SHELF LIFE PREDICTION OF DRIED FRUIT AND VEGETABLES: A QUANTITATIVE APPROACH

A THESIS PRESENTED IN PARTIAL FULFILMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY IN FOOD TECHNOLOGY
AT MASSEY UNIVERSITY

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1989

ABSTRACT

The quantitative approach to shelf life prediction of foods is a relatively new field of food technology and the paucity of published studies in this area indicates a need for further research. The present study was undertaken to develop and evaluate a methodology for the shelf life prediction of packaged dried foods using a quantitative approach.

The development of a technique for the shelf life prediction of packaged dried foods, specifically onion flakes, sliced green beans, and apricot halves, involved the mathematical modelling of product and package characteristics as functions of environmental conditions, i.e. temperature and humidity.

The WVTR and permeability constants of LDPE (60 μm), PET (12 μm) and a laminate of both films (30 μm LDPE and 12 μm PET) were determined at different temperatures and humidities. A general model was developed which satisfactorily predicted permeances of the three films as a function of external relative humidity and temperature.

The moisture sorption isotherms of the three products were determined at 20, 30, and 40^{o}C. The GAB model adequately described the isotherms using a direct nonlinear regression analysis.

The kinetics of the deteriorative reactions limiting the shelf life of the three dried products and their acceptable limits were determined. Storage trials were conducted on the three products under different relative humidity (32% to 59% RH for dried onion flakes and green beans; 59% to

81% RH for dried apricot) and temperature (20°C to 40°C) conditions.

Nonenzymic browning in onion flakes and chlorophyll a loss in green beans were better described by a zero-order reaction model. Thiolsulphinate loss in onion flakes, nonenzymic browning in apricot, and SO_2 loss in both green beans and apricots were better described by a first-order reaction model. For onion flakes and green beans, the rates of reactions were found to increase with an increase in the water activity of the products. Empirical equations were derived describing the relationship between the rates of reactions and water activity. The Arrhenius equation satisfactorily described the relationship between rate constants and temperature.

Nonenzymic browning and sulphur dioxide loss in dried apricots exhibited a trend wherein the rate increased with water activity until a maximum was reached and then decreased with a further increase in water activity. The reactions followed the Arrhenius equation at all three water activity levels.

Mathematical models of quality deterioration in the dried foods were developed based on the theoretical and empirical equations obtained on the kinetics of the deteriorative reactions as functions of storage time, water activity and temperature. There was close agreement between the actual and predicted shelf lives of the unpackaged dried foods stored under variable temperature and relative humidity conditions.

In order to predict the shelf life of the dried products packaged in polymeric films, a computer iterative technique was developed which combined the models describing the permeability characteristics of the packaging films, the sorption properties of the product, the kinetics of

deterioration in the products and the mass transport equation. By solving these equations numerically with the aid of a computer, moisture gain, quality loss and shelf life of the products were satisfactorily predicted under various storage conditions.

ACKNOWLEDGEMENTS

I wish to thank my supervisor, Professor Gordon L. Robertson, for all the help, time and encouragement he provided during the course of this work. Appreciation is also extended to Dr Ian Boag for his assistance in the statistical and mathematical aspects of the study.

I am grateful to Dr Robert Holland for reviewing the chapter on permeability; to Mr G. Radford, Mrs M.C. Bewley, Mr M. Conlon and Mr H. van Til for their technical assistance; and to Unilever (N.Z.) Ltd. for providing the dried vegetables.

This work would not have been possible without funding from the New Zealand and Philippine governments, to whom I am indebted. I also wish to thank Dr Alicia Lustre and my company the Food Development Centre for their support.

Finally, to Mark, my family and friends for their continual moral support, I shall always be very grateful.

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CHAPTER 1
INTRODUCTION

The term 'shelf life' is generally understood to be the duration of that period, between the packaging of a product and its consumption, for which the quality of the product remains acceptable to the product user. The prediction of the shelf life of packaged foods is of obvious importance to the food industry. Shelf life studies are an essential part of product development, with the manufacturer attempting to provide the longest, practicable shelf life consistent with costs and the pattern of handling and use by distributors, retailers and consumers.

Traditionally, most food companies who determine the shelf life of packaged foods do so by conducting actual storage tests which are specific to a product/package combination by holding the foods under specific environmental conditions until they become unacceptable. In contrast, some companies simply determine the shelf life by making judicious guesses based on experience.

However, over the past decade there has been an increasing interest in quantitative approaches to the analysis of food quality deterioration during processing and storage which has been motivated in part by a growing consumer awareness, and in part by mandatory governmental requirements in many countries. Developments have also been made in accelerated testing methods, which significantly decrease testing time. The analytical approach to food quality deterioration and shelf life prediction allows a wider scope of investigation which may lead to alternative processes and packaging materials, different storage conditions, or more efficient operations, thus minimising undesirable changes and optimising quality retention in the foods.

Despite this interest in quantitative approaches, the use of analytical methods in shelf life prediction in the food industry is not widespread, due in part to the lack of basic data on the effect of extrinsic factors on the rates of deteriorative reactions, in part to ignorance of the methodology required, and in part to a healthy scepticism of the advantages to be gained from using sophisticated shelf life prediction procedures.

The application of quantitative approaches to the shelf life determination of foods packaged in polymeric films is even less widespread, since data on the effects of different temperatures and humidities on film permeabilities is often unavailable. Even if it is, accounting for these effects complicates the situation further. At present, food companies choose their packaging materials largely on a trial and error method which usually results in overprotection and thus higher than necessary packaging costs.

The basic approach to shelf life prediction is based on the following five assumptions (Karel, 1975a):

First, properties of the food which determine quality depend on the initial condition of the food and on reactions which change these properties with time. These reactions, in turn, depend on the internal environment of the package. It is assumed that deteriorative mechanisms limiting shelf life and their dependence on environmental parameters (i.e. water activity, temperature and oxygen pressure) can be described by a mathematical, although not necessarily analytical, function.

Second, the maximum acceptable deterioration level can be determined by correlating objective tests of deterioration with organoleptic or toxicological parameters.

Third, the internal environment depends on the conditions of the food, on package properties, and on the external environment. It is assumed that changes in environmental parameters can be related to food and package properties.

Fourth, barrier properties of the package can in turn be related to internal and external environments.

Fifth, the various equations can be combined and solved with or without the aid of a computer. The solution predicts shelf life or required package properties for given storage conditions.

During the past several years, studies have been conducted to develop techniques to predict the shelf life of foods, and reviews of this subject have been published by Labuza (1973), Karel (1975a) and Saguy and Karel (1987).

Mizrahi et al. (1970) developed mathematical models for predicting the shelf life of dehydrated cabbage in flexible pouches, deteriorating by nonenzymic browning. An iteration technique for the prediction of the browning, using a computer and a method for estimation of the variance of the predicted values, was devised. They also studied the feasibility of accelerated tests for obtaining the kinetic data needed to formulate the model. Simon et al. (1971) used numerical techniques for prediction of the storage stability of space food items as a function of package properties, considering only one limiting deterioration mechanism. The predictions were considered sufficiently accurate to be of practical value in package design. Both of the above mentioned studies were conducted using a single temperature condition and the study of Simon et al. (ibid.) used a constant low humidity condition. Hence, the variability of the reactions and the permeability of the packaging materials at different

temperature and humidity conditions was not considered in these studies.

Quast et al. (1972) and Quast and Karel (1972) investigated the storage behavior of potato chips undergoing deterioration by two simultaneous mechanisms: loss of crispness due to moisture adsorption and oxidative rancidity due to oxygen adsorption. The approach to model-building included a theoretical consideration of reaction kinetics, as well as empirical data fitting. The work resulted in the formulation of functions, which with the aid of a computer, made it possible to simulate the shelf life of potato chips under various conditions. An actual investigation of the packaging aspect was not included in the study.

Studies on the prediction of nutrient stability was carried out by Wanninger (1972), who postulated a mathematical model for the rate of ascorbic acid degradation based on the chemistry of ascorbic acid. This theoretical model was verified and its applicability tested only on unpackaged flour and flour-based foods. Singh et al. (1983) studied the storage stability of intermediate moisture apples (IMA). Based on kinetic data, mathematical models were developed to predict nonenzymic browning and ascorbic acid loss in IMA as a function of temperature and a_w. The model was found adequate in describing the deteriorative reactions in unpackaged IMA.

Riemer and Karel (1978) investigated the mathematical modelling of ascorbic acid retention in dehydrated tomato juice as a function of time, temperature and water activity using theoretical, empirical and statistical considerations. This method was combined with equations describing the transport of water to the food utilizing experimentally obtained mass transport parameters for the packages and sorption characteristics of the food. By

solving these equations numerically with the aid of a computer, ascorbic acid retention was simulated for various conditions. A packaging permeability equation was not included in the computer iteration procedure (i.e. permeability of the packaging material was assumed to be constant). Despite this simplifying assumption, there was reasonable agreement between experimentally observed losses of ascorbic acid and those predicted by the computer simulation program.

Cardosa and Labuza (1983) developed a mathematical model to predict moisture gain and loss for packaged pasta under controlled unsteady-state conditions of temperature and humidity. A computer iterative technique combining the sorption properties of the product and the permeability characteristics of the packages was developed. Good predictions were obtained.

All of the above studies involved determination of kinetic models for the deteriorative reactions and subsequent simulation of storage behavior. In contrast, a method was developed by Mizrahi and Karel (1977 a,b) for the prediction of shelf life of moisture sensitive products that does not require prior knowledge of the kinetic model of effects of moisture on the rate of deterioration. The method can be applied to dried food products when the index of deterioration is dependent only on moisture content, which changes continuously during storage.

The results of the different studies reviewed above show the great potential for the quantitative approach to shelf life prediction. The present availability of numerical methods and powerful computers has made simulation and prediction easier to conduct. The limiting factor to its development is the availability of appropriate models describing quality deterioration in foods, and packaging barrier properties.

Although numerous studies have been conducted to determine the kinetics of deteriorative reactions in various food products, there is a lack of kinetic models of general applicability to a range of foods. There is also a paucity of published studies on the development of mathematical models relating the permeability characteristics of packaging films to environmental factors.

Most of the published studies discussed above on the quantitative approach to shelf life prediction were conducted on unpackaged dried foods. Excluding the packaging aspect gives an unrealistic situation since dried foods are always packaged in some form, commonly in flexible film materials. Disregarding the effect of the packaging material on the system may lead to erroneous shelf life estimates and packaging requirements.

Thus, there is great need for further research into quantitative approaches to shelf life prediction of food products, particularly those approaches that consider the total product/package/environment system. This is a relatively new field of food technology and the potential of prediction modelling and accelerated shelf life testing methods has yet to be fully exploited.

With the above factors in view, the present study was conducted with the following general objectives:

a. To develop mathematical models of deteriorative reactions of general applicability to dried food products.

b. To develop models describing the relationship between the permeability of certain packaging films as a function of environmental factors such as temperature and humidity.

c. To develop and critically assess a technique for the shelf life prediction of packaged dried foods.

In order to meet the above objectives, three major dried products of economic importance in New Zealand were used in the study. They were dried onion flakes, sliced green beans, and apricot halves.

CHAPTER 2
MOISTURE SORPTION ISOTHERMS

2.1 INTRODUCTION

Moisture sorption isotherms have an important role to play in the prediction of the shelf life of dried foods because of their sensitivity to moisture changes. Sorption isotherms are also necessary in the prediction of moisture transfer into foods through permeable films. This chapter is concerned with the determination of water sorption isotherms for dried foods (specifically onion flakes, sliced green beans, and apricot halves) and the fitting of mathematical models to the isotherm data.

Most of the sorption data for foods published in the literature has been obtained at only one temperature, typically the normal storage condition. However, sorption data over a wide temperature range are essential for modelling storage stability of dried foods, since storage temperatures generally vary quite widely.

An analytical expression for the isotherm is also required to predict the shelf life of a dried product in a packaging material of known permeability.

This study was conducted with the following objectives:

a. to determine the sorption isotherms of dried apricot, green beans, and onion at different temperatures
b. to determine the applicability of a suitable model to describe the sorption isotherms of the three products at different temperatures.

2.2 LITERATURE REVIEW

The water sorption isotherm of foods shows the equilibrium relationship between the moisture content of foods and the water activity (a_w) at constant temperatures and pressures (Labuza, 1968). At equilibrium, the water activity is related to the relative humidity (RH) of the surrounding atmosphere by:

$$a_w = \frac{p}{p_o} = \frac{\%RH}{100} \qquad (2\text{-}1)$$

where:

p = the water vapour pressure exerted by the food material

p_o = the water vapour pressure of pure water at temperature T_o, the equilibrium temperature of the system

Water sorption isotherms are usually presented as a plot of the amount of water sorbed as a function of water activity, giving rise in most (but not all) cases to curves of sigmoid shape (Figure 2.1).

The sorption isotherm is characteristic of a specific product and although each product's sorption isotherm is different, it is possible to group the isotherms into classes having certain characteristics in common. As illustrated in Figure 2.1, the isotherms are different depending on whether they are established by drying from the fully saturated state (desorption isotherm) or by wetting from the fully dried state (adsorption isotherm). This effect is called the moisture sorption hysteresis whereby at any given moisture content the equilibrium RH corresponding to the desorption process is always less than that of the corresponding adsorption process (Rockland,

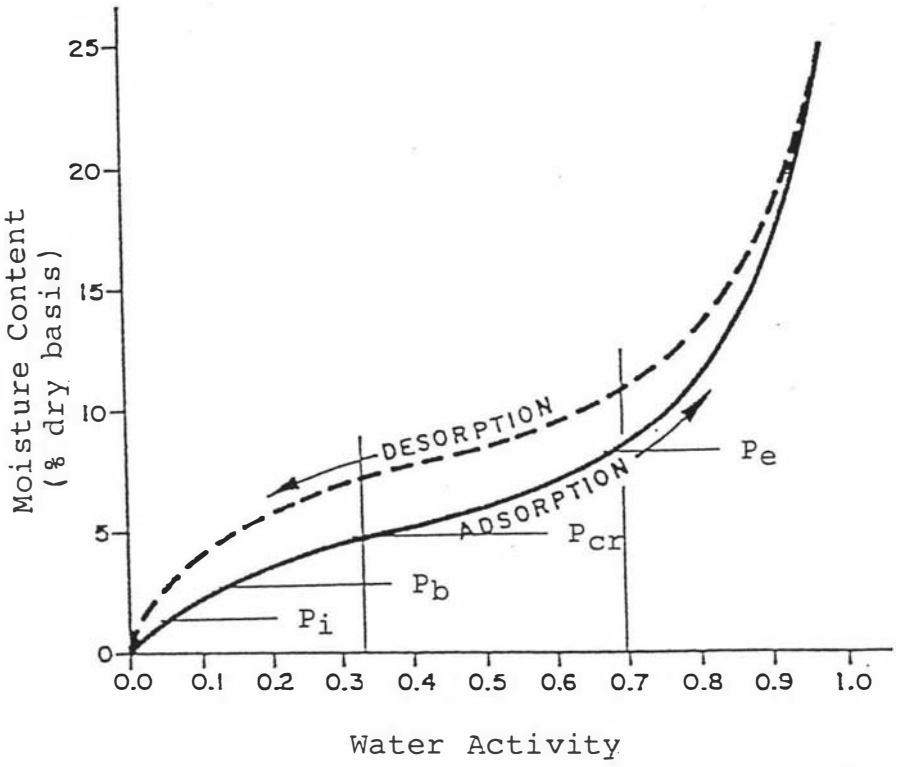


Fig. 2.1. Schematic sorption isotherm with typical marking points.

1969; Kapsalis, 1981).

The desorption isotherm is important for nearly all drying processes, whereas the adsorption isotherm is the important one in most cases for studying and predicting the effect of storage on dried products. Thus, it is the adsorption process which is of particular interest in this study. The adsorption process has been discussed in detail by van den Berg and Bruin (1981) and will not be discussed further here.

Gal (1983) reported that the sorption isotherm is just one characteristic of a food product, the other being the so-called marking points along the isotherm. These marking points are shown in Figure 2.1 and are:

P_i = Initial point of the packaged food (or end-point of the processing)

P_b = Point b (so-called monolayer value) which marks the end of the first curved part of the isotherm

P_{cr} = Critical point that should not be exceeded during storage and distribution

P_e = Point corresponding to equilibrium with the environmental atmosphere

The sorption isotherm is only of limited value without the knowledge of its critical marking points.

