondly, addition of new product ranges have not been proven to maintain their quality for the total shelf life periods and could therefore impact negatively on the perceived quality of this value-added product should problems arise (J. Schoeman, SAD, personal communication).

Feasibility

Probably the biggest reason for the failure of some new IMF products is that the market never wanted such products at the time. Figure 1 gives a simplified decision pathway to determine the feasibility of a new product.

Water activity

Deciding on the water activity range of the product is the next important step in the development of IMF. This will influence the type of product and the microbiological, chemical and physical stability.

Water activity plays the central role in the primary problems, i.e. growth of food spoilage micro-organisms and non-enzymatic browning, confronting the development of intermediate moisture foods (Bone, 1973). Other quality characteristics of food that are influenced by changes in a_w value are the sensory characteristics such as colour, smell and taste; the stability of the composition; the reaction to ambient humidity and temperature; the solubility of the texture, and the durability (Hattingh, 1995). Humectants such as glycerol and even sugars can lower the a_w in a specific food product (Ames, 1990).

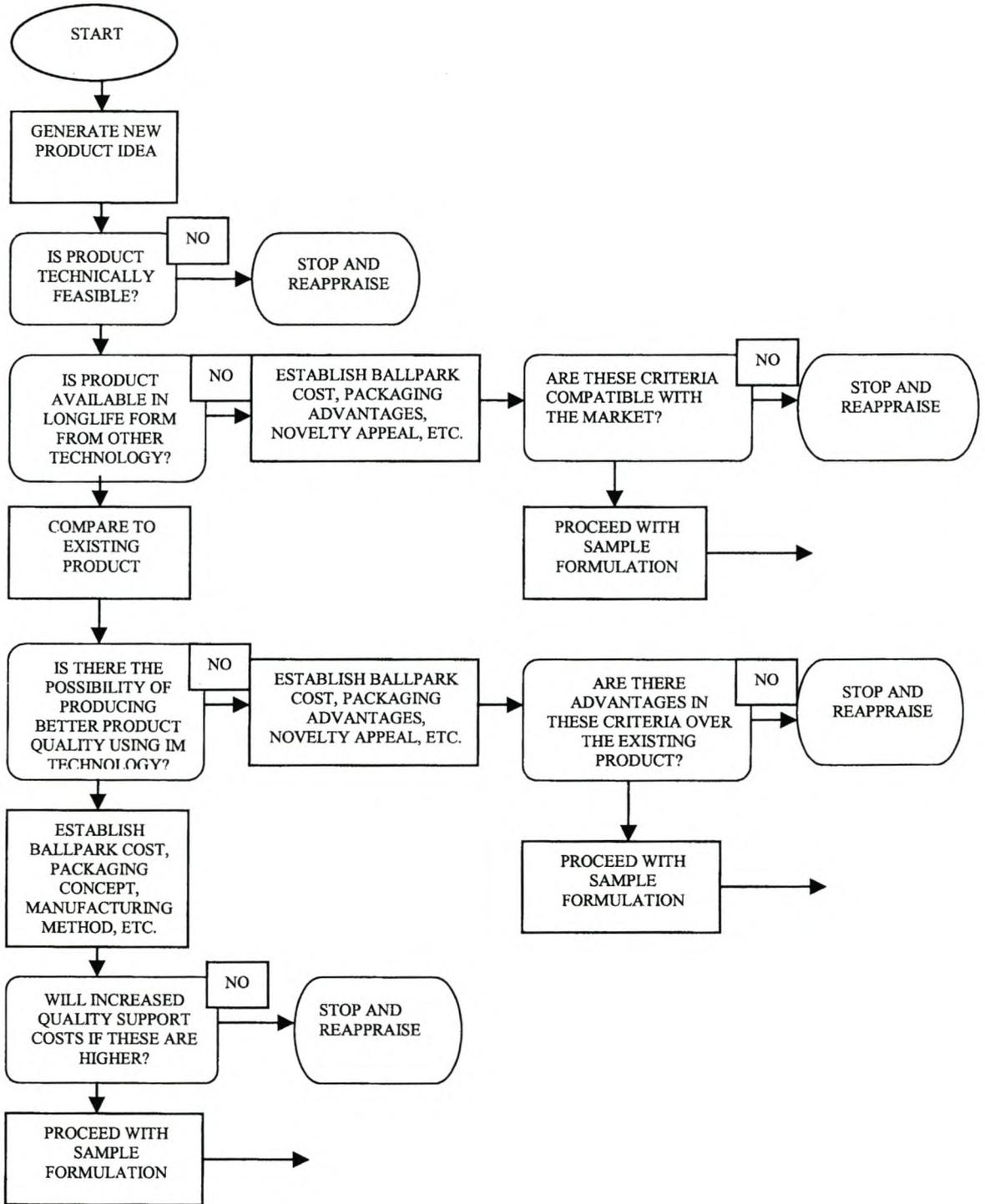


Figure 1. Schematic IMF feasibility decision pathway (adapted from Brimelow, 1985).

Maximum browning occurs in most foods between a_w 0.3 and 0.7, depending on the type and specific composition of the food. At higher water activities the decrease in reaction rate has generally been attributed to dilution of the reactants (Eichner & Karel, 1972).

Traditional IMF's with a water activity of between 0.65 and 0.90 and moisture contents of between 10 and 40% are usually divided into three classes: those consumed "as-is", those that need dehydration and those that need rehydration. The "as-is" product is obviously the most convenient of the three, since it needs no further preparation (Brimelow, 1985).

It is important to note that it is mostly not sufficient to use reduced water activity alone to preserve food. There are significant advantages in a combined factor approach generally known as hurdle technology. The use of anti-oxidants, mixed humectants, blocking agents and preservatives are usually required in conjunction with low water activity (Brimelow, 1985).

Packaging

At the same time as deciding on the product formulation and the a_w range of the product, the packaging specification and format should also be considered. Although there will be individual requirements for each product, there is a common checklist of packaging criteria (Brimelow, 1985):

- The package must ensure the required shelf life by providing sufficient barrier against oxygen, moisture and light;
- The package must be capable of being filled successfully with product at the desired throughput;
- The package must provide a sufficient degree of protection against handling or mishandling damage;
- The package should be attractive and satisfy market requirements; and
- The package should be low in cost.

Manufacturing

Methods of manufacture of IMF may be divided into three types (Brimelow, 1985):

- Moist infusion, also known as desorption processing, in which full moisture food particles are soaked or cooked in a solution of humectants to obtain a product with the target water activity;
- Dry infusion, in which food pieces are dehydrated before soaking in a solution of humectants; and
- Blending, in which a mixture of dry and full moisture ingredients are blended in the required proportions to give the target a_w .

There are also variations and combinations to the methods mentioned above and there are certainly problems inherent with all of them. Great care should be taken to choose a method or combination of methods to produce a satisfying and safe product (Brimelow, 1985).

Quality assurance

Some of the possible requirements of a quality assurance (QA) scheme for an IMF product can be listed as follows (Brimelow, 1985):

- Control of the humectant infusion solution composition, if applicable;
- Monitoring of the a_w of certain key ingredients, directly or indirectly, if applicable;
- Monitoring of product a_w , directly or indirectly, at every stage of a multi-stage process; and
- Other QA checks which are normal for any product (weight control, pack integrity, storage checks, etc.).

The essence of a good QA scheme is the ability to be able to check rapidly the quality of the product (Brimelow, 1985). In this respect the situation with regard to high moisture dried fruit is not very good, for there are still no rapid methods for direct monitoring of a_w (Brimelow, 1985).

McBean & Pitt (1965) were responsible for some of the earlier work done on the subject of high-moisture dried fruit in 1965. They rehydrated prunes by placing it in boiling water for 15-25 min. to reach moisture contents of up to 37%. Although the whole line was filled with steam, the packed pouches needed subsequent heat treatment to ensure that the product became commercially sterile.

Water activity

Water activity can be defined as the measure of the freedom of water in a hygroscopic product (Labuza, 1968; Rockland, 1969; Van den Berg, 1986; Hattingh, 1995).

Water activity (a_w) is the most frequently used concept of expressing the reactivity of water in food and is expressed as:

$$a_w = \frac{P_{eq}}{P_o}$$

Where, P_{eq} represents the partial vapour pressure of water in equilibrium with the solution and P_o the vapour pressure of pure water at the same conditions of temperature and atmospheric pressure (Troller, 1993).

The a_w value is determined by the relative humidity inside a product which, in return, is determined by the partial water vapour pressure on the surface of a product. The actual a_w value will depend on the composition, the temperature and the water content of a product. The chemical composition will determine with what force the water molecules will be bound. Strongly bound water molecules will have a negative effect on a_w since those molecules will not readily react with other molecules because of their inhibited movement (Troller, 1993). A high temperature translates to higher kinetic energy for the water molecules and will cause a higher a_w due to the higher mobility (Hattingh, 1995).

Measurement of a_w

Water activity can be measured by several different methods, which include measuring the vapour pressure (manometry), freezing point depression, boiling point elevation, psychrometric evaluations, suction potential, or by using the isopiestic method, bithermal equilibrium, electric hygrometers, and hair hygrometers (Barbosa-Cánovas & Vega-Mercado, 1996).

Vapour pressure

The a_w of a product is directly related to the water vapour pressure that a product would exert in a closed atmosphere at a constant temperature. Therefore a_w can be measured by water vapour pressure using a vapour pressure manometer. This

method has relatively high precision and is inexpensive, but the glass manometer is fragile and unable to measure over a wide range of vapour pressure (Barbosa-Cánovas & Vega-Mercado, 1996).

Freezing point depression and boiling point elevation

A_w can be determined by measuring the freezing point depression or the elevation in the boiling temperature of solutions, relative to that of pure water. However, this method can only be used with solutions and not with solid foods (Barbosa-Cánovas & Vega-Mercado, 1996).

Dew point hygrometer

The dew point of a product is measured and related via a psychrometric chart to the relative humidity and a_w . This method cannot measure the change in a_w due to the slow release of water vapour from fatty products. Measurements are also time-consuming (Barbosa-Cánovas & Vega-Mercado, 1996).

Thermocouple psychrometer

Water activity is measured based on wet bulb depression. A thermocouple is cooled in the chamber where the sample is equilibrated, and the water is condensed over the thermocouple. Once the thermometer is wet, the water is allowed to evaporate, causing a decrease in temperature. The drop in temperature is related to the rate of water evaporation from the surface of the thermometer, which is a function of the relative humidity in equilibrium with the sample (Barbosa-Cánovas & Vega-Mercado, 1996).

Isopiestic methods and graphic interpolation

The isopiestic method consists of equilibrating both a sample and a reference material in an evacuated desiccator for 24 h at 25°C. The moisture content of the reference material is then determined and the a_w obtained from its sorption isotherm. Because the sample was in equilibrium with the reference material, the a_w of both would be the same (Barbosa-Cánovas & Vega-Mercado, 1996).

Hair hygrometry

This procedure is based on the ability of human or animal hair to stretch when hydrated. Early measurements were achieved by means of a container with a human hair attached to a mechanical dial. As the hair stretched the dial would indicate the a_w . This method is, however, time consuming and a single measurement can take as long as 8 hours (Barbosa-Cánovas & Vega-Mercado, 1996).

Electric hygrometry

The electric hygrometer uses the ability of water adsorbing and desorbing material to change its resistance electrically. The sensors can be either electrolytic or capacitive. The sensor must show no hysteresis otherwise the instrument will give inaccurate results. This instrument is easy to use and calibrate and is very accurate. It is, however, very expensive (Barbosa-Cánovas & Vega-Mercado, 1996). Stekelenburg & Labots (1991) investigated the specific problems arising from the use of an electric hygrometer (type EEJA-6, Novasina Ltd, Zürich, Switzerland). They concluded that this instrument enables a simple, rapid and reliable measurement of a_w if some precautions are taken. The a_w value is taken only when it has been constant for 10 min. The humidity sensors must be calibrated regularly to compensate for drift. Separate calibration curves must be made for each sensor. Sensors must be calibrated at the same temperature at which the samples are measured. The a_w must be measured in duplicate and there must not be a difference of more than 0.005-0.010 units. Differences in temperature between sample and sensor should always be avoided because of possible formation of condensate.

Water potential

The instrument to measure water potential consists of a porous cup or membrane that is permeable to water and solutes, but not to air and macromolecules. The cup is filled with water and connected to a manometer or vacuum gauge so that the suction potential can be measured (Barbosa-Cánovas & Vega-Mercado, 1996).

Moisture sorption isotherms

In effect, water activity and water content are two very different entities. The former has already been defined while the latter is the total amount of water both free and

bound, that is present in food (Troller, 1993). Food moisture sorption isotherms are graphical representations of the amount of water sorbed at equilibrium as a function of water activity (Iglesias & Chirife, 1983).

Moisture sorption isotherms usually exhibit a sigmoid shape (Figure 2) and two distinct curves exist, depending on whether the data were obtained by desorption or adsorption of moisture (Puiggali, 1993).

In the past the terms adsorption, desorption and sorption were used to describe different things. According to Iglesias & Chirife (1983) the term adsorption refers to the gaining of weight, desorption refers to the loss in weight and sorption refers to an isotherm where some points are obtained through adsorption and the other points were obtained through desorption.

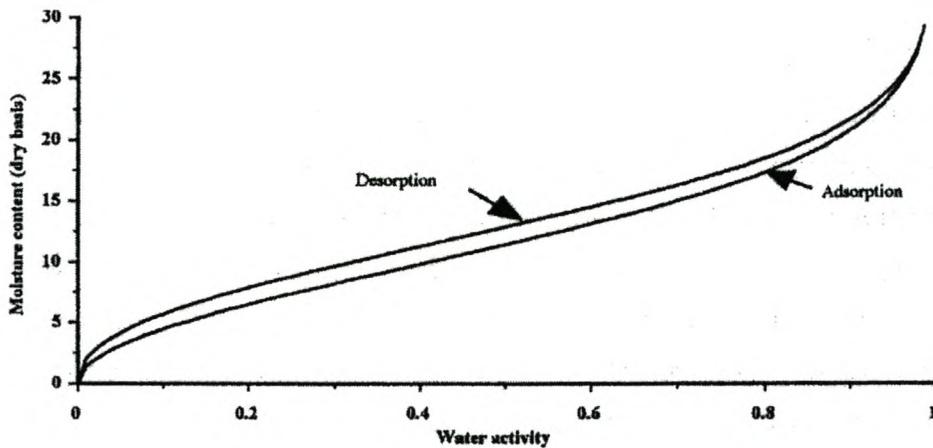


Figure 2. Typical moisture sorption isotherm with hysteresis (Hansmann, 1996).

Toledo (1994) stated that the curve could be divided into three zones depending on the mechanism for water sorption. Zone A, extending from *ca.* 0 to 0.45 a_w represents monolayer adsorption and this region has no free water. In zone B, extending from *ca.* 0.45 to 0.75 a_w , water is held in the solid matrix by capillary adsorption. In this region water may still exist in the liquid phase. Zone B shows maximum stability for dried fruits. Zone C extends above 0.75 a_w and insoluble solids do not influence water activity to any significant effect in this region. Water activity is only dependant on the solute and water content of the sample.

The difference in desorption and adsorption curves is termed hysteresis (Labuza, 1968). A wide variety of hysteresis loop shapes are observed in foods. In high sugar, high pectin foods (for example air-dried apple) hysteresis is restricted to the lower moisture content region. Although hysteresis is large for this type of product, no hysteresis is exhibited above a_w 0.65. In high protein foods (for example freeze-dried pork) hysteresis begins in the high a_w region and extends down to zero a_w . In starchy foods (for example freeze-dried rice) a large hysteresis loop is exhibited with a maximum effect at 0.70 a_w (Kapsalis, 1987).

Temperature exerts a relative large effect on hysteresis. At low temperature the hysteresis effect is increased, and is reduced as temperature increases, until at about 80°C where no hysteresis effects is found (Van den Berg, 1986). It is also widely accepted that an increase in temperature results in decreased equilibrium moisture content. It is important to keep the effect of hysteresis in mind, since a_w may differ at the same moisture content under different conditions (adsorption or desorption) (Hill & Rizvi, 1982). The importance of moisture sorption isotherms is discussed later in this review.

Methods for the determination of moisture sorption isotherms

There are three principal methods for determining moisture sorption isotherms (Iglesias & Chirife, 1983):

- Gravimetric
- Manometric
- Hygrometric

Gravimetric

The gravimetric method can be divided into methods with continuous registration of mass changes and methods with discontinuous registration of mass changes (Iglesias & Chirife, 1983).

The continuous measurement of mass change is achieved through a balance that is a fixed part of the apparatus. This method is usually carried out in an evacuated system to accelerate diffusion of water molecules from the reservoir to the sample. This method can also be a dynamic system where circulated air is the carrier for the transfer of water vapour to and from the sample. Precise weightings are possible at a constant air flow rate around the sample (Iglesias & Chirife, 1983).

The discontinuous methods have no balance as a fixed part of the apparatus and can also be a static or a dynamic system. The static system is the most commonly used method. The material is placed in vacuum desiccators (or closed jars) containing saturated salt solutions or sulphuric acid solutions at different concentrations, which give a certain equilibrium relative humidity. Data for the equilibrium relative humidities at different salt solutions are available (Table 2) (Labuza *et al.*, 1976; Troller & Christian, 1978; Mazza *et al.*, 1994). A vacuum may be created to accelerate equilibrium (Iglesias & Chirife, 1983). With a dynamic system an air stream of known relative humidity is forced to pass over the sample (Iglesias & Chirife, 1983).

Table 2. The relative humidity values for a variety of salts at different temperatures.¹

Salt	2°C	10°C	25°C	40°C	55°C
LiCl	11	11	11	11	11
CH ₃ COOK	23	23	23	22	21
MgCl ₂	34	34	33	32	30
Mg(NO ₃) ₂	60	57	53	48	45
CuCl ₂	65	68	67	67	67
NaCl	76	76	75	75	74
KCl	88	87	84	82	81
KNO ₃	96	96	94	89	84

¹ Adapted from Mazza *et al.* (1994).

Manometric

The vapour pressure of water in equilibrium with a food at a given moisture content is measured by a sensitive manometric device (Iglesias & Chirife, 1983). The principles of this method were discussed earlier.

Hygrometric

The equilibrium relative humidity of a small amount of air in contact with a food at a given moisture content is measured by a hygrometer device. Dew point or electric hygrometers are frequently used (Iglesias & Chirife, 1983). The principles of this method were discussed earlier.

Mathematical description of isotherms

Equations for fitting moisture sorption isotherms in foods are of special interest in many aspects of food preservation by dehydration. Among them are the predictions of drying times, the shelf life of a dried product in a packaging material, or equilibrium conditions, after mixing products with various water activities. In addition to practical considerations, the isotherm equation is also needed for evaluating the thermodynamic functions of the water sorbed in foods. This means that the adsorption and desorption behaviour of water under different temperature conditions can be evaluated (Iglesias *et al.*, 1976). Labuza (1968) has pointed out the need for mathematical models in order to use the isotherm with computer techniques to solve the type of problem mentioned above (Iglesias & Chirife, 1983).

Several mathematical equations have been reported in the literature for describing moisture sorption isotherms of food materials (Karel, 1973). Each model, empirical, semi - empirical or theoretical, has had some success in reproducing equilibrium moisture content data. However, none of these have been able to give accurate results throughout the whole range of water activity. This is mainly because moisture sorption isotherms of food products represent the integrated hygroscopic properties of numerous constituents, and the depression of water activity is due to a combination of factors, each of which may be predominant in a given range of water activity (Karel, 1973).

Chirife & Iglesias (1978) have compiled and discussed most of the isotherm equations that have been reported in the literature. Göğüş *et al.* (1998) listed the six

equilibrium isotherm equations most frequently used to fit experimental data. These equations are listed in Table 3.

However, these equations cover a wide range of food products and do not necessarily fit the data acquired from dried fruit very well. Ayranci *et al.* (1990) investigated the moisture sorption isotherms of dried apricot, fig and raisins at 20°C and 36°C. The Iglesias & Chirife, Halsey, BET and GAB equations (Table 3) were tested to correctly predict the data. The authors found that the GAB model described the moisture sorption isotherms for dried apricot at 20°C and 36°C and of raisins at 20°C the best.

Table 3. Mathematical models most frequently used to fit the experimental data for the prediction of a_w .

Model	Equation	Reference
BET	$\frac{a_w}{(1 - a_w)} = \frac{1}{M_0 \cdot C} + \frac{(C - 1)}{M_0 \cdot C} \cdot a_w$	Chirife & Iglesias (1978)
GAB	$M = \frac{CKM_0}{[(1 - Ka_w)(1 - Ka_w + CKa_w)]} \cdot a_w$	Mir & Nath (1995)
Iglesias & Chirife	$\ln[M + \sqrt{M + M_{0.5}}] = Ca_w + K$	Chirife & Iglesias (1978)
Halsey	$a_w = \exp\left(-\frac{C}{M^K}\right)$	Lomauro <i>et al.</i> (1985)
Henderson	$(1 - a_w) = \exp(-KM^C)$	Boquet <i>et al.</i> (1978)
Chung & Pfof	$\ln a_w = -\frac{C}{RT} \cdot \exp(-KM)$	Chung & Pfof (1967)

C and K = constants in sorption models; M = moisture content (% dry basis); M_0 = monolayer moisture content (% dry basis); $M_{0.5}$ = Moisture content at $a_w = 0.5$; T = absolute temperature (K); R = Gas constant (8.314 J.mol⁻¹.K⁻¹).

The Halsey equation was best for isotherms of dried fig at 36°C and raisins at 36°C, while the Iglesias & Chirife equation described the isotherm of dried fig at 20°C the best. Tsami *et al.* (1990) also investigated the moisture sorption isotherms of raisins, currants, figs, prunes and apricots. They found that the GAB equation proved

successful in fitting experimental data over almost the entire a_w range from 0 to 0.95. This is in agreement with Lomauro *et al.* (1985) who investigated the moisture sorption isotherm equations of fruit, vegetable and meat products. The GAB model fitted their data for fruits the best. The GAB model gave the best fit for 50% or more of the foods in the fruit category. It can thus be concluded that the GAB model is most satisfactory to fit the data acquired from dried fruits.

Browning reactions

Colour is the most important attribute of appearance, the criteria by which the initial quality of food is judged (MacLaren, 1980). It plays an important role in consumer acceptance of a product and can often account for 40% of the criteria for acceptance (Baardseth *et al.*, 1988). During the production and subsequent storage, dried fruit are susceptible to enzymatic and non-enzymatic browning reactions, which can cause deterioration in quality (Bolin *et al.*, 1985).

Enzymatic browning

Enzymatic browning is the discoloration that results when monophenolic compounds of plants, in the presence of atmospheric oxygen and polyphenol oxidase (PPO), are hydroxylated to o-diphenols, and the latter are oxidised to o-quinones (Mayer & Harel, 1979; Vamos-Vigyazo, 1981; McEvily *et al.*, 1992). Enzymatic browning is important during the production of dried fruit while at high moisture contents. This is not a problem when the fruit are at *ca.* 19% moisture content at which stage the fruit are delivered to storage depots before further processing (E. Joubert, ARC Infruitec-Nietvoorbij, personal communication). Therefore, this review will concentrate on non-enzymatic browning.

Non-enzymatic browning

Dried fruit are susceptible to non-enzymatic browning during storage even at moisture contents of 19% or less. Joubert (1997) demonstrated discoloration of dried apricots, peaches and pears during storage of fruit at moisture contents less than 20%.

According to Wedzicha (1984) non-enzymatic browning reactions include the reaction between reducing sugars and amino compounds, also known as the Maillard reaction (Figure 3). It also includes ascorbic acid browning, caramelisation and lipid browning. A common feature of all these reactions is the participation of carbonyl compounds as the reactive intermediates and the formation of coloured products named melanoidins.

The Maillard reaction limits the shelf life of various dehydrated fruits and vegetables, citrus products and juices (Hodge, 1953; Labuza & Schmidl, 1986; Handwerk & Coleman, 1988). Although browning reactions between reducing sugars and amino acids or proteins (Maillard reaction) are important in many products, browning may also result from sugar degradation (Lee & Nagy, 1988) or from the oxidative degradation of ascorbic acid and further reaction of the carbonyl compounds formed via aldol condensation or reaction with amino groups to yield brown pigments (Kacem *et al.*, 1987; Wong & Stanton, 1989; Löscher *et al.*, 1991). In addition to causing discoloration, non-enzymatic browning reactions also result in destruction of nutrients such as essential amino acids and ascorbic acid, reduced protein digestibility, inhibition of digestive enzymes, and interference with mineral metabolism through metal iron complexation (Namiki, 1988; O'Brien & Morrissey, 1989).

The extent of non-enzymatic browning in foods depends on product composition, e.g. Maillard reaction precursors or ascorbic acid content (Wong & Stanton, 1989; Kennedy *et al.*, 1990), pH (Wedzicha & Goddard, 1988; O'Brien & Morrissey, 1989), water activity (Monsalve *et al.*, 1990), and storage time and temperature (Nagy *et al.*, 1990). Non-enzymatic browning in fruit and vegetable products can be inhibited by refrigeration control or manipulating product water activity to reach levels of minimum browning (Labuza & Saltmarch, 1981).

Water has a dominant effect on the rate of browning in systems that contain carbonyl compounds. Usually, browning increases with water content up to a maximum, which depends on specific conditions. The reaction is rather complex, but increased water content, up to the maximum, causes a shortened induction period to the Maillard reaction and an increase in browning rate. This is mainly due to increased availability and mobility of reactants. The effect on induction time may indicate that formation of pigment has a different pathway at the lower a_w , which

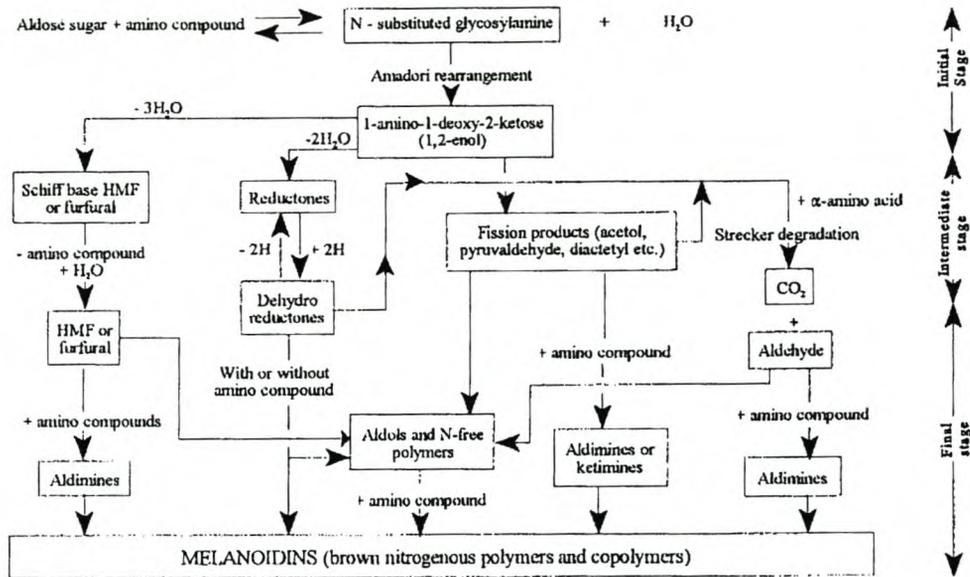


Figure 3. Maillard reaction pathways (Ames, 1990).

The fourth pathway involves trans amination of the Schiff base. The fifth pathway starts with a second substitution of the amino-deoxy-ketose. The final step of the advanced Maillard reaction is the formation of many heterocyclic compounds such as pyrazines and pyrroles (Mauron, 1981).

Brown melanoidin pigments are produced in the final stage of the Maillard reaction. The pigments are formed by polymerisation of the reactive compounds produced during the advanced Maillard reactions, such as unsaturated carbonyl compounds and furfural. The polymers have a molecular weight greater than 1000 and are relatively inert (Leung, 1987).

Factors influencing the Maillard reaction

The most important variables which can be manipulated in order to control the Maillard reaction in a food process, are temperature, time, pH, a_w , type of reactants and availability of reactants (Lingnert, 1990).

- *Temperature*

The temperature dependence of chemical reactions is often expressed as the activation energy, E_A , in the Arrhenius equation:

$$k = k_0 e^{-E_A/RT}$$

Where:

k_0	=	pre-exponential factor
R	=	gas constant in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
T	=	temperature in K
E_A	=	extra energy (activation energy) needed by the reaction component to have a high probability of forming the product (Labuza & Riboh, 1982).

The higher the value of E_A , the more temperature dependent is the reaction rate. Activation energy data for the Maillard reaction have been reported within a wide range, (10-160 $\text{kJ}\cdot\text{mol}^{-1}$), depending on, amongst others, the effect of the reaction that has been measured. The activation energy is highly dependent on water activity, being increased at low water activities (Eichner *et al.*, 1985).

- *pH*

In most cases, the Maillard reaction rate has been found to increase with increasing pH. There is a general increase in colour formation with increasing pH from 4 up to 8 at 100°C and at 110°C. Generally it is considered that the Maillard reaction is favoured by high pH, but even here interactions with other variables have to be taken into account (Lingnert, 1990).

- *a_w*

Since water is produced in the Maillard reaction, the reaction may also be influenced by the water activity (Lingnert, 1990). The rate of the Maillard reaction is generally considered to have a maximum at some intermediate water activity of between 0.3 and 0.7 a_w (Ames, 1990). It has been shown that the water influence is highly temperature dependent, although data on this aspect is very limited. Water activity is undoubtedly an important factor for the Maillard reaction in food

processing, and during dehydration of food the product should pass through the critical a_w range as rapidly as possible to minimise optimal browning conditions (Lingnert, 1990). The browning rate in a sugar-amino system is not simply related to water activity alone. Optimum browning conditions are determined by the amount of water and the state of water binding in a distinct system, and by the mobility of reactants in the system. The maximum browning depends on the extent to which these conflicting influences affect the reaction (Eichner & Karel, 1972).

- *Reactants*

Several model studies on the browning potential of various combinations of sugars and amino acids are reported in the literature (Denehy & Pigman, 1951; Eichner & Ciner-Doruk, 1979; Saltmarsh & Labuza, 1982). In general, pentoses yield stronger colour intensity than hexoses, which in turn are more reactive than reducing disaccharides. The influence of specific reactants is perhaps more interesting in relation to specific effects of the Maillard reaction products i.e. flavour, antioxidative effect, antimicrobial effect and mutagenic effect (Eichner *et al.*, 1985).

Ascorbic acid browning

Under anaerobic conditions L-ascorbic acid is readily decarboxylated and dehydrated to yield 3-deoxypentosulose and furfural (Kurata & Sakurai, 1967). As these products are intermediates in the Maillard browning of pentoses, it can be assumed that the coloured products are similar to Maillard reaction products (Davies & Wedzicha, 1993). The development of colour is enhanced in the presence of amino compounds. Ascorbic acid is unstable in strong acid medium and its stability increases with increasing pH until pH 2.3. Above this pH value increasing pH causes reduced stability until a minimum stability is reached at pH 4.0 (Wedzicha, 1984).

In the presence of oxygen, browning of ascorbic acid proceeds via dehydroascorbic acid. Further reactions involve opening of the lactone ring to yield 2,3-diketo-gulonic acid followed by further degradation reactions, including decarboxylation. The exact course of the reaction at this stage is not clear. Labile, red coloration is also obtained which ultimately lead to brown pigments. Ascorbic

acid is also susceptible to autoxidation catalysed by metal ions. The maximum autoxidation rate of L-ascorbic acid occurs at pH 5 (Wedzicha, 1984).

Caramelisation

Caramelisation of carbohydrates (degradation in the absence of amines) entails the formation of 3-deoxyosuloses and continued dehydration leads to the formation of 5-substituted furan-2-aldehydes. The reaction shares similarities with the Maillard reaction with the exemption that amines do not participate and the coloured products are nitrogen-free. In systems containing amines, the Maillard reaction will be favoured practically exclusively due to the much higher energy requirements of caramelisation (Wedzicha, 1984).

Lipid Browning

Lipid browning occurs as a result of oxidation of unsaturated glyceride components and tends to be favoured by the presence of amines or proteins (Wedzicha, 1984). Since dried fruit contains no significant amount of lipids, lipid browning will not be discussed.

Colour

Colour is a matter of perception and is important in product acceptability (Baardseth *et al.*, 1988). It is a major quality attribute of any food including dried fruits, such as peaches and apricots, since consumers prefer naturally coloured products (Salunke *et al.*, 1991). The colour of food is quantified for three major reasons. The first of these is the standardisation of food products for efficient quality control. The second is the use of colour as a measure of economic worth i.e. a deep red strawberry is worth more than one that is still green. The third reason is the use of colour to measure pigments or the colour effect of ingredients. The effect of different formulations, processing and storage on colour could thus be investigated (Clydesdale, 1985).

The need for objective colour measurement arises from the difference in human perception of colour. Terms like dark red, musty yellow or lavender pink means a different colour for different people (Clydesdale, 1978). People observing

the exact same colour will describe the colour in a different way using different terms due to differing perspectives (Francis, 1977). The first attempt at a numerical system of colour classification was devised by A.H. Munsell, who divided colour into three attributes, namely value (lightness to darkness), hue (specific colour) and chroma (intensity of colour). The three-dimensional model consisted of a vertical axis representing the value. The hue is represented around the parameter of a circular plane at the centre of which is the value axis and the chroma is the distance from the centre of the circular disc. The Munsell Book of Colour was first published in 1929 (Clydesdale, 1978).

Tristimulus colorimetry

The development of tristimulus colorimetry is based on the principle that colour is a combination of three primary colours, red (R), green (G) and blue (B) (Figure 4) (MacDougall, 1988). The Commission Internationale de l'Éclairage (CIE) devised a system in 1931 that uses imaginary primaries X, Y and Z instead of R, G and B. This change in colour system eliminated negative values (Clydesdale, 1969; MacDougall, 1988). The 1931 CIE x, y, z system has one serious fault; values are far from being equally visually spaced. Since 1931 several modifications in this regard have been made in constructing three dimensional colour scales. The three near-uniform colour spaces of practical importance today are the Hunter L, a, b, the 1976 CIELUV and CIELAB spaces. The CIELUV was mainly implemented by the textile industries, while CIELAB was implemented by the food industries. Today CIELAB is considered the standard system for food colour measurement (MacDougall, 1988).

The scale of the CIELAB system can be more readily visualised and interpreted. For instance an increase in +a represents an increase in red; -a an increase in green; +b an increase in yellow and -b an increase in blue. An increasing value of L represents an increase in whiteness or lightness. Further descriptive information is given by hue angle and the saturation index or chroma (Hutchings, 1994). Hue is the attribute of visual sensation according to which an area appears to be similar to one, or two proportions, of the perceived colours red, yellow, orange, green, blue and purple. Chroma is the attribute of a visual sensation according to which a nonluminous related colour appears to exhibit more or less chromatic colour, judged in proportion to the average brightness of its surroundings (Hunt, 1978).

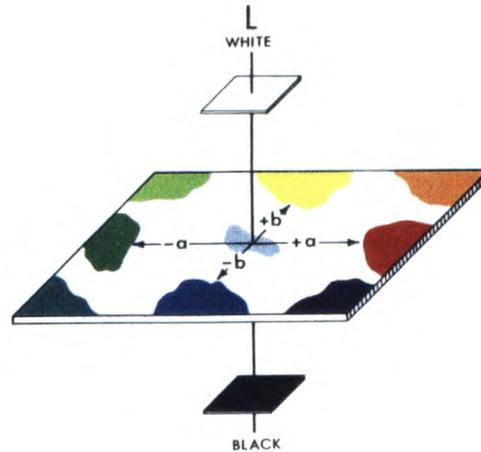


Figure 4. The three dimensions of tristimulus colorimetry (Gardner colour measurement manual).

Colour differences

Since colour measurement was introduced in 1931, the desirable target was to determine the colour difference between a sample and a standard (McLaren, 1980).

The total colour difference, ΔE_{CIE} , between two samples can be calculated as follows for the CIE ($L^*a^*b^*$) colour space (Clydesdale, 1978; MacDougall, 1988):

$$\Delta E_{CIE}(L^*a^*b^*) = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

Where: $\Delta L^* = L^* \text{ sample} - L^* \text{ standard}$

$$\Delta a^* = a^* \text{ sample} - a^* \text{ standard}$$

$$\Delta b^* = b^* \text{ sample} - b^* \text{ standard}$$

This equation gives the best results when investigating food products and no other equation gives a higher correlation coefficient against visual data (McLaren, 1980).

The colour difference can also be split into the three attributes lightness, chroma and hue:

Lightness difference,

$$\Delta L^* = L^* \text{ sample} - L^* \text{ standard}$$

Chroma difference,

$$\Delta C^* = C^* \text{ sample} - C^* \text{ standard}$$

Hue difference,

$$\Delta H^* = [(\Delta E^*)^2 + (\Delta L^*)^2 + (\Delta C^*)^2]^{1/2}$$

Colour measurements of dried fruit and extent of browning

Food product samples differ in composition and individual properties and in the way it interacts with light to produce unique human and instrumental observations. Critical to this process is adequate sample preparation and presentation together with the development of measuring techniques specific for the product under investigation. A major problem of food colour measurement is that foods exist in many physical forms (Hutchings, 1994). In the case of dried fruit it is necessary that the preparation procedure should not mask superficial browning, since browning usually occurs first at the surface of the fruit. The texture of fruit e.g. the hair on peaches and irregular surfaces, have an effect on light reflection. The fruit must thus be presented in an identical manner for every measurement. Ideally the surface must be flat, but the nature of the product does not allow for that except with significant product manipulation such as maceration, which is unacceptable in the case of measurement of surface colour. Another problem is the small diameter of dried fruit when it is placed on an apparatus with a large measuring aperture. Care must be taken to standardise the background by placing a black cover over the sample to exclude light from the laboratory that would interfere with the readings. However, the use of a black cover will result in lower colour values (E. Joubert, ARC Infruitec-Nietvoorbij South Africa, personal communication).

Only a few studies have been published which describe the use of tristimulus colour measurement for quantification of dried fruit colour. Joubert (1997) investigated the discoloration of dried Elberta peaches during storage before and after processing. The changes in a^* , b^* , hue and chroma obtained with increasing storage temperatures, indicated a shift towards yellow with more colour saturation. Increased colour saturation also resulted from an increase in moisture and sulphur dioxide contents from the fruits. The decrease in L^* under these conditions was consistent with non-enzymatic browning of food products as reported for peaches (Bolin *et al.*, 1976) amongst others. Sadie & Joubert (1998) investigated the probability of using a

single attribute of colour to determine the quality of dried fruit. They found that chroma gave the best results for peaches and apricots while lightness correlated the best with pear quality as evaluated by a panel. It is important to note that these fruit had a low moisture content (20%).

Joubert *et al.* (2001) investigated the effect of moisture content and storage temperature on discoloration of dried pears during storage. Colour was quantified in terms of CIE L*, a*, b*, hue and chroma. Discoloration was expressed as a decrease in all colour parameters, except a* which showed an opposite effect. Any increase in browning rate were confirmed by a decrease in the L* values and coincided with an increase in storage temperature and moisture content. In conclusion they found that by using the L* parameter the impact of storage temperature, fruit moisture content and initial fruit colour on colour retention and thus quality could be illustrated (Joubert *et al.*, 2001).

Modified-atmosphere packaging (MAP)

Modified-atmosphere packaging (MAP) is the replacement of air in a pack by a different mixture of gases, where the proportion of each component is fixed when the mixture is introduced, but no further control is exercised during storage (Davies, 1995).

The ability of MAP to preserve foodstuffs has been known and investigated for many years. It started in the 1920s in the UK with work done on apples (Davies, 1995). In the 1930s the storage life of beef carcasses were doubled with the use of carbon dioxide. Today foods packaged in modified atmospheres include raw and cooked meats, poultry and fish, vegetables and fruit, fresh pasta, cheese, bakery products, potato crisps, coffee and tea (Davies, 1995).

The use of modified atmosphere packaging in food preservation by hurdle technology is widely recognised (Grijspaart-Vink, 1994). However, although the influence of packaging material on fresh apricots under MAP (Pretel *et al.*, 1993) and the browning inhibition in fresh-cut pears through MAP (Sapers & Miller, 1998) and even the effect of CO₂ partial pressure on fruit respiration (Beaudry, 1993) have been studied, the only study on MAP and dried fruit that could be found was by Bolin *et al.* (1976) that investigated the effect of nitrogen on colour retention.

Advantages of MAP include increased shelf life, greater economic gain, decreased distribution costs, higher product quality, centralised packaging and portion control, improved presentation and little or no need for chemical preservatives. There is, however, a certain amount of disadvantages which include visible added cost, temperature control, different gas formulations, special equipment, increased pack volume and the benefits are lost once the pack is opened or leaks (Davies, 1995).

Role of gases

Although several different gases can be used in MAP, there are three major gases namely oxygen, nitrogen and carbon dioxide. Other gases include carbon monoxide, sulphur dioxide, nitrous oxide, ozone and chlorine. The use of these gases has, however, been limited due to safety, legislation, organoleptic properties and cost (Davies, 1995).

Air consists of about 78% nitrogen, a colorless, tasteless gas that is essentially biologically inert in its gaseous form. Nitrogen is used in packaging primarily as a filler and to exclude other more active gasses. Nitrogen is easily purified and inexpensive and used in many modified atmosphere packages (Zagory, 1994).

Oxygen is a atmospheric gas that constitutes about 20.9% of the atmosphere. It is also a reactive gas that can form compounds with virtually any chemical compound (Zagory, 1994).

Air also contains about 0.03% carbon dioxide (CO₂). It is very soluble in water, especially in cold water (179.7 cm³.100⁻¹ ml at 0°C) and thus is absorbed by high-water-content foods. When CO₂ dissolves in water it produces carbonic acid, which causes a drop in pH. This acidification, as well as direct antimicrobial effects, can suppress growth of many spoilage microorganisms. For this reason CO₂ is essential in many extended shelf life food processes. However, too much CO₂ can be damaging to plant tissues. The solubility of CO₂ in water can lead to package collapse (due to take-up from the surrounding environment). CO₂ permeates most packaging materials more rapidly than other atmospheric gasses (Zagory, 1994).

Packaging material

In the last few years there have been several developments in the packaging material and equipment. Much of the development work has centered on retail packs and includes the development of microwaveable and resealable MAP packs. One of the most significant recent developments is the use of in-line non-destructive leak detectors. The detection of leakers is one of the major challenges facing the MAP producer (Davies, 1995).

Controlling the Maillard reaction in dried fruit with MAP

Not much work has been done on controlling non-enzymatic browning reactions in fruit with the help of MAP. In a scientific status summary, Sapers (1993) clearly illustrates the requirement of O₂ in browning reactions and he even suggests the use of MAP in the preserving of fresh produce. The importance of the presence of O₂ during storage is also emphasised by Mahmutoğlu *et al.* (1996). Another important point is the production of CO₂ via the Strecker degradation in the Maillard reaction (Sapers, 1993). It can thus be said that browning of dried fruit is usually accompanied by the production of CO₂. The rate of CO₂ production is also closely related to temperature. CO₂ production increases about 4 times for 10°C rise in temperature over the range 22°C – 49°C (Stadtman, 1948). Carbon dioxide is produced almost as rapidly under anaerobic conditions as in air, however, as oxygen pressure increases so does the rate of CO₂ formation (Stadtman, 1948). The use of nitrogen is recommended to replace oxygen (Stadtman, 1948). The use of CO₂ however, seems to be a more logical option since it does not only replace the oxygen in the packet but reverses the Maillard reaction by raising the concentration of the reaction products.

Conclusions

The production of shelf stable, intermediate moisture dried fruit can only be achieved through a combination of preservation factors. These factors include choosing the optimal product a_w and processing temperature to minimise non-enzymatic browning and still render a microbiologically safe product. Rehydration of the dried fruit must be effective and the target moisture content should be obtained as quickly as possible.

The physical characteristics of colour and texture play an important role in consumer acceptance and must be considered at all times.

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Chapter 3

Moisture sorption isotherms of dried Royal type apricots and nectarines using a static gravimetric method

Abstract Moisture sorption isotherms, depicting the relationship between moisture content (g water.100 g solids⁻¹) and water activity (a_w) of a specific product and used to predict a_w of food at specific moisture contents, were determined for Royal type apricots and nectarines at 25° and 40°C. Samples of *ca.* 3 g equilibrated at relative humidities in the range of 11-97% were obtained using saturated salt solutions in a static gravimetric method. Isotherms were found to be of type I, typical of dried fruit. Six mathematical models namely: BET, GAB, Iglesias and Chirife, Halsey, Henderson, and Chung and Pfoest were fitted to experimental data. The GAB model predicted the a_w of both apricots and nectarines the best at 25°C and 40°C with the Henderson equation second best in all instances. The binding energy as a function of moisture content was calculated to determine energy requirements for drying.

Introduction

The moisture sorption isotherm of food is an extremely important tool in food science, because it can be used to predict changes in food stability and water activity (a_w) at different moisture contents and temperatures. It can also be used to analyse processes like preservation, drying, storing, packaging and mixing (Tsami *et al.*, 1990).

Dried fruit are traditionally dried on the farm in South Africa to a moisture content of *ca.* 18%. Further processing entails washing to remove superficial dirt and to increase the moisture content to *ca.* 22-26%, depending on the market (Joubert *et al.*, 2001). For production of a newly developed “soft-eating” fruit, the fruit are subjected to an additional water treatment before packaging to render a product with a moisture content of *ca.* 36% (J. Schoeman, SAD, personal communication). At this

relatively high moisture content the water activity reaches levels of *ca.* 0.86. The physical properties of this dried fruit product with its relative high moisture content and subsequent higher water activity are unknown. Several studies have been done on dried fruit to determine sorption data (Bolin, 1980; Iglesias & Chirife, 1982; Roman *et al.*, 1982; Saravacos *et al.*, 1986; Vagenas *et al.*, 1986; Abdelhag & Labuza, 1987; Maroulis *et al.*, 1988). The dried fruits investigated included raisins, currants, figs, prunes and Turkish apricots. However, no moisture sorption data are available for nectarines or any other dried fruit produced in South Africa. Due to different weather and soil conditions the composition of locally produced fruit is different from that of fruit produced elsewhere (Fourie & Hansmann, 1992). The need thus arose for moisture sorption data applicable to locally produced dried fruit.

The purpose of the study was to determine the moisture sorption isotherms of South African Royal type apricots and nectarines over a range of water activities at 25° and 40°C. The data were also fitted to six well known models to determine important parameters such as monolayer moisture content, for determination of the amount of water available to take part in chemical reactions, and to use the best model to make predictions of water activity under different temperature and relative humidity conditions e.g. binding energy.

Material and methods

Material

Choice grade dried Royal type apricots and nectarines were obtained from the South African Dried Fruit Co-op (SAD), which is the major processor of dried fruit in the Western Cape, South Africa. Saturated salt solutions (*ca.* 100 ml) of lithium chloride (LiCl), potassium acetate (CH₃COOK), magnesium chloride (MgCl), potassium carbonate (K₂CO₃), magnesium nitrate (Mg(NO₃)₂), cupric chloride (CuCl₂), sodium chloride (NaCl), potassium chloride (KCl), potassium sulphate (K₂SO₄) (Rockland, 1960; Mazza *et al.*, 1994) were used to respectively maintain a range of constant vapour pressures at 25° and 40°C (Table 1) in sealed 1 litre glass preserving jars. Reagent grade chemicals used in the preparation of saturated salt solutions were obtained from Saarchem Holpro Analytic (Pty) Ltd (RSA), Riedel-de-Haën Laborchemikalien and Merck N. T. Laboratory Supplies (Pty) Ltd (RSA).

Table 1. Salts used in the determination of moisture sorption isotherms with corresponding relative humidities at 25°C and 40°C.

Salt	RH at 25°C	RH at 40°C
Lithium chloride ¹	11	11
Potassium acetate ¹	23	22
Magnesium chloride ¹	33	32
Potassium carbonate ²	43	40
Magnesium nitrate ¹	53	48
Cupric chloride ¹	67	67
Sodium chloride ¹	75	75
Potassium chloride ¹	84	82
Potassium sulfate ²	97	96

¹ Mazza *et al.*, 1994

² Rockland, 1960

Methods

Dried Royal type apricots and nectarines were macerated once with a Bizerba (Columbit, Cape Town) meat mill equipped with a special gearbox and samples of *ca.* 3 g were spread in a thin layer (*ca.* 1 mm) in small plastic Petri dishes (40 mm diameter; 5 mm depth). These samples were subsequently dried in a vacuum oven at 30°C for 48 h (Ayranci *et al.*, 1990).

The samples were then placed in 1000 ml preserving jars that had been equipped with suspended sample holders to keep the samples above the saturated salt solution, sealed and placed in temperature-controlled rooms (25° and 40°C). The samples were weighed every second day until equilibrium was reached. Equilibrium was assumed when two consecutive readings differed less than 0.1% of the initial mass (Mazza *et al.*, 1994). After equilibration the moisture content of the samples was determined according to a modified AOAC vacuum oven drying method (Williams, 1984) by drying for 16 h at 70°C. Equilibration time was about 2-3 w, depending on the relative humidity and temperature.

Analysis of data

The data obtained were fitted to six three-parameter equations (Table 2) namely: BET; GAB; Iglesias and Chirife; Halsey; Henderson; Chung and Pfof (Chung & Pfof, 1967; Boquet *et al.*, 1978; Chirife & Iglesias, 1978; Lomauro *et al.*, 1985; Mir & Nath, 1995).

The constants for the mathematical models used to predict a_w were evaluated using a nonlinear optimisation technique. The parameter selected to measure the adequacy of fit was the R^2 value. All statistical analyses were performed using SAS/STAT (6.08) statistical software (Anon, 1990).

Heat and binding energy of sorption

The thermodynamic function used to express the temperature dependence of vapour pressure was the Clausius-Clapeyron equation for phase transition from an adsorbed liquid to the vapour phase. With at least two different temperatures this equation can provide thermodynamic data on isosteric heat of sorption through the use of the integrated form (Rizvi & Benado, 1984):

Table 2. Mathematical models used to fit the experimental data of South African dried Royal type apricots and nectarines for the prediction of a_w .

Model	Equation	Reference
BET	$\frac{a_w}{(1 - a_w)} = \frac{1}{M_0 C} + \frac{(C - 1)}{M_0 C} \cdot a_w$	Chirife & Iglesias (1978)
GAB	$M = \frac{CKM_0}{[(1 - Ka_w)(1 - Ka_w + CKa_w)]} \cdot a_w$	Mir & Nath (1995)
Iglesias & Chirife	$\ln[M + \sqrt{M + M_{0.5}}] = Ca_w + K$	Chirife & Iglesias (1978)
Halsey	$a_w = \exp\left(-\frac{C}{M^K}\right)$	Lomauro <i>et al.</i> (1985)
Henderson	$(1 - a_w) = \exp(-KM^C)$	Boquet <i>et al.</i> (1978)
Chung & Pfof	$\ln a_w = -\frac{C}{RT} \cdot \exp(-KM)$	Chung & Pfof (1967)

C and K = constants in sorption models; M = moisture content (% dry basis); M_0 = monolayer moisture content (% dry basis); $M_{0.5}$ = moisture content at $a_w = 0.5$; T = absolute temperature (K); R = gas constant (8.314 J.mol⁻¹.K⁻¹).

$$\ln(a_{w1}/a_{w2}) = - (q_{st}/R) [(T_1/T_2) - (1/T_1)]$$

where: $q_{st} = Q_{st} - \cong H_{vap}(H_2O)$

In these equations a_{w1} and a_{w2} are the a_w at a given moisture content at temperatures T_1 and T_2 , respectively. Q_{st} is the isosteric heat of sorption, $\cong H_{vap}(H_2O)$ is the enthalpy of vaporisation of water ($43 \text{ kJ}\cdot\text{mol}^{-1}$ for this temperature range) and R the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$).

Another similar measure of the interaction of water vapour with a solid substrate is the binding energy of sorption ($\cong H_B$), defined as the difference ($Q_{st} - \cong H_O$), where Q_{st} is the isosteric heat of sorption and $\cong H_O$ is the heat of condensation of water vapour at the given temperature ($\cong H_O = 10.53 \text{ kcal}\cdot\text{mol}^{-1}$ at 25°C). At a given moisture content, $\cong H_B$ can be estimated from sorption data at two different temperatures (T_1 and T_2), using an integrated form of the Clausius-Clapeyron equation (Soekarto & Steinberg, 1981):

$$\ln\left(\frac{a_{w2}}{a_{w1}}\right) = \frac{\Delta H_B}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Where: a_{w1} and a_{w2} are the water activities at temperatures T_1 and T_2 , respectively, and R is the gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$).

Results

Water sorption isotherms

The sorption isotherms of dried Royal type apricots and nectarines at temperatures 25° and 40°C are shown in Fig. 1 and 2, respectively. Each data point represents the mean value of three replications. In general, all of the isotherms showed characteristics of type I isotherm (Labuza, 1984; Ayranci *et al.*, 1990).

The isotherms of both apricots and nectarines (Fig. 1 and 2) showed definite temperature dependence and the same pattern was observed in both cases. The isotherm constructed at 40°C showed lower water activities at any given moisture content than the isotherm constructed at 25°C .

Fitting of sorption data to various equations

The six mathematical models were fitted to the experimental data to determine which model predicted a_w for dried apricots and nectarines the best. The constants and R^2 values for the different mathematical models are summarised in Tables 3, 4, 5, and 6. The GAB model predicted both the a_w of apricots and nectarines at 25° and 40°C the best, as reflected by the R^2 values (0.999 in all instances). The water sorption isotherms obtained using the GAB model at 25° and 40°C, are shown in Fig. 1 and 2 for dried apricots and nectarines, respectively.