2.2.1 Sorption Isotherm Models

The physical chemistry of surfaces has provided food scientists with a large number of theoretical isotherms proceeding from different molecular models that can fit various experimental water sorption results. More than 75 isotherm equations have been reported in the literature for describing water sorption isotherms of biological materials over a smaller or larger range of a_w or even over the whole isotherm (Chirife and Iglesias, 1978; van den Berg and Bruin, 1981). Each of the models proposed (empirical, semi-empirical or theoretical) has had some success in reproducing equilibrium moisture content data of a given type of food and a given range of water activity.

Some of these models were reviewed by Labuza (1968). Chirife and Iglesias (1978) summarised 23 isotherm equations and surveyed their origin, range of applicability (both to type of food and water activity) and use in food science. Boquet et al. (1978) and Iglesias and Chirife (1975, 1976a) evaluated the usefulness of a number of two-parameter isotherm equations in describing moisture sorption isotherms of different foods.

From these studies it is apparent that a number of sorption isotherm models may be used to reasonably fit experimental

data for a given product. However, as noted by Labuza (1968), the usefulness of a sorption model will depend on the desired objectives of the user. For instance, for the prediction of the shelf life of packaged dried foods, the user is interested in an equation which fits as closely as possible the experimental data, rather than the correctness of the theory. The other important factor in selecting a sorption model is the simplicity (i.e. minimum number of parameters) which improves the usability of the equation.

BET Equation

Among the multilayer models for sorption, the most popular theory is that described by the Brunauer-Emmett-Teller (BET) equation which since its conception in 1938 has acted as the useful compromise between theory and practice. The BET equation is:

$$\frac{a_w}{(1-a_w)\,W} = \frac{1}{W_o C} + \frac{(C-1)\,a_w}{W_o C} \qquad (2\text{-}2)$$

where:

W = equilibrium moisture content, % dry basis
W_o = the monolayer moisture content, % dry basis
C = the constant related to the net heat of sorption.

The equation was derived based on the assumptions that the number of adsorbed layers at saturation pressure is infinite, and that the properties of the second and higher adsorbed layers of vapour are the same as bulk liquid. These assumptions are not entirely correct and therefore result in an equation that is only applicable between 0.05 and 0.45 a_w. However, this gives enough data so that the parameters W_o and C can be calculated (Labuza, 1968).

Although the BET analysis is based on over-simplified assumptions (Labuza, ibid.) which are certainly not expected to hold for water sorption in foods, the monolayer concept is useful because of its relationship with several aspects of the physical and chemical deterioration in dehydrated foods (Iglesias and Chirife, 1976b).

Over 300 monolayer values corresponding to almost 100 foods and food components were reported by Iglesias and Chirife (1976b).

Because of its limitation, the BET theory has been the subject of modification, extension, or critical analyses, but the general picture it offers of multilayered adsorption has not been invalidated. The simple form in which the BET equation is presented also makes it highly attractive. After considerable work on the theory, Hill (1946) formed the opinion that any future improvement on it must be in the form of a refinement rather than a modification of the basic theory. Brunauer et al. (1969) considered the Anderson-Guggenheim equation to be an important improvement of the BET equation.

GAB Equation

A moisture isotherm equation that has emerged over the past decade as applicable to most foods is the Guggenheim-Anderson-deBoer or GAB isotherm equation which is normally written in the following form:

$$W = \frac{CkW_m a_w}{(1-ka_w)(1-ka_w+Cka_w)} \qquad (2-3)$$

where:

W = the moisture content of the material on a dry basis

a_w = water activity

W_m = water content corresponding to saturation of all primary sites by one water molecule (formerly called the monolayer in BET theory)

C = the Guggenheim constant

$$= C_o \exp(\Delta H_1/RT) \qquad (2\text{-}4)$$

k = factor correcting properties of the multilayer molecules with respect to the bulk liquid

$$= k_o \exp(\Delta H_2/RT) \qquad (2\text{-}5)$$

where:

T = the absolute temperature (K)

R = the gas constant (8.31 $Jmol^{-1}\ K^{-1}$)

$$\Delta H_1 = H_m - H_n \qquad (2\text{-}6)$$

$$\Delta H_2 = H_1 - H_n \qquad (2\text{-}7)$$

where:

H_m and H_n = the heats of sorption of the monolayer and the multilayer of water respectively

H_1 = the heat of condensation of water vapour at the given temperature ($kJmol^{-1}$)

C_o and k_o = are adjusted constants for the temperature effect.

It is a three-parameter equation based on the BET sorption theory and developed independently from principles of statistical mechanics and kinetics. The parameters of the equation have physical significance, W_m being a monolayer moisture value and C and k relating to interaction energies between water and food, and between the multiple layers of water, respectively. For k=1 the equation reduces to the BET sorption isotherm equation.

The GAB equation has been applied very successfully to a large number of foods in the range of 0 to 0.9 a_w. It has been shown that the GAB equation fits food isotherms in

that range as well or better than other equations with four or more parameters (van den Berg, 1985). The GAB equation can also describe water activity dependence on temperature since W_m, C, k are exponential functions of inverse absolute temperature (1/T) (Weisser, 1985). It has become the standard sorption isotherm equation used in Europe (COST 90 project on water activity) and is being established in U.S. laboratories (Labuza, 1984a). A tabulation of GAB isotherms for more than 160 foods has been published by Lomauro et al. (1985a, b).

2.2.2 Effect of Temperature

One use to which isotherms obtained at two or more temperatures can be put is to predict sorption values at other temperatures. Food isotherms at several temperatures usually show a decrease in the amount sorbed with an increase in temperature at constant water activity (Labuza, 1968; Iglesias and Chirife, 1976c; Bandyopadhyay et al., 1980). This means that these foods become less hygroscopic with an increase in temperature. From the well known thermodynamic relationship:

$$\Delta F = \Delta H - T\Delta S \qquad (2\text{-}8)$$

where:

ΔF = the change in free energy

ΔH = the change in enthalpy

ΔS = the change in entropy

T = absolute temperature

As $\Delta F < 0$ (sorption is a spontaneous process) and $\Delta S < 0$ (the sorbed molecule has less freedom), then:

$$\Delta H < 0$$

and therefore from a thermodynamic point of view, an increase in temperature will not favour water sorption.

However, it is known that some sugars (or foods containing sugars) show an opposite trend in their isotherms; i.e. they become more hygroscopic at higher temperatures because of the dissolution of sugar in water (Audu et al., 1978; Bandyopadhyay et al., 1980).

Usually sorption phenomena in foods obey the Clausius-Clapeyron relationship (Iglesias and Chirife, 1976c). The temperature dependence of the isotherm may be expressed as

$$\ln a_w = \frac{Q_s}{R}\left(-\frac{1}{T}\right) + \text{constant} \qquad (2\text{-}9)$$

where:

a_w = the water activity at temperature T (K)
R = the gas constant (8.31 J mol^{-1} K^{-1})
Q_s = the net isosteric heat of sorption (J mol^{-1})

The net isosteric heat of sorption may be calculated from equation 2-9 by plotting ln a_w versus 1/T and determining the slope which equals $-Q_s/R$.

In this way it is possible to predict the water activity at some unknown temperature in the range covered by the known sorption isotherms. Because of some irreversible changes in food materials subjected to high temperatures, predictions should be limited to temperature ranges not very far from the actual temperature, otherwise deviations may occur (Bandyopadhyay et al., 1980).

In some cases the temperature dependence of water sorption isotherms can be estimated using isotherm equations

containing additional constants characteristic of the food material (Chen and Clayton, 1971; Iglesias and Chirife, 1976d).

2.2.3 Moisture sorption isotherms of dried onion, green beans and apricot

Studies have been conducted to determine the sorption properties of onions (Mazza and Le Maguer, 1978), green beans (Gane, 1950; Lafuente and Pinaga, 1966) and apricots (McBean and Wallace, 1967; Harel et al., 1978; Abdelhaq and Labuza, 1987; Maroulis et al., 1988).

It was observed from these results that differences in temperature and drying methods led to variations in the sorption curves obtained. It should be realised that there is not a single isotherm for a given product; pretreatments, maturity, variety, and chemical changes may all influence the shape of the isotherm (Iglesias and Chirife, 1982).

In the above studies conducted to obtain isotherms, no attempt was made to fit the experimental data to any isotherm model. However, Iglesias and Chirife (1975; 1976a; 1982) did statistical analysis on the fitting abilities of various two-parameter equations as applied to each experimental isotherm collected. Their results gave the model that best fitted the data for the given a_w range and temperature.

2.3 METHODOLOGY

2.3.1 Background

The method of Lang et al. (1981) was used to determine the moisture sorption isotherms of the three food products at different temperatures. The method is based on the use of saturated salt solutions to maintain a fixed relative humidity, and relatively small containers which permit rapid equilibration of samples with the test atmosphere. This method has also been used by Chinachoti and Steinberg (1986) in their isotherm studies.

A sample of known moisture content and weight was placed in the proximity equilibration cell (PEC) over salt solutions that maintained an atmosphere of known humidity. The sample absorbed/desorbed depending on the atmosphere in the PEC and its original moisture content. Equilibrium was reached relatively rapidly and the amount of water absorbed was calculated. An isotherm plot was then made of moisture content versus water activity (a_w).

Use of this technique results in a considerable decrease in equilibration time as compared to the use of the conventional dessicator method. Other advantages of using the PEC are:

a. The materials needed for making the PEC are readily available, cheap and easy to assemble.
b. A large number of PECs at different humidities and temperatures can be set-up simultaneously.
c. The method has good reliability for measuring sorption isotherms (as will be discussed in Section 2.3.3).

2.3.2 Materials

PEC

The cell and sample holder can be constructed from any chemically inert material. The dimensions of the cell are not critical; however, the smaller the volume of air in the cell, the faster equilibrium will be reached.

Figure 2.2 gives the schematic diagram of the PEC that was used in this study. A high density polyethylene specimen jar was used for making the cell. Cut-out polystyrene yoghurt containers were used as sample holders; they fitted snugly inside the specimen jar but could easily be removed for weighing. The sample holder was modified by removing a 38 mm diameter circular section from its bottom. This was replaced with Whatman No.54 filter paper which had been formed into a 'cup' that fitted the bottom of the sample holder. The filter paper supported the sample while allowing transmission of moisture.

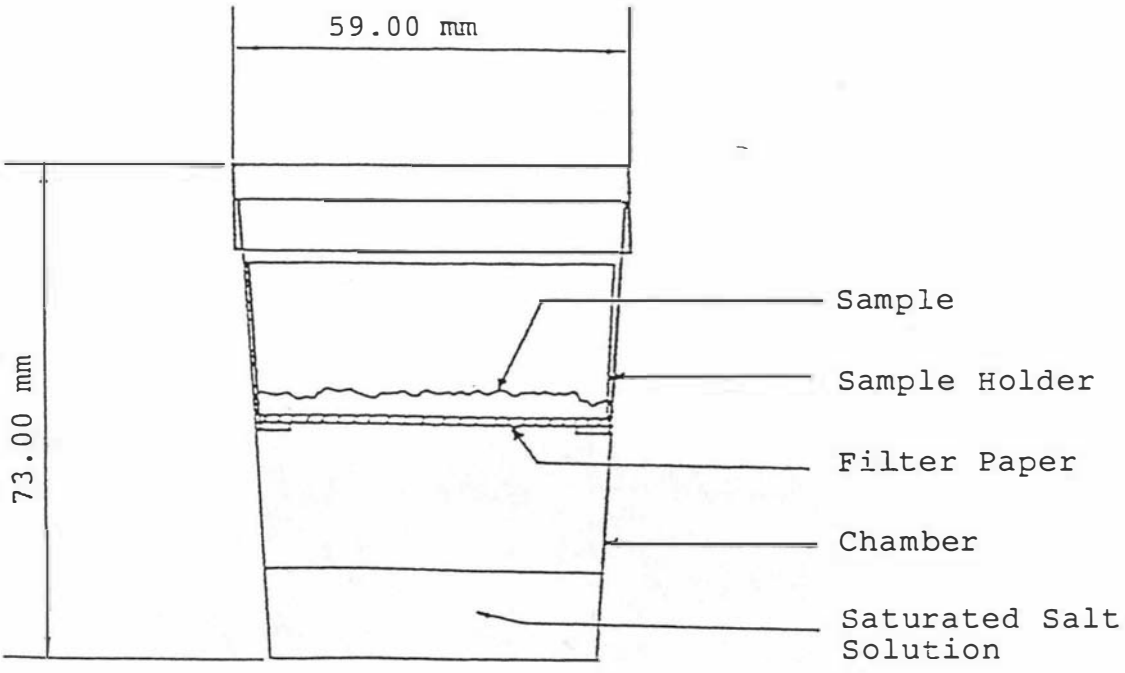


Fig. 2.2. Schematic diagram of the proximity equilibration cell.

Saturated Salt Solutions

The standard salts used and the corresponding water activities of their saturated solutions at different temperatures are given in Table 2.1.

Table 2.1. Water activity of the saturated salt solutions at different temperatures[1].

Salt	Temperature (°C) 20	30	40
Lithium Chloride	0.11	0.11	0.11
Potassium Acetate	0.23	0.22	0.19
Magnesium Chloride	0.33	0.32	0.32
Potassium Carbonate	0.43	0.43	0.43
Magnesium Nitrate	0.54	0.51	0.48
Sodium Bromide	0.59	0.56	0.53
Cobalt Chloride	0.68	0.62	0.55
Potassium Iodide	0.70	0.68	0.66
Sodium Chloride	0.75	0.75	0.75
Ammonium Sulfate	0.81	0.81	0.80
Potassium Chloride	0.85	0.84	0.82
Potassium Nitrate	0.95	0.92	0.89

[1] From Greenspan (1977)

Reagent grade salts and distilled water were used in preparing the saturated salt slurries following the recommendations of Labuza (1984a) and the COST 90 project (Wolf et al., 1985). The slurry was made up to the 30 mm mark of the PEC. The resulting salt solution surface to vapour volume ratio in the PEC was 0.19 as compared to 0.0335 cm^2 per mL for the conventional dessicator (Lang et al., 1981).

2.3.3 Reliability of the Method

To determine the reliability of the method in terms of accuracy and precision, an adsorption isotherm of microcrystalline cellulose (MCC) was measured according to the standard method set by the COST 90 group (Wolf et al., 1984). The results obtained were compared to the mean value and precision data of the collaborative study. These results are given in Appendix 2.1.

Good agreement is said to be obtained if the difference between the experimental mean value X and the reference value X_o is equal to or smaller than a critical difference D_{cr}. In the COST 90 collaborative study, the mean critical difference had the value $D_{cr} = 0.498$ at the 95% probability level. The mean moisture content values obtained in the present study at the different a_w levels fell within the range $X_o + D_{cr}$, indicating good agreement with the recommended sorption isotherm in the collaborative study.

The standard deviation s was also compared to the repeatability standard deviation s_r as established in the collaborative study. The mean s obtained in the present study was equal to the reference mean s_r of 0.06 at a 95% probability level. Out of the 9 a_w levels used, only the $a_w = 0.44$ gave an s value bigger than the corresponding s_r. Since s was equal to or smaller than s_r for almost all of the a_w levels, the PEC method can be considered to have good reliability for measuring sorption isotherms, provided care is taken in handling the PECs and in the weighing procedure.

2.3.4 Sample Preparation

The dried onion flakes and sliced green beans were processed commercially and supplied by Unilever (N.Z.) Ltd,

Hastings. The dried apricot halves were produced commercially in Alexandra, N.Z. by C. and M. Harrex.

The initial moisture contents (wet basis) of the three products were 5.5% for onion flakes, 6.8% for sliced green beans and 18.7% for apricot. The products were further dried by exposure to anhydrous $CaSO_4$ in a dessicator. This was to ensure that the isotherm obtained was an adsorption curve.

The dried onion flakes and sliced green beans were ground to a fine powder (20 mesh) and the apricot halves to tiny pieces using a domestic coffee mill. This was done immediately before weighing to avoid any changes in moisture content.

2.4 EXPERIMENTAL

The sample holders were fitted inside the PECs and placed in incubators set at controlled temperatures for 24 hours to allow the filter paper to equilibrate over the salt slurries. Three temperatures were used: 20, 30, and 40^{o} C. There were five replicates for each treatment. A thermometer was attached to one of the PECs to monitor the actual temperature inside the cells, as it had been noted by Scott and Bernard (1983) that it is important to measure and report the temperature of the sample itself rather than the incubator temperature.

The PECs were removed from the incubator for weighing one treatment at a time to avoid temperature change and condensation which could affect the weight of the samples.