The Henderson equation gave the second best fit for all the data tested. The R^2 values ranged between 0.996 and 0.998. The Iglesias & Chirife equation gave the 3rd best fit for the data obtained from the dried apricots and nectarines with R^2 values of 0.989 and 0.988, respectively. These equations were followed by the Chung & Pfof and Halsey equations in 4th and 5th place, respectively.

Heat of sorption

The integrated form of the Clausius-Clapeyron equation was used to fit the sorption data from both the apricots and nectarines (Fig. 3). An estimate of the binding energy ($\cong H_B$) as a function of moisture content was plotted using the two temperatures, 25° and 40°C. The binding energy was found to be negative for the entire range of data points. Below a moisture content of 20%, the binding energy increased significantly. Between 20 and 40% moisture content, the binding energy decreased slightly and above 40% moisture content the binding energy increased again, especially in the case of the dried apricots.

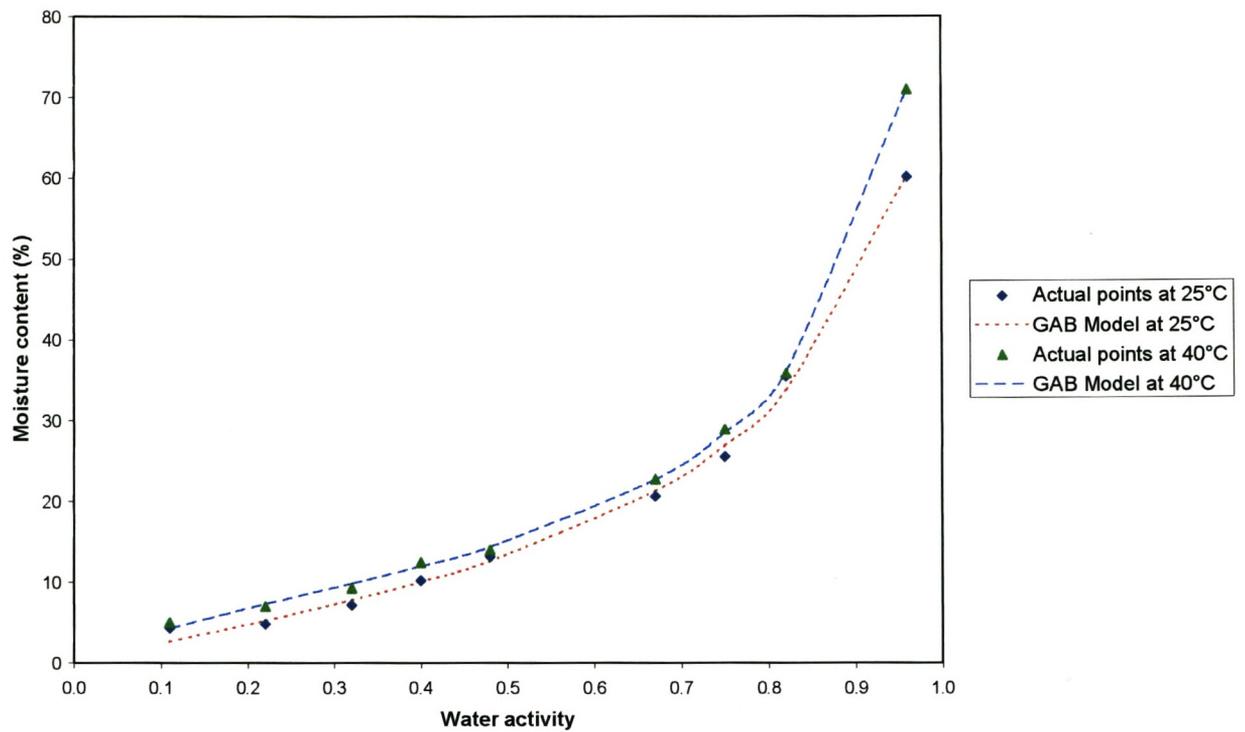


Figure 1. Moisture sorption isotherms of Royal apricot samples at 25° and 40°C with actual data points and the fitted GAB Model.

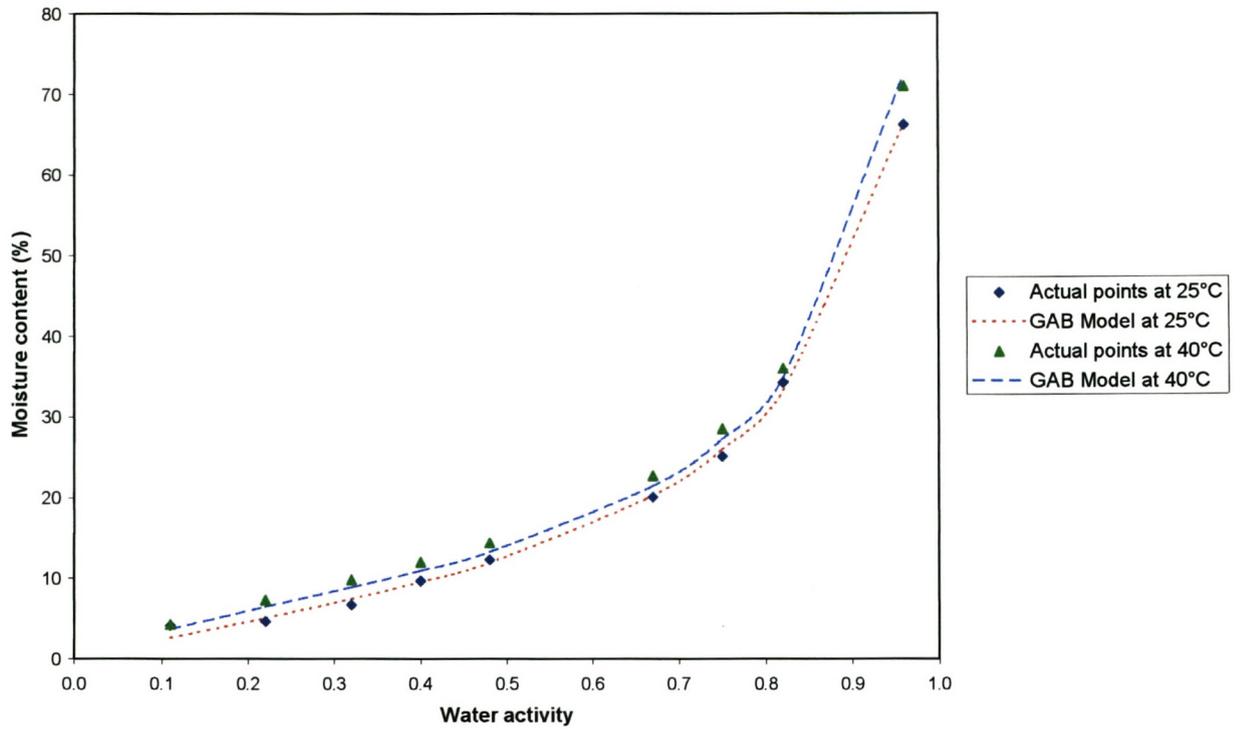


Figure 2. Moisture sorption isotherms of nectarine samples at 25° and 40°C with actual data points and the fitted GAB Model.

Table 3. Constants and the R^2 values of moisture sorption data obtained for dried apricot at 25°C using the BET, GAB, Iglesias and Chirife, Halsey, Henderson and Chung and Pfof equations.

Model	C	K	M_0	$M_{0.5}$	R^2
BET	-35.667	-	3.9438	-	0.703
GAB	2.352	0.8514	12.0611	-	0.999
Iglesias and Chirife	3.3578	1.5378	-	14.14	0.996
Halsey	16.9619	6	-	-	0.819
Henderson	0.0524	1	-	-	0.997
Chung and Pfof	5007.491	0.0682	-	-	0.989

C and K = constants in the sorption models; M = moisture content (% dry basis); M_0 = monolayer moisture content (% dry basis); $M_{0.5}$ = moisture content at $a_w = 0.5$; T = absolute temperature (K) and R = gas constant ($8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$).

Table 4. Constants and the R^2 values of moisture sorption data obtained for dried nectarines at 25°C using the BET, GAB, Iglesias and Chirife, Halsey, Henderson and Chung and Pfof equations.

Model	C	K	M_0	$M_{0.5}$	R^2
BET	-113.619	-	4.1523	-	0.755
GAB	2.71099	0.0891	10.2040	-	0.999
Iglesias and Chirife	3.7809	1.2158	-	13.52	0.992
Halsey	3.0372	1	-	-	0.865
Henderson	0.0502	1	-	-	0.997
Chung and Pfof	4544.127	0.0629	-	-	0.981

C and K = constants in the sorption models; M = moisture content (% dry basis); M_0 = monolayer moisture content (% dry basis); $M_{0.5}$ = moisture content at $a_w = 0.5$; T = absolute temperature (K) and R = gas constant ($8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$).

Table 5. Constants and the R^2 values of moisture sorption data obtained for dried apricot at 40°C using the BET, GAB, Iglesias and Chirife, Halsey, Henderson and Chung and Pfof equations.

Model	C	K	M_0	$M_{0.5}$	R^2
BET	-28.933	-	4.4988	-	0.753
GAB	5.5139	0.8969	10.1437	-	0.999
Iglesias and Chirife	3.498	1.5424	-	14.45	0.989
Halsey	31.6409	9.6617	-	-	0.851
Henderson	0.04614	1	-	-	0.998
Chung and Pfof	5281.245	0.0698	-	-	0.984

C and K = constants in the sorption models; M = moisture content (% dry basis); M_0 = monolayer moisture content (% dry basis); $M_{0.5}$ = moisture content at $a_w = 0.5$; T = absolute temperature (K) and R = gas constant (8.314 J.mol⁻¹.K⁻¹).

Table 6. Constants and the R^2 values of moisture sorption data obtained for dried nectarines at 40°C using the BET, GAB, Iglesias and Chirife, Halsey, Henderson and Chung and Pfof equations.

Model	C	K	M_0	$M_{0.5}$	R^2
BET	-49.888	-	4.44655	-	0.776
GAB	4.6957	0.9084	9.5356	-	0.999
Iglesias and Chirife	3.8028	1.2715	-	12.80	0.988
Halsey	32.9983	10	-	-	0.874
Henderson	0.0464	1	-	-	0.996
Chung and Pfof	4889.501	0.0588	-	-	0.978

C and K = constants in the sorption models; M = moisture content (% dry basis); M_0 = monolayer moisture content (% dry basis); $M_{0.5}$ = moisture content at $a_w = 0.5$; T = absolute temperature (K) and R = gas constant (8.314 J.mol⁻¹.K⁻¹).

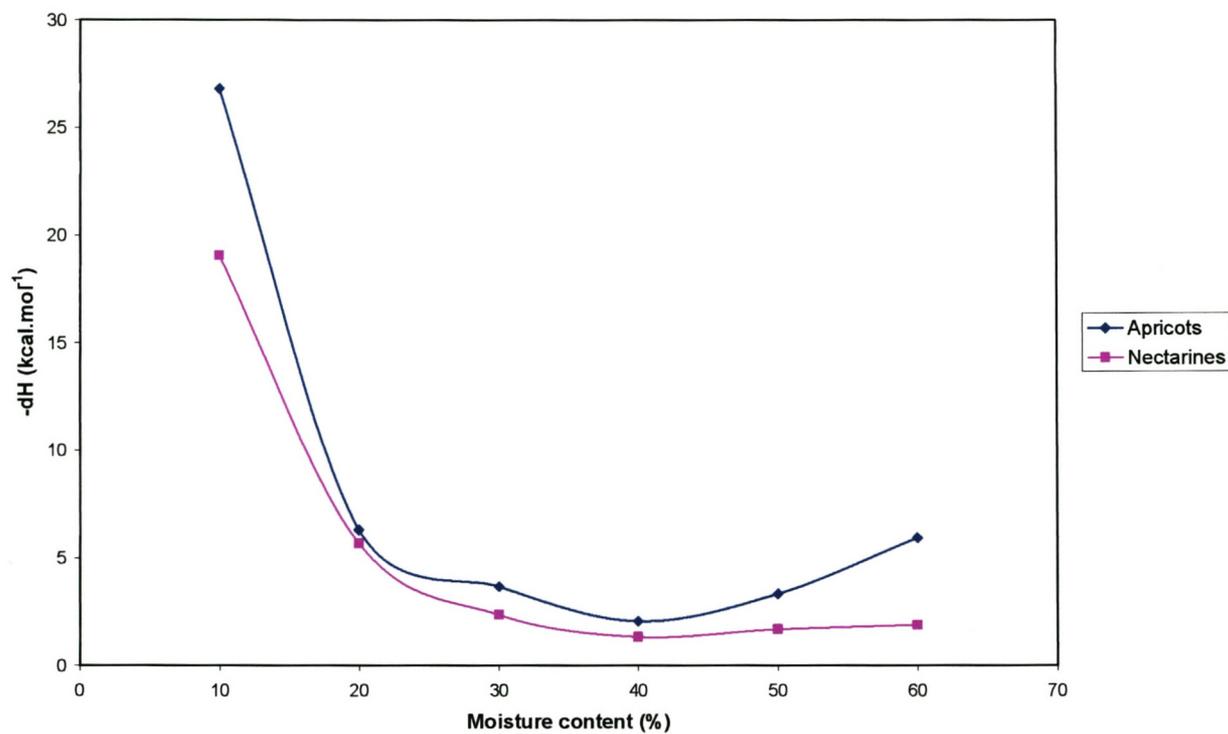


Figure 3. Differential isosteric heat of sorption as a function of moisture content of dried Royal type apricots and nectarines.

Discussion

The sigmoid shape of the sorption isotherms (Fig. 1 and 2) is characteristic of materials with high sugar content (Weisser, 1985) with the shape of this isotherm generally recognised as a type I (Labuza, 1984). Ayranci *et al.* (1990) found similar results for dried Malatya apricots, figs and raisins. Small amounts of water are sorbed at low water activities, due to the water sorption of biopolymers, which usually accompany the sugars (Saravacos *et al.*, 1986). At low water activities, water can be absorbed only to surface - OH sites of crystalline sugar (Saltmarch & Labuza, 1980). At high water activities, dissolution of sugar occurs and crystalline sugar is converted into amorphous sugar. The amount of water to be adsorbed increases greatly after this transition, because of the increase in the number of adsorption sites upon breakage of the crystalline structure of sugar (Maroulis *et al.*, 1988). These factors give rise to the nonlinear relationship between moisture content and a_w .

In general, a_w would be expected to increase with increasing temperature at any given moisture content due to the higher activity of the water molecules. This was, however, not the case. The effect of temperature on the isotherms can be explained with reference to sorption energy. As the energy involved in sorption is the algebraic sum of the endothermic heat of dissolution of solute and the exothermic heat of sorption of nonsolute solids, the net effect of the temperature on the isotherms would depend on the magnitude of both (Roman *et al.*, 1982). The effect of temperature on the isotherms can be explained with reference to the dissolution of sugars. With more sugar being dissolved at higher temperatures, more water was thus being held by the dried fruit at the higher temperature resulting in a lower a_w for the same moisture content. This was evident throughout the entire a_w range.

Contrary to the findings of Ayranci *et al.* (1990) and Tsami *et al.* (1990), the apricot isotherms constructed at different temperatures (25° and 40°C) (Fig. 1 and 2), never crossed and thus showed no inversion (intersection) point. This means that the sugars of the dried fruit behave differently in the low a_w range. These unexpected results can be attributed to the specific type and concentration of sugars contained in the fruit, which differs from country to country due to different soil and weather conditions. Saravacos *et al.* (1986) found that at high water activities, the sugars are the determining factor of water sorption. The dissolution of sugars increases significantly as the temperature is raised, offsetting the opposite effect of temperature

on the sorption of nonsugar solids. At higher temperatures the sugars are in solution and bind with water molecules to lower the water activity of the samples. This phenomenon is applicable to all the data points. Roman *et al.* (1982) investigated the isotherms of Granny Smith apples and found no inversion point. The isotherms constructed in their study, showed the same pattern as was found in this study. This phenomenon was ascribed to the specific sugar (58% reducing sugars; 18% sucrose) composition of the apples. Hansmann & Nortjé (1979) found a sucrose content of 60.46 % in Royal type apricots. Wills *et al.* (1983) found a sucrose content of 61% for apricots and 65 % for nectarines. No temperature data for nectarines could be found in literature. The nectarines isotherm does, however, exhibit similar properties to that of apricots and it can be concluded that the specific sugar content has the same effect in the case of nectarines.

The GAB equation gave the best fit for both apricots and nectarines at both temperatures in this study. This model can thus be used with a high degree of accuracy for these South African dried fruit types. According to Lomauro *et al.* (1985) the GAB model gave the best fit for 50% or more of the foods they tested in the fruit category. Other researchers also recognised the GAB equation as the most satisfactory theoretical isotherm equation (Van den Berg, 1984; Weisser, 1985; Wolf *et al.*, 1985; Kapsalis, 1987; Multon, 1988). Different equations have found suitable applications to different food products. Ayranci *et al.* (1990) used the Iglesias and Chirife, Halsey, BET and GAB equations to fit the data they obtained for dried apricots (Malatya), figs and raisins. The GAB and Henderson equations are often used to predict data obtained from dried fruit and vegetables (Saravacos *et al.*, 1986; Tsami *et al.*, 1990; Samaniego-Esguerra *et al.*, 1991). In addition to the Henderson, Halsey and GAB equations the Chung and Pfoest equation was used by Mazza *et al.* (1994) to fit data obtained from dried mustard seeds. In all these cases the GAB equation showed the best fit for the sorption data.

Fitting data to the GAB model provides not only the value of monolayer moisture content (M_0), but also other useful information related to heat of sorption of both monolayer and multilayer. The M_0 values decreased with an increase in temperature. This was consistent with the results obtained by Labuza *et al.* (1985) on cornmeal and Ayranci *et al.* (1990) on dried Malatya apricots, figs and raisins. This effect may be due to a reduction in the total number of active sites for water binding as a result of physical or chemical changes induced by temperature (Iglesias & Chirife,

1976). The M_0 value is used in several thermodynamic functions and is of great importance in the accurate prediction of a_w at specific moisture contents. It is also used to determine the amount of water available for chemical and microbiological reactions and to study the energy requirements for drying fruit (Caurie, 1981).

The Henderson equation was found to fit data from starch and starch containing foods very well (Crapiste & Rotstein, 1982; Boki & Ohno, 1991). It was thus surprising to find that the Henderson equation also gave a very good fit for all the data tested.

Boquet *et al.* (1978) found good results when fitting the Iglesias and Chirife equation on data obtained from high sugar and starchy foods. This equation gave the 3rd best fit for the data obtained from the dried apricots and nectarines.

In the past, one of the most popular food isotherm equations was the BET equation (Brunauer *et al.*, 1938). This equation also provides the value of the monolayer moisture content. However, the BET equation gave the poorest results in this study and the use of this model proved to be unsatisfactory.

A special form of the Clausius-Clapeyron equation was used to fit the sorption data from both the apricots and nectarines. The binding energy is negative for the entire range of data points, indicating an exothermic reaction. An increase in $-\Delta H_B$ was observed at low moisture contents (< 20%). This is in agreement with findings of Roman *et al.* (1982), Saravacos *et al.* (1986), Ayranci *et al.* (1990) and Göğüş *et al.* (1998) on a variety of products, ranging from fresh Granny Smith apples to Turkish delight. At these lower moisture contents, water is much less mobile and it takes more energy to release water molecules than at a higher moisture contents (Göğüş *et al.*, 1998). At higher moisture contents the binding energy approaches zero, meaning that the isosteric heat of sorption is equal to the heat of condensation of water. A simple interpretation of Fig. 3 is that the energy needed to dry both apricots and nectarines up to a moisture content of 20% remain fairly constant. Drying to below 20% moisture content requires a greatly increased energy input.

Saravacos *et al.* (1986) found the binding energy of water in raisins to decrease as the temperature was increased from 22° to 32°C in the low moisture region. The effect of temperature was reversed at higher moisture contents evidently due to the endothermic dissolution of fruit sugars, which would result in binding of the water, therefore preventing it from evaporating easily. The 32°C line increases again at high

moisture levels (> 60%). This effect was also observed where the binding energy increased above moisture contents of 40% for both apricots and nectarines.

Conclusions

Comparisons were made with data from the literature on dried Malatya apricots and other dried fruit products. It was found that there are similarities (e.g. Type I isotherm) and differences (e.g. no inversion point). Differences were attributed to the compositional differences of South African fruit and to the specific method (static gravimetric) that has been used. The results showed that the GAB model could be employed to study South African dried apricots and nectarines. Using the GAB model, the energy requirements for the drying of these fruit can be estimated, but further studies are needed. It remains to be seen what the effect of water activity and moisture content will have on the colour stability and thus shelf life of high moisture dried fruit.

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Chapter 4

Effect of moisture and sulphur dioxide contents on colour deterioration of high moisture dried macerated Royal type apricots and nectarines at accelerated storage conditions

Abstract Discolouration of high moisture dried Royal type apricots and nectarines during accelerated storage as affected by moisture (32, 36, and 40%) and sulphur dioxide (SO₂) contents (2500, 3000 and 3300 mg.kg⁻¹ for apricots; 1800, 2200 and 2600 mg.kg⁻¹ for nectarines) were investigated. Fruit preparation entailed rehydration, maceration and adjustment to the required moisture and SO₂ contents with water or a sodium metabisulphite solution. The macerated samples were stored at 30°, 40°, 50° and 60°C. Colour was quantified in terms of the L* value of the CIELab system. Moisture and SO₂ affected both the initial fruit colour and the rate of discolouration. The highest L* values, i.e. lightest fruit colour, were obtained for fruit at 40% moisture content and the highest SO₂ levels. Increasing storage temperature accelerated loss of moisture and SO₂. Q₁₀ and a_w values for apricot ranged between 1.96 - 2.47 and 0.833 - 0.890 respectively, while Q₁₀ values of 1.50 - 4.61 and a_w values of 0.844 - 0.890 were obtained for nectarines.

Introduction

Traditionally fruit are sulphured and dried to a moisture content of *ca.* 18% (m/m) and lower to ensure a relatively stable product before further processing. This entails washing and rehydration of the fruit to moisture contents of 26 to 28% to improve product texture. However, the demand for a “soft-eating” product resulted in the development of products with a moisture content of *ca.* 36%. These developments included conventional dried fruit and a macerated form of dried fruit used in the production of fruit bars and fruit dainties. At this relatively high moisture content,

shelf life of less than three months due to unacceptable browning was realised for “soft-eating” nectarines, while “soft-eating” Royal type apricots could not be used, due to poor colour stability (J. Schoeman, 1999, SAD, personal communication).

The browning process in dried fruit is partially inhibited by SO₂ and low temperature (Harel *et al.*, 1978). During storage dried fruit lose SO₂, with the effect more evident at higher temperatures (Joubert *et al.*, 2001).

Only a few studies have addressed colour stability of dried apricots as affected by moisture content, SO₂ content and storage temperature (McBean & Wallace, 1967; Bolin & Jackson, 1985; Abdelhag & Labuza, 1987; Mahmutoğlu *et al.*, 1996; Joubert, 1997), while only one study on nectarines had been reported (Joubert, 1997). McBean & Wallace (1967) concluded that a moisture content of 22% for the rehydrated dried apricots did not adversely affect the shelf life of the product provided the sulphur dioxide level was *ca.* 3000 mg.kg⁻¹, and the storage temperature not higher than 10°C. These recommendations have practical implications for the South African situation, as the permitted dried fruit SO₂ level is only 2000 mg.kg⁻¹ (Anonymous, 1991) and storage at 10°C is unlikely during retail. Even lower SO₂ levels are required for some international markets. Joubert (1997) studied the effect of fruit moisture content, storage temperature and SO₂ on the colour stability of Royal type apricots and Elberta peaches over a period of 100 w. An increase in fruit moisture content resulted in a lighter colour product initially, but accelerated browning. Resulphuring after rehydration slowed down browning. Storage at 0°C was effective in ensuring colour stability for at least 100 w, but noticeable colour deterioration, accompanied by loss in SO₂, occurred during storage at 25°C. This study was, however, limited to fruit at a maximum moisture content of 28%. Mahmutoğlu *et al.* (1996) found that the SO₂ content of dried apricots at 24% moisture content, declined considerably with storage at 5° and 13°C, while colour remained fairly constant.

The objective colour parameter L* (CIELab system), as an indication of lightness and darkness, has been used to quantify browning in dried fruit. Examples include peaches (Kluter *et al.*, 1994), nectarines and apricots (Joubert, 1997), pears (Sapers & Douglas, 1987; Joubert *et al.*, 2001), apples (Bolin & Steele, 1987) and sultanas (Cañellas *et al.*, 1993; Joubert, 1997).

The purpose of this study was to determine the impact of SO₂ content, moisture content and storage temperature on colour retention of homogenised high

moisture dried apricots and nectarines and to investigate the stability of this processed form as a final product. L^* , a_w and Q_{10} values were used to assess product stability.

Material and methods

Sample preparation

Choice grade, large, dried Royal type apricots and nectarines from the 1999 harvest were obtained from SAD, Worcester, South Africa. The apricots and nectarines had average moisture contents of 19.5 and 15.5% moisture (wet basis), respectively. The dried fruit were stored for a maximum of three months in sealed plastic containers to prevent any moisture loss prior to sampling and processing. Storage took place at *ca.* 0°C to prevent discoloration.

A schematic representation of the experiment to determine the influence of moisture content on shelf life is given in Fig. 1. For both dried apricots and nectarines, the fruit were divided into three batches, which were rehydrated separately by dipping in tap water at 45°C for 90 sec. The rehydrated dried fruit were then macerated once with a Bizerba meat mill (Columbit, Cape Town) equipped with a special gearbox and the moisture content determined. The macerated dried fruit were allowed to equilibrate overnight at *ca.* 0°C, and thereafter water was added to obtain final moisture contents of 32, 36 and 40%, respectively. Each batch was macerated again to ensure a homogenous mixture. Three hundred and sixty samples (10 samples x 4 temperatures x 3 moisture contents x 3 replicates) of each batch were prepared by filling 65 mm plastic petri dishes leaving *ca.* 1 mm of headspace. The petri dishes were sealed with insulation tape to prevent excessive moisture loss. The samples were then equally divided and placed in temperature-controlled laboratory incubators pre-set at 30°, 40°, 50° and 60°C. Colour, moisture and SO₂ measurements of the 30°C samples were done every 4th day (for 36 d), the 40°C samples every 3rd day (for 27 d), the 50°C samples every 2nd day (for 18 d) and the 60°C samples every day (for 9 d). Initial analyses were done on day 0. These analyses included colour, moisture and SO₂ measurements and were performed on samples, which underwent the same treatment as the rest of the samples, but were randomly selected prior to the samples being placed in the incubators.