The sample holders were weighed and then approximately 2 grams of the sample was spread on the bottom of the sample

Unless otherwise stated, 1 kg sub-samples were drawn from 20 kg bags of the products obtained directly from the manufacturers.

Sample sizes were chosen to ensure that heterogeneity was accommodated.

holders. An accurate weight was then taken to four decimal places. The PECs were tightly covered and immediately returned to the incubator.

The samples were weighed every 24 hours until equilibrium was reached. Equilibrium was considered to have been reached when the moisture content (dry basis) did not change by more than 1 mg/g of sample (0.5%) during three consecutive sampling periods. The equilibrium moisture content was considered to be the first in the series of three consecutive readings. According to Lomauro et al. (1985c) a change of 0.5% in the moisture content represents a weight change of about 1mg/g, which equals the accuracy of a typical balance found in a food analysis laboratory.

At high a_ws (greater than 0.85), equilibrium was considered to have been reached when the moisture content did not change by more than 10 mg per day over three consecutive samplings. This assumption was made on the basis that at higher water activities where more sorption sites are exposed to the water vapour, the deviations are more pronounced than at lower activities (Spiess and Wolf, 1983). More complex sorption processes are involved so that equilibrium conditions are not reached in any case. This is particularly true for high sugar foods where dissolution of sugars can take place at high water activities.

At a_ws greater than 0.70 a small piece of sponge was glued inside the lid of the PECs and a few drops of toluene was added to it to inhibit microbial growth, following the suggestion of Labuza (1984a).

Calculation

The moisture content (% dry basis) was calculated using the equation:

$$m = \frac{(W_f - W_i) + \left(\frac{m_i}{100} \times W_i\right)}{\frac{W_i \times \left|100 - m_i\right|}{100}} \qquad (2\text{-}10)$$

where:

m = % moisture content (dry basis)

m_i = % initial moisture content (wet basis)

W_f = final weight of sample after equilibrium at specific relative humidity

W_i = initial weight of sample in PEC

2.5 RESULTS AND DISCUSSION

2.5.1 General Observations

The results of the experimental measurements of the equilibrium moisture contents of dried onions, green beans and apricots at 20, 30 and 40°C are given in Tables 2.2 to 2.4. Equilibrium was reached after different time periods for different a_ws: 4 to 14 days for green beans, 3 to 10 days for onion (except for a_w = 0.92 where it took around 20 days), and 4 to 18 days for apricot (except for a_w = 0.95 where it took around 25 days). The standard deviations between the replicates generally increased with an increase in a_w, with a significantly higher standard deviation at a_ws greater than or equal to 0.90. As was mentioned earlier, this may be explained on the basis that at higher water activities there are more sorption sites exposed to the water vapour. More complex sorption processes are involved so that at very high water activities equilibrium conditions are not reached. Maroulis et al. (1988) reported that for dried fruits

Table 2.2. Equilibrium moisture contents (% dry basis) of dried onion at different water activities and temperatures.[1]

Temp. (°C)	a_w	Replicates 1	2	3	4	5	sd
20	.23	5.13	5.10	5.10	5.03	5.17	.05
	.33	5.82	5.79	5.73	5.68	5.68	.06
	.54	11.83	11.76	11.73	11.76	11.70	.05
	.59	14.71	14.55	14.98	14.87	14.66	.17
	.75	25.56	25.67	25.43	25.89	25.75	.18
	.85	39.26	38.82	39.58	39.54	39.26	.30
	.95	71.53	75.68	75.27	74.35	---	1.87
30	.22	4.32	4.26	4.19	4.10	4.16	.09
	.32	5.17	5.13	5.21	5.11	5.13	.04
	.51	10.10	10.02	10.01	10.07	10.00	.04
	.56	11.77	11.70	11.79	11.76	11.77	.03
	.62	13.75	13.83	13.97	13.94	13.96	.10
	.75	23.27	22.95	23.12	23.42	23.12	.18
	.84	35.18	35.77	34.85	35.54	---	.40
	.92	64.55	66.24	---	---	---	1.20
40	.11	2.31	2.27	2.34	2.26	2.32	.03
	.19	3.04	2.98	3.03	3.04	3.00	.03
	.32	4.60	4.58	4.60	4.54	4.58	.02
	.43	7.34	7.32	7.31	7.27	7.30	.03
	.48	8.97	8.96	8.98	8.96	8.87	.04
	.53	10.69	10.63	10.63	10.69	10.61	.04
	.66	16.73	16.71	16.54	16.67	16.75	.09
	.75	23.70	23.88	23.55	23.52	23.99	.21
	.80	29.41	29.00	29.47	---	---	.26
	.82	33.01	33.47	32.97	33.09	32.98	.21
	.89	50.03	50.87	50.72	49.68	49.96	.52

[1] Blanks represent excluded results due to error.

Table 2.3. Equilibrium moisture contents (% dry basis) of dried green beans at different water activities and temperatures.

Temp. (°C)	a_w	Replicates 1	2	3	4	5	sd
20	.23	4.68	4.75	4.49	4.61	4.48	.12
	.33	5.58	5.56	5.56	5.50	5.54	.03
	.43	7.68	7.76	7.71	7.92	---	.11
	.54	11.44	11.43	11.47	11.35	11.34	.06
	.59	14.15	14.08	14.43	14.60	---	.24
	.75	25.49	25.70	25.41	25.78	24.58	.48
	.85	38.60	38.42	39.54	40.27	39.16	.75
	.95	75.05	74.38	75.35	74.12	76.62	.98
30	.22	3.61	3.59	3.63	3.59	3.59	.02
	.32	4.78	4.78	4.77	4.73	4.77	.02
	.43	7.00	6.95	6.98	6.93	6.95	.03
	.51	9.35	9.33	9.37	9.36	9.34	.02
	.56	10.95	10.93	10.91	10.90	10.90	.02
	.62	13.09	13.03	13.03	13.06	13.10	.03
	.68	16.33	16.20	16.22	---	---	.07
	.75	22.17	22.03	21.94	22.02	22.12	.09
	.81	26.39	26.44	26.42	---	---	.03
	.84	31.87	31.97	31.96	32.06	32.00	.07
	.92	52.91	51.40	49.81	51.36	---	1.27
40	.19	2.96	2.97	2.92	2.91	2.97	.07
	.32	4.28	4.20	4.18	4.23	4.24	.04
	.43	6.71	6.57	6.56	6.59	6.56	.06
	.48	7.85	7.74	7.78	7.80	7.80	.04
	.53	9.20	9.22	9.22	9.21	9.18	.02
	.66	14.59	14.34	14.54	14.36	14.52	.11
	.75	21.56	21.88	21.01	21.23	21.07	.37
	.80	27.51	26.95	27.45	---	---	.31
	.82	29.34	29.39	29.51	30.08	---	.34
	.89	46.23	46.04	46.93	---	---	.47

Table 2.4. Equilibrium moisture contents (% dry basis) of dried apricot at different water activities and temperatures.[1]

Temp. (°C)	a_w	Replicates 1	2	3	4	5	sd
20	.54	14.28	14.20	14.31	14.34	14.28	.05
	.59	17.08	17.09	17.19	17.19	17.20	.06
	.75	32.47	32.49	32.62	32.75	32.57	.11
	.85	53.23	54.25	53.70	54.06	53.70	.39
	.95	112.81	113.56	110.37	112.57	---	1.37
30	.51	12.22	12.21	12.24	12.30	12.16	.05
	.56	14.66	14.60	14.61	14.59	14.61	.03
	.62	17.81	17.89	17.79	17.76	17.86	.05
	.75	31.18	31.25	31.12	31.02	31.03	.10
	.84	47.62	47.80	47.72	47.45	46.89	.36
	.92	83.88	83.03	84.80	84.95	---	.89
40	.53	10.25	10.31	10.37	10.43	10.18	.10
	.55	12.40	12.30	12.36	12.40	---	.05
	.66	18.78	18.61	18.71	18.67	18.60	.07
	.75	29.51	29.52	29.03	29.45	29.34	.20
	.80	37.31	36.47	36.40	---	---	.51
	.82	42.74	42.71	43.48	43.21	43.63	.42
	.89	73.71	70.31	72.27	72.21	---	1.40

[1] Blanks represent excluded results due to error.

large deviations were found at high water activities because of the difficulty of determining a constant equilibrium moisture content due to the gradual dissolution of fruit sugars.

The sorption isotherms of the three products at the three temperatures are shown in Figures 2.3 to 2.5. Each point on the curves represents the mean value of four to five replications, and the lines are the calculated GAB isotherm curves.

The shapes of the isotherms are characteristic of high sugar foods, which sorb relatively small amounts of water at low water activities and large amounts at high relative humidities. The sugar content of apricots is about 80% of the total solids on a wet basis (Abdelhaq and Labuza, 1987) and the remaining solids consist mainly of biopolymers such as polysaccharides, pectins and proteins. Dried apricots have around 51% (dry basis) sugar content (Young, 1975). According to Saravacos et al. (1986) the slight sigmoid shape of the first part of the isotherms in dried fruits is caused by the water sorption of the biopolymers, and the sharp increase in moisture content at high water activities is due to the sugars. At low water activities the physical state of the sugars may have an important effect on the sorption properties. Amorphous sugars are known to sorb more water than the crystalline materials (Chinachoti and Steinberg, 1984).

Mazza and LeMaguer (1978) also concluded that the shape of the adsorption isotherm for dried onion at low water activities may be directly dependent on the amount of sugars in the crystalline form. Sugars constitute about 80% (wet basis) of the total solids of onion and the sugar content of dried onion is around 50% (dry basis) (Warburton and Pixton, 1977).

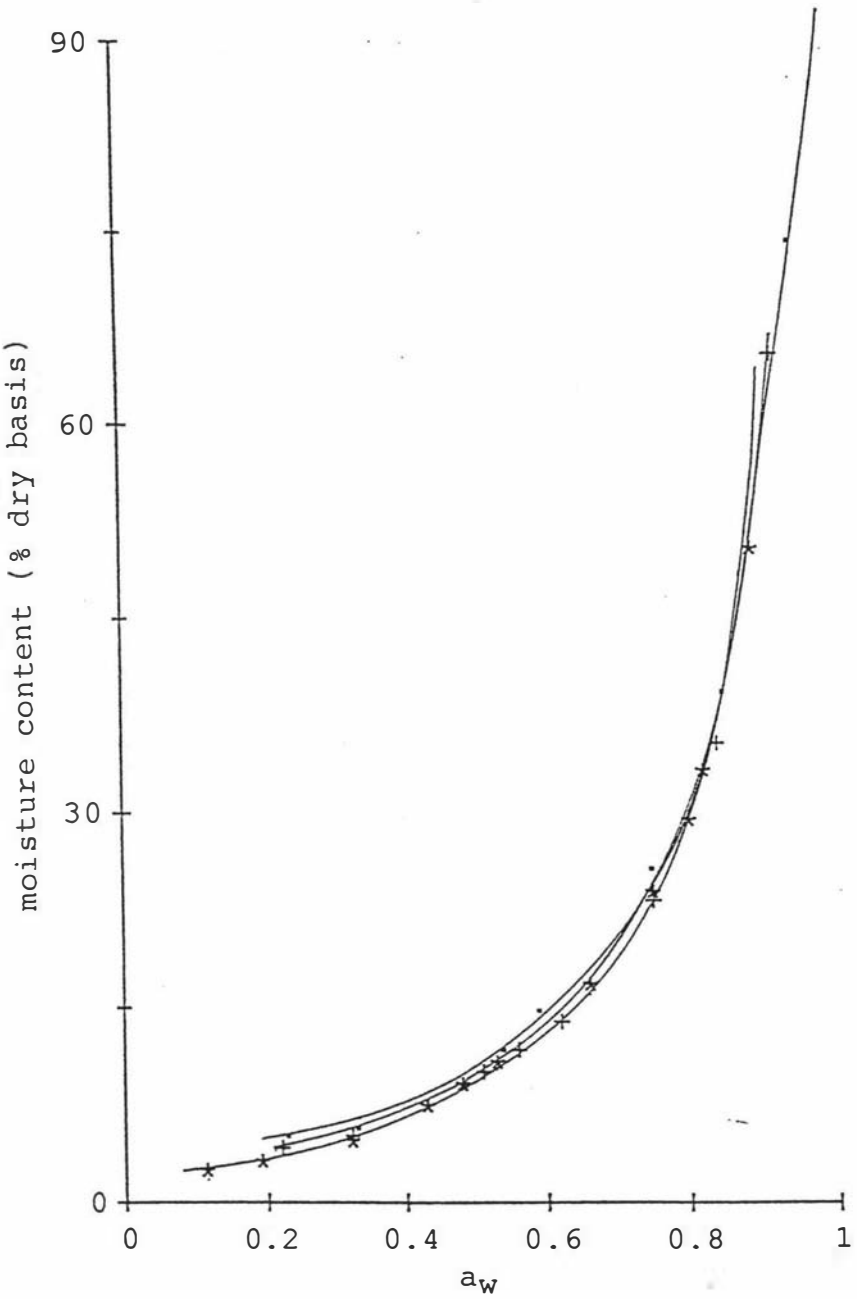


Fig.2.3. Moisture sorption isotherms of dried onions at 20°C (·), 30°C (+) and 40°C (*). The various points represent the means of the observed values; the lines are the calculated GAB curves.

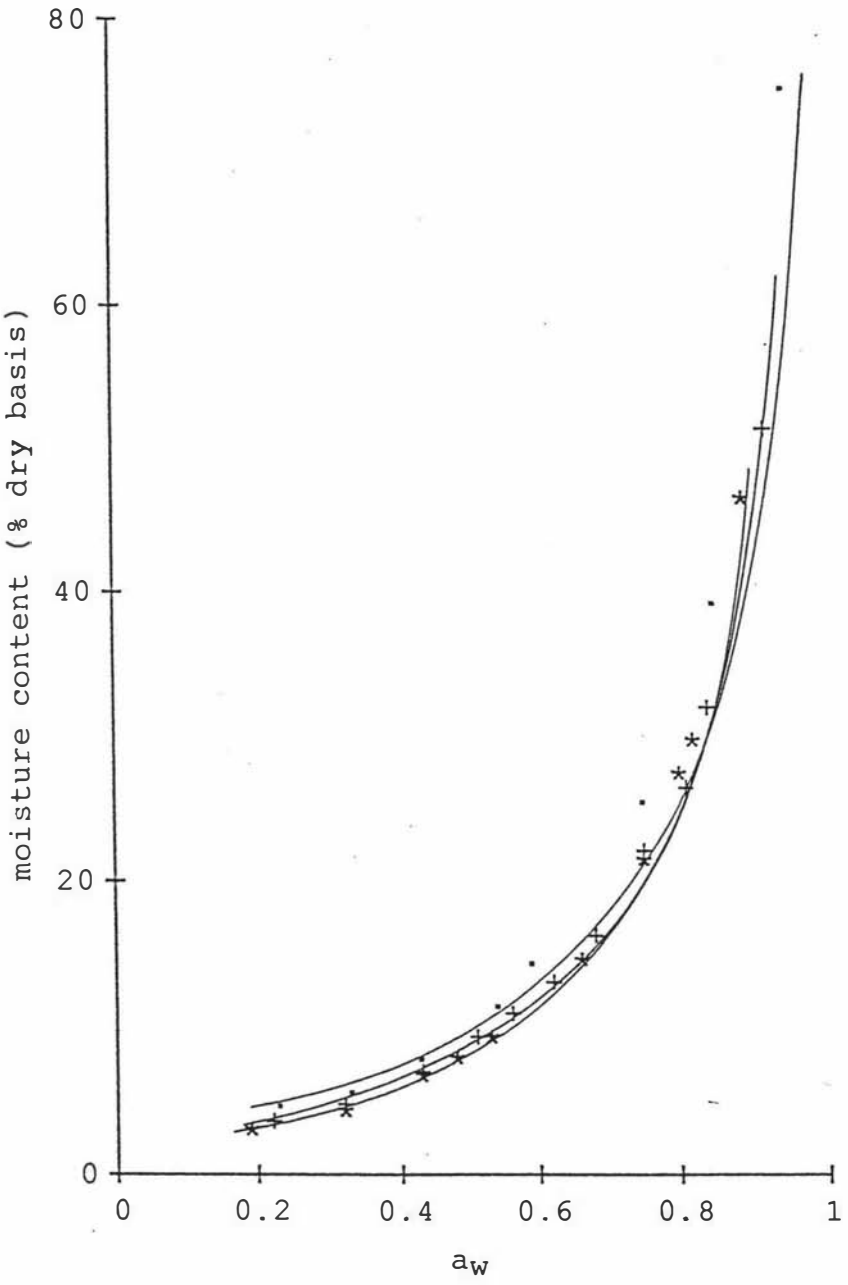


Fig.2.4. Moisture sorption isotherms of dried green beans at 20°C (·), 30°C (+) and 40°C (*). The various points represent the means of the observed values; the lines are the calculated GAB curves.

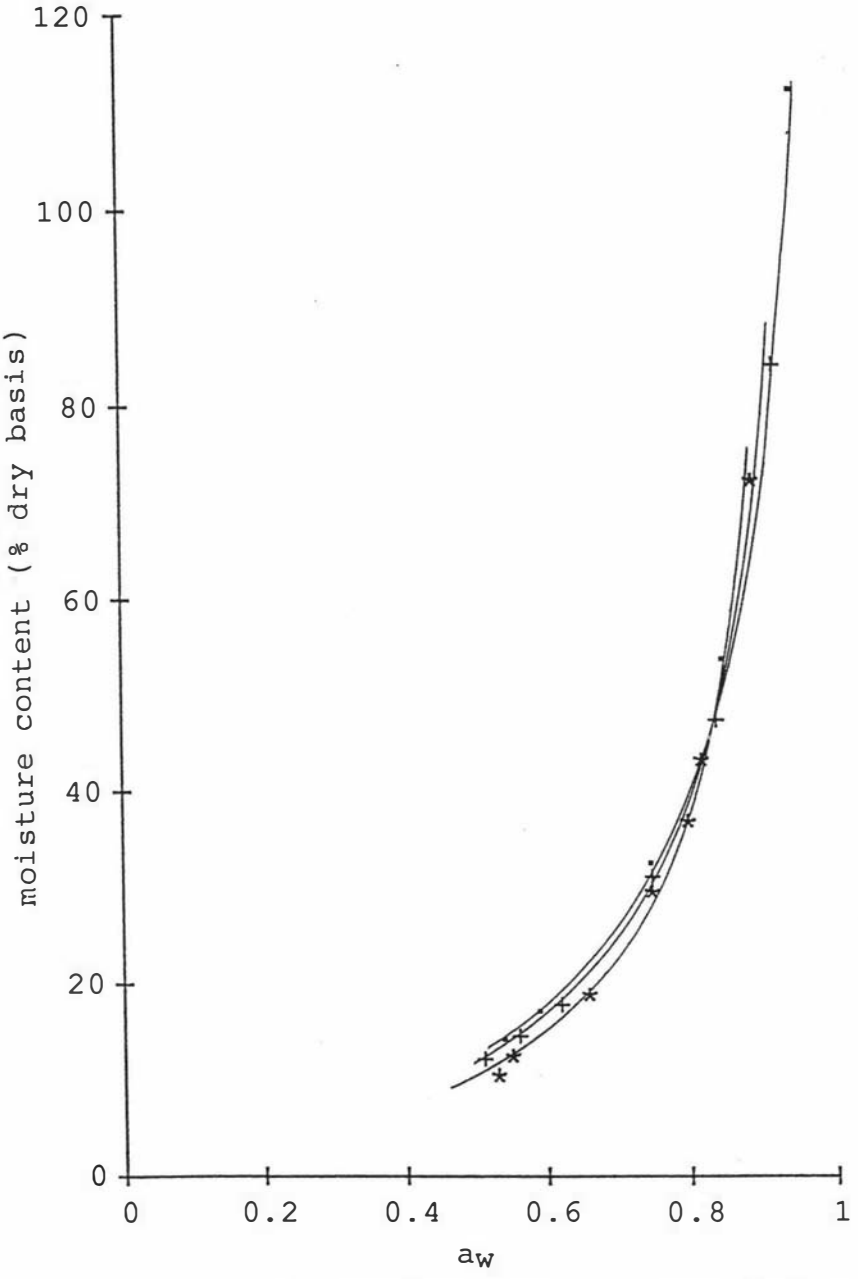


Fig. 2.5. Moisture sorption isotherms of dried apricot at 20°C (·), 30°C (+), and 40°C (*). The various points represent the means of the observed values; the lines are the calculated GAB curves.

The same explanation is probably true for dried green beans which exhibited a similar shaped isotherm. The green beans absorbed less water at high a_ws (i.e. lower moisture contents) compared to the onion and apricot. This may be due to the lower sugar content of green beans. According to Maroulis et al.(1988) the high moisture contents of dried fruits at high water activities are related to the sugar content of the products.

At low and intermediate water activities (a_w less than 0.80), temperature had the normal effect predicted by the theory of physical adsorption, i.e., at a constant a_w the equilibrium moisture content of the three dried products decreased significantly as the temperature increased from 20 to 40^{o}C. As pointed out by Iglesias and Chirife (1982) this tendency can be explained by the thermodynamic relationship given in equation 2-8. Therefore, an increase of temperature represents a condition unfavourable to water sorption.

The opposite temperature effect was observed at higher water activities (greater than 0.80 a_w), with the foods sorbing more water at higher temperatures. Thus in the high humidity region the water activity at constant moisture content decreased as the temperature increased.

The change in sorption properties of the dried products may be due to the dissolution of the sugars in water (Loncin et al., 1968; Saravacos et al., 1986). Evidence for this was provided by the observation that at water activities higher than 0.70 for onion and 0.80 for apricot, an exudate, possibly containing sugar, occurred, which was more pronounced at higher temperatures; all the sample (i.e. apricot pieces and exudate) was used in the moisture analysis. The isotherms crossed-over (Figures 2.3 to 2.5) at around the a_w of 0.80 for onion, 0.85 for apricot and 0.90 for green beans. Similar results were reported by

Furthermore, some deteriorative reactions such as nonenzymic browning result in the production of water, thus further complicating the interpretation of the sorption data.

Mazza and LeMaguer (1978) for onion, Abdelhaq and Labuza (1987) for apricot, and Maroulis et al. (1988) for dried fruits.

The a_w at which the crossing-over was observed appears to be related to the sugar content of the dried product, with a higher sugar content resulting in a lower a_w at which crossing-over occurred. According to Kapsalis (1987), the quantity of sugars present plays a role in whether or not crossing of isotherms with temperature at high water activities will take place. This is supported by the work of Roman et al. (1982) who reported that temperature had the normal effect on the desorption isotherms of apples at 20 to 60°C, with no crossing of the curves at high water activities. This was attributed to the lower percentage of monosaccharides in the apples.

At high water activities, the sugars are the major factor determining water sorption in dried fruits such as raisins, prunes and apricots (Saravacos et al., 1986 and Maroulis et al., 1988) and other high-sugar foods such as onion. The dissolution of sugars (an endothermic process) increases significantly as the temperature is raised, off-setting the opposite effect of temperature on the sorption of water on nonsugar solids. The net result is an increase of the moisture content (crossing-over) of the isotherms. This tendency has been observed in starch-glucose model systems (Saravacos and Stinchfield, 1965). Similar effects of temperature have been reported by Audu et al. (1978) for sugars, and Weisser et al. (1982) for sugar alcohols. Chinachoti and Steinberg (1984) found that sucrose added to starch gels increased sharply the sorption of water at water activities higher than 0.85. A strong interaction of amorphous sucrose with gelatinised starch was detected by measuring the sorption isotherms of freeze-dried gels.

2.5.2 Sorption Isotherm Equations

The GAB equation can be rearranged into a second degree polynomial as follows:

$$\frac{a_w}{W} = \alpha a_w^2 + \beta a_w + \gamma \qquad (2\text{-}11)$$

where:

$$\alpha = \frac{K}{W_m}\left(\frac{1}{C} - 1\right)$$

$$\beta = \frac{1}{W_m}\left(1 - \frac{2}{C}\right)$$

$$\gamma = \frac{1}{W_m CK}$$

Equations 2-3 and 2-11 will be referred to in this text as standard and transformed GAB equations, respectively. Regression analyses were performed using BMDP computer programs (Dixon, 1985). Three regression procedures were conducted:

a. Polynomial regression with the transformed GAB equation
b. Indirect (successive) nonlinear weighted regression with the standard GAB equation (three parameters)
c. Direct nonlinear weighted regression with the standard GAB equation (six parameters).

The transformed GAB equation is easiest to compute, but has two important disadvantages. The transformation of the measured data leads to an incorrect weighting of the data. Moreover, confidence intervals for the GAB constants cannot be obtained directly (Schar and Ruegg, 1985). The standard deviations of these constants have to be estimated on the basis of the Gauss Law of error propagation. Despite these

disadvantages, the transformed GAB model is still useful as a means of obtaining initial estimates of the different parameters that may be used in the nonlinear method. The transformed polynomial regression method was used by Bizot (1983) and Weisser (1985) in their isotherm studies.

Nonlinear regression analysis based on the standard GAB equation does not have the disadvantages mentioned above. However, the values at high water activity are usually associated with a high experimental error (as evidenced by the high standard deviation) and therefore strongly influence the resulting constants. The residuals at high a_w account for a high proportion of the sum of squares which is minimised. This unfavourable effect was avoided by weighting the squares of residuals with the variance of the data at each a_w level.

In a recent study on the evaluation of BET constants it was concluded that a weighted, nonlinear least squares procedure was the most reliable technique (Toupin et al., 1983). It was pointed out that a transformation of nonlinear models to evaluate BET constants was unsatisfactory. The parameters were shown to depend on the kind of regression analysis. A similar situation exists for the GAB equation (Schar and Ruegg, 1985).

Linear regression of the GAB model has been found less accurate than nonlinear regression, because the transformation of the GAB model into a linear equation (in respect of the three constants), results in large mean relative errors between the experimental and the predicted values of the equilibrium moisture content (Schar and Ruegg, 1985).

There are two methods of nonlinear regression analysis for estimating the constants of the GAB equation from experimental moisture sorption data: the direct and the

indirect method. In the indirect (successive) method, the three GAB constants W_m, C and k are estimated at each temperature by regression analysis of equation 2-3, and then the constants C_o, k_o, ΔH_1 and ΔH_2 are estimated by regression analysis of equations 2-4 and 2-5. The experimental data are grouped at various temperatures for the first regression, and they are subsequently represented by derived values. The derived values may introduce significant uncertainties into the second and third regressions. Thus, the application of the indirect (successive) regression method depends very much on the confidence limits and regions of the constants W_m, C and k, which are obtained from the first approximation (Maroulis et al., 1988).

In the direct regression method the six GAB constants W_o, C_o, k_o, ΔH, ΔH_1, and ΔH_2 are estimated by substituting equations 2-4, 2-5, and 2-12 in equation 2-3. The experimental data are weighted.

Maroulis et al. (1988) compared the two regression methods in their study on dehydrated fruits (including apricot) but in the direct method they used only five parameters in their nonlinear regression model instead of six parameters. They did not consider the relationship of W_m (monolayer moisture content) with temperature as shown in equation 2-12. This resulted in a constant W_m value for the different temperatures which is not expected to be the case. Weisser (1985) and Iglesias and Chirife (1984) reported that W_m decreases with an increase in temperature and had proposed the following relationships:

$$W_m = W_o \exp(\Delta H/RT) \qquad \text{(Weisser, 1985)} \qquad (2\text{-}12)$$

$$\ln W_m = \beta + \alpha T \qquad \text{(Iglesias and Chirife, 1984)} \qquad (2\text{-}13)$$

where β and α are constants and T is temperature in ^{o}C.

Maroulis et al. (1988) did not use a weighted regression method (i.e. all the experimental data were used directly with the same weight) despite the differences in the variance of the data. This could have affected the GAB equation that they obtained.

The results of the transformed polynomial regression analysis of the experimental results are given in Table 2.5. These results were only used to estimate initial values for the nonlinear regression and thus no further statistical analyses of the data (i.e. standard error, RMS) were made. The W_m values for the three products are realistic indicating that the transformed model may be used to estimate W_m if access to modern software packages which include nonlinear regression procedures is not available.

Table 2.5. Results of the transformed, polynomial regression analysis.

Product	Temp. (°C)	a_w Range	Parameters		
			W_m[1]	C	k
Onion	20	.23 - .95	7.26	3.39	0.97
	30	.22 - .92	6.20	3.50	1.00
	40	.11 - .89	5.87	3.35	1.02
Green Beans	20	.23 - .95	7.09	2.97	0.97
	30	.22 - .92	6.51	2.60	0.97
	40	.19 - .89	5.31	2.99	1.02
Apricot	20	.54 - .95	13.24	1.09	0.94
	30	.51 - .92	11.16	1.33	0.96
	40	.53 - .89	13.16	0.64	0.94

[1] W_m = g/100g dry weight

Table 2.6 shows the results of the indirect (successive) nonlinear regression method. The monolayer moisture content values (W_m) of apricot and green beans decreased as temperature increased, as was to be expected. The same trend was not observed for onion. There was no clear correlation between the value of C (Guggenheim constant) and temperature, although this would be expected from equation 2-4. The value of k (factor relating to interaction energies between the multiple layers of water) appeared to increase slightly with temperature for the three products.

Table 2.6. Results of the weighted, nonlinear, three parameter GAB equation.

Product	Temp. (°C)	a_w Range	Parameter			Std Dev.		
			W_m[1]	C	k	s_w	s_c	s_k
Onion	20	.23-.95	7.58	2.97	0.96	.36	.37	.01
	30	.22-.92	7.42	2.21	0.97	.23	.14	.01
	40	.11-.89	7.76	1.78	0.97	.44	.17	.01
Green	20	.23-.95	8.94	1.69	0.94	.32	.10	.01
Beans	30	.22-.92	7.00	2.32	0.95	.24	.16	.01
	40	.19-.89	6.88	1.73	0.97	.20	.10	.01
Apricot	20	.54-.95	13.28	1.09	0.94	.14	.02	.00
	30	.51-.92	11.58	1.24	0.95	.43	.08	.01
	40	.53-.89	9.87	1.05	0.99	.89	.16	.01

[1] W_m = g/100g dry weight

Because no clear relationships between the three parameters and temperature were obtained for the three products, these results have limited use, i.e. they can only be used at the specific temperatures at which they were derived. They

cannot be used for predictive purposes over the temperature range of 20 to 40°C.

Thus it was necessary to use the direct regression method (with six parameters) to obtain an equation that included temperature as a variable. The results of the direct nonlinear regression analysis are shown in Table 2.7.

Table 2.7. Estimates of the six parameters and their asymptotic standard deviations for the nonlinear GAB equations.

Product	Parameter	Estimate	Std Dev.	Coef. of Var.
Onion	W_o	4.13	2.44	0.59
	$\Delta H/R$	176.30	198.56	1.13
	C_o	0.02	0.02	1.43
	$\Delta H_1/R$	1524.78	503.51	0.33
	k_o	1.25	0.13	0.10
	$\Delta H_2/R$	-76.60	37.55	-0.49
Green Beans	W_o	1.68	2.20	1.31
	$\Delta H/R$	432.59	402.72	0.93
	C_o	0.06	0.19	2.99
	$\Delta H_1/R$	1093.15	884.75	0.81
	k_o	1.14	0.28	0.25
	$\Delta H_2/R$	-54.13	74.56	-1.38
Apricot	W_o	0.12	0.15	1.22
	$\Delta H/R$	1378.12	277.64	0.20
	Co	0.99	2.47	2.50
	$\Delta H_1/R$	44.69	594.53	13.30
	k_o	1.98	0.21	0.10
	$\Delta H_2/R$	-220.39	18.00	-0.08

The W_m, C and k values at the different temperatures were interpolated using the equations given in Table 2.7, and are shown in Table 2.8.

Table 2.8. Calculated isotherm constants based on the nonlinear, 6 parameter GAB equations given in Table 2.7.

Product	Temp. (°C)	a_w Range	Parameters		
			W_m[1]	C	k
Onion	20	.23 - .95	7.54	2.72	0.96
	30	.22 - .92	7.39	2.29	0.97
	40	.11 - .89	7.26	1.95	0.98
Green Beans	20	.23 - .95	7.34	2.58	0.94
	30	.22 - .92	6.99	2.28	0.95
	40	.19 - .89	6.68	2.03	0.96
Apricot	20	.54 - .95	13.54	1.15	0.93
	30	.51 - .92	11.59	1.15	0.96
	40	.53 - .89	10.03	1.14	0.98

[1] W_m = g/100g dry weight

The W_m values for all three products decreased with an increase in temperature, as was expected, but to different degrees. The ΔH value indicates the degree of W_m change with temperature. The W_m values for apricot decreased significantly with temperature while the changes of W_m for onion and green beans were very slight. Iglesias and Chirife (1976b and 1984) showed that the W_m response against temperature change is different for different foods (i.e. the ΔH value differs for different foods).