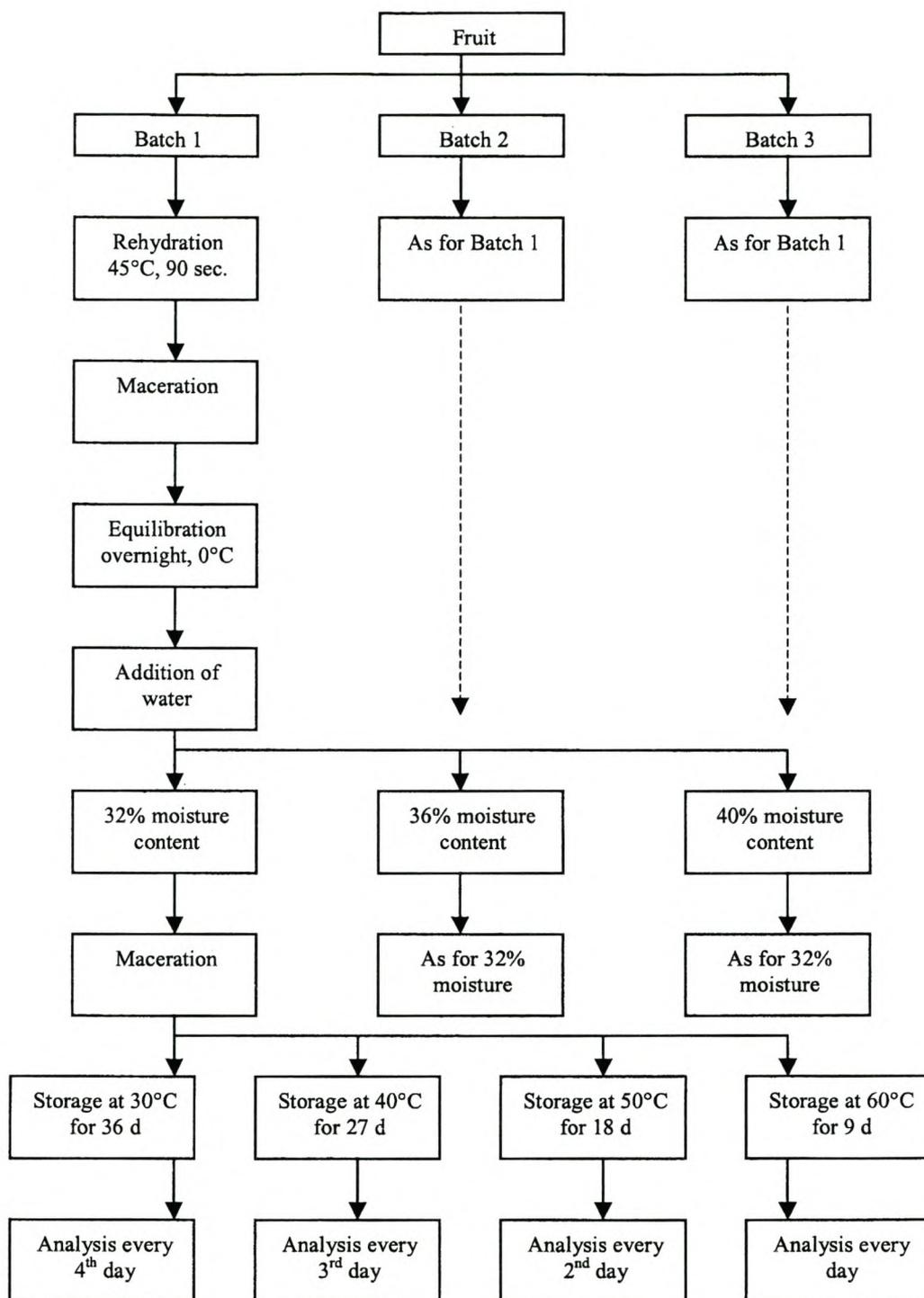


Figure 1. Schematic representation of experiment to determine the influence of moisture content and storage time on the shelf life of dried Royal type apricots and nectarines.

For the samples with different SO₂ contents, the fruit were prepared as described above. A schematic representation of the experiment to determine the influence of SO₂ content on shelf life is given in Fig. 2. The moisture content of all the samples was adjusted to 36%. The SO₂ concentration of the samples was adjusted with sodium metabisulphite solutions to 2488, 3062 and 3330 mg.kg⁻¹ for apricots and 1800, 2260 and 2666 mg.kg⁻¹ for nectarines. The SO₂ concentration of the apricots and nectarines were initially 2100 and 1840 mg.kg⁻¹, respectively. An initial analysis of colour, moisture and SO₂ was done on day 0 as described above. The samples of each SO₂ concentration were stored at 30°, 40°, 50° and 60°C, respectively. In this case the colour measurements of the 30°C samples were measured every 5th day (45 d), the 40°C samples every 4th day (36 d), the 50°C samples every 3rd day (27 d) and the 60°C samples every 2nd day (18 d). The moisture and SO₂ contents were determined with every second colour analysis.

Objective colour measurements

The L* value of samples was determined using a Gardner Colorgard 2000/05 system (BYK-Gardner GmbH, Germany), employing 45° illumination/0° viewing and a 32 mm aperture calibrated with a black zero reference standard and a standard white tile (X=84.30; Y=86.52; Z=100.71) supplied by BYK-Gardner. The lids of the petri dishes were removed, and the samples were placed directly over the aperture with the open end of the petri dish facing down. A quartz glass plate was not used on the aperture. A black cover was placed over the sample to prevent external light reaching the sample. Two measurements were performed on each sample by rotating the sample 90° after the first reading.

Moisture content determinations

Moisture contents of the fruit were determined according to a slightly modified version of the AOAC vacuum oven drying method (Williams, 1984) by drying a *ca.* 5 g sample for 16 h at 70°C.

Sulphur dioxide measurements

The SO₂ concentrations were determined directly after completion of the colour measurements without further maceration. Duplicate samples (10 g) of the macerated dried fruit were distilled for 7 min (Fourie, 1997) with a Gerhardt

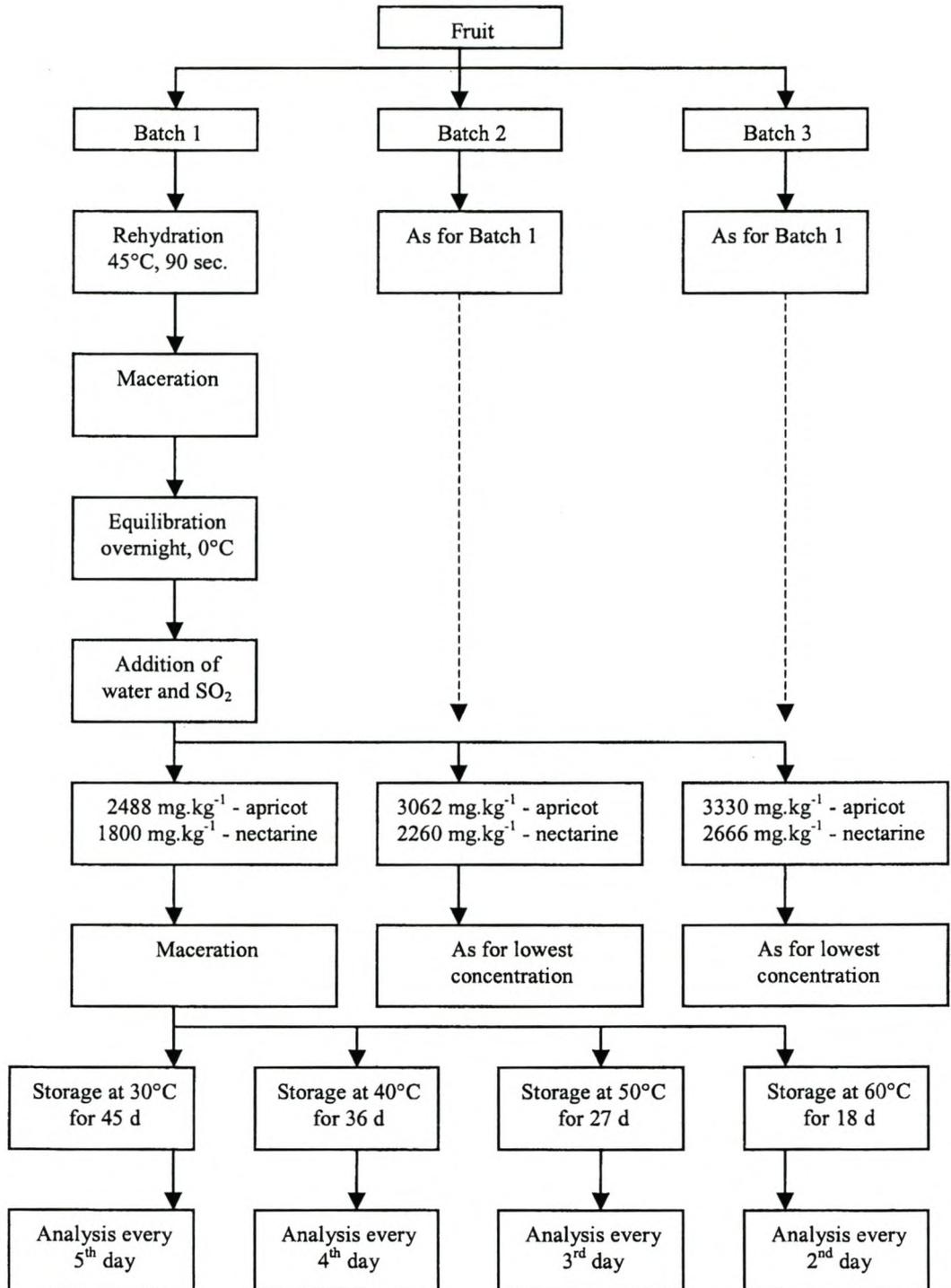


Figure 2. Schematic representation of experiment to determine the influence of sulphur dioxide (SO₂) content and storage temperature on shelf life of dried Royal type apricots and nectarines.

Vapodest 1 unit (Laboratory and Scientific Equipment (Pty) Ltd, Cape Town) according to the method described by Anon (1978).

Determination of a_w

The a_w of the fruit samples was determined with an electric hygrometer (Novasina Thermoconstanther TH-200, equipped with a TH-2 temperature regulator; manufactured by Defensor AG, Pfäffikon, Switzerland). The Universal filter eVC-26 was used to protect the sensor, which consisted of a conductivity cell. The sensor was calibrated using saturated salt solutions of $MgCl_2$, $Mg(NO_3)_2$, NaCl, and $BaCl_2$ each respectively corresponding to an a_w of 0.328, 0.529, 0.753 and 0.901 at 25°C, as standards. These solutions were supplied by the manufacturer. The macerated dried fruit were sealed in disposable plastic dishes (40 mm diameter x 12 mm deep) supplied with the apparatus and stored at 4°C until determination of water activity at 25°C.

Calculation of Q_{10} values

The colour data obtained during the various experiments were used for calculation of the Q_{10} values. The Q_{10} value can be defined as the increase in deterioration rate for every 10°C increase in temperature (Labuza & Saltmarch, 1981):

$$Q_{10} = \theta_S (T^\circ C) / \theta_S (T+10^\circ C)$$

where: $\theta_S (T^\circ C)$ = the shelf-life at any given temperature

$\theta_S (T+10^\circ C)$ = the shelf life at 10°C above that temperature

For the purpose of this study, the calculated rate of change in L^* at different temperatures, was used to determine Q_{10} .

Statistical analysis

Data obtained with the storage trials were tested for normality, using the Shapiro-Wilk test (Shapiro & Wilk, 1965), and submitted to analysis of variance. In order to determine whether significant changes in colour occurred over time separate regression functions (linear and quadratic) were fitted to each moisture content x storage temperature combination as well as SO_2 x storage temperature combination. A good fit was obtained with linear regression ($R^2 > 0.998$ for all colour parameters) and the intercepts and slopes of the resultant lines were subsequently compared, using

Student's t-LSD ($P = 0.05$). When not significantly different, the data were pooled and a single function fitted to the data. In all cases all the data points of the samples stored at 30° and 40°C were used. Only the first five data points of the samples stored at 50°C and only the first 4 data points of the samples stored at 60°C, were used.

Results

Change in moisture content, SO₂ content and a_w of rehydrated dried fruit during storage

The initial moisture contents of the rehydrated macerated dried apricot and nectarine samples for the study on the effect of moisture content are given in Table 1. Included are also the corresponding values after storage at 30°, 40°, 50° and 60°C, respectively. Moisture losses occurred during storage with the extent depending on temperature and storage time. The maximum moisture losses for both the apricot and nectarine samples occurred at 40°C (27 d) storage temperature. The samples subjected to shorter storage periods at 50°C (18 d) and 60°C (9 d) retained more moisture.

The initial and final SO₂ content of the samples with different initial moisture contents is given in Table 2. Maximum losses of SO₂ occurred at 60°C in all samples, with the exception of the apricot sample with 32% moisture content. Thus an increase in storage temperatures resulted in a steady decline in final SO₂ levels.

The SO₂ losses of the dried apricots and nectarines at different initial SO₂ levels during storage are given in Fig. 3 and 4, respectively. For all initial levels of SO₂, the SO₂ losses increased with increasing temperature. The samples stored at 30°C showed a steady decline in SO₂ concentration and reached levels ranging from 1014 to 1381 mg.kg⁻¹ for apricots and 1172 and 1838 mg.kg⁻¹ for nectarines after 40 d, depending on the initial SO₂ concentration. Samples stored at 40°C showed the same trend, but with the nectarine samples declining to 225 to 475 mg.kg⁻¹ and the apricot samples declining to 518 to 975 mg.kg⁻¹, after 32 d. The samples stored at 50°C reached levels between 418 and 517 mg.kg⁻¹ for apricots and 207 and 284 mg.kg⁻¹ for nectarines after only 24 d. Samples stored at 60°C underwent a rapid loss in SO₂. Both the apricot and nectarine samples showed the same tendencies with the samples reaching SO₂ levels of *ca.* 450 and 320 mg.kg⁻¹, respectively, after 16 d.

Table 1. The initial moisture content (m.c.) (% m/m) of Royal type apricots and nectarines with different initial moisture contents and their corresponding final moisture content after storage at 30° (36 d), 40° (27 d), 50° (18 d) and 60°C (9 d).

Fruit	Initial m.c. ¹	Final m.c. ¹			
		30°C	40°C	50°C	60°C
Apricots	32.42	31.02	28.08	29.76	30.82
	36.10	34.26	32.86	33.46	34.11
	40.14	38.05	36.73	36.73	38.65
Nectarines	31.65	29.97	28.46	28.49	30.02
	35.47	33.78	31.50	32.21	33.16
	39.42	37.03	35.36	35.88	37.09

¹ Results expressed on wet basis.

Table 2. The initial SO₂ contents (mg.kg⁻¹) of Royal type apricots and nectarines with different initial moisture contents (m.c.) (% m/m) and their corresponding SO₂ contents after storage at 30° (36 d), 40° (27 d), 50° (18 d) and 60°C (9 d).

Fruit	Initial m.c. ¹	Initial SO ₂	Final SO ₂			
			30°C	40°C	50°C	60°C
Apricots	32.42	2278	1608	1489	836	892
	36.10	2473	1823	1410	998	673
	40.14	2454	1810	855	886	604
Nectarines	31.65	1544	1165	515	411	332
	35.47	1416	1211	508	417	339
	39.42	1255	1117	337	265	259

¹ Results expressed on wet basis.

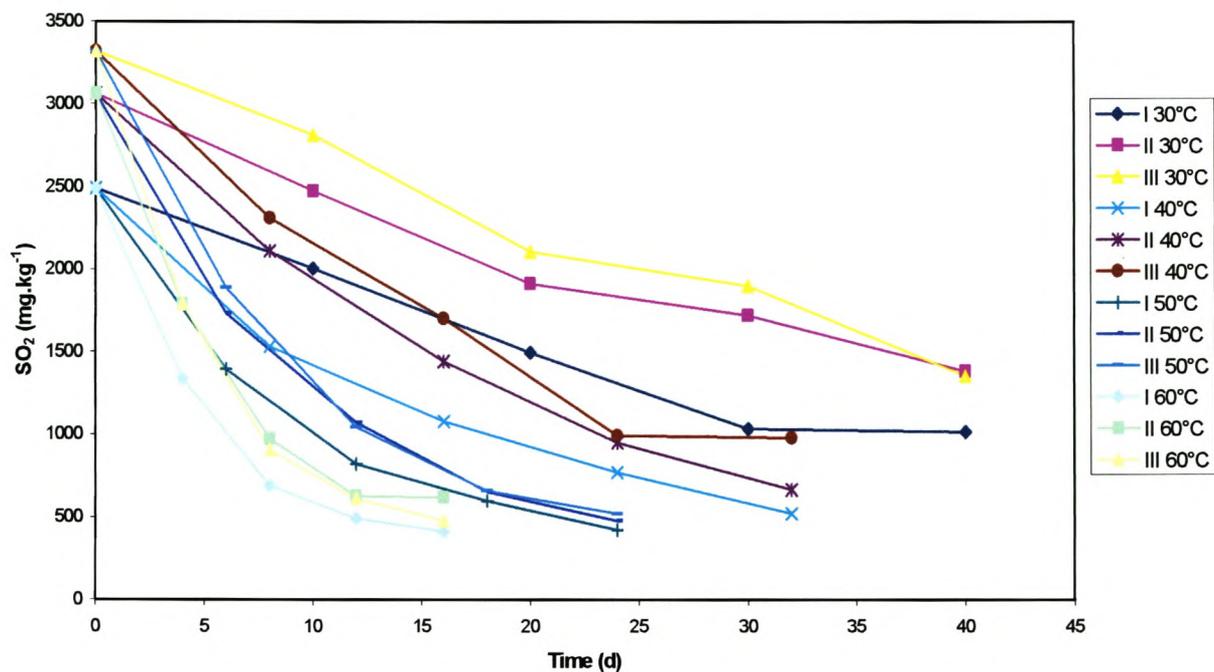


Figure 3. SO₂ content of macerated Royal type apricots (36% moisture content) with different initial SO₂ contents (I - 2490, II - 3060 and III - 3320 mg.kg⁻¹) during accelerated storage at 30°, 40°, 50° and 60°C.

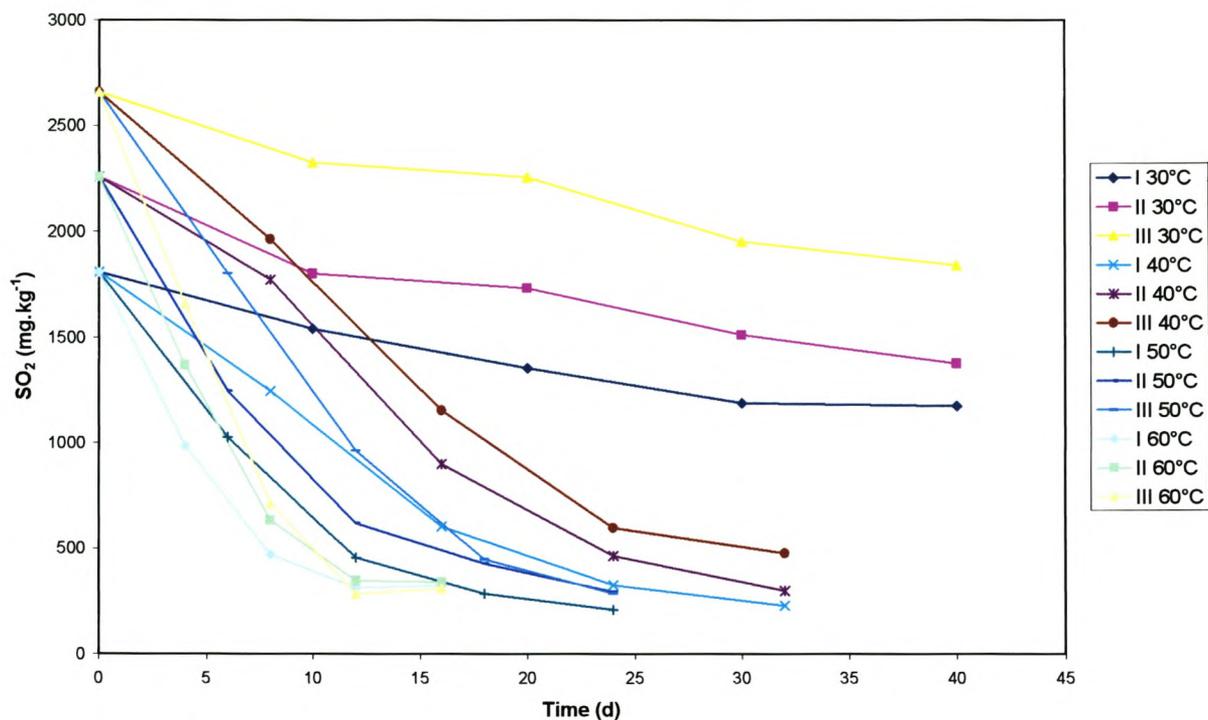


Figure 4. SO₂ content of macerated nectarines (36% moisture) with different initial SO₂ contents (I - 1800, II - 2260 and III - 2660 mg.kg⁻¹) during accelerated storage at 30°, 40°, 50° and 60°C.

From Fig. 5 it can clearly be seen that the a_w of the samples is related to the moisture content. A specific relationship between moisture content and a_w over the limited moisture range was established for both apricots and nectarines (Fig. 5). The a_w levels increased as the moisture content increased. The a_w levels showed the same tendency to that of the moisture content. The apricot samples with different initial moisture contents showed minimum values at 40°C. The apricot sample with initial moisture content of 40.14% showed the same a_w value at 30° and 40°C storage temperature. Nectarine samples with initial moisture content of 31.65% showed the same minimum a_w value at 50° and 60°C of 0.801, while the samples with an initial moisture content of 35.47% showed a minimum value at 50°C of 0.830. The samples with initial moisture content of 39.42% showed the minimum value at 40°C of 0.859.

Effect of moisture content on initial colour at different storage temperatures

The intercepts of the regression lines for the change in L^* values of apricot and nectarine samples with storage at different temperature and moisture content combinations are summarised in Tables 3 and 4, respectively. In all cases the relative order for initial L^* (intercept) was 40% > 36% > 32%, except in the case of nectarines stored at 50°C. The higher L^* value indicates lighter colour. The different moisture content data were pooled for a specific storage temperature to determine the effect of temperature only. Likewise, the data for different storage temperatures were pooled to determine the effect of moisture content only. Data are summarised in Tables 5 and 6. For the effect of moisture content only, the initial L^* value of the macerated apricot samples with 36 and 40% initial moisture content did not differ significantly, but both differed significantly ($P < 0.05$) from the samples with 32% initial moisture content. Nectarines samples with 40% initial moisture content differed significantly ($P < 0.05$) from the samples with 32 and 36% initial moisture content, while these two samples did not differ significantly.

Effect of SO_2 content on initial colour at different storage temperatures

For the apricots the relative order for initial L^* (intercept) was 3062 > 3330 > 2488 (Table 7). The data for samples at different SO_2 contents were pooled for a specific storage temperature to determine the effect of temperature only. Likewise, the data for different storage temperatures were pooled to determine the effect of SO_2 content only. Data are summarised in Table 8.

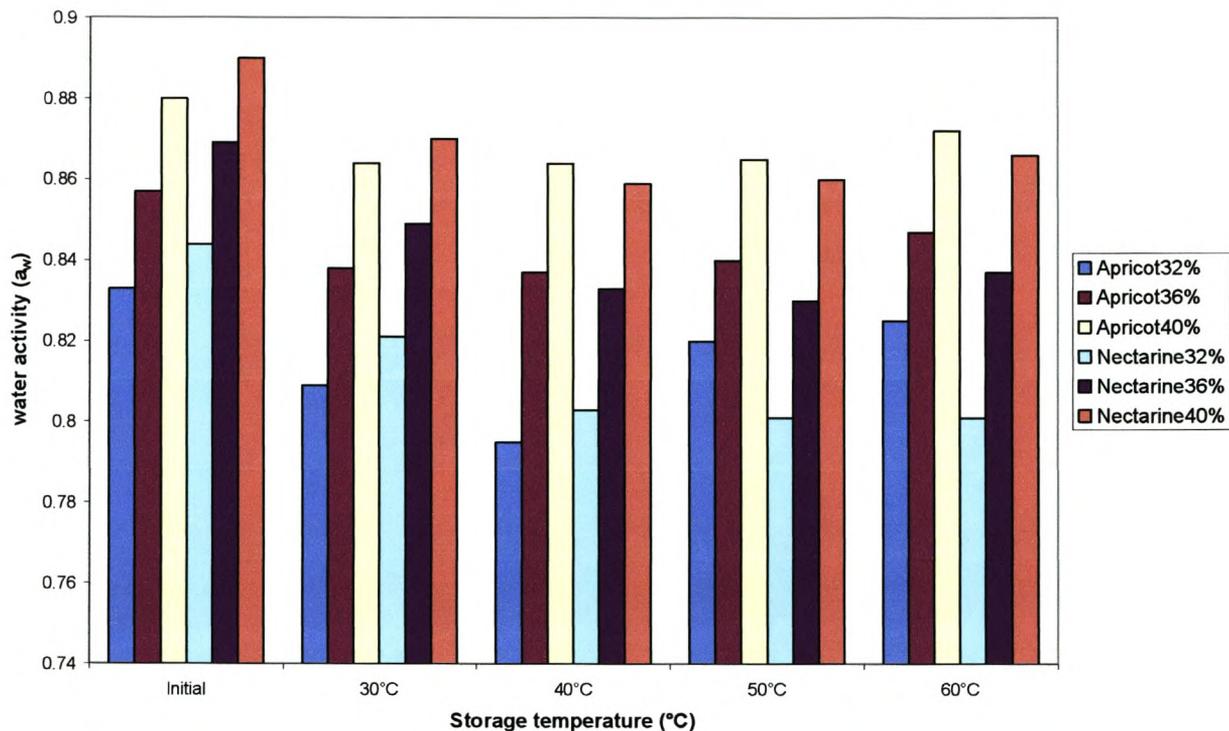


Figure 5. The initial a_w of macerated Royal type apricots and nectarines with different initial moisture contents and their corresponding a_w content after storage at 30° (36 d), 40° (27 d), 50° (18 d) and 60°C (9 d).

Table 3. The initial L* values and rates of deterioration (L*/d) obtained for macerated, dried Royal type apricots at different moisture contents (%) and storage temperature combinations.

Treatment combination¹	Initial L* value	Average	Rate of deterioration	Average
30 / 32	47.31		-0.1477	
30 / 36	48.10	48.26	-0.1358	-0.1402
30 / 40	49.39		-0.1371	
40 / 32	48.66		-0.6703	
40 / 36	49.96	49.69	-0.6605	-0.6482
40 / 40	50.46		-0.6138	
50 / 32	48.60		-1.587	
50 / 36	50.39	49.94	-1.590	-1.545
50 / 40	50.85		-1.459	
60 / 32	48.12		-3.494	
60 / 36	50.25	49.71	-3.441	-3.387
60 / 40	50.78		-3.228	

¹ Treatment combination shows the storage temperature first in °C and then the moisture content in % (30° and 40°C-all data points; 50°C -first 5 data points; 60°C -first 4 data points).

Table 4. The initial L* values and rates of deterioration (L*/d) obtained for macerated, dried nectarines at different moisture contents (%) and storage temperature combinations.