This inverse relationship between W_m and temperature has been reported for other food materials by a number of workers (Mazza and LeMaguer, 1978; Iglesias and Chirife, 1984; Labuza et al., 1985) including Iglesias and Chirife (1976b) who stated that the decrease in the monolayer with increasing temperature 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. Physical changes which could be responsible for the observed phenomena include: the degree of crystallinity of high polymers such as cellulose, pectin, hemicellulose, starch, and conformational changes in proteins. The number of potential binding sites may also be decreased through nonenzymic browning reactions or protein-lipid interactions leading to crosslinking of proteins. This could also explain the differences in W_m response against temperature change for different foods.

The W_m values for apricot obtained in the present study are comparable to that reported by Maroulis et al. (1988) for the "average" dried fruit of 12.4% (15 to 60°C) but are lower than the reported W_m for dried apricot of 15.1% (dry basis). Maroulis et al. (ibid.) considered this latter value to be relatively high for a dried fruit.

Mazza and Le Maguer (1978) obtained the following BET monolayer values for onion: 6.67% (10°C), 6.20% (20°C) and 4.71% (30°C). Using the data of Mazza and Le Maguer (ibid.), Lomauro et al.(1985a) computed the GAB W_m value at 30°C (0.11 to 0.86a_w) to be 8.11%. The values of W_m obtained in the present study range from 7.26% to 7.54% and fall within the published results.

Labuza et al.(1985) concluded that the GAB model was comparable to the BET model for prediction of the monolayer value. The BET monolayer values for onion and green beans were determined using equation 2-2 and are given in Table

2.9. The W_m values for apricot were not determined using this model because of the limited a_w range used. The results show that the GAB monolayer values were higher than the BET monolayer values for both products at all temperatures tested. Other workers who have compared the BET and GAB equations reported higher GAB monolayer values than BET values for potato starch (van den Berg et al., 1975), fishflour and cornmeal (Labuza et al., 1985), starch polymer (van den Berg, 1985) and wild rice (Gencturk et al., 1986).

Table 2.9. Results of the BET analysis.

Product	Temp. (°C)	a_w Range	W_m (% dry basis)	R^2 (%)
Onion	20	.23 - .54	5.85	77.8
	30	.22 - .43	5.10	92.9
	40	.11 - .43	5.02	87.4
Green Beans	20	.23 - .54	6.23	87.8
	30	.22 - .56	6.09	92.3
	40	.19 - .53	5.57	86.4

The initial moisture contents of the onion flakes (5.4% wet basis) and the green beans (6.7%) as they were obtained from the commercial processor, were lower than the calculated W_m values indicating that they had been dried to a lower moisture content than was necessary.

The value of C decreased gradually with temperature, while k increased slightly, in agreement with the results of Weisser (1985) for ground coffee and Maroulis et al. (1988) for sultana raisins. The values ΔH_1 and ΔH_2 represent the mean values of the heats of sorption of water on the dried product. ΔH_1 is the difference in enthalpy between

monolayer and multilayer sorption (eqn 2-4), which is expected to have a positive value, due to the strong exothermic interaction of water vapour with the primary sorption sites of the food. The ΔH_1 for apricot (0.37 kJ mol^{-1}) was considerably smaller than those for onion (12.68 kJ mol^{-1}) and green beans (9.09 kJ mol^{-1}) and much less than the value value of 21.1 kJ mol^{-1} reported for dried apricot by Maroulis et al. (ibid.).

The large difference between the literature value and the experimental value obtained for apricot is probably due to the difference in the a_w range used. Maroulis et al. (1988) used an a_w range of 0.11 to 0.92 in their study, while a narrower range of 0.54 to 0.95 was used in this study. At lower water activities, interaction between water vapour and the primary sorption sites of apricot would be expected to be higher, resulting in higher heats of sorption (ΔH_1).

The small negative value of ΔH_2 corresponds to a heat of sorption of the multilayer slightly greater than the heat of condensation of water (eqn 2-5). The value obtained for apricot (-1.83 kJ mol^{-1}) is comparable to that reported by Maroulis et al. (1988) of -2.05 kJ mol^{-1} for apricot and -1.63 kJ mol^{-1} for an "average" dried fruit. The ΔH_2 values for onion (-0.64 kJ mol^{-1}) and green beans (-0.45 kJ mol^{-1}) were smaller. It should be noted that at high moisture contents, ΔH_2 may reach a slightly positive value due to the endothermic dissolution of fruit sugars (Saravacos et al., 1986).

2.5.3 Fit of the GAB Model

Tables 2.10 to 2.12 give the experimental and calculated mean moisture content values at the different a_w levels at the three temperatures. The GAB isotherm equation fitted

Table 2.10. Experimental and calculated mean moisture content values for dried onion.

Temperature (°C)	a_w	Mean Moisture Content (% dry basis)		
		Experimental	Indirect Nonlinear	Direct Nonlinear
20	.23	5.11	4.46	4.22
	.33	5.74	6.44	6.18
	.54	11.76	12.04	11.75
	.59	14.75	13.97	13.67
	.75	25.66	24.16	23.88
	.85	39.29	38.87	38.68
	.95	74.21	86.35	86.96
30	.22	4.21	3.52	3.60
	.32	5.15	5.34	5.45
	.51	10.04	9.99	10.15
	.56	11.76	11.70	11.89
	.62	13.89	14.23	14.46
	.75	23.18	23.07	23.51
	.84	35.34	35.83	36.80
	.92	65.40	63.82	66.80
40	.11	2.30	1.52	1.55
	.19	3.02	2.72	2.75
	.32	4.58	5.00	4.98
	.43	7.31	7.44	7.36
	.48	8.95	8.81	8.69
	.53	10.65	10.41	10.24
	.66	16.66	16.34	16.06
	.75	23.73	23.44	23.15
	.80	29.29	29.67	29.50
	.82	33.10	32.97	32.91
	.89	50.25	51.73	53.03

Table 2.11. Experimental and calculated mean moisture content values for dried green beans.

Temperature (°C)	a_w	Mean Moisture Content (% dry basis)		
		Experimental	Indirect Nonlinear	Direct Nonlinear
20	.23	4.60	3.62	3.93
	.33	5.55	5.58	5.77
	.54	11.41	11.48	10.94
	.59	14.32	13.53	12.71
	.75	25.39	24.06	21.76
	.85	39.20	38.15	34.10
	.95	75.10	75.80	68.82
30	.22	3.60	3.36	3.34
	.32	4.77	5.06	5.04
	.51	9.35	9.30	9.28
	.56	10.92	10.83	10.82
	.62	13.06	13.07	13.07
	.75	22.06	20.68	20.74
	.84	31.97	31.12	31.30
	.92	51.37	51.97	52.56
40	.19	2.93	2.38	2.55
	.32	4.23	4.39	4.56
	.43	6.60	6.56	6.67
	.48	7.79	7.78	7.84
	.53	9.21	9.20	9.18
	.66	14.47	14.53	14.09
	.75	21.35	20.94	19.80
	.80	27.30	26.60	24.72
	.82	29.58	29.61	27.28
	.89	46.40	46.92	41.33

Table 2.12. Experimental and calculated mean moisture content values for dried apricot.

Temperature (°C)	a_w	Mean Moisture Content (% dry basis)		
		Experimental	Indirect Nonlinear	Direct Nonlinear
20	.54	14.28	14.27	14.77
	.59	17.15	17.17	17.70
	.75	32.58	32.58	33.01
	.85	53.79	53.80	53.63
	.95	112.33	112.36	107.98
30	.51	12.23	12.16	11.86
	.56	14.61	14.57	14.27
	.62	17.82	18.16	17.89
	.75	31.12	30.71	30.67
	.84	47.50	48.35	48.86
	.92	84.16	84.45	86.89
40	.53	10.31	11.14	11.54
	.55	12.36	12.05	12.45
	.66	18.67	18.90	19.22
	.75	29.37	28.77	28.77
	.80	36.73	37.88	37.40
	.82	43.15	42.86	42.04
	.89	72.12	73.30	69.40

the experimental data reasonably well for apricot and onion at all temperatures (Figures 2.3 and 2.5). A poor fit was obtained for green beans at 20°C (Figure 2.4), but the fit at the two higher temperatures was quite good. For the three products the best fit was achieved in the medium a_w range, the range that is of most practical importance in the shelf life prediction of dried foods. The data at the highest a_ws had the biggest residuals as expected. The standard deviations between replicates at these a_w levels were the highest and, consequently, were given the lowest weights in calculating the isotherm equations resulting in the higher residuals.

It is suggested that with complex foods such as dried fruits and vegetables or foods with high sugar content, the GAB equation (or any other equation) is not applicable to a_ws greater than 0.90 due to the inherent problem of large deviations among replicates and the difficulty of determining equilibrium conditions, especially when phase changes of sugars occur. Previous studies by various workers which had concluded that the GAB equation was suitable for describing isotherms to a_ws higher than 0.90 had been carried out on less complex foods or food components such as starch, MCC and flour (Bizot, 1983; van den Berg et al., 1975 and van den berg, 1985). Thus, on the basis of the present study, it is recommended that extrapolations should not be made outside the range of a_w over which data was collected, especially at high a_w levels.

The above discussion further supports the proposition that a weighted regression should be used. If no weights had been assigned to the data, the unreliable values at the higher a_ws would have adversely influenced the calculated GAB equation.

The indirect (3 parameter) nonlinear GAB equation generally fitted the experimental data better than the direct GAB equation. Thus, if prediction is to be made at the specific temperature tested, then the use of the indirect nonlinear method seems adequate and simpler to use. However, as was stated before, the indirect method is not suitable for predictive purposes at other temperatures.

The residual plots for the weighted regression equations are shown in Figure 2.6. The plots show no definite pattern or structure indicating the usefulness of the weighted regression and adequacy of the models that were obtained.

The asymptotic standard deviations of the six parameters shown in Table 2.7 indicates the relatively low precision or high uncertainties of the parameters. The parameters were correlated among themselves. Some caution is needed in interpreting these values. Nonlinear regression applied to models with Arrhenius-type relationships generates very highly correlated parameter estimates. This leads to an elongated joint confidence region and apparent lack of precision.

2.6 CONCLUSIONS

The moisture sorption isotherms of dried onion, green beans and apricot were determined at 20, 30 and 40^{o}C. The GAB model was adequate for the description of the isotherms of the three products at the three temperatures. A direct weighted nonlinear regression analysis of the data is recommended for prediction purposes.

Although the estimated constants of the GAB model W_m, C_o, k_o, ΔH, ΔH_1, and ΔH_2 have relatively low precision, the parameters have acceptable physical significance.

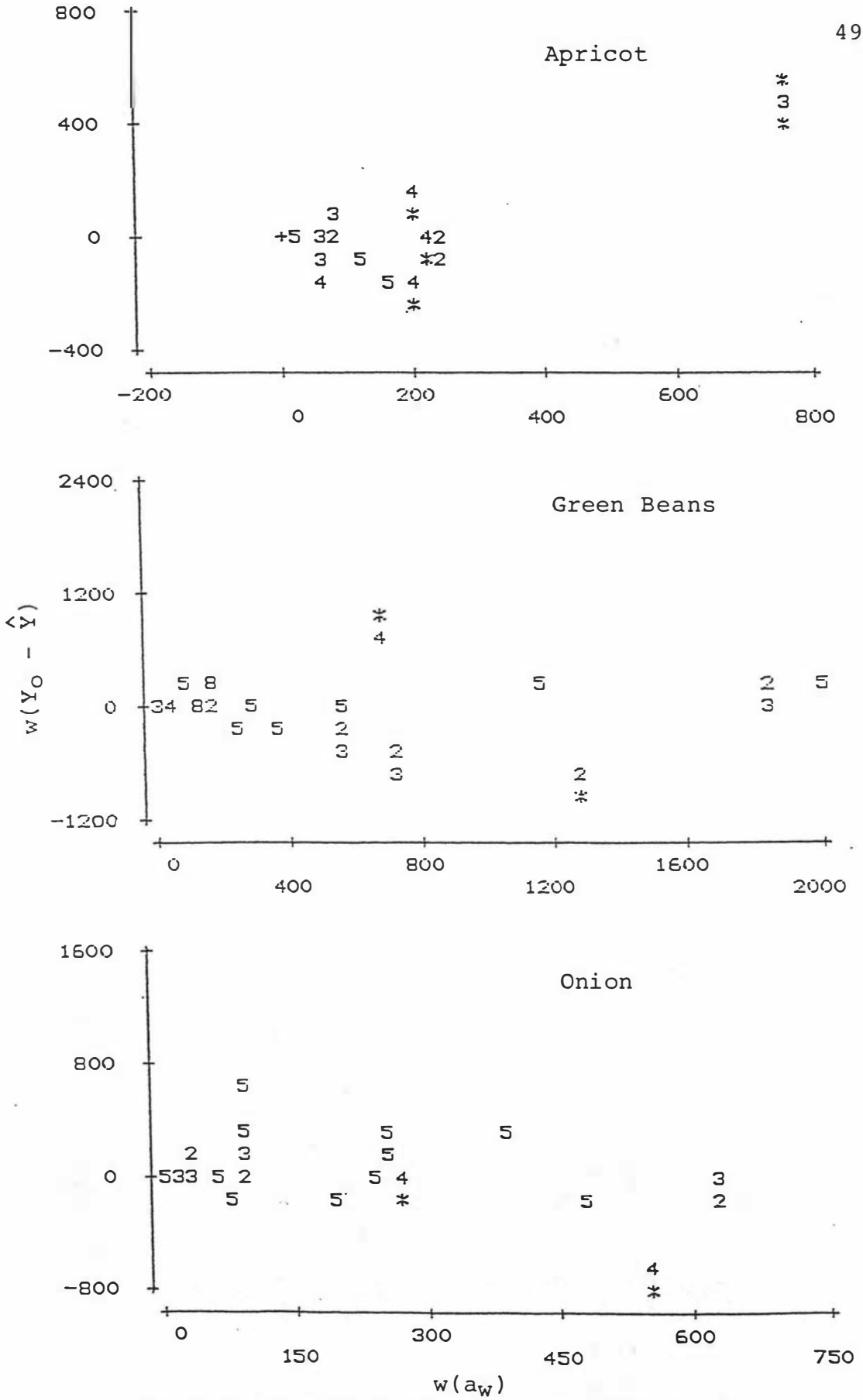


Fig.2.6. Residual plots for the weighted regression analysis of the GAB equations (w = weight; numbers indicate number of data points).

GAB constants should always be reported together with the type of regression procedures used for their estimation. Extrapolations should not be made, especially at high a_w values. Therefore, constants of isotherm equations must be reported together with the range of water activities over which the measurements were made.

CHAPTER 3
PERMEABILITY OF PACKAGING FILMS

3.1 INTRODUCTION

The selection of the proper package for any food product should be based on the knowledge of firstly, the characteristics and requirements of the food and secondly, the protective properties of the packaging material. The first factor is discussed in Chapters 2 and 4. This chapter is concerned with the second factor, the permeability properties of selected plastic films.

The permeability of flexible plastic films to gases and vapours plays a major role in the retention of product quality during distribution and storage. This is particularly true for packaged dehydrated products which are sensitive to moisture gain.

A number of studies have been previously conducted to determine the permeability characteristics of most of the commercial films available today. However, most of these studies apply only to specific conditions i.e. a particular temperature and relative humidity (RH). In some instances not even this information has been reported. Thus the results are of limited use for prediction purposes.

To be able to use permeability data in the prediction of shelf life, there is a need for mathematical equations that describe the relationships between the permeability characteristics of the films and environmental factors such as temperature and RH so that the permeability of the films can be predicted at different storage conditions.

This study was conducted with the following objectives:

a. to determine the water vapour permeability of several commonly used packaging films at different temperatures and humidities;
b. to develop equations describing the relationship between permeability, temperature and humidity.

The packaging films used in the study were low density polyethylene (60 μm), polyethylene terephthalate (12 μm) and a laminate of both films (12 μm polyester and 30 μm polyethylene). These films are readily available commercially and are commonly used for packaging dried food products.

3.2 LITERATURE REVIEW

Gases and vapours can permeate through macroscopic or microscopic pores and pinholes in materials, or they may diffuse by a molecular mechanism, known as "activated diffusion" (Karel, 1975a). In activated diffusion the gas is considered to dissolve in the packaging material at one surface, to diffuse through the packaging material by virtue of a concentration gradient, and to evaporate at the other surface of the packaging material.

Under steady-state conditions, diffusion of gases and vapours through the polymer at constant temperature and differential partial pressure can be described by Fick's law of diffusion:

$$\frac{\delta W}{\delta t} = -D \frac{\delta c}{\delta x} \qquad (3\text{-}1)$$

where:

$\delta W/\delta t$ = the rate of transport of gases or water vapour through the film

D = the diffusion constant

$\delta c/\delta x$ = the concentration gradient across a thickness δx

By integration and applying Henry's law (which states that concentration is proportional to pressure, the proportionality constant being the solubility constant), and by defining permeability (P) as the product of solubility constant (S) and diffusion constant (D), the following equation is obtained for evaluating the permeability constant (Karel, 1975a; Mannheim and Passy, 1985):

$$P = D.S = \frac{X \,.\, Q}{A.t.\Delta p} \qquad (3\text{-}2)$$

where:

Q = the quantity of gas or water vapour permeating through the polymer

t = time

A = area of film

X = thickness of the film

Δp = pressure difference

The above treatment assumes that D and S are independent of concentration but in practice deviations do occur. Equation 3-2 does not hold for heterogeneous materials such as coated or laminated film, or when there is interaction such as occurs between hydrophilic materials (e.g. regenerated cellulose, glassine and some of the polyamides) and water vapour. Permeabilities of polymers to water vapour are often presented as the Water Vapour Transmission Rate (WVTR) of the material which is defined as:

$$WVTR = \frac{Q}{A.t} \qquad (3\text{-}3)$$

The RH on both sides of the film, the temperature, and the material thickness and type must be specified .

Composites of multilayer materials such as laminates are considered as a number of barriers arranged in series. The overall resistance to flow (which is the reciprocal of permeability) is given by the individual film permeabilities according to the following equation:

$$\frac{1}{P} = \sum_{i=1}^{n} \frac{Xi}{L} \cdot \frac{1}{P_i} \qquad (3\text{-}4)$$

where:

P = the overall permeability of the laminate,

P_i = the permeability of ply i which has a thickness X_i

L = the total thickness.

This relationship is valid, provided the individual permeabilities are independent of pressure and concentration, and there is no interaction with the diffusing gases. The permeability of the laminate will approximate that of the least permeable ply, and therefore the equation is only useful when the plies have similar permeabilities. When any P_i is pressure dependent, as is the case for hydrophilic films, the above equation is no longer valid and the overall permeability is affected by the order in which the layers are assembled.

The permeability of a film can change with temperature and the relative humidity present on either side of the film. This is because the water can dissolve in the film, plasticise it, cause it to swell, and influence the

temperature at which the polymer may undergo a phase transition from the amorphous to the crystalline state (Labuza, 1982a). Thus, any single P or WVTR value generally applies only to one condition of temperature and humidity.

3.2.1 Effect of Relative Humidity

The standard equation for mass transfer (eqn 3-2) assumes that the water sorption properties for a film are linear; however, the more polar the film the less this holds true (Labuza and Contreras-Medellin, 1981). Thus, many films will show a change in WVTR or P depending on vapour pressure conditions on each side of the film.

The permeability of films to water vapour usually increases rapidly at high relative humidities. This effect is attributed to an increase in the diffusion constant due to the plasticising effect of the vapour, and an increase in the solubility coefficient with increasing pressure (i.e deviation from Henry's law). Karel (1975a) studied the effect of different RHs on one side of the film on the permeability of several films. He reported that with the relatively hydrophobic films (e.g. polypropylene, polyester, rubber hydrochloride and polyethylene) the permeability constants are independent of pressure. The calculation of water transport through such materials as polyamide, cellulose, polyvinyl alcohol, and others which show a humidity-dependent permeability can be made only if this dependence can be characterised by a suitable mathematical function.

In an earlier study, Karel et al. (1959) concluded that a linear relationship existed between WVTR and the partial pressure differential for hydrophobic plastics including polyvinylidene chloride, polyester, polystyrene, and

polyethylene. Similar results have been reported by de Leiris (1986) for polyester and polypropylene. Othomer and Frohlich (1955) showed that a plot of log P versus log p was linear for many films. However, this has been criticised by Labuza and Contreras-Medellin (1981) on the basis that log/log functions tend to straighten out any data and may have no theoretical meaning.

3.2.2 Effect of Temperature

Permeability constants are affected by temperature according to the Arrhenius relationship:

$$P = D.S. = D_o \exp(-E_d/RT) \cdot S_o \exp(-\Delta H_s/RT)$$

$$= P_o \exp(-E_p/RT) \qquad (3\text{-}5)$$

where:

E_d = energy of activation for diffusion
ΔH_s = heat of solution
E_p = energy of permeation
$E_p = E_d + \Delta H_s$

Heiss (1958), Karel et al. (1959) and de Leiris (1986) have shown that most of the common types of packaging films follow equation 3-5, including polyvinylchloride, polyethylene, polyamide, polyvinylidene chloride, polystyrene, polyester, and polypropylene. For those films in which a straight-line relation for equation 3-5 does not hold true, Kumins et al. (1957) proposed that at a certain temperature the film undergoes amorphous to crystalline changes in the polymer that significantly affect P. The temperature at which this transition occurs is called the glass-transition temperature (T_g). At this temperature an amorphous polymer changes from a brittle, glassy state to a flexible, rubbery state or vice-versa. This phenomenon is

not relevant in this study because the T_gs for low density polyethylene (-25°C) and polyester (69°C) (Bikales, 1967) are well outside the temperature range (20 to 40°C) that was used in these experiments.

Labuza and Contreras-Medellin (1981) studied the effect of both relative humidity and temperature on the P values of ten food packaging films. There seemed to be no clear-cut relationship between P, external RH (0 to 75%), and temperature (-30 to 35°C). However, it was shown that by using the Arrhenius relationship, a plot of log P versus the reciprocal of absolute temperature gave a straight line for each relative humidity. They reported that, in general, at the higher temperature (35°C) , the larger the driving force (Δp), the higher the P. Their results, however, show that such was not the case for polyethylene and polyethylene terephthalate; no specific trend could be concluded from their results.

The above authors used water filled into the bags to obtain the 100% internal RH and this could have led to deviations in their results. Barrier properties of a plastic material to liquid penetrants and to the corresponding saturated vapours should be identical if the equilibrium between the two phases is maintained. However, higher permeability values are sometimes found for liquid penetrants, probably due to the conditions used in which the equilibrium is not maintained, and to the conditioning effect of the liquid which may alter the morphology of the polymer (Yasuda and Stannett, 1985).

3.2.3 Effect of Pinholes

The prediction of moisture gain or loss is based on the package being integral, i.e., that the folding , creasing, code-date stamping, etc., do not create pinholes through

which water vapour can flow. Using the Poynting equation for the underwater vacuum test, Labuza and Contreras-Medellin (1981) have calculated the rate of moisture transport through pinholes. They showed that the leak rate through a pinhole is not very large if the pinhole size is small. For a package that just passes a vacuum test of 507 mm Hg of H_2O, the pinhole size would be 8.7×10^{-3} mm, and 100 holes of that size in a package would pass about 8 g of water in a year under the standard WVTR conditions. Assuming more realistic conditions (e.g. 25°C with a food at 0.2 a_w and the surrounding air at 60 %RH), a single hole would not pass more than 20 mg of water in one year. Thus, if the film-making and packaging operations are properly controlled, pinholes are of no consequence to moisture transport (Labuza, 1982a). Therefore, the possible effect of pinholes was not considered further in this research.

3.2.4 Other Factors

The barrier properties of films depend on the specific molecular structures of the polymers involved. A structure that provides a good barrier to gases may provide a poor water vapour barrier.

Some of the factors that influence the barrier properties of polymers include:

1. degree of polarity
2. chain stiffness
3. inertness to the permeant
4. molecular symmetry or order, crystallinity or orientation
5. bonding or attraction between chains
6. glass transition temperature (T_g)

These factors are discussed in detail by Ashley (1985), Rogers (1985) and Pascat (1986).

3.3 METHODOLOGY

3.3.1 Background

The method used for determining the water vapour permeability of the packaging films was based on the detector film method developed by Holland and Santangelo (1982). A transparent cellulose film containing anhydrous cobalt chloride as moisture detector was sandwiched in a brass microcell between two pieces of the film to be tested. The system was held at a controlled temperature and humidity, and the amount of water vapour permeating through the test film was determined at intervals by measuring the decrease in absorbance of the detector film at 690 ηm. This method requires little equipment and is claimed to be highly reproducible and rapid, a characteristic which is of particular importance in accelerated storage studies. Holland and Santangelo (ibid.) observed a good correlation between the permeability values obtained using this spectrophotometric method and the standard gravimetric method.

3.3.2 Procedure

Detector Film

Cobalt chloride is blue when dry and pink under humid conditions, both in the solid state and in a number of solvent media. Cellulose films (30 μm thick) were soaked in 2.5M aqueous cobalt chloride solutions for about 30 min. The films were removed, wiped on filter paper, dried in a stream of warm air until the colour changed from pink to bright blue, and then stored in a dessicator. The initial absorbance of the resulting detector at 690 ηm was around 1.5.

Holland and Santangelo (1982) had used a higher concentration of cobalt chloride resulting in initial absorbance readings of 1.7-1.9.* However, detector films with such high initial absorbance readings were observed to develop cloudy streaks after an absorbance change of around 0.5, while those with initial absorbance readings of less than 1.5 allowed changes of around 0.7 without the cloudiness occurring.

Because the dried films were brittle, they were cut to shape for the cell before drying.

Microcells

A diagram of the microcells used in the study is presented in Figure 3.1.

The microcells were made from two identical brass plates (31 x 44 mm) with a circular aperture (11 mm dia.) at the centres. A rubber-modified nitrile copolymer o-ring slightly larger than the apertures (18 mm dia.) was used as a seal. A strip of detector film (larger than the o-ring) was sandwiched between two pieces of test film and laid over the aperture of one of the brass plates. The o-ring was placed on top of the film, and the second brass plate was placed on top and screwed to the bottom plate with screws placed at each corner of the cell. Hence the o-ring sealed the detector film in a watertight envelope and defined the permeation area. The apertures allowed the water vapour from a controlled atmosphere access to both the exposed surfaces of the test film. The cell was removed at intervals from the controlled atmosphere and placed in a spectrophotometer, where the change in absorbance of the detector film was monitored through the apertures in the cell.

* It was implicitly assumed in the present study that the lower initial absorbance value did not affect the validity of the method. A Beer's law plot would have made the technique unequivocal.

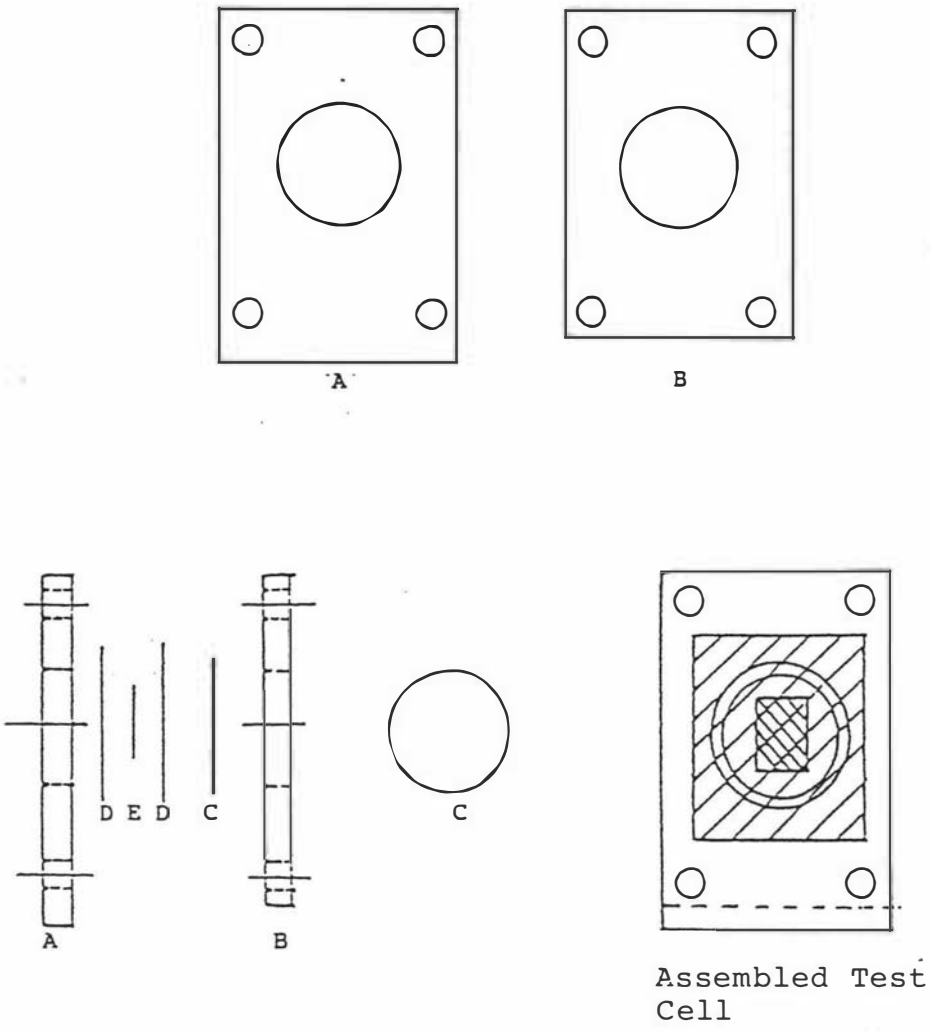


Fig. 3.1. Diagram of the microcell used for the determination of the WVTR of packaging films (drawn to actual size) where:

A - brass vertical support plate
B - brass front plate
C - rubber 'o' ring
D - test film
E - detector film

3.3.3 Calculations

The quantity of water absorbed by the detector film (Q) was calculated using the equation :

$$Q = 6\ \Delta a.A_o/\varepsilon \qquad (3\text{-}6)$$

where:

Δa = the change in absorbance of cobalt chloride in the detector film

ε = the molar extinction coefficient

A_o = the area of the detector film

factor 6 = corresponds to the number of water molecules per molecule of cobalt chloride

The permeability constants of the film for water vapour at a fixed temperature were calculated using equation 3-2 and the WVTR using equation 3-3.

Whose equation ?

3.3.4 Materials

The films used for the permeability measurements were low density polyethylene (60 µm) (hereafter abbreviated LDPE), polyethylene terephthalate (12 µm)(hereafter abbreviated PET) and a laminate of both films (12 µm PET and 30 µm LDPE). The plastic films were supplied by Courtaulds Films N.Z. Ltd., a converter of packaging films.

3.4 EXPERIMENTAL

A range of humidity conditions (55, 75 and 90% RH) and three temperatures (20, 30, 40°C) were chosen as the experimental variables. The constant humidity conditions

were attained by using saturated salt slurries of NaBr, NaCl, and KNO_3 in PEC cells (as described in Section 2.3). The PEC cells were placed in incubators that had been set to the different temperatures. The actual humidity values obtained at the different temperatures are given in Table 3.1a.

The steady-state internal RH was assumed to be 23% for LDPE and the laminate at all temperatures and external RHs. This is based on the results of Holland and Santangelo (1982), who showed that the detector film does not absorb water vapour below 23% RH. This was interpreted by Holland (1989) as a competitive situation between the cellulose and water; until an RH of 23%, cobalt chloride is bound to cellulose; at higher RH values the detector film becomes increasingly permeable and reacts increasingly quickly with water vapour. Because the transmission rates for PET were much higher than the two other films, the steady-state internal RHs were expected to be higher with time. The internal RHs were obtained by interpolating the slope of the detector response against slopes obtained at known vapour pressures (as given in Holland and Santangelo, ibid.). The assumed internal RH values for PET are given in Table 3.1b.

The test films were cut to the required size (2 x 2 cm) and were conditioned to the different treatment conditions by holding them overnight in representative PEC cells in the incubators.

At the start of the experiment, the detector films were sealed between the test films in the microcells following the procedure given in Section 3.3.2. In the case of the laminate, the film was laid over the aperture of the brass cell such that the LDPE side was facing the detector film and the PET side was exposed to the external RH. An initial reading of the detector film was taken and the

Table 3.1a. Saturated salt solutions and their corresponding RH (%) at different temperatures.[1]

Temperature (°C)	Saturated Salt Solution		
	NaBr	NaCl	KNO_3
20	59.1	75.5	94.6
30	56.0	75.1	92.3
40	53.2	74.7	89.0

[1] Greenspan (1977)

Table 3.1b. Assumed internal relative humidities (%) for PET film.[1,2]

Temperature (°C)	External RH (%)		
	55	75	90
20	23	23	23
30	23	24	25
40	24	26	27

[1] The assumed internal RHs for LDPE and Laminate are 23% for all temperature and external RH conditions.