Treatment combination¹	Initial L* value	Average	Rate of deterioration	Average
30 / 32	48.26		-0.3780	
30 / 36	48.54	48.76	-0.3801	-0.3859
30 / 40	49.49		-0.3995	
40 / 32	46.72		-0.8811	
40 / 36	47.18	47.61	-0.9180	-0.9283
40 / 40	48.94		-0.9857	
50 / 32	47.62		-1.680	
50 / 36	47.17	48.19	-1.637	-1.691
50 / 40	49.80		-1.756	
60 / 32	47.71		-3.404	
60 / 36	48.81	48.90	-3.447	-3.423
60 / 40	50.20		-3.418	

¹Treatment combination shows the storage temperature first in °C and then the moisture content in % (30° and 40°C-all data points; 50°C -first 5 data points; 60°C -first 4 data points).

Table 5. Statistical data showing the differences in L* values and rates of deterioration obtained for macerated, dried Royal type apricots at three moisture contents (32, 36 and 40%) and stored at 30°, 40°, 50° and 60°C. Table shows combined effect of moisture content and temperature, respectively.

Variable	Moisture content		Temperature	
	Moisture (%)	T Grouping ¹	Temperature (°C)	T Grouping ¹
Initial L*	40	A		
Initial L*	36	A		
Initial L*	32	B		
Rate ²	40	A	30	A
Rate	36	B	40	B
Rate	32	B	50	C
Rate			60	D

¹ Means with the same letter are not significantly different.

Alpha = 0.05; df = 24; Critical value of T = 2.06.

² Rate of change in L* (L*/d)

Table 6. Statistical data showing the differences in L* values and rates of deterioration obtained for macerated, dried nectarines at three moisture contents (32, 36 and 40%) and stored at 30°, 40°, 50° and 60°C. Table shows combined effect of moisture content and temperature, respectively.

Variable	Moisture content		Temperature	
	Moisture (%)	T Grouping ¹	Temperature (°C)	T Grouping ¹
Initial L*	40	A		
Initial L*	36	B		
Initial L*	32	B		
Rate ²	40	A	30	A
Rate	36	A	40	B
Rate	32	A	50	C
Rate			60	D

¹ Means with the same letter are not significantly different.

Alpha = 0.05; df = 24; Critical value of T = 2.06.

² Rate of change in L* (L*/d)

Table 7. The initial L* values and rates of deterioration (L*/d) obtained for macerated, dried Royal type apricots at different SO₂ contents and storage temperature combinations.

Treatment combination¹	Initial L* value	Average	Rate of deterioration	Average
30 / 2488	46.63		-0.2437	
30 / 3062	48.14	47.49	-0.1831	-0.1954
30 / 3330	47.69		-0.1594	
40 / 2488	47.14		-0.7989	
40 / 3062	49.28	48.48	-0.7542	-0.7665
40 / 3330	49.04		-0.7464	
50 / 2488	47.46		-1.757	
50 / 3062	49.66	48.72	-1.821	-1.770
50 / 3330	49.05		-1.732	
60 / 2488	47.52		-4.008	
60 / 3062	49.27	48.45	-3.682	-3.834
60 / 3330	48.56		-3.813	

¹ Treatment combination shows the storage temperature first in °C and then the SO₂ content in mg.kg⁻¹ (30° and 40°C-all data points; 50°C -first 5 data points; 60°C -first 4 data points).

Table 8. Statistical data showing the differences in L* values and rates of deterioration obtained for macerated, dried Royal type apricots at three SO₂ contents (2488, 3062 and 3330 mg.kg⁻¹) and stored at 30°, 40°, 50° and 60°C). Table shows combined effect of SO₂ concentration and temperature, respectively.

Variable	SO ₂ concentration		Temperature	
	Initial SO ₂ (mg.kg ⁻¹)	T Grouping ¹	Temperature (°C)	T Grouping ¹
Initial L*	3062	A		
Initial L*	3330	B		
Initial L*	2488	C		
Rate ²	3062	A	30	A
Rate	3330	A	40	B
Rate	2488	A	50	C
Rate			60	D

¹ Means with the same letter are not significantly different.

Alpha = 0.05; df = 24; Critical value of T = 2.06.

² Rate of change in L* (L*/d)

If the effect of the SO₂ content only is considered (Table 8), the intercept value of all the macerated apricot samples differed significantly ($P < 0.05$) from each other. This result is, however, unexpected because it was not the highest SO₂ concentration that resulted in the highest L* value. This is attributed to experimental variation in the initial colour of the dried fruit used.

The initial L* values of the nectarines with different SO₂ contents are given in Table 9. Initial SO₂ content did not influence initial L* values (Table 10).

Effect of moisture content on colour retention

In Fig. 6 and 7 the colour deterioration of the apricot and nectarine samples with different moisture levels (32, 36 and 40%), is depicted. In most cases, the rate of change in L* of apricots and nectarines with storage, decreased with moisture content (Table 3). The rate of change at 40% moisture content was significantly ($P < 0.05$) lower than at 36% and 32%, but no significant difference was observed between these latter samples (Table 5).

The effect of moisture (at different storage temperatures) on colour deterioration of nectarines was less pronounced than for apricots (Figures 6 and 7). Samples with higher moisture contents had higher initial L* values, but the L* values at the different moisture contents slowly converged. Overall, moisture content had no significant effect on the rate of change in L* (Table 6).

Effect of SO₂ content on colour retention

The effect of SO₂ on colour retention of apricots and nectarines during storage at 30°, 40° 50° and 60°C, is depicted in Fig. 8 and 9, respectively. Increasing the SO₂ content of apricots from 2488 to 3062 mg.kg⁻¹ did not improve the colour retention during storage. No significant difference was obtained for the rate of change in L* (Table 8). However, for nectarines, SO₂ content had a significant effect (Table 10) and the increase in SO₂ content from 1800 to 2666 generally decreased the rate of change in L* (Table 9).

Table 9. The initial L* values and rates of deterioration (L*/d) obtained for macerated, dried nectarines at different SO₂ contents and storage temperature combinations.

Treatment Combination¹	Initial L* value	Average	Rate of deterioration	Average
30 / 1800	47.31		-0.3245	
30 / 2260	47.45	47.42	-0.2556	-0.2623
30 / 2666	47.50		-0.2069	
40 / 1800	46.09		-0.8293	
40 / 2260	46.57	46.74	-0.7806	-0.7856
40 / 2666	47.56		-0.7471	
50 / 1800	48.05		-1.988	
50 / 2260	47.81	47.97	-1.717	-1.747
50 / 2666	48.06		-1.536	
60 / 1800	48.94		-4.588	
60 / 2260	48.53	48.60	-3.888	-4.030
60 / 2666	48.35		-3.613	

¹ Treatment combination shows the storage temperature in °C followed by the SO₂ content in mg.kg⁻¹ (30° and 40°C-all data points; 50°C -first 5 data points; 60°C -first 4 data points).

Table 10. Statistical data showing the differences in L* values and rates of deterioration obtained for macerated, dried nectarines at three SO₂ contents (1800, 2260 and 2666 mg.kg⁻¹) and stored at 30°, 40°, 50° and 60°C. Table shows combined effect of SO₂ concentration and temperature, respectively.

Variable	SO ₂ concentration		Temperature	
	Initial SO ₂ (mg.kg ⁻¹)	T Grouping ¹	Temperature (°C)	T Grouping ¹
Initial L*	2666	A		
Initial L*	1800	A		
Initial L*	2260	A		
Rate ²	2666	A	30	A
Rate	2260	B	40	B
Rate	1800	C	50	C
Rate			60	D

¹ Means with the same letter are not significantly different.

Alpha = 0.05; df = 24; Critical value of T = 2.06.

² Rate of change in L* (L*/d)

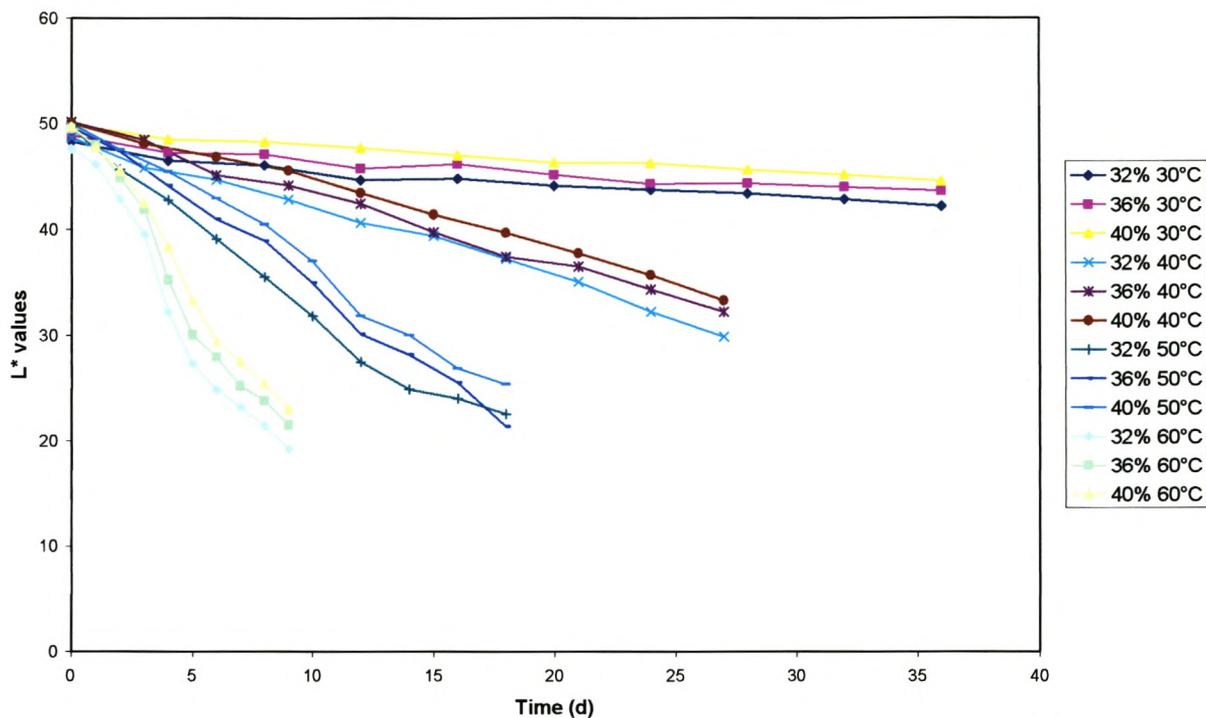


Figure 6. Changes in the L* values of macerated, dried Royal type apricots with different initial moisture contents (32, 36 and 40%) during storage at 30°, 40°, 50° and 60°C.

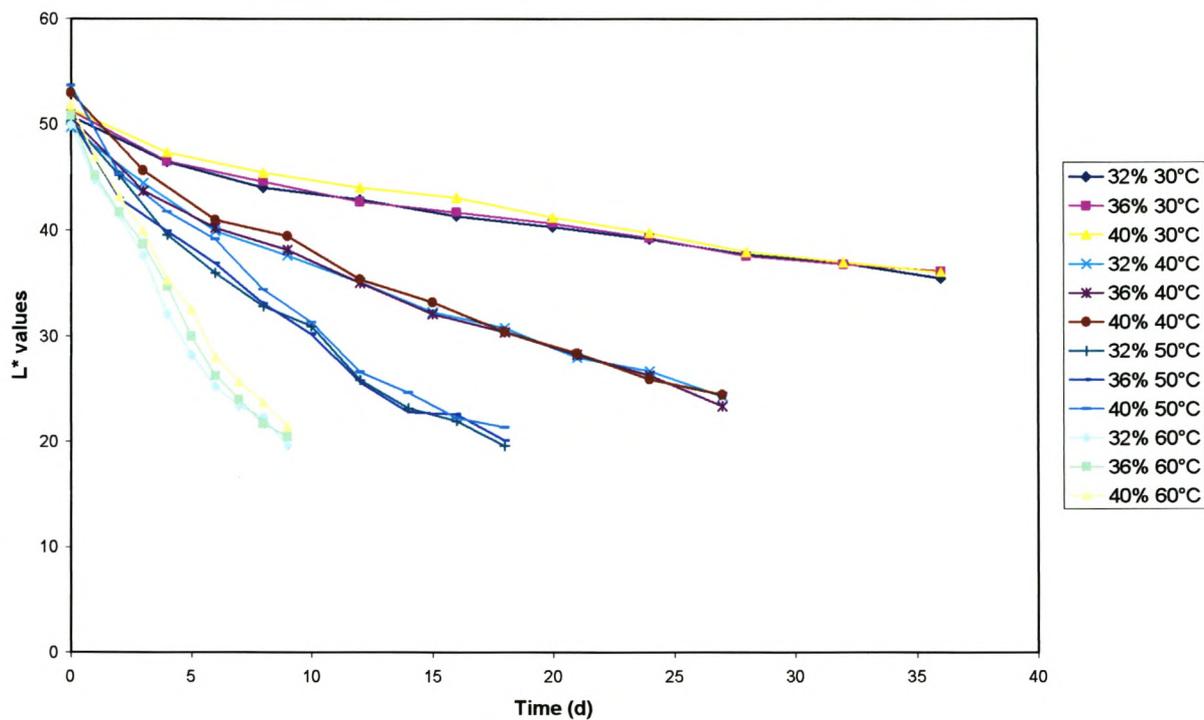


Figure 7. Changes in the L* values of macerated, dried nectarines with different initial moisture contents (32, 36 and 40%) during storage at 30°, 40°, 50° and 60°C.

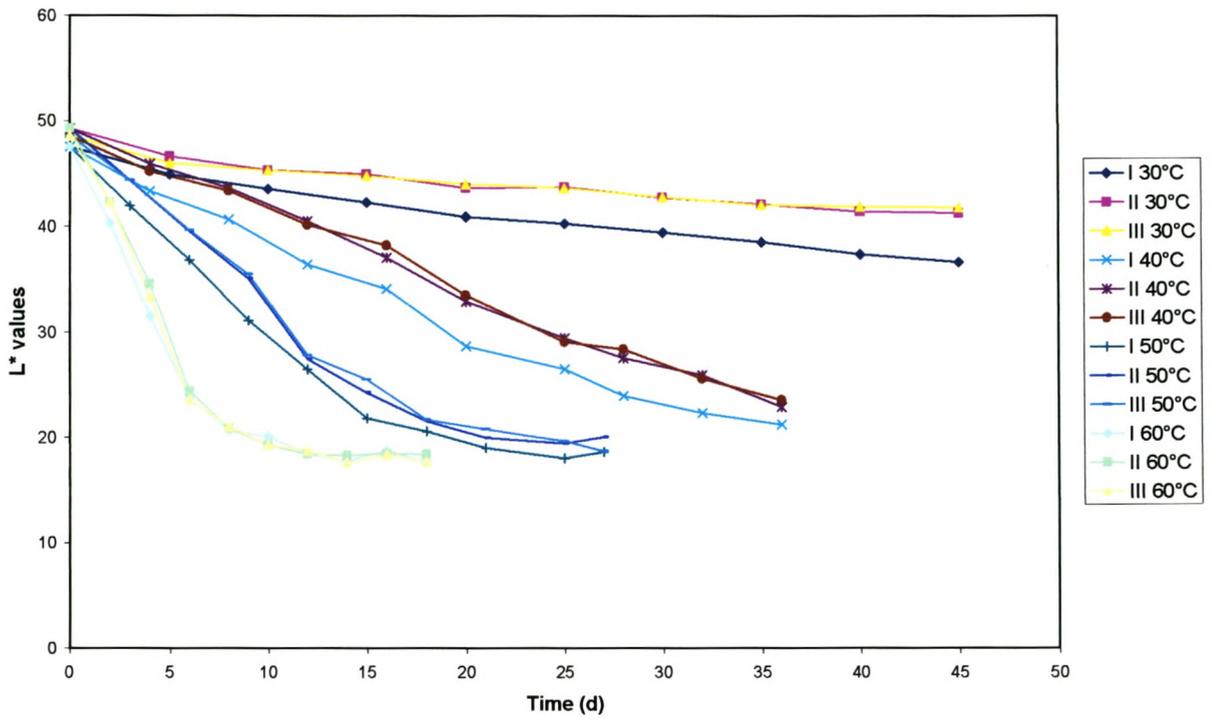


Figure 8. Changes in the L* values of macerated, dried Royal type apricots with different initial SO₂ contents (I: 2488, II: 3062 and III: 3330 mg.kg⁻¹) during storage at 30°, 40°, 50° and 60°C.

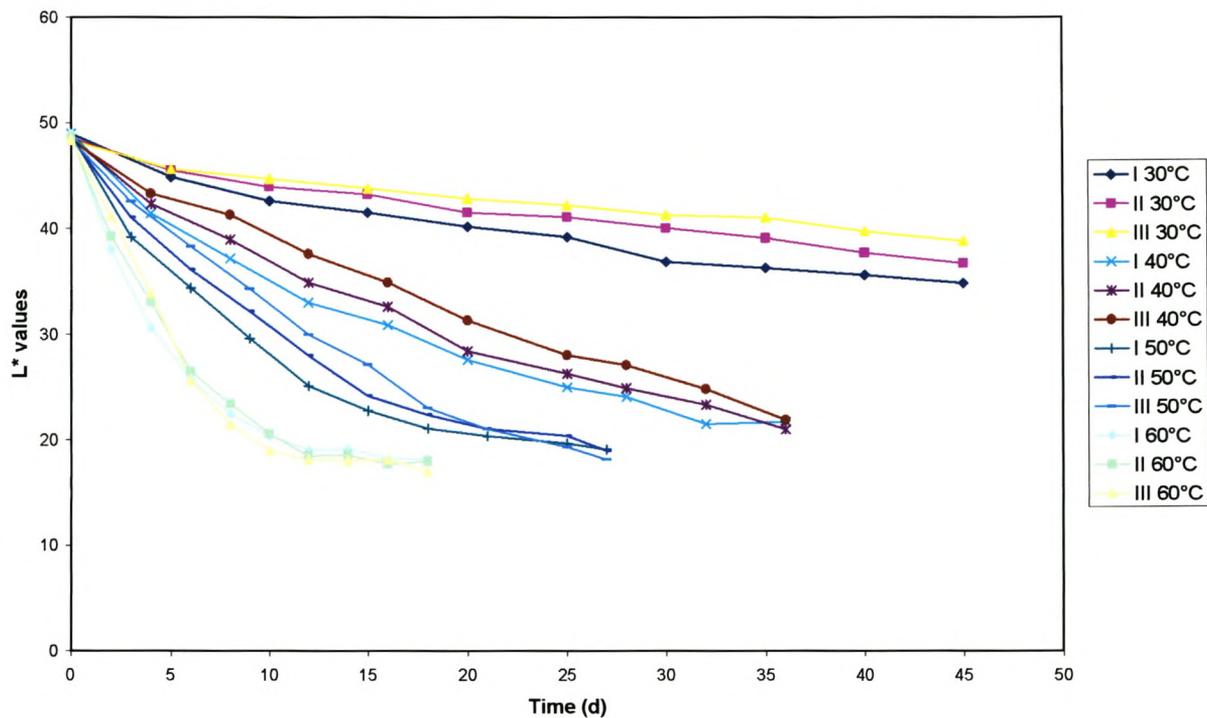


Figure 9. Changes in the L* values of macerated, dried nectarines with different initial SO₂ contents (I: 1800, II: 2260 and III: 2666 mg.kg⁻¹) during storage at 30°, 40°, 50° and 60°.

Effect of storage temperature on colour retention

The data in Fig. 6 shows the decrease in L^* for apricot with actual moisture contents, 32.42, 36.10 and 40.14%, stored at 30°, 40°, 50° and 60°C. The rates of deterioration for the respective moisture x temperature combinations are given in Table 3. Temperature had a significant effect ($P < 0.05$) on the rate of change in L^* (Table 5) with higher rates at higher temperatures (Table 3). Nectarines at 31.65, 35.47 and 39.42% moisture contents followed the same trends (Fig. 7) than for apricots (Fig. 6), but in this case, the rate of change in L^* at the respective storage temperatures was higher (Table 4) than for apricots (Table 3), and especially noticeable at 30° and 40°C. The data in Fig. 8 and 9 show the decrease in L^* for apricots and nectarines at different SO_2 contents during storage at 30°, 40°, 50° and 60°C. The moisture content of the fruit was 36%. The rate of change in L^* for the different SO_2 and temperature treatment combinations, as well as the average values at the respective temperatures is given in Tables 7 and 9 for apricots and nectarines, respectively. Increasing storage temperature significantly ($P < 0.05$) increased the rate of change in L^* for both apricots and nectarines (Tables 8 and 10).

Q_{10} values

The Q_{10} values were determined by using the rate of change in L^* found in Tables 3, 4, 7 and 9. The calculated values for all the samples are given in Table 11. The average deterioration rates of apricots (different moisture contents) for the temperature range 30° to 40°C, 40° to 50°C and 50° to 60°C are 4.62, 2.38 and 2.16 respectively. The corresponding rates for apricots with different SO_2 contents are 3.92, 2.31 and 2.17.

Nectarines, with different moisture contents, for the temperature range of 30° to 40°C had an average deterioration rate of 2.41, decreasing to 1.82 and 2.02 for the temperature range 40° to 50°C and 50° to 60°C, respectively. At these temperature ranges the average Q_{10} values for samples with different SO_2 levels, were 3.00, 2.22 and 2.31, respectively.

Table 11. Q_{10} values for macerated dried Royal type apricots and nectarines including averages for the temperature ranges.

Sample	30°-40°C		40°-50°C		50°-60°C		
Apricot	32% ¹	4.54		2.37		2.20	
	36%	4.86	4.62	2.41	2.38	2.16	2.19
	40%	4.48		2.38		2.21	
Nectarine	32%	2.33		1.91		2.03	
	36%	2.42	2.41	1.78	1.82	2.11	2.02
	40%	2.47		1.78		1.95	
Apricot	2488 ²	3.28		2.20		2.28	
	3062	4.12	3.92	2.41	2.31	2.02	2.17
	3330	4.68		2.32		2.20	
Nectarine	1800	2.56		2.40		2.31	
	2260	3.05	3.00	2.20	2.22	2.26	2.31
	2666	3.61		2.06		2.35	

¹ Moisture content (% m/m).² SO₂ content (mg.kg⁻¹).

Discussion

The extent of moisture loss by the samples during storage can be attributed to a combination of temperature and time of exposure. The maximum losses did not occur at the highest storage temperatures, since shorter storage periods were used. These losses can be attributed to water vapour escaping through the sides of the petri dishes. This was aggravated by the headspace. Although samples were left to reach ambient temperature before opening of the petri dish, some residual water was still to be found on the lid of the dish. This water did not re-equilibrate with the sample upon standing before analysis.

The a_w of each sample was closely correlated to the moisture content with higher moisture content resulting in higher a_w values. The correlation was not linear as explained in Chapter 3. The a_w of dried Turkish apricots with moisture contents of 25 and 35% at 20°C was 0.75 and 0.85, respectively (Mahmutoğlu *et al.*, 1996). This corresponds to results found in this study. The a_w of the product affects the extent of nonenzymatic browning during storage. In the a_w range above 0.80, the reactants of nonenzymatic browning reactions are diluted and the browning rate decreased (Leung, 1987). Aguilera *et al.* (1987) found maximum browning a_w for Sultana grapes to be 0.84. Above this a_w ($a_w > 0.84$) the nonenzymatic browning rate decreased. This was the case for the apricot samples when the moisture content was increased from 36 to 40% (corresponding a_w values of 0.857 and 0.880) and the positive effect on colour retention was confirmed with the higher L^* values for samples with higher a_w values. The samples with higher a_w showed better colour retention than found for the apricot samples with lower a_w values. This was not true for the nectarine samples where the trend was a reverse, except for samples stored at 50°C. The reason for the difference in the fruit is probably due to the fact that the a_w value for maximum browning for nectarines is higher than for apricots due to compositional differences between the fruit. The nectarine samples had not reached the maximum browning point and this would explain why the rate of browning increased with an increase in a_w in the nectarine samples.

Since most spoilage bacteria cannot grow below an a_w value of 0.90, they hold no danger for this high moisture product. At 40% moisture content the apricots and nectarine samples had an a_w of 0.88 and 0.89, respectively. This does, however, make the product susceptible for yeast and mould growth, as it requires a minimum a_w of

0.88 and 0.80 respectively to proliferate (Jay, 1996). A product with a moisture content of 40% will necessitate a thorough pasteurisation. The a_w of all the other samples were above 0.80, but below 0.88. This would make the product susceptible only to mould spoilage. Since SO_2 has a well documented antimicrobial activity (Taylor *et al.*, 1986), its presence will help to further stabilise the product.

Substantial losses in SO_2 occurred during storage due to high storage temperatures. At higher temperatures SO_2 will be more susceptible to loss through permeation into the atmosphere and the maceration of the fruit probably exacerbated the loss of SO_2 . With these high rates of SO_2 loss the fruit would become more susceptible to browning, than when considering only the effect of temperature on the rate of the Maillard reaction. In dried apples, the loss of free SO_2 was shown to be a function of storage temperature (Sayavedra & Montgomery, 1983). The Maillard reaction is temperature dependent (Labuza & Saltmarsh, 1981) and the reaction rate is increased at higher temperatures and thus the free SO_2 takes more readily part in the resulting inhibitory reaction. The reaction of sulfites with the carbonyls generated by nonenzymatic browning accounts for most of the loss of sulfites (Wedzicha *et al.*, 1984), consequently resulting in a lower final free SO_2 content (Davis *et al.*, 1973).

An increase in moisture content of the fruit led to changes in the initial colour values, i.e. higher L^* values were obtained for apricots and nectarines. This phenomenon is probably due to the dilution effect on the constituents of the dried fruit as the fruit is less concentrated at higher moisture contents. It can also be contributed to a change in the texture of the fruit. The increased moisture content then causes the fruit to expand and became more swollen. This, in turn, causes a change in surface texture.

An increase in moisture content (36 to 40%) resulted in a decrease in the rate of change in L^* for apricots. The positive effect of increased moisture content on colour retention of apricots can be contributed to the dilution effect of water on the reactants of the Maillard reaction. By the laws of mass reaction, the rate of a reaction is proportional to concentration, and a decrease in concentration through the dilution with water will decrease the reaction rate (Labuza *et al.*, 1970; Eichner & Ciner-Doruk, 1981). The combination of a higher initial L^* and slower rate of change with increasing moisture content would therefore ensure a longer shelf life. This effect was not evident in the nectarines for the same reasons as explained above with regards to the a_w . The small advantage that the nectarines with the higher moisture contents

appeared to have could solely be attributed to the higher initial L^* value, with addition of more free water. It is rather the combined effect of the higher initial value and smaller rate of change that caused the higher moisture samples to retain colour better than the other samples with lower moisture contents.

The reason for the strong influence of temperature on colour retention of the samples can be attributed to several factors. The first of these is the greater reaction rate of the Maillard reaction at higher temperatures (Labuza & Saltmarch, 1981), which has dark coloured melanoidins as final product and darkens the product. According to Labuza & Saltmarch (1981) the Maillard reaction exhibits a very high temperature coefficient ($2 \leq Q_{10} \leq 8$) with the result that increasing the temperature increase the reaction rate. Another important consideration is the accelerated loss of SO_2 and moisture content at higher temperatures found in this study.