[2] The vapour pressure difference (Δp) was calculated using the equation:

Δp = p of pure H_2O at specific T x(external RH - internal RH)

microcells placed in the PEC cells. There were three replicate cells for each treatment condition.

The cells were removed at intervals from the controlled atmosphere and immediately placed in a spectrophotometer, where the change in absorbance at 690 ηm of the detector film was monitored through the apertures in the cell. Sampling and reading were done one treatment at a time to avoid delay and subsequent condensation.

3.5 RESULTS AND DISCUSSION

3.5.1 WVTR and Permeance

The raw data of the change in absorbance of the detector films over time are given in Appendices 3.1 to 3.9.

Regression equations were determined to calculate the slope of the curve which is equivalent to the change of absorbance over time ($\Delta a/t$). This value is required in the calculation of the WVTR. Only the linear portion of the curves was considered in determining the regression equations, i.e. data at t=0 was omitted when a lag was observed; for the samples at the high RHs and temperature, the readings were stopped once the formation of cloudy streaks in the detector film was observed. A steady-state condition can be assumed to exist during the linear portion of the curve and Δp can be taken to be constant during this period. The $\Delta a/t$ results are given in Table 3.2.

The WVTR values were calculated using equation 3-3 and a value for Q calculated from equation 3-6. The WVTR data were plotted against the difference in partial pressure between the two sides of the wall formed by the film (Δp).

Table 3.2. Change of absorbance of the detector film as a function of time (hr^{-1}).

Film	Temperature (^{o}C)	Saturated Salt Solution NaBr	NaCl	KNO_3
LDPE	20	.006	.008	.012
	30	.011	.017	.025
	40	.019	.035	.052
PET	20	.052	.084	.117
	30	.094	.160	.218
	40	.147	.270	.348
Laminate	20	.008	.013	.018
	30	.015	.025	.036
	40	.029	.052	.071

As can be seen in Figures 3.2 to 3.4 and Table3.3, it was observed that WVTR was a linear function of Δp. Good correlations were obtained for all the regression equations. LDPE and PET are nonpolar, hydrophobic films, i.e. the water vapour does not interact with the polymer. Thus, the classic laws of diffusion (eqns 3-1 and 3-2) are expected to apply, with an increase in the driving force (Δp) resulting in a linear increase in the transmission rates. Similar trends were reported by Karel et al.(1959) and de Leiris (1986) for these two films.

The regression lines for each temperature are nearly parallel to each other for all three films. This parallel relationship was reported by de Leiris (1986) for PET. At a constant Δp, WVTR increased with temperature for LDPE and the laminate. The opposite trend was observed for PET.

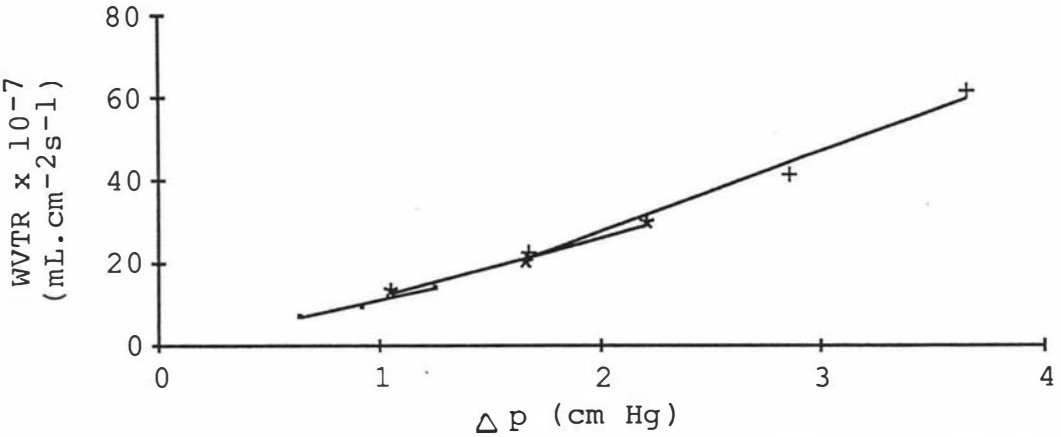


Fig. 3.2. Relationship between WVTR and vapour pressure difference (Δp) for LDPE at 20°C (·), 30°C (*) and 40°C (+).

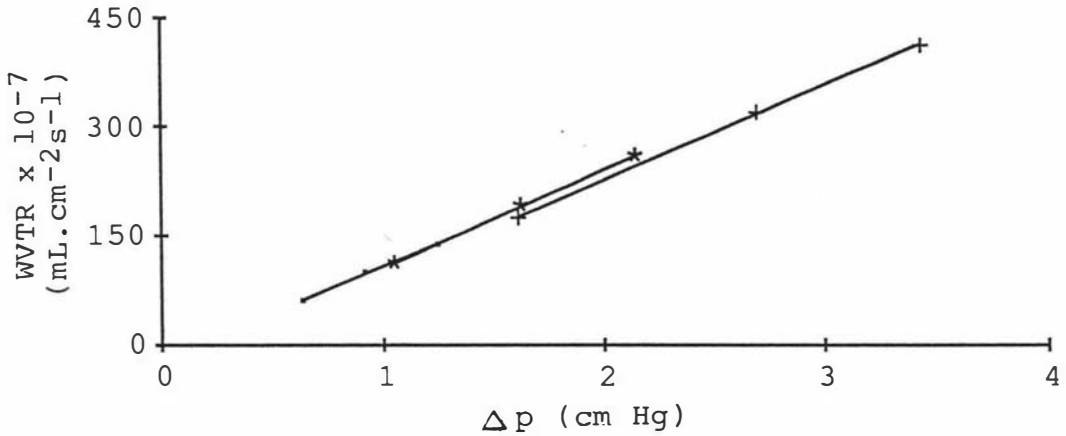


Fig. 3.3. Relationship between WVTR and Δp for PET at 20°C (·), 30°C (*) and 40°C (+).

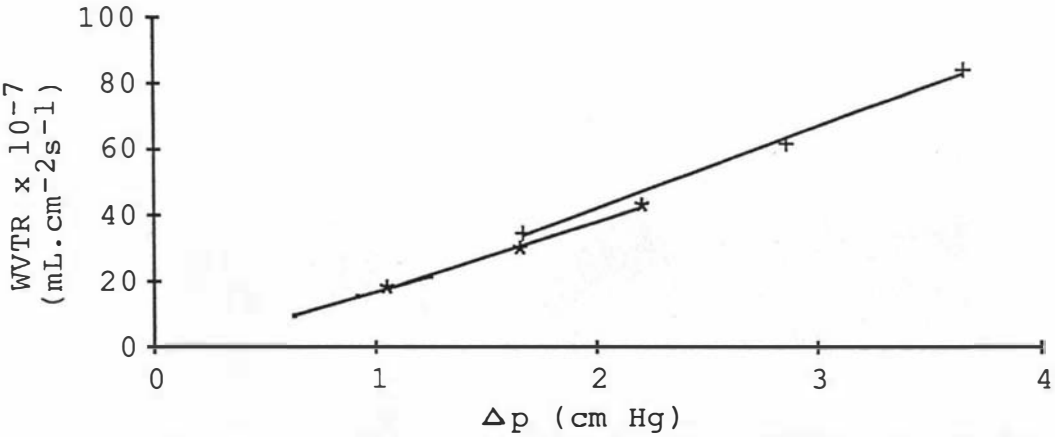


Fig. 3.4. Relationship between WVTR and Δp for the laminate film at 20°C (·), 30°C (*), and 40°C (+).

Table 3.3. Results of the regression equations for WVTR ($mL.cm^{-2}.s^{-1}$) as a function of the difference in vapour pressure Δp (cm Hg).[1]

Film	Temp. (^oC)	Coefficients a ($\times 10^{-6}$)	b ($\times 10^{-6}$)	R^2 (%)
LDPE	20	-0.05	1.15	97.9
	30	-0.25	1.43	98.8
	40	-1.10	1.94	98.3
PET	20	-1.58	12.32	99.9
	30	-2.99	13.43	100.0
	40	-3.65	13.09	100.0
Laminate	20	-0.24	1.90	99.8
	30	-0.52	2.14	99.7
	40	-0.79	2.48	99.4

[1] $WVTR = a + b\Delta p$

Rearranging equations 3-2 and 3-3 give the following equation for WVTR:

$$WVTR = \frac{P\ \Delta p}{X} = \frac{D\ S\ \Delta p}{X} \qquad (3\text{-}7)$$

The results indicate that for LDPE, P increases with temperature at a constant Δp while for PET, P decreases with temperature at a constant Δp. P is a product of D and S which are properties specific to a polymer/permeant combination which could be the reason for the difference in trends for LDPE and PET.

To attain the same difference in vapour pressure (Δp) at different temperatures, the difference in RH (external RH

minus internal RH) must be reduced at higher temperatures. Karel (1975a) and de Leiris (1986) showed that it is not only the vapour pressure difference that affects P but also water vapour concentration itself. Higher water vapour concentrations may plasticise the polymer, resulting in higher P values. However, for hydrophobic films such as LDPE and PET, the plasticisation effect would not be expected to be significant when compared to the effect of Δp (which is a function of temperature) on permeability.

The WVTR values for PET were much higher than those for LDPE under the same humidity and temperature conditions. LDPE is a good water vapour barrier. As expected, the WVTR values for the laminate film are lower than those for polyester because of the polyethylene layer in the laminate (30 um).

The WVTR of the laminate may also be calculated using the equation:

$$\frac{1}{WVTR_L} = \frac{1}{WVTR_1} + \frac{1}{WVTR_2} + \ldots\ldots + \frac{1}{WVTR_i} \qquad (8)$$

where 1,2 and i refer to each individual polymer web comprising a laminate of i layers. The WVTR for the 30 µm LDPE in the laminate was obtained by doubling the values for the 60 µm LDPE. This is based on Fick's law which states that the transmission rate is inversely proportional to thickness X.

The calculated WVTR values for the laminate were around 10% higher than the actual values obtained (Table 3.4). These differences may be due to an effect from surfaces and interfaces or a deviation from Ficks'law. According to Pascat (1986) permeability is proportional to X^{-n}, where n = 0.8 to 1.2.

Table 3.4. WVTR at constant external RH ($mL.cm^{-2}.s^{-1}$) ($\times 10^{-6}$).

Film	Temperature (^{o}C)	External RH (%) 55	75	90
LDPE	20	0.59	1.00	1.30
	30	1.20	2.11	2.79
	40	2.32	4.46	6.07
PET	20	5.33	9.65	12.90
	30	10.69	18.81	24.79
	40	18.80	31.84	41.97
Laminate				
Experimental Results				
	20	0.82	1.49	1.99
	30	1.66	3.03	4.05
	40	3.61	6.36	8.42
Calculated Results[1]				
	20	0.97	1.65	2.16
	30	1.96	3.45	4.56
	40	3.72	6.97	9.42

[1] WVTR calculated using equation 3-8

To show the relationship between temperature and WVTR, the ln WVTR was plotted against the reciprocal of temperature (1/T) (Figures 3.5 to 3.7). The WVTR values for constant RH conditions (55, 75, 90% RH) were calculated using the regression equations in Table 3.3 and are given in Table 3.4. A linear relationship was observed for all three films. This relationship can be described by the general equation (Table 3.5):

$$\ln WVTR = a - b(1/T) \qquad (3\text{-}9)$$

which is similar in form to the Arrhenius equation.

Table 3.5. Results of the regression equations for ln WVTR ($ml.cm^{-2}.s^{-1}$) versus the reciprocal of temperature (K^{-1}) (equation 3-9).

Film	External RH (%)	Coefficients a	b	R^2 (%)
LDPE	55	6.83	6204	100.0
	75	9.45	6823	100.0
	90	10.36	7015	100.0
PET	55	7.42	5730	99.6
	75	6.98	5426	99.5
	90	7.05	5362	99.6
Laminate	55	8.87	6714	99.9
	75	9.08	6599	100.0
	90	9.25	6564	100.0

The straight lines obtained at different external relative humidities are parallel, indicating that WVTR is not affected by the external vapour pressure concentration, i.e. WVTR response to temperature change is the same under

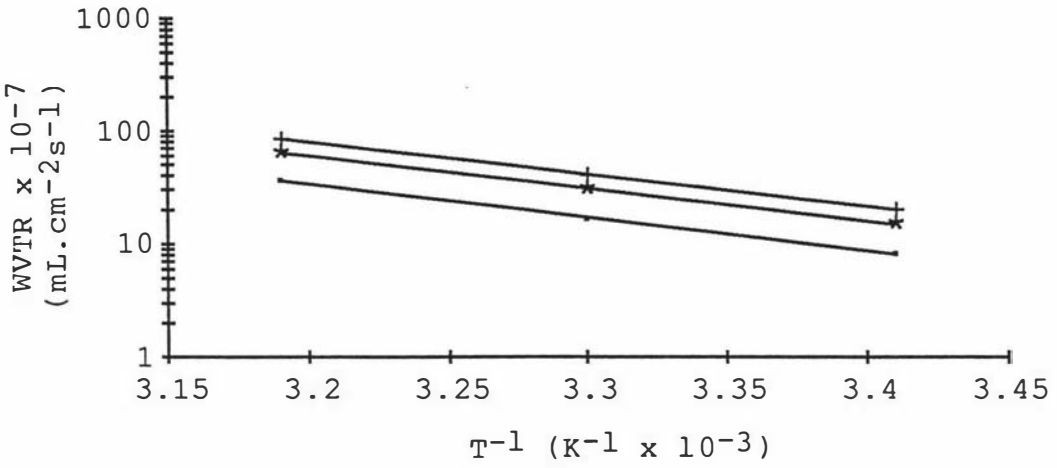


Fig. 3.5. Plot of ln WVTR against the reciprocal of temperature (T^{-1}) for LDPE film at 55% (·), 75% (*), and 90% (+) external RH.

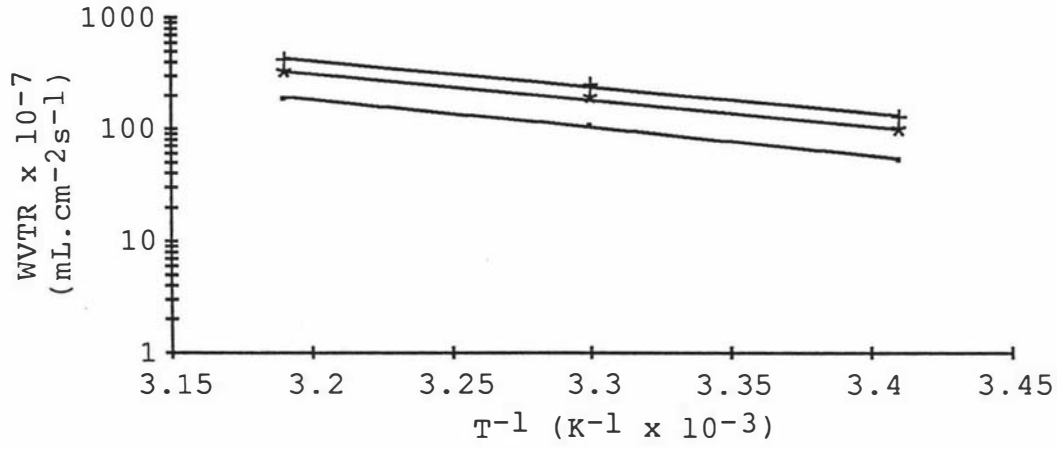


Fig. 3.6. Plot of ln WVTR against T^{-1} for PET film at 55% (·), 75% (*) and 90% (+) external RH.