The SO_2 content had a profound effect on colour retention with higher SO_2 concentrations giving rise to better colour retention. This was expected, since the effect of SO_2 on colour retention is widely reported in the literature (McBean *et al.*, 1967; Harel *et al.*, 1978; Bolin & Jackson, 1985; Ames, 1990; Sapers, 1993; Rossellò *et al.*, 1994). Rossellò *et al.* (1994) reported good colour retention for dried apricot samples with 18% moisture content and SO_2 content of 1400 mg.kg^{-1} , stored at 20° - 25°C . Harel *et al.* (1978) concluded that a storage temperature of 4°C was needed to preserve rehydrated apricots with moisture contents of 27 - 38% and SO_2 contents of 630 mg.kg^{-1} for 26 months. It is also clear from the results that the apricots lost SO_2 more readily than the nectarines. This can be contributed to compositional differences.

The method for determining the Q_{10} values differed from the method used by Labuza & Saltmarch (1981). The rate of change in L^* was used, rather than the actual L^* values, due to the fact that the initial L^* values of the samples differ slightly. Using the rate of change in L^* will thus render a more accurate result. The Q_{10} values of 1.78 to 4.86 are an indication of a relatively high temperature coefficient for the browning reaction and are consistent with results found by Labuza & Saltmarch (1981), which varied between 2 to 8. The greater the Q_{10} value the greater the influence of temperature. Data obtained suggest that the influence of temperature on shelf life is greater at lower temperatures, which resembles realistic storage temperatures. The deterioration rate increased for apricot samples stored at 30° , 40° ,

50° and 60°C varied between 2.02 and 4.86, with values decreasing as the storage temperature increased, which means that the browning reaction is less influenced by temperature at elevated temperatures. Values of between 2.33 and 3.61 were found for nectarines stored at 30°C compared to an average value of 2.09 for nectarine samples stored at 40°, 50° and 60°C. The shelf life of nectarine samples with different moisture contents stored at 40°C was half that of the corresponding samples stored at 30°C. The shelf life of nectarine samples with different SO₂ contents stored at 40°C was 2.2 times lower than the corresponding samples stored at 30°C. It is therefore of great importance that the high moisture product be kept at cold chain temperatures (5°C) during distribution and sale.

Conclusions

Fruit moisture and SO₂ contents, as well as storage temperature, are important factors in determining the shelf life of “soft-eating” macerated dried fruit. A combination of high SO₂, high moisture and low temperatures gave the best colour retention, based on the L* value of the CIELab system. A high SO₂ level will increase the initial L* values and also decrease the rate of deterioration. High moisture levels will not necessarily decrease the rate of deterioration, but will increase the initial L* value and thus increase shelf life. Low temperatures are of extreme importance in prolonging the shelf life of the high moisture dried fruit products since it decreases the rate of discolouration. The effect of these factors must still be investigated using whole dried fruit halves.

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Chapter 5

Evaluation of effective rehydration and pasteurisation techniques for the production of high moisture dried Royal type apricots and nectarines tested for colour retention under accelerated and normal storage conditions

Abstract Whole dried nectarine fruit halves were rehydrated using three different methods to reach moisture contents of 36 and 40%, respectively. Dry heat and steam pasteurisation techniques were used to render a microbiologically safe product. Commercial packaging material i.e. aluminium laminated pouch was used and the atmosphere was modified with CO₂ to lower the O₂ concentration in the headspace. A two-step rehydration at 45°C, steam pasteurisation at 90°C for 150 min and packaging under a high CO₂ atmosphere rendered a product with the best colour retention under accelerated storage conditions of 40°C for eight weeks. These conditions were evaluated for Royal type apricot and nectarine halves against the standard method used by the industry in a shelf life study. Samples were stored at 5° and 25°C for a period of 30 weeks to determine shelf life. Samples were tested every 5 weeks to determine gas composition and concentration in headspace, colour retention and SO₂ concentration. Objective colour measurement (L*) was used as an indication of colour retention. Both apricots and nectarines achieved a shelf life of 89 weeks at 5°C but only 32 weeks at 25°C.

Introduction

The South African dried fruit industry produces a high moisture, “soft-eating” dried fruit with moisture content of *ca.* 36% (m/m). These include Royal apricots and nectarines. The colour stability of these products is unsatisfactory due to rapid browning resulting in a poor shelf life. Nectarines are the most sensitive to these non-

enzymatic browning reactions (J. Schoeman, 2000, personal communication, SAD). The non-enzymatic Maillard browning reaction is accelerated through prolonged exposure to high temperatures (Harel *et al.*, 1978). This temperature damage occurs during the pasteurisation process employed by industry. Due to the high moisture content, the products are susceptible to attack by micro-organisms and an effective pasteurisation process is vital for a safe and successful product since micro-organisms are not entirely inhibited by SO₂ (Ames, 1990).

The product, packed under normal atmospheric conditions, is sealed in a laminated foil pack, which does not allow for gas transfer. The resulting presence of O₂ allows the growth of micro-organisms (Jay, 1996) and reacts with the SO₂ to form an inactive sulphate (Wedzicha, 1984). The introduction of high levels of CO₂ could suppress the growth of micro-organisms (Jay, 1996) and also slow down the reaction rate of the Maillard reaction by forcing the Strecker degradation in the opposite direction (Sapers, 1993).

In Chapter 4 it was found that the shelf life of an unpasteurised macerated dried fruit product could be prolonged by increasing the moisture content from 36 to 40% in addition to an initial SO₂ content of 2000 mg.kg⁻¹ and storage at low temperatures. The use of modified atmosphere packaging and an adequate pasteurisation, in addition to the above mentioned parameters, remains to be tested on whole dried fruit halves.

The aims of this study were: (i) to find an effective rehydration technique, which is fast, causes little or no browning and also keeps the texture integrity of the fruit intact; (ii) to find a pasteurisation process that does not cause excessive browning, but still results in a microbiological stable product; (iii) to investigate the influence of high CO₂ on colour retention in a modified atmosphere packed product; and (iv) to evaluate the optimum rehydration, pasteurisation and modified atmosphere packaging conditions in a shelf life study.

For the first three objectives only nectarines were used due to the susceptibility of these fruit to browning reactions thereby giving an indication of the effect of the different parameters on colour retention. The treatments and combinations thereof were tested under accelerated storage conditions. The second part of this investigation entailed the shelf life study, using both dried Royal type apricots and nectarines and comparing it to the existing process used by industry.

Material and methods

Accelerated storage

Fruit

Choice grade large dried nectarines, obtained from SAD, Worcester, South Africa, were used to determine the best rehydration technique, pasteurisation process, packing atmosphere and combination thereof. The nectarines, with an average moisture content of 15.5% (wet basis), were stored at *ca.* 0°C for a maximum of three months in sealed plastic containers to prevent any moisture loss. A schematic representation of the experiment to determine the influence of rehydration method, moisture content, pasteurisation method and packaging atmosphere on colour retention of dried nectarines in an accelerated shelf life trial is given in Fig. 1.

Rehydration of fruit

The efficiency of different rehydration techniques was investigated. A first rehydration step was carried out at 45°C for 60, 90 and 120 sec, respectively, to increase moisture content to *ca.* 22-26%. Rehydration was performed by dipping the dried fruit halves in a stainless steel basket in water. Superficial water was shaken off and the fruit were placed overnight in sealed containers at 0°C to allow the moisture content to equilibrate. This was followed by a second rehydration step to increase the moisture content to 36 and 40% respectively, according to three procedures: (i) addition of the required mass of free water to the fruit in the pouches according to the method used by industry; (ii) rehydration under atmospheric pressure at 45°C for 90, 120 or 180 sec; and (iii) rehydration under vacuum at initial water temperature of 40°C for 90, 120 or 180 sec. The rehydrated fruit were packed in containers, which were left open for *ca.* 30 min to allow evaporation of excess superficial moisture before determination of moisture content. Final contact times were 90 and 120 sec, and 90 and 210 sec to reach 36 and 40% moisture content, respectively.

Samples of *ca.* 5 kg were prepared for the accelerated storage trial. The nectarines were subjected to each of the above-mentioned six rehydration (2 moisture contents x 3 rehydration methods) treatments. The rehydrated nectarines of each treatment were randomly subdivided into samples (*ca.* 250 g; 10 fruit halves; packed in aluminium foil pouches (Kohler), supplied by SAD, Worcester). These samples were subjected to the following pasteurisation procedures:

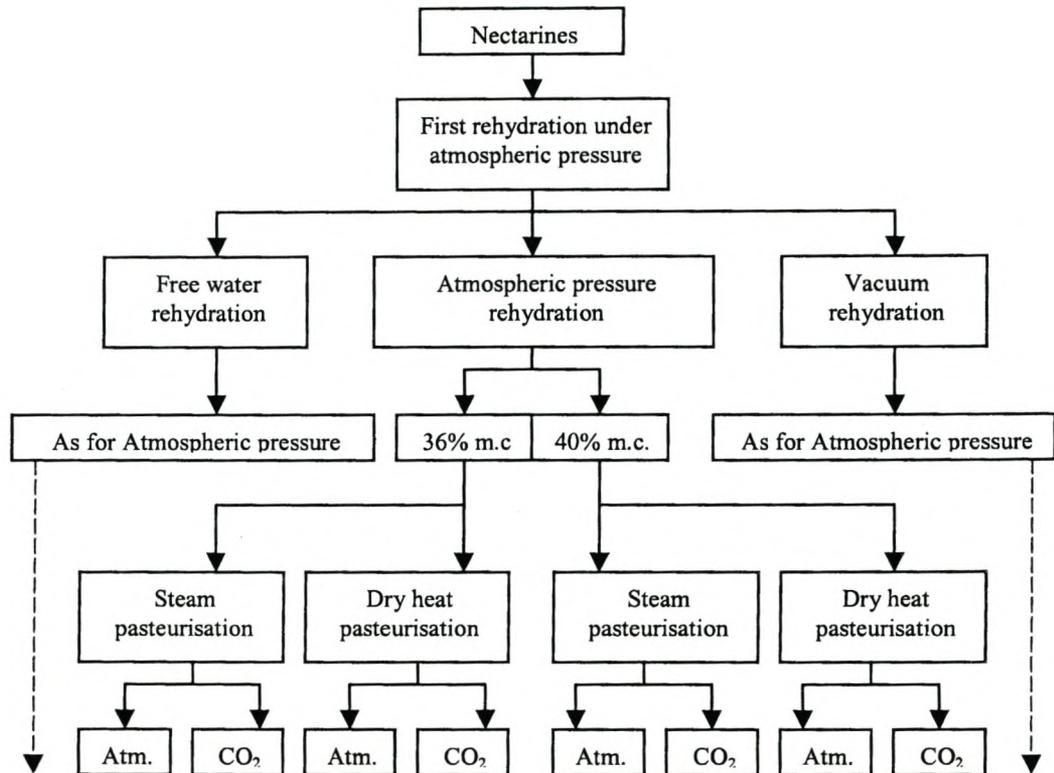


Figure 1. Schematic representation to determine the influence of rehydration method, moisture content (m.c.), pasteurisation method and packaging atmosphere on colour retention of rehydrated dried nectarines in an accelerated shelf life trial of 8 weeks at 40°C. Study was repeated with a second batch of nectarines.

Pasteurisation of pouches

The sealed pouches were pasteurised at 80°C for 7 h in a drying tunnel in a manner similar to that used during commercial production. The other pasteurisation technique employed was to put open pouches in an enclosed steam box and flush the pouches with direct steam at 90°C for 2.5 h. The pouches were positioned in such a way that allowed steam to enter the pouch and to allow the fruit maximum steam contact. All treatments were repeated with a second batch of dried nectarines.

Modified atmosphere packaging

Half of the samples were flushed with CO₂ at a flow rate of 25 l.min⁻¹ for 20 sec, whilst the remainder were packed under normal atmosphere. The samples that were pasteurised in the dry air tunnel were flushed and sealed before pasteurisation. The steam-pasteurised samples were firstly subjected to the heat treatment and then flushed with CO₂ and sealed.

Accelerated storage

All pouches were subjected to accelerated storage conditions at 40°C in a temperature-controlled room. One pouch of each treatment combination was randomly removed at 0, 2, 4, 6 and 8 w for determination of the CO₂ and O₂ contents of the headspace, and colour and SO₂ content of the samples. All analyses were performed within 24 h.

Shelf life study

Fruit

Choice grade dried Royal type apricots and nectarines were used to determine the shelf life of the products using both the standard method employed by the industry and the new process developed in this study. In addition to the nectarines, Choice grade, large dried Royal apricots (19.5% moisture) were also obtained from SAD, Worcester, South Africa. The dried fruit were stored at *ca.* 0°C for a maximum of three months in sealed plastic containers before commencement of the experiment. A schematic representation of the experiment to determine the influence of pasteurisation method, packaging atmosphere and storage temperature on colour retention of high moisture dried Royal type apricots and nectarines in the shelf life trial is given in Fig. 2.

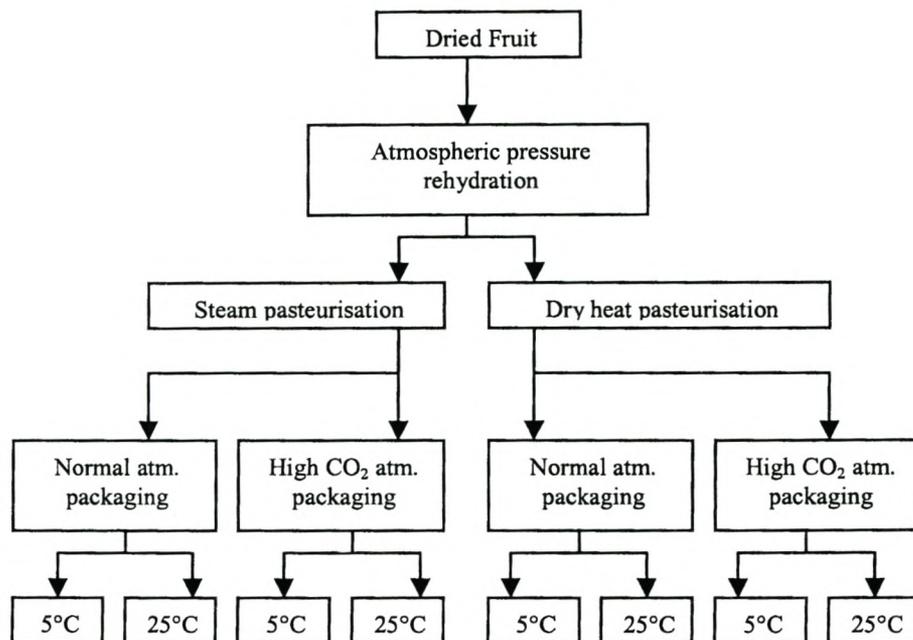


Figure 2. Schematic representation to determine the influence of pasteurisation method, packaging atmosphere and storage temperature on colour retention of rehydrated dried Royal type apricots and nectarines in a shelf life trial of 30 weeks at 5° and 25°C. Study was repeated 3 times with a second and third batch of dried fruit.

Rehydration of fruit

The first rehydration step was carried out at 45°C for 90 sec to increase moisture content to *ca.* 26%. Superficial water was shaken off and the moisture content of the samples were allowed to equilibrate overnight in sealed containers at 0°C. The exact moisture content was determined before the second rehydration step was implemented to increase the moisture content to 40%. In the standard method used by the industry, this consisted of the addition of the required mass of free water to the dried fruit in the pouches. It was accepted that the fruit would absorb all the water. For the newly developed method it consisted of a second rehydration step under atmospheric pressure at 45°C for 180 sec to reach 40% moisture content.

The fruit was packed in containers and left open for *ca.* 30 min to allow evaporation of excess moisture before determination of the moisture content. The rehydrated apricots and nectarines of each rehydration method were randomly subdivided to give 48 samples (3 replicates; *ca.* 250 g per treatment combination) for each of the fruits. The samples were divided in two batches, which were stored in temperature-controlled rooms at 5° and 25°C, respectively.

Pasteurisation and modified atmosphere packaging

Samples were treated as previously described, except that the dry air pasteurisation was performed in the commercial tunnel in the commercial factory used by SAD to simulate commercial conditions as closely as possible.

Storage

Pouches were subjected to storage at 5° or 25°C, in temperature-controlled rooms. Three pouches of each treatment combination were randomly removed after 0, 5, 10, 15, 20, 25 and 30 w for determination of the CO₂ and O₂ contents of the headspace, colour and SO₂ content of the high moisture dried fruit.

Analytical analyses

CO₂ determination

The CO₂ concentration (v/v) in the headspace (1 ml sample volume) of the pouches was determined by gas chromatography method (procedure used for gas analysis of fruit; J. Hannie, ARC Infruitec-Nietvoorbij, personal communication). The analysis was done every week for the accelerated shelf life trial and at week 10,

15, 25 and 30 for the shelf life trial. The standard gas mixture for calibration (CO₂: 1%; O₂: 10,1%) was supplied by Air Products (Pty) Ltd, Cape Town.

Objective colour measurement

Objective colour measurement was performed on the samples using a measuring system as described in Chapter 4. Samples were measured every week for the accelerated shelf life trial and every 5th week for the shelf life trial. Initial colour measurements were performed within 24 h of production. The fruit halves were placed directly on the quartz glass with the skin side facing down. Fruit halves were turned 90° after the first measurement for a second measurement.

Sulphur dioxide, moisture content and water activity

The SO₂ concentration and moisture content of the samples were determined directly after completion of the colour measurements as described in Chapter 4. Water activity (a_w) of the fruit samples was determined using an electric hygrometer as described in Chapter 4.

Statistical analysis

Data obtained during the storage trials were tested for normality, using the Shapiro-Wilk test (Shapiro & Wilk, 1965), and submitted to analysis of variance. In order to determine whether significant changes in colour occurred over time, separate regression functions (linear and quadratic) were fitted to each moisture content x storage temperature combination. A good fit was obtained with linear regression ($R^2 > 0.998$ for all colour parameters) and the intercepts and slopes of the resultant lines were subsequently compared, using the Student's t-LSD ($P = 0.05$). When not significantly different, the data were pooled and a single function fitted to the data.

Results

Accelerated storage

Rehydration of fruit

The rehydration of the nectarines was relatively successful for all the methods tested. Less free water was visible inside the pouches that had been rehydrated by dipping rather than by the addition of free water. The different treatment

combinations (contact times) with corresponding moisture contents are summarised in Table 1. The second stage rehydration resulted fruit with moisture contents of 36 and 40% at both atmospheric pressure (120 and 210 sec, respectively) and under vacuum (180 and 240 sec, respectively). Rehydration under atmospheric pressure, however, produced the required moisture content within a slightly shorter time.

Change in moisture content and a_w during storage

The moisture content of the samples, irrespective of treatment method, remained more or less the same during storage, due to the excellent moisture barrier properties of the pouches. The average initial and final moisture content of all the samples pasteurised with steam was 39.28 ± 1.91 and $39.76 \pm 1.78\%$, respectively. The average initial and final moisture content of all samples pasteurised with dry air was 38.13 ± 1.93 and $37.81 \pm 2.15\%$, respectively. The initial a_w for the fruit varied from 83.50 to 89.40% (Table 2). The average a_w for samples pasteurised with steam and dry air was 86.91 ± 1.47 and $85.68 \pm 1.38\%$, respectively. This corresponds to the slightly higher initial moisture content of the samples pasteurised with steam.

Change in SO_2 content during storage

The total SO_2 levels of the samples decreased during the storage period of 8 w (Fig. 3). The SO_2 loss of the fruit subjected to packaging under normal air was more than those packed under high CO_2 levels (Fig. 3). The SO_2 levels of samples packed under normal atmosphere decreased from 1467 ± 174 to 582 ± 23 $mg.kg^{-1}$, while the SO_2 levels of samples packaged under high CO_2 , decreased from 1522 ± 155 to 822 ± 68 $mg.kg^{-1}$. That is a decrease of 885 and 700 $mg.kg^{-1}$ SO_2 , respectively.

Change in CO_2 content of headspace during storage

The data in Fig. 4 shows the average initial and final CO_2 (v/v) levels for all the samples packed under normal atmosphere and under high CO_2 conditions. The CO_2 levels in the headspace of the samples increased with storage. The CO_2 levels of samples packed under normal atmosphere increased from 3.66 to 10.43%, while the CO_2 levels of samples packed under high CO_2 , increased from 40.02 to 69.74%. In the case of samples packed under air the percentage increase in CO_2 formation were higher than when packed under high CO_2 atmosphere.

Table 1. Moisture levels (% m/m) of rehydrated dried nectarines after two-stage rehydration. The second stage consisted of dipping the fruit under atmospheric pressure and under vacuum, respectively.

Method	First rehydration ¹			
	Second rehydration ²	60	90	120
Atmospheric	90	32.65	35.05	36.40
	120	35.10	36.05	38.75
	180	37.00	37.95	38.90
	210	38.45	40.15	41.35
	240	40.75	42.10	43.00
Vacuum	90	33.60	34.15	35.70
	120	35.75	35.15	36.55
	180	35.95	36.05	38.55
	210	37.05	38.20	39.00
	240	37.90	39.25	39.85

¹The first rehydration step under atmospheric pressure at 45°C and contact time in sec.

²The second rehydration step under atmospheric pressure and under vacuum at 45° and 40°C, respectively. Contact time is in sec.

Table 2. Initial a_w levels of nectarines obtained for the rehydration methods (standard method, dipping under atmospheric pressure and dipping under vacuum) measured at week 0 after final packaging and pasteurisation. Results are the average of two replicates.

Sample ¹	Standard	Atmospheric	Vacuum
36% Atm. Steam	85.02	85.02	87.25
36% Atm. Dry heat	85.20	83.50	84.95
36% CO ₂ Steam	85.75	85.45	87.35
36% CO ₂ Dry heat	84.45	84.00	85.70
40% Atm. Steam	87.40	86.45	89.40
40% Atm. Dry heat	86.40	86.30	88.40
40% CO ₂ Steam	86.70	88.10	89.05
40% CO ₂ Dry heat	85.75	86.20	87.30

¹Notation indicates moisture content, packaging atmosphere and pasteurisation method used.

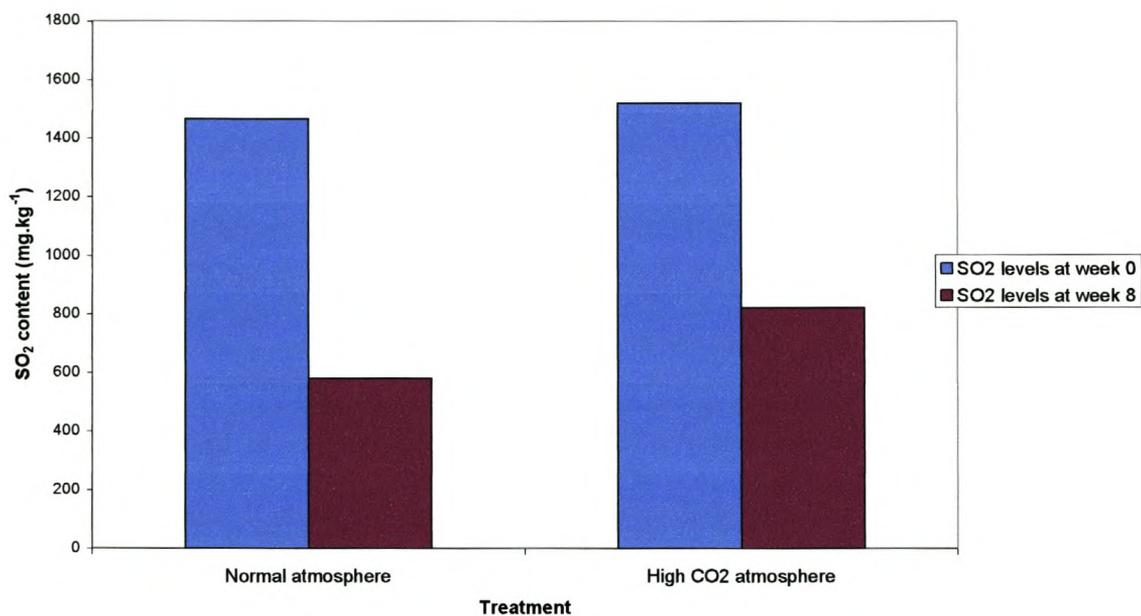


Figure 3. Initial and final SO₂ levels of nectarine samples packed under normal and high CO₂ atmosphere, respectively. The values given are the average of all the rehydration methods.

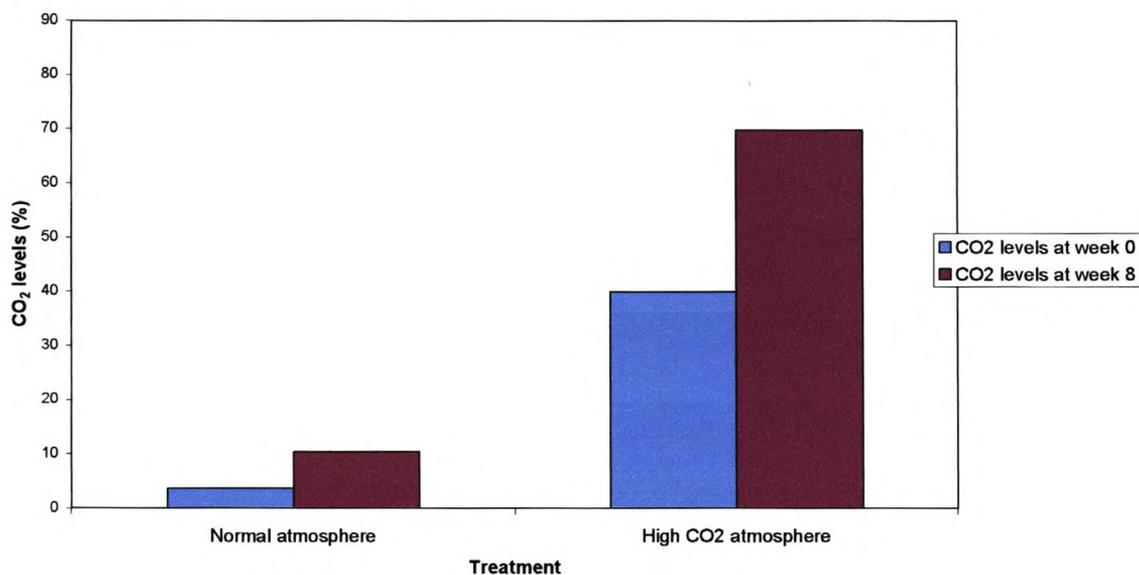


Figure 4. Initial and final CO₂ (v/v) levels of nectarine samples packed under normal and high CO₂ atmosphere, respectively. The values given are the average of all the rehydration methods.

Change in L value as measure of colour retention of samples during storage*

The data in Fig. 5 shows the changes in colour in terms of L* for rehydrated nectarines subjected to different treatments. The main trends were verified by the visual colour of the fruit (Fig. 6). The initial L* values of the fruit were influenced by the different processing treatments (Table 3). The samples that were subjected to steam pasteurisation and then packed under high CO₂ atmosphere, had the highest initial L* values (46.36). Samples pasteurised in the dry air tunnel and packed under normal atmosphere had the lowest initial L* values (34.72). Moisture content had no significant influence on initial L* values, but packaging atmosphere and pasteurisation method did have a significant influence (Table 4) with high CO₂ atmosphere packaging and steam pasteurisation having a positive effect on initial L* values.

The rate of deterioration was the smallest for the samples with 40% moisture content, pasteurised with steam and packed under high CO₂ atmosphere (Table 3). The fastest deterioration rate was observed for samples with 36% moisture content, pasteurised with dry heat and packaged under high CO₂ atmosphere (Table 3). Statistical analysis did, however, show that moisture content, packaging atmosphere and pasteurisation method had no significant influence on rate of deterioration (Table 4).

The relative order of highest final L* values corresponds to the order of the initial L* values. The highest final average L* value (33.42) were achieved by samples that were pasteurised with steam and packed under high CO₂ atmosphere. The lowest final average L* value (20.44) were obtained for samples pasteurised in the dry air tunnel and packed under normal atmosphere.

Shelf life study

For this part of the study whole dried Royal type apricot and nectarine halves were rehydrated, pasteurised and packed according to the standard method currently employed by the industry and the new method developed in this study. Optimum processing conditions obtained with the accelerated storage study were verified at simulated ambient (25°C) and cold storage (5°C) temperatures.

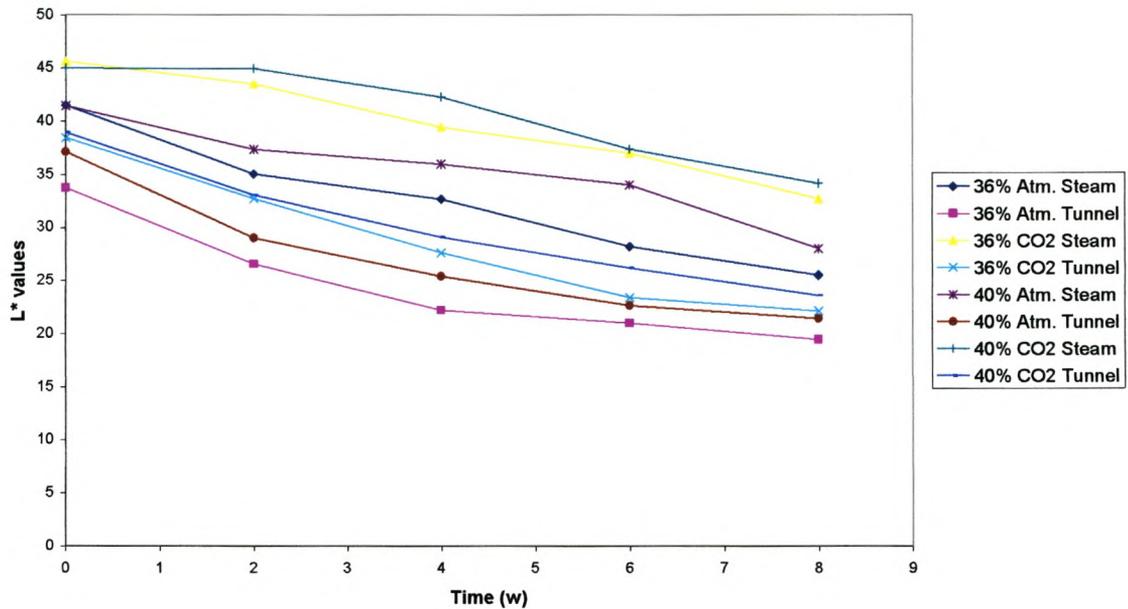


Figure 5. L^* values of nectarine samples with different moisture levels (36 and 40%), packed under different atmospheres (normal and high CO_2 atmosphere) and subjected to dry heat and steam pasteurisation. The values given are the average of the rehydration methods.

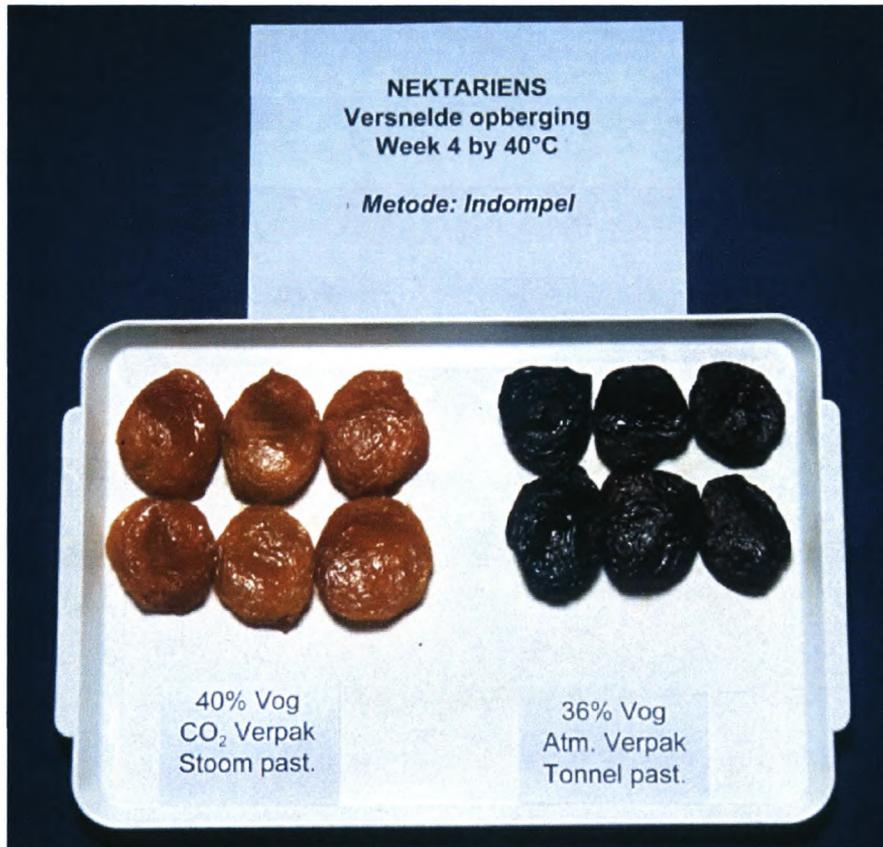


Figure 6. Photo of nectarines after accelerated storage of 4 w at 40°C. Samples depicted are of 40% moisture content, high CO₂ packaging and steam pasteurisation (left) vs 36% moisture content, normal atmosphere packaging and dry heat pasteurisation (right).

Table 3. The initial L* values and rates of deterioration (L*/w) obtained for dried nectarines rehydrated to 36 and 40% moisture, packed under normal atmosphere and CO₂ and pasteurised with a dry heat and steam, and stored at 40°C. Data from the different rehydration techniques were pooled.

Treatment Combination¹	Initial L* value²	Rate of deterioration
40% Atm. Steam	41.41	-1.511
40% Atm. Dry heat	34.67	-1.888
40% CO ₂ Steam	46.59	-1.462
40% CO ₂ Dry heat	37.68	-1.879
36% Atm. Steam	40.34	-1.941
36% Atm. Dry heat	34.77	-1.705
36% CO ₂ Steam	46.13	-1.621
36% CO ₂ Dry heat	37.23	-2.095

¹ Treatment combination shows the moisture content (%), packaging atmosphere and means of pasteurisation.

² Initial colour measurements took place after pasteurisation, gas flushing and packaging.

Table 4. Statistical data showing the differences in initial L* values and rates of deterioration obtained for dried nectarines rehydrated to 36 and 40% moisture, packed under normal atmosphere and CO₂ and pasteurised with dry heat and with steam and stored at 40°C. Data from the different rehydration techniques were pooled.

Variable	Mean Initial L*		Mean Rate of deterioration²	
		T Grouping¹		T Grouping¹
Moisture content:	40%	40.09 A	-1.685	A
	36%	39.61 A	-1.840	A
Packing atmosphere:	Atm	37.80 B	-1.761	A
	CO ₂	41.91 A	-1.764	A
Pasteurisation:	Steam	43.62 A	-1.634	A
	Dry air	36.09 B	-1.892	A

¹ Means with the same letter are not significantly different.

Alpha = 0.05; df = 24; Critical value of T = 2.06.

² Rate of change in L* (L*/w)

Changes in headspace CO₂ concentrations of apricot and nectarine samples during storage

The CO₂ concentration in the headspace of samples was measured at weeks 10, 15, 25 and 30, respectively. The average CO₂ levels in the headspace of the apricot samples packed under high CO₂, ranged between 76.9 and 82.8% at week 10 (Fig. 7). Carbon dioxide levels decreased to between 15.4 and 19.1% after 30 w of storage. These CO₂ levels of the apricot samples packed under normal atmosphere remained more or less the same with an average initial value of 3.9% decreasing to an average value of 2.2% (Fig. 7). The average initial value for the nectarine samples packed under high CO₂ ranged between 69.0 and 74.7% (Fig. 7). The concentrations decreased to average values of between 16.1 and 23.9% after storage of 30 weeks. The CO₂ concentrations of the nectarine samples that were packed under normal atmosphere remained at low values throughout storage with an average initial value of 6.0% decreasing to an average value of 3.5% (Fig. 7).

Changes in SO₂ concentrations of apricot and nectarine samples

The change in the SO₂ concentration in the apricot and nectarine samples over the 30-week storage period is depicted in Fig. 8. The SO₂ concentration in the dried fruit samples stored at 25°C decreased during storage, while the samples stored at 5°C remained more or less the same. Some of the variation in the results is contributed to the variation in the initial fruit product used. Another important point to note is the impact that the pasteurisation method had on the initial SO₂ content of both the apricot and nectarine samples. In the case of apricots, the average initial SO₂ value for samples pasteurised with steam was 2050 mg.kg⁻¹, while the value for the samples pasteurised in the dry air tunnel was 1522 mg.kg⁻¹, constituting in a decrease of 25.76%. The nectarine samples pasteurised with steam had an average initial SO₂ value of 2383 mg.kg⁻¹, while the samples pasteurised with the dry heat was 1652 mg.kg⁻¹. In this case the decrease in SO₂ content was 30.68%. The final SO₂ levels of apricot samples pasteurised with steam and stored at 5° and 25°C were 1878 and 1390 mg.kg⁻¹, respectively. The final SO₂ levels of the apricot samples pasteurised with dry heat and stored at 5° and 25°C were 1422 and 837 mg.kg⁻¹, respectively. The final SO₂ levels of nectarine samples pasteurised with steam and stored at 5° and 25°C were 2599 and 1086 mg.kg⁻¹, respectively, while the final SO₂ levels of the samples pasteurised with dry heat were 1892 and 931 mg.kg⁻¹, respectively.

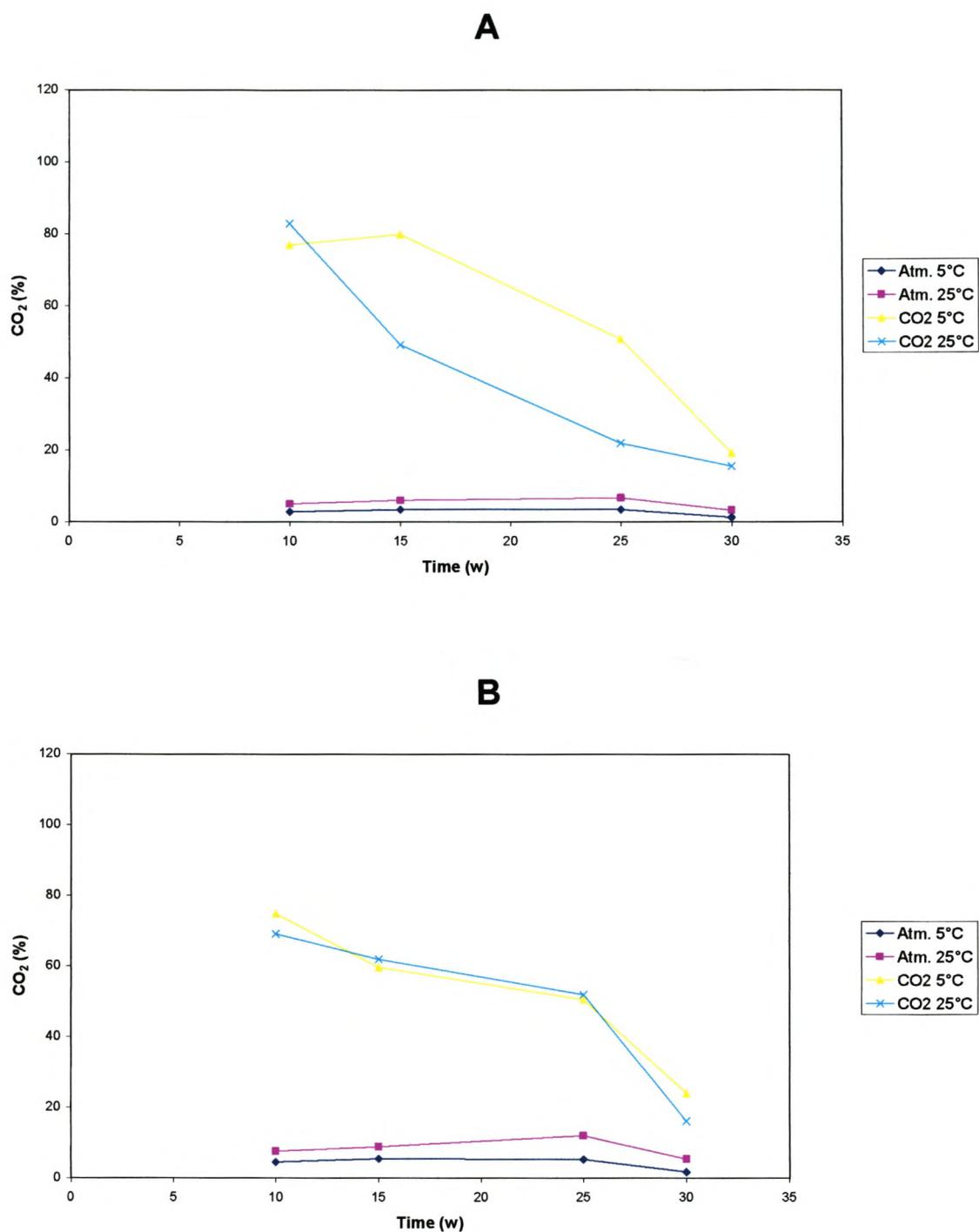


Figure 7. The headspace CO₂ concentration of rehydrated Royal type apricot (A) and nectarine (B) samples packed under normal and high CO₂ atmospheres and stored at 5° and 25°C for a period of 30 w. The values are the mean of dry air and steam pasteurisation methods.

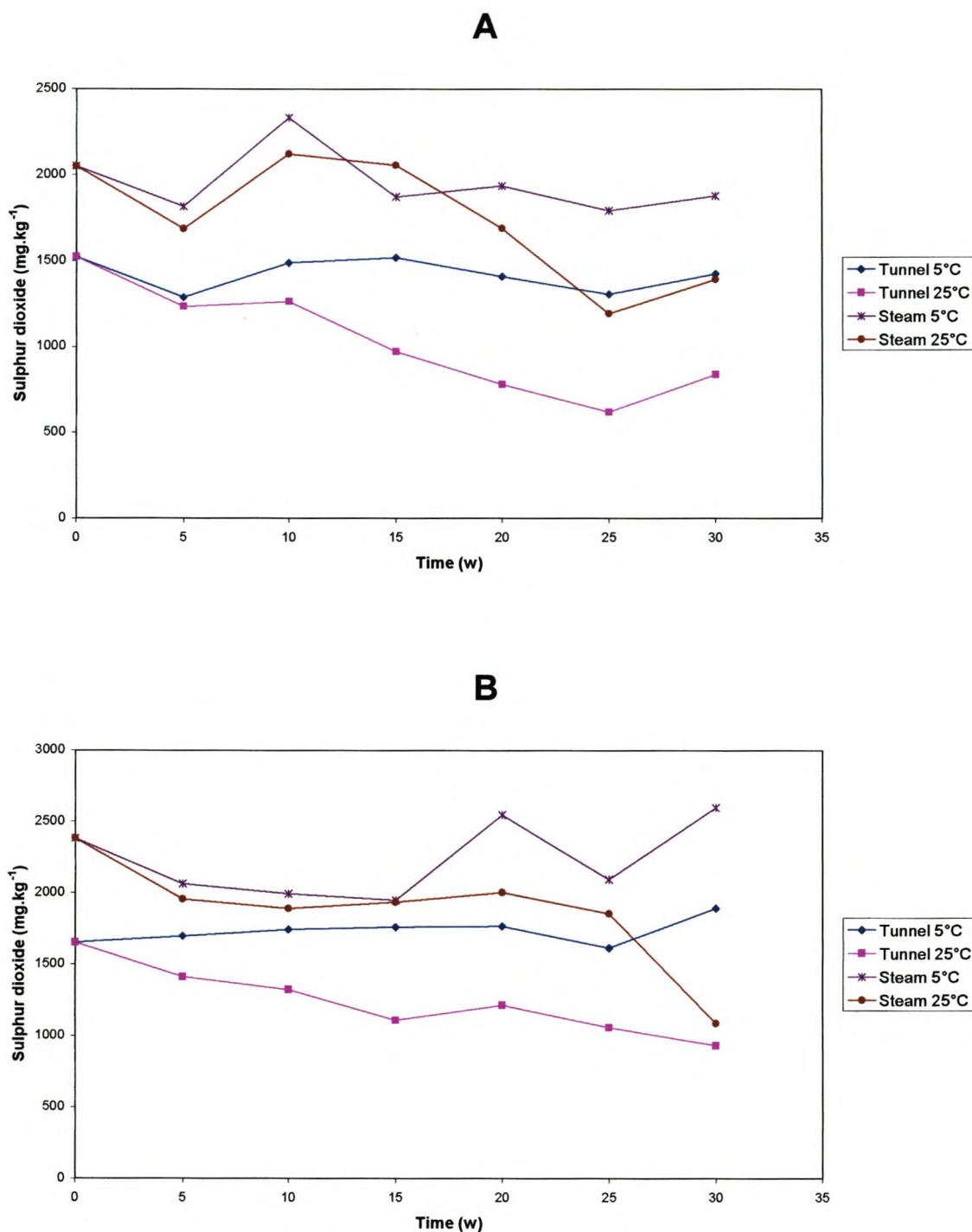


Figure 8. The SO₂ content of rehydrated Royal type apricot (A) and nectarine (B) samples pasteurised with dry air and steam respectively, and stored at 5° and 25°C for a period of 30 w. The values are the mean of the samples packed under normal and high CO₂ atmospheres.

Changes in moisture content of apricot and nectarine samples during storage

In the case of both the apricots and nectarines, the moisture content remained more or less the same during the shelf life storage trial. The samples pasteurised with steam tended to have a higher moisture content throughout the trial. It is important to note that the initial moisture content of both the apricot and nectarine samples pasteurised with steam, was higher than the samples pasteurised with dry air. In the case of apricots the values were 45.11 and 42.12%, respectively. The values for the nectarines were 39.89 and 39.44%, respectively. The final moisture content for apricots decreased to 43.21 and 41.10%, respectively while the final levels for nectarines decreased to 39.88 and 38.81%, respectively. The minimal decreases in moisture content are ascribed to losses during colour measurements.

Changes in L value as measure of colour retention of apricot samples during storage at 5° and 25°C*

The changes in L* values of the apricot samples, stored at 5° and 25°C, are given in Fig. 9 and the visual can be seen in Fig. 10. The initial L* values and rate of deterioration for the different treatments are summarised in Table 5. The pasteurisation technique had a significant effect on initial L* values, (Table 6) with steam pasteurisation giving rise to higher initial L* values (Table 5). For both pasteurisation techniques, the addition of CO₂ to the packaging atmosphere had a positive effect on the initial L* values (Tables 5 and 6), but the addition of CO₂ increased the rate of deterioration (Tables 5 and 6). The positive effect of the addition of CO₂ to the steam pasteurised packs on colour retention, is attributed to the rapid cooling effect of the CO₂. The storage temperature had a significant influence on the rate of deterioration with the lower storage temperature, giving rise to a slower rate of deterioration (Table 6).

The general trend was that the samples pasteurised with steam and packed under CO₂ had the highest L* values throughout the storage period. The lowest L* values were measured for the samples that were pasteurised in the dry air tunnel and packed under normal atmosphere. This was the case for the samples stored at 5°C. For the samples stored at 25°C, this was also the trend with the exception of the samples pasteurised with dry air that inverted at week 15. This is ascribed to variation in the colour of the initial dried fruit (Fig. 9).

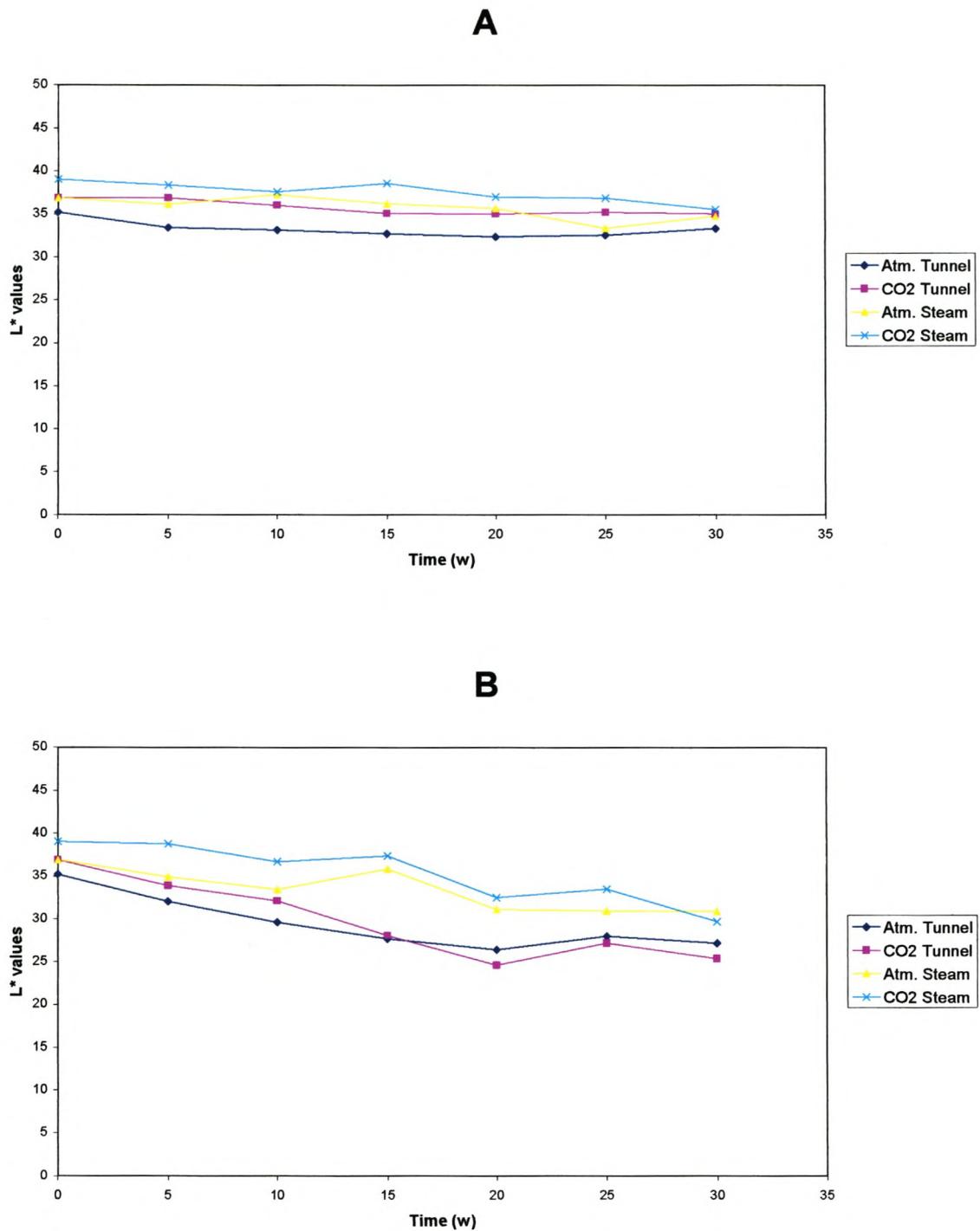


Figure 9. Changes in the L^* values of rehydrated Royal apricot samples pasteurised with dry heat and steam, packed under normal and high CO_2 atmospheres and stored at 5° (A) and 25°C (B) for a period of 30 w.

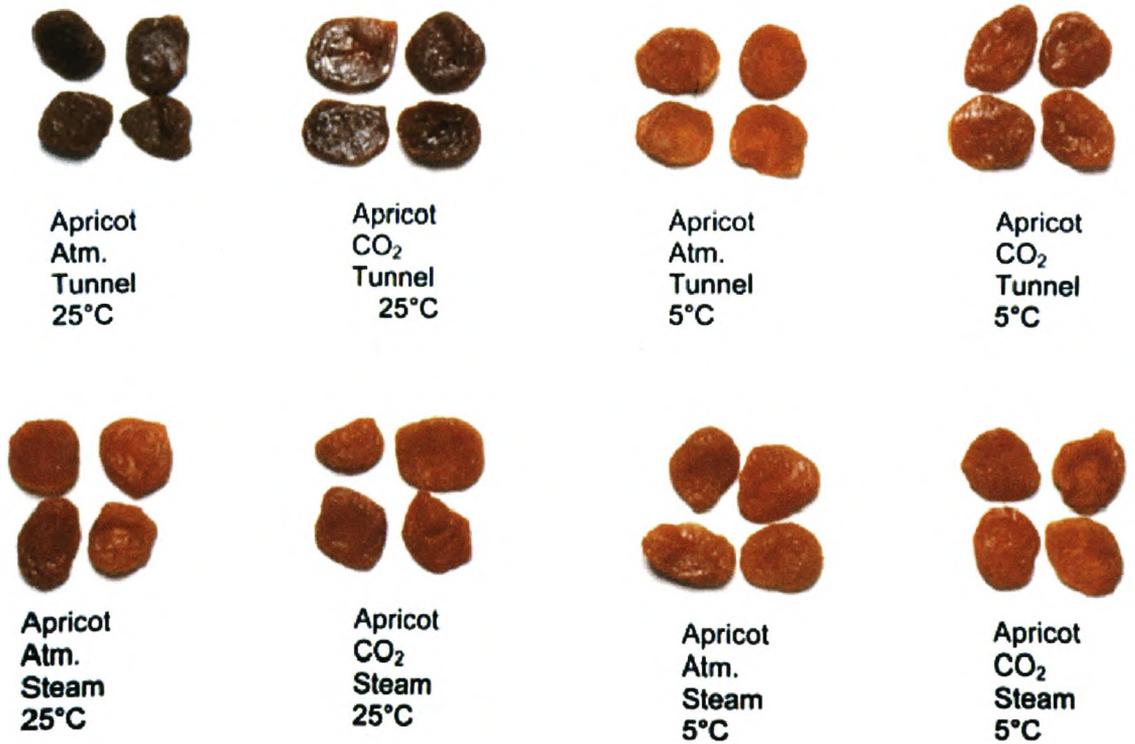


Figure 10. Photo of the rehydrated dried Royal type apricots after 30 w storage at 5° and 25°C. Samples were subjected to different packaging atmospheres (normal and high CO₂ atmospheres) and pasteurisation processes (dry heat and steam).

Table 5. The initial L* values and rates of deterioration (L*/5 w) obtained for rehydrated dried Royal type apricots packed under normal and high CO₂ atmospheres, pasteurised with dry heat and steam, and stored at 5° and 25°C.

Treatment combination¹	Initial L* value	Rate of deterioration
Atm. Dry heat 5°C	34.07	-0.3020
Atm. Dry heat 25°C	33.20	-1.264
Atm. Steam 5°C	37.18	-0.4839
Atm. Steam 25°C	36.43	-1.012
CO ₂ Dry heat 5°C	36.78	-0.3554
CO ₂ Dry heat 25°C	35.66	-1.986
CO ₂ Steam 5°C	39.04	-0.5028
CO ₂ Steam 25°C	39.90	-1.529

¹ Treatment combination shows the storage atmosphere, means of pasteurisation and storage temperature in °C.

Table 6. Statistical data showing the differences in initial L* values and rates of deterioration obtained for the rehydrated dried Royal type apricots packed under normal and high CO₂ atmosphere, pasteurised with dry heat and steam, and stored at 5° and 25°C. The data shows the combined effect of packaging atmosphere, pasteurisation and storage temperature.

Variable	Mean Initial L*		Mean rate of deterioration²	
		T Grouping¹		T Grouping¹
Pack atmosphere:	Atm	35.22 B	-0.7654	A
	CO ₂	37.85 A	-1.093	B
Pasteurisation:	Dry air	34.93 B	-0.9767	A
	Steam	38.14 A	-0.8820	A
Storage Temp.:	5°C		-0.4110	A
	25°C		-1.448	B

¹ Means with the same letter are not significantly different.

Alpha = 0.05; df = 16; Critical value of T = 2.16.

² Rate of change in L* (L*/5 w).

Changes in L value as a measure of colour retention of nectarine samples during storage at 5° and 25°C*

The changes in L* values of the nectarine samples stored at 5° and 25°C, are illustrated in Fig. 11. The visual changes in the colour of the nectarines can be seen in Fig. 12. The initial L* values and rates of deterioration for the different treatments are summarised in Table 7. The pasteurisation technique had a significant effect on initial L* values and rates of deterioration (Table 8) with the steam pasteurisation giving rise to higher initial L* values and slower rates of deterioration (Table 7). For both pasteurisation techniques, the addition of CO₂ to the packaging atmosphere had a positive effect on the initial L* values (Table 7), but its effect on the deterioration rate was not significant (Table 8). The storage temperature had a significant effect on the deterioration rate with the lower storage temperature, giving rise to a slower rate of deterioration (Table 8).

Overall the samples that were pasteurised with steam and packed under CO₂ had the highest L* values throughout the storage period. The lowest L* values were measured for the samples that were pasteurised in the dry air tunnel and packed under normal atmosphere.

Estimated shelf life

The estimated shelf life was calculated using the initial L* values and the deterioration rates (Table 9). The cut-off point for shelf life was taken as L*=30 for apricots and L*=40 for nectarines.

Apricots stored at 5°C all reached an estimated shelf life of at least 65 weeks, while steam pasteurised samples stored at 25°C reached a maximum of only 32 weeks. The highest estimated shelf life was achieved with the samples pasteurised with dry heat and packed under a high CO₂ atmosphere.

The nectarines pasteurised with the steam method and stored at 5°C, all reached an estimated shelf life of at least 90 weeks, while samples pasteurised with dry heat and stored at 25°C only reached a maximum of 8 weeks. The highest estimated shelf life was achieved by the sample pasteurised with steam, packed under high CO₂ atmosphere and stored at 5°C. Under these conditions it was estimated that this sample could reach a calculated shelf life of 600 weeks.

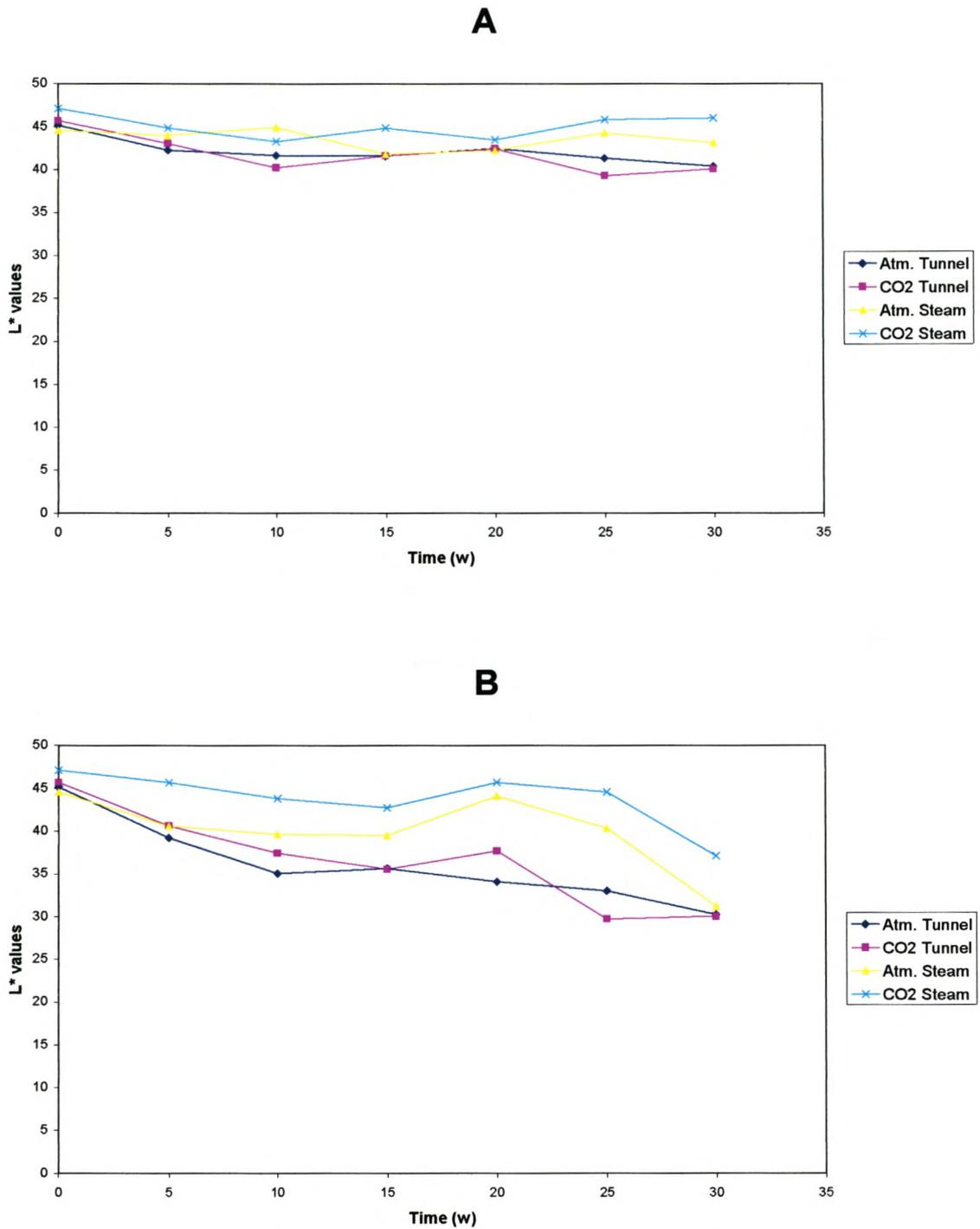


Figure 11. Changes in the L^* values of rehydrated nectarine samples pasteurised with dry heat and steam, packed under normal and high CO_2 atmospheres and stored at 5° (A) and 25°C (B) for a period of 30 w.

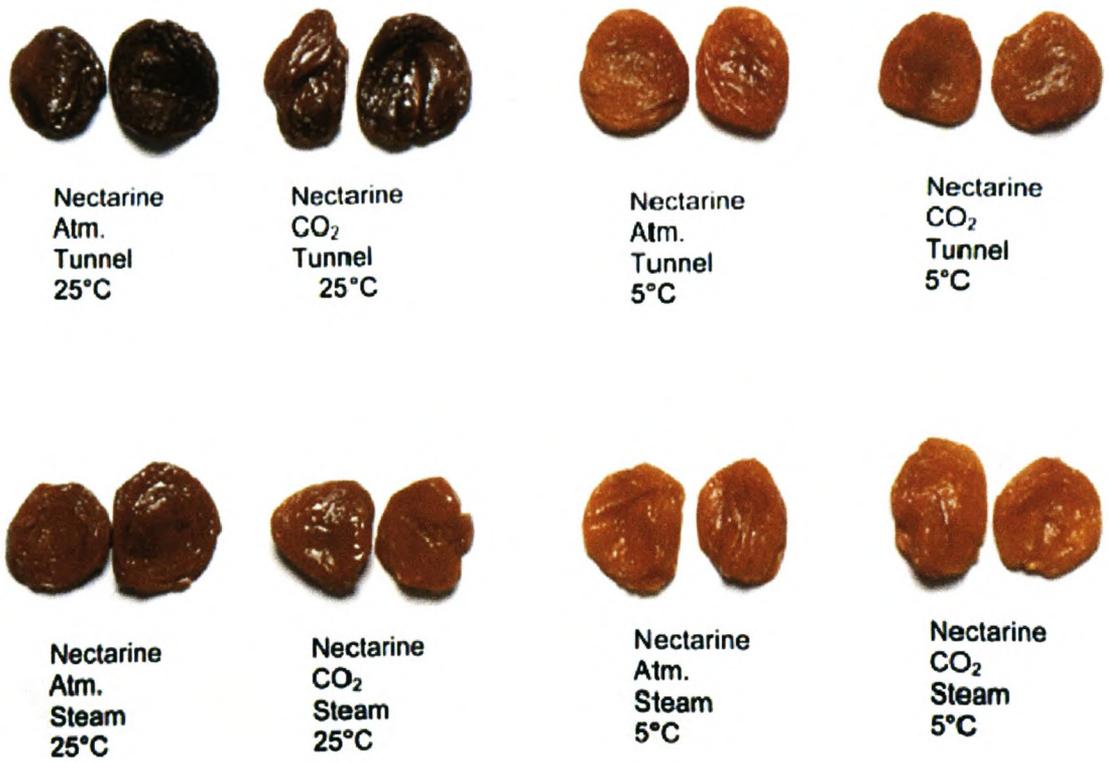


Figure 12. Photo of the rehydrated dried nectarines after 30 w storage at 5° and 25°C. Samples were subjected to different packaging atmospheres (normal and high CO₂ atmospheres) and pasteurisation processes (dry heat and steam).

Table 7. The initial L^* values and rates of deterioration ($L^*/5 w$) obtained for rehydrated dried nectarines packed under normal and high CO_2 atmospheres, pasteurised with dry heat and steam, and stored at 5° and $25^\circ C$.

Treatment combination ¹	Initial L^* value	Rate of deterioration
Atm. Dry heat $5^\circ C$	43.72	-0.5616
Atm. Dry heat $25^\circ C$	42.26	-2.077
Atm. Steam $5^\circ C$	44.23	-0.2315
Atm. Steam $25^\circ C$	43.84	-1.296
CO_2 . Dry heat $5^\circ C$	44.11	-0.7929
CO_2 . Dry heat $25^\circ C$	44.00	-2.452
CO_2 . Steam $5^\circ C$	45.14	-0.0426
CO_2 . Steam $25^\circ C$	47.03	-1.087

¹ Treatment combination shows the storage atmosphere, means of pasteurisation and storage temperature in $^\circ C$.

Table 8. Statistical data showing the differences in initial L^* values and rates of deterioration obtained for rehydrated dried nectarines packed under normal and high CO_2 atmospheres, pasteurised with a dry heat and steam, and stored at 5° and $25^\circ C$. The data show the combined effect of packaging atmosphere, pasteurisation and storage temperature.

Variable	Mean Initial L^*		Mean rate of deterioration ²	
		T Grouping ¹		T Grouping ¹
Packing atmosphere:	Atm	43.51 B	-1.041	A
	CO_2	45.07 A	-1.094	A
Pasteurisation:	Dry air	43.52 B	-1.471	B
	Steam	45.06 A	-0.6642	A
Storage Temp:	$5^\circ C$		-0.4071	A
	$25^\circ C$		-1.728	B

¹ Means with the same letter are not significantly different.

Alpha = 0.05; df = 16; Critical value of T = 2.16.

² Rate of change in L^* ($L^*/5 w$).

Table 9. Estimated shelf life (in weeks) obtained with the rehydrated dried Royal type apricots and nectarines packed under normal and high CO₂ atmospheres, pasteurised with dry heat and steam, and stored at 5° and 25°C. Cut off points for shelf life was taken as L*=30 for apricots and L*=40 for nectarines.

Treatment Combination¹	Shelf life (w)¹	
	Royal type apricots	Nectarines
Atm. Dry heat 5°C	67.38	33.12
Atm. Dry heat 25°C	12.66	5.44
Atm. Steam 5°C	74.19	91.36
Atm. Steam 25°C	31.77	14.81
CO ₂ Dry heat 5°C	95.39	25.98
CO ₂ Dry heat 25°C	14.25	8.16
CO ₂ Steam 5°C	89.90	603.29
CO ₂ Steam 25°C	32.37	32.34

¹ Calculated according to initial L* values and rates of deterioration as found in this study.

Discussion

One of the detrimental characteristics of the soft-eating dried fruit products currently being produced by the industry in South Africa, is the presence of free water inside the sealed pack. This results in some of the sugars from the fruit dissolving in this free water and forming a sticky syrup. Rehydrating the fruit until it reached the required moisture content before it is packed solved this problem. The two-stage rehydration process under atmospheric pressure achieves this result in a shorter time and with minimal technology input. The two-step rehydration process was therefore chosen as the rehydration procedure for the shelf life trial. Özkan *et al.* (2003) also used a two-step rehydration process and found it to be sufficient for rehydrating dried Malatya apricots. Rehydration under vacuum did not lead to a faster rehydration time, as one would have expected. This may be due to the quick lowering in temperature as a result of the decrease in boiling point, which led to a slower rate of rehydration.

Both dry heat and steam pasteurisation rendered a microbiologically safe product (Engelbrecht, 2000). However, steam pasteurisation achieved this result in a substantially shorter time (2.5 h vs 7 h). Pasteurisation of the product is necessary to render a safe product, but any heat treatment had a negative effect on colour retention initially and during storage, as was found for both the accelerated and shelf life storage trials. Harel *et al.* (1978) found that high moisture dried Raanana apricots subjected to a heat treatment prior to storage at 25°C showed a rapid increase in browning compared to samples that did not receive the initial heat treatment. This is due to the relatively high temperature coefficient associated with the Maillard reaction, which produces brown polymers, called melanoidins (Ames, 1990). The effect of pasteurisation on the initial colour of dried fruit is not well documented. As shown in this study, this aspect is of great importance and will determine the shelf life of the product.

The steam pasteurisation process developed requires 65% less time that it takes for the dry air tunnel as is currently used by industry. The reduction in time does not only make the pasteurisation more time efficient, but also reduces the negative effect on colour retention. The effect of the different pasteurisation techniques was more evident for apricots than for nectarines.

In the accelerated storage trial the samples that had been pasteurised with steam had a slightly higher moisture contents and thus corresponding a_w . This was attributed to additional water absorption during the steam pasteurisation process. This phenomenon was also observed for the shelf life trial, although to a lesser extent. A higher moisture content and corresponding a_w can lead to a slower browning rate as explained in Chapter 4. This may have contributed to the better colour retention of the samples subjected to steam pasteurisation as was found for the nectarines in the extended shelf life trial. Another important point is the effect of initial moisture content on initial L^* values. Özkan *et al.* (2003) and Joubert *et al.* (2001, 2003) found that moisture content affected the L^* values of dried apricots and dried Bon Chretien pears and Elberta peaches. In the case of the apricots, the L^* values increased with 9.3 units with moisture increases from 15.5 to 30.2%. According to Özkan *et al.* (2003), the change in L^* values, due to the increase in moisture content, may be attributed to the change in wavelength of the light reflected from the fruit due to the change on the surface of the rehydrated dried fruit. During rehydration water enters the air spaces between tissues and changes the texture of the surface and thus the wavelength of the light reflected. A higher initial L^* value due to increased moisture content may also contribute to a longer shelf life.

Rossellò *et al.* (1994) showed that dried apricots with a low SO_2 content (300 $mg.kg^{-1}$) had found lower L^* values than apricots with a high SO_2 content (1400 $mg.kg^{-1}$). In addition to the fact that the steam process is much shorter than the existing process, it was also found that steam pasteurised rehydrated dried fruit had a higher initial SO_2 value than samples pasteurised with dry air. This is probably due to the greater reaction rate of the Maillard reaction during the dry air pasteurisation, where SO_2 is used to retard the reaction and thus lower the final concentration. The higher SO_2 values therefore contribute to the higher initial L^* values and resulting shelf life. The SO_2 loss of the fruit subjected to packaging under normal atmosphere was more than those packed under high CO_2 levels. The reduction of the Maillard reaction rate in a low O_2 atmosphere will cause less SO_2 to be used as an inhibitory substance for the Maillard reaction. Furthermore, the loss of SO_2 , partly due to sulphate formation in the presence of oxygen (Davis *et al.*, 1973; Bolin & Jackson, 1985), was suppressed. It is clear that the presence of CO_2 in the packaging contributed to a longer shelf life due to the preservation of SO_2 . This phenomenon was confirmed with the colour data.

The increase in CO₂ levels in the headspace of the samples was attributed to the formation of CO₂ as intermediary reaction product of the Maillard reaction. Increased headspace CO₂ is an indication of an increase in the rate of the Strecker degradation reaction, and the intermediate products of the Maillard reaction (Labuza & Saltmarch, 1981). The reduction in CO₂ in the headspace after extended storage can be attributed to the solution of the CO₂ in water.

A high CO₂ content was effective in increasing shelf life, but whether it can be ascribed to suppressing the Maillard reaction, is not clear at this stage. Bolin *et al.* (1976) found that packaging under vacuum or nitrogen is also effective in reducing browning. Dried peaches were found to be lighter in colour compared to those packed under air. The storage life of apricots of a range of moisture contents (5-25%) was found to increase with decreasing O₂ in the product headspace.

In the case of both Royal type apricots and nectarines, it was shown that samples stored at 5°C and packed under a high CO₂ atmosphere, had the highest estimated shelf life. Storage temperature plays a major role when it comes to colour retention. Rossellò *et al.* (1994) and Joubert *et al.* (2001, 2003) found an intense increase in the browning of dried apples, pears and peaches, at higher storage temperatures. The improved colour retention for samples stored at 5°C compared to 25°C suggests that a cold chain should be introduced by industry if a long storage life is to be realised. The results showed that steam pasteurisation lowered the rate of browning significantly during storage of nectarines. Although it was not significant, apricots also exhibited a lower rate. This suggests that the industry should consider implementing a steam pasteurisation process to facilitate a lower browning rate.

The addition of CO₂ to the atmosphere increased initial L* values, but led to a significant increase in browning rate of apricots, while the difference in browning rate for nectarines was not significant. The initial increase in L* values, however, is crucial to the final shelf life since it prolonged the shelf life. The preserving action of the CO₂ on the steam pasteurised samples is attributed to the rapid cooling effect that is caused by the CO₂ gas during gas flushing. The steam pasteurisation resulted in a higher CO₂ concentration, which in turn led to a higher SO₂ concentration, and thus subsequently better colour retention. This suggests that industry should consider high CO₂ atmosphere packaging or a CO₂ treatment prior to final packaging.

The higher moisture content also led to a lower reaction rate as was seen in the accelerated storage trial, although the difference was not significant, which resulted in

less SO₂ used, leading to a better a colour preserving action. Industry should thus consider increasing final product moisture content, taking texture deficiencies into account.

Conclusions

It can be concluded that the higher final L* values that were achieved in the shelf life study can be attributed to a combination of factors. These factors include SO₂, CO₂ and moisture concentrations, pasteurisation and storage temperatures. They all influence initial L* values and/or the rate of browning. The new processing method developed in this study was more successful in retaining fruit colour than the existing method used by the industry.

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Chapter 6

General discussion and conclusions

Background

Dried fruit is an age-old and well-known product that has been produced using the same process for many decades. Over the last few years a definite international trend has developed for a relatively high moisture dried fruit product in the intermediate moisture range with a moisture content of *ca.* 36 – 40% (m/m). The South African Dried Fruit Co-operation Ltd., the major South African dried fruit producer, has placed such a product on the market but with limited success.

To produce high moisture dried fruit, the fruit are treated with a washing process, which increases the moisture content from *ca.* 18% to *ca.* 26%. The additional rehydration of conventional dried fruit, to increase the moisture content to *ca.* 36%, is carried out by the addition of free water to the final package before pasteurisation. This process leads to the formation of an undesirable sticky syrup inside the pack. The product is packaged and sealed under normal atmospheric conditions. Due to the increased moisture content, the product is susceptible to microbiological spoilage and therefore a heat pasteurisation process must be applied. At present this commercial pasteurisation process is carried out in an air drying tunnel at 80°C for 7 h. Although this process is sufficient to pasteurise the product, it causes excessive browning, which renders a visually unacceptable product.

Thus, it is necessary to investigate the extent of influence of the factors, which cause browning, and to evaluate the effect of a change in these factors on colour retention of rehydrated dried Royal type apricots and nectarines at elevated moisture content levels of 36 – 40%. The information acquired in initial studies was then used to develop a new processing method with different rehydration, pasteurisation and packaging atmosphere parameters so as to render an acceptable final product with an acceptable shelf life.

Influence of a_w and moisture content

The importance of moisture content is overshadowed by the importance of a_w since browning reaction rates and the ability of microorganisms to grow are dependent on a_w rather than on the moisture content. In this study it was found that there is a correlation between moisture content and a_w that is not linear and very specific. This correlation is best described for dried Royal type apricots and nectarines evaluated by the GAB three-parameter equation ($R^2 = 0.999$ for both apricots and nectarines). However, the moisture content is used as a specification because it directly impacts on the texture and appearance. The specified moisture content of the existing high moisture product is 36%, but it was found that a moisture content of 40% is more preferable for colour retention.

The non-enzymatic browning reactions are dependent on the availability of free water. It was found for both macerated fruit and fruit halves that free water increased the non-enzymatic browning reaction rate up to an optimum a_w of *ca.* 0.83 (Labuza & Saltmarch, 1981), whereafter a further increase in a_w led to a dilution effect and the browning rate subsequently decreased. An increased initial moisture content of 40% also gave rise to increased initial L^* values. Both of these phenomena proved to be vital in the long-term colour preservation of the product since increased moisture content led to a longer shelf life.

Influence of SO_2 content

The obvious positive influence of an increased SO_2 concentration on the colour retention was shown in the accelerated storage of both macerated and fruit halves, as well as in the extended shelf life trial of fruit halves. Increased SO_2 also led to increased initial colour of the rehydrated dried fruit halves, confirming the results of Joubert *et al.* (2003). The initial elevated L^* values proved to be significant in extending the shelf life of the rehydrated fruit since SO_2 levels tended to equalise after extended storage. A high SO_2 content is vital for colour retention and must be maintained throughout processing and pasteurisation or alternatively it must be compensated for by a higher initial SO_2 content, keeping in mind the maximum legally permitted levels of SO_2 . The best way to preserve SO_2 during storage is to

keep the product at refrigerated temperatures (5°C), and to lower or remove O₂ from the packaging atmosphere so as to prevent the formation of inactive sulphates.

Influence of modified atmosphere

Modified atmosphere packaging has been used for many years to preserve a variety of products (Davies, 1995). It was thus a logical decision to change the pack atmosphere and lower the oxygen concentration. The choice of CO₂ to replace the normal atmosphere was influenced by the fact that CO₂ is a reaction product of the Maillard reaction and that the reaction, under the laws of mass action, would thus be slowed down. The presence of CO₂ in the pack atmosphere proved to have a significant preservative action in retaining colour, giving an average shelf life of 112.71 weeks, while control samples packed under normal atmospheric conditions only reached an average shelf life of 41.34 weeks. It still remains to be proven that the preservation action of the high CO₂ atmosphere was due to slowing down the Maillard reaction, as was seen for nectarines, or due to a more effective retention of SO₂ by samples packed under normal atmosphere or due to a combination of both factors. The rapid decrease in product temperature, directly after steam pasteurisation, during CO₂ flushing also had a positive effect on colour retention.

Influence of pasteurisation

The influence of the pasteurisation treatment on the final shelf life of rehydrated dried fruit and the need to manipulate this process was one of the most important conclusions reached in this study. The use of direct steam as a pasteurisation medium by the industry should save time and result in higher initial L* values and a decreased rate of browning while obtaining a satisfactory microbial preservative action (Engelbrecht, 2000). The use of the steam pasteurisation method led to a decrease in loss of SO₂ during the heat treatment period and also slightly higher moisture content. Both of these additional factors contributed to an extended shelf life.

Influence of storage temperature

Storage temperature, a critical factor in colour retention of dried fruit (Joubert, 1997), was also a significant factor in colour retention of high moisture content dried Royal type apricots and nectarines. Samples stored at 5°C had a longer shelf life (135.08 weeks) than samples stored at 25°C (18.98 weeks), regardless of any other parameter. It is well known that increased storage temperatures will lead to an increase in the reaction rate of the non-enzymatic browning reactions (Sapers, 1993). After the accelerated storage trial it was shown that samples stored at 60°C did not even last a week, while samples stored at 5°C in the shelf life trial were still acceptable after 30 weeks. Increased temperatures lead to decreased SO₂ content by not only increasing the browning reaction rates, but also facilitate the evaporation of SO₂ from the product. A lower SO₂ content gives rise to a shorter shelf life as already discussed.

Recommendations

The final process as developed in this study differs in almost every aspect from the existing commercial method. To obtain a good quality product with extended shelf life it is recommended that rehydration is performed by using a two-stage rehydration process, which will render the desired moisture content for the rehydrated product before pasteurisation and will prevent the formation of the sticky syrup in the pouch. It was also found that a higher moisture content (40%) led to a reduction in browning rate and an increased initial L* value. Effective pasteurisation may be obtained by direct steam contact on final packaging for a period of 2.5 h. Based on the results obtained it is recommended that after pasteurisation, the packs should be flushed with CO₂ gas to expel most of the O₂ present to prevent the formation of inactive sulphates. A final recommendation is that this product must be distributed and displayed at refrigerated temperatures (5°C). The implementation of the above mentioned recommendations will ensure an excellent quality product with a longer shelf life.

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