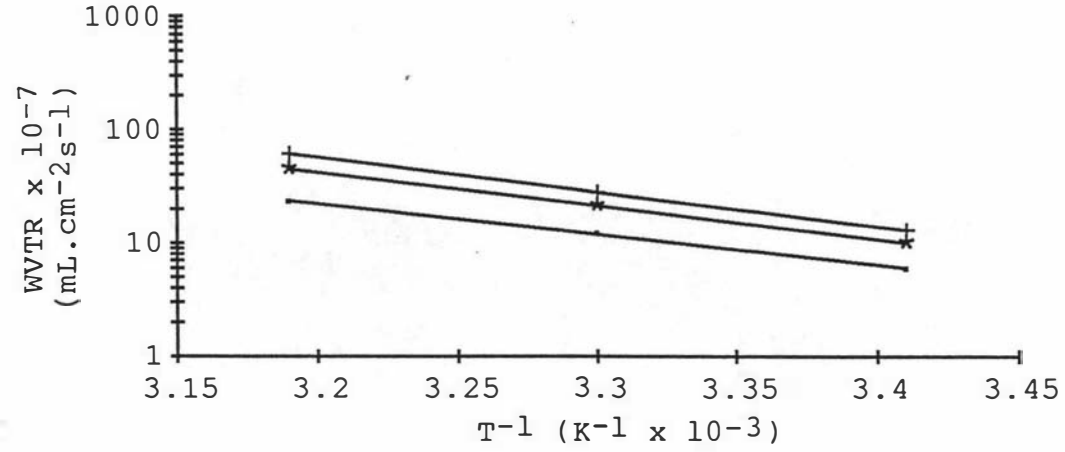


Fig. 3.7. Plot of ln WVTR against T^{-1} for laminate film at 55% (·), 75% (*) and 90% (+) external RH.

the different conditions of external relative humidity. Similar results were reported by de Leiris (1986).

Because the WVTR includes neither pressure nor concentration of permeant in its dimensions, it is necessary to know either the vapour pressure at saturation or the concentration of permeant under the conditions of the measurement in order to correlate the WVTR with the permeability coefficient P of the permeant in the polymer. Since the WVTR is not a real constant which is characteristic for a polymer, it is only used as a means of comparing barrier properties. For this reason Labuza (1981) recommended that WVTR should not be used in shelf life predictions.

The permeability constants for polyethylene and polyester were determined using equation 3-2; this equation does not hold for heterogeneous materials such as laminated films. Each web in a laminate of two or more polymers provides a different barrier to the permeation of a gas or vapour so that a permeability coefficient cannot be specified. Hence, permeance (P/X) is used to describe the permeability property of laminates or composite films with no absolute thickness. To be able to compare the three films, the permeance at the different conditions were calculated and the results are presented in Table 3.6. The permeability constants for LDPE and PET are given in Table 3.7.

The permeability constants obtained are comparable to those that have been published previously by several authors; these are summarized in Table 3.8.

In Figures 3.8 to 3.10, the permeances are plotted against the reciprocal of temperature (1/T). For ideal conditions these plots should result in straight lines with a negative slope. It is evident from the results, that this relationship was followed in general for all relative

Table 3.6. Water vapour permeance (P/X) ($mL.cm^{-2}.s^{-1}.cm\ Hg^{-1}$) (x 10^{-6}).

Film	Temperature (^{o}C)	External RH (%) 55	75	90
LDPE	20	1.06	1.09	1.10
	30	1.18	1.27	1.31
	40	1.31	1.55	1.64
PET	20	9.50	10.58	10.98
	30	10.50	11.59	11.98
	40	10.96	11.74	12.04
Laminate	20	1.47	1.63	1.69
	30	1.63	1.83	1.90
	40	2.04	2.21	2.27

Table 3.7. Water vapour permeability constants ($mL.cm.cm^{-2}.s^{-1}.cm\ Hg^{-1}$) (x 10^{-9}).

Film	Temperature (^{o}C)	External RH (%) 55	75	90
LDPE	20	6.34	6.55	6.62
	30	7.08	7.65	7.85
	40	7.87	9.31	9.82
PET	20	11.4	12.7	13.2
	30	12.6	13.9	14.4
	40	13.2	14.1	14.4

Table 3.8. Summary of published results of permeability constants.

Source	Water Vapour Permeability Constants ($mL.cm.cm^{-2}.s^{-1}.cm\ Hg^{-1}$)	
	LDPE ($\times 10^{-9}$)	PET ($\times 10^{-8}$)
Davis (1970) 25° C, 65% RH	9.41	1.29
Holland and Santangelo (1982) 25° C, 75% RH	8.09[a]	1.14[a]
Ashley (1985) 25° C, 90% RH	8.0	1.30
Rogers (1985) 25° C	9.0	1.30
Yasuda and Stannett (1985) 30° C	10.0	1.75

[a] Recalculated results due to an error in the published paper.

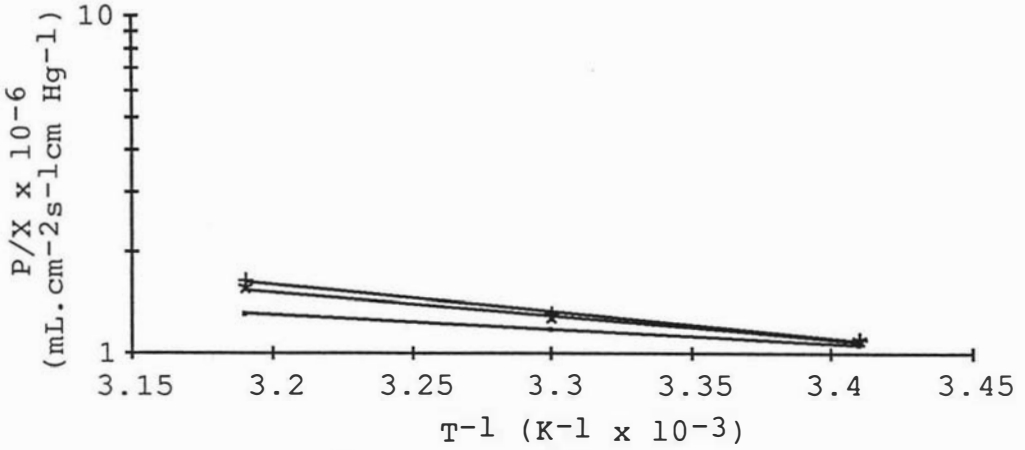


Fig. 3.8. Plot of ln P/X against T^{-1} for LDPE film at 55% (·), 75% (*) and 90% (+) externaL RH.

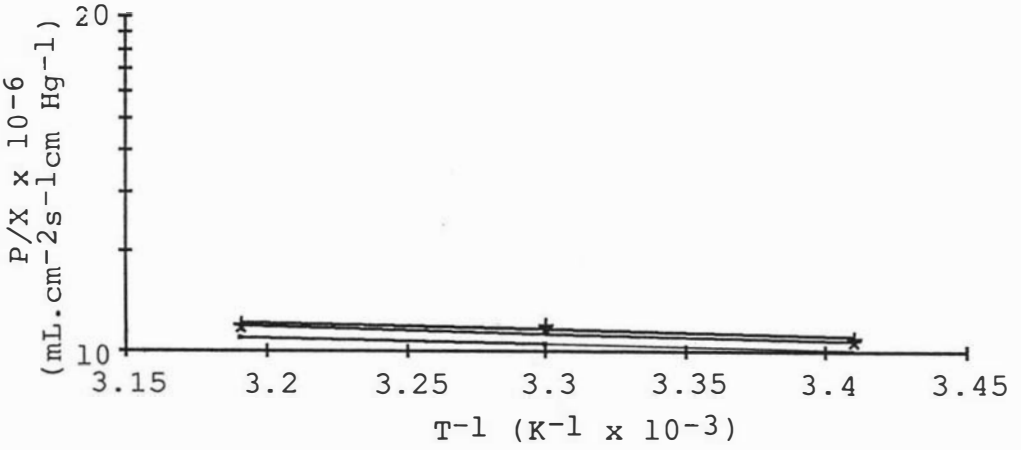


Fig. 3.9. Plot of ln P/X against T^{-1} for PET film at 55% (·), 75% (*) and 90% (+) external RH.

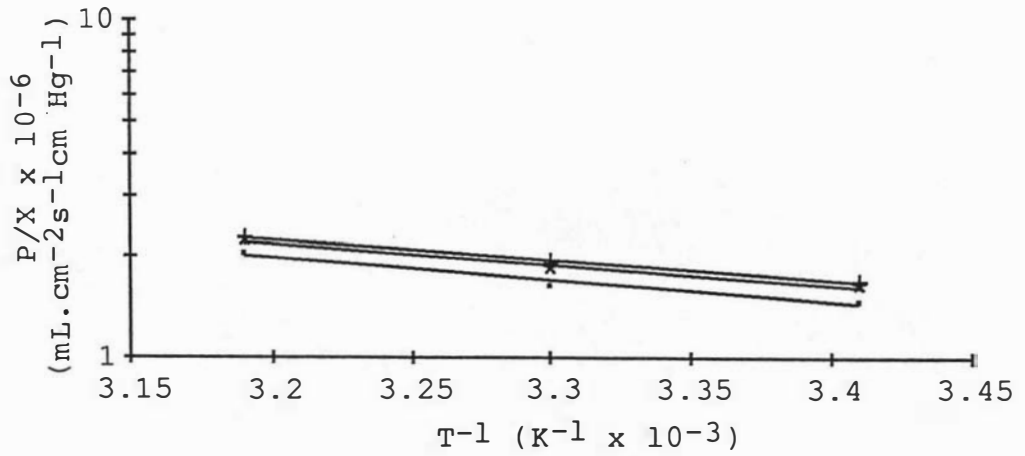


Fig. 3.10. Plot of ln P/X against T^{-1} for the laminate film at 55% (·), 75% (*) and 90% (+) external RH.

humidities and thus can be described by equation 3-5 (Table 3.9).

The activation energies for permeation (E_p) were calculated from the Arrhenius equations and are given in Table 3.9. The E_p values for LDPE increased with an increase in partial pressure difference. The opposite trend was observed for PET. The E_p for the laminate seems to be independent of Δp. Labuza and Contreras-Medellin (1981) reported that the activation energies of flexible films (including LDPE and PET) generally increased with the driving force Δp although the relationship was not very clear-cut. This led to their conclusion that if the activation energies of films had to be considered it could make shelf life predictions very complex.

Table 3.9. Results of the Arrhenius equations for permeance P/X ($mL.cm^{-2}.s^{-1}.cm\ Hg^{-1}$).

Film	External RH (%)	$\ln (P/X)_o$	E_p ($kJ.mol^{-1}$)	R^2 (%)
LDPE	55	-10.4	8.1	100.0
	75	-8.23	13.4	99.5
	90	-7.49	15.2	99.2
PET	55	-9.25	5.6	96.5
	75	-9.79	4.0	86.5
	90	-10.0	3.4	76.6
Laminate	55	-8.37	12.4	95.6
	75	-8.62	11.5	98.1
	90	-8.73	11.2	98.6

Cardosa and Labuza (1983) concluded that for polyethylene and polypropylene, the activation energy of permeation increased as the external RH decreased (internal RH was zero) over an RH range of 11 to 83% at 30, 37 and 45°C. The temperature range studied was comparatively high and a "inflexion point" was exhibited at around 45°C. At 30 and 37°C, P increased with RH; however, at 45°C the opposite trend was observed. Hence, the observed relationship between E_p and external RH. It is questionable whether the same trend would have been observed at a lower temperature range.

The activation energies that were obtained for LDPE in the present study are lower than the published results of Labuza and Contreras-Medellin (1981) of 21 to 31 $kJ.mol^{-1}$. This could be due to the difference in the systems used (liquid water in their study as opposed to water vapour in the present study). The calculated E_p values for LDPE are within the range of that found by Cardosa and Labuza (1983), of 4 to 14 $kJ.mol^{-1}$ over RH conditions of 53 to 75%; they used water vapour rather than liquid water. The E_p value for PET at 90% external RH is comparable to that reported by Yasuda and Stannett (1985) of 2.93 kJ mol^{-1}. Karel et al. (1959) also showed that the permeability constant of PET changed very little with temperature.

The permeability constant is a combination of the two functions solubility (S) and diffusion (D) as shown in equation 3-5. The diffusion constant always increases when the temperature increases. For condensable vapours such as water, S decreases with increases in temperature. The net result would depend on the relative changes of these properties as they vary with temperature. This would partly explain the complex relationship between temperature and permeability.

For the relatively hydrophobic films such as LDPE and PET, it was expected that the permeability constants would be independent of pressure. However, as can be seen from Table 3.7, the larger the Δp, the higher the P value obtained at a constant temperature indicating some dependence of the permeability constant on vapour pressure. Similar results were reported by Labuza and Contreras-Medellin (1981) who stated that this was most likely due to the effects of moisture in plasticising the film, resulting in increases in the diffusion rates. Clustering of water molecules in hydrophobic films is said to occur at high relative pressures (Yasuda and Stannett, 1962). The dependence of the permeability constant on vapour pressure does not appear significant when compared to the magnitude of the effect of Δp on the permeability constants of hydrophilic films (Karel et al., 1959).

3.5.2 Development of the Permeability Model

In order for the permeability data to be useful for the prediction of the shelf life of packaged dried food products, the dependence of the permeance of the packaging films on the environmental parameters (RH and temperature) must be described by a mathematical function.

An attempt was made to develop an empirical model relating P/X, external RH and temperature using the data obtained above.

P/X was found to follow the Arrhenius equation (eqn 3-5):

$$\frac{P}{X} = \left(\frac{P}{X}\right)_o \exp\left(\frac{-E_p}{RT}\right) \qquad (3\text{-}5)$$

The $(P/X)_o$ and E_p values obtained from equation (3-5) (given in Table 3.9) were observed to be dependent on RH. The SP123 computer program (Walonick, 1987) was used to determine the correlations of the different transformations of $(P/X)_o$ and RH, and E_p and RH for the three films. A high correlation for all three films was obtained for the functions given in Equations 3-10 and 3-11:

$$\left(\frac{P}{X}\right)_o = \alpha \exp\left(\frac{\beta}{RH}\right) \qquad (3\text{-}10)$$

$$E_p = \gamma + \frac{\delta}{RH} \qquad (3\text{-}11)$$

where α, β, γ, and δ are constants.

These two equations were tested using the linear regression analysis, and the resulting correlation coefficients were found acceptable (Tables 3.10 and 3.11).

Parameters $(P/X)_o$ and E_p were then substituted into equation 3-5, and the resulting equation tested with the BMDP AR program (Dixon, 1985):

$$\frac{P}{X} = \alpha \exp\left(\frac{\beta}{RH}\right) \cdot \exp -\left(\gamma + \frac{\delta}{RH}\right) \cdot \frac{1}{RT} \qquad (3\text{-}12)$$

The four constants for the three films were determined and the results are presented in Table 3.12. The residual values were fairly small and randomly scattered, indicating a good overall fit.

Equation 3-12 is a mathematical model expressing permeance as a function of external RH and temperature. This model can be used to predict permeance of the three types of film at different RH and temperature conditions.

Table 3.10. Results of the regression equations describing $\ln (P/X)_o$ as a function of external RH (equation 3-10).

Film	Coefficients		R^2 (%)
	$\ln \alpha$	β	
LDPE	-2.78	-417.40	99.6
PET	-11.20	106.93	99.9
Laminate	-9.30	51.02	99.9

Table 3.11. Results of the regression equations describing E_p as a function of RH (equation 3-11).

Film	Coefficient		R^2 (%)
	γ	δ	
LDPE	26.80	-1024.67	99.5
PET	-0.21	319.46	99.9
Laminate	9.25	172.30	99.5

Table 3.12. Estimates of the parameter constants of the permeability model.

Film	Parameter	Estimate	Asymptotic Standard Deviation
LDPE	α	0.090	0.094
	β	-438.630	73.756
	γ	27.525	2.662
	δ	-1061.489	186.917
PET	α	0.00002	0.00002
	β	91.494	99.080
	γ	0.341	3.552
	δ	-274.980	250.206
Laminate	α	0.0001	0.0002
	β	66.021	131.865
	γ	9.097	4.740
	δ	214.329	334.462

3.5 CONCLUSION

The WVTR and permeability constants of LDPE, PET and a laminate of both films were determined at different temperatures and humidities. The results support the following general conclusions:

a. A linear relationship exists between WVTR and vapour pressure difference for the three plastic films.

b. The Arrhenius relationship for the dependence of permeability on temperature fits the data well in the range of temperatures between 20 and 40 ^{o}C for the three films at each relative humidity condition. Permeability

measurements at two temperatures would probably be sufficient to define this relationship over a temperature range of this magnitude, given the good linear relationship.

c. A generalised relationship between the activation energy of permeation and vapour pressure difference can not be made for all three films.

d. Although the permeability constant is dependent on the difference in vapour pressure across the film with an increase in Δp resulting in a higher permeability constant, this dependence appears to be of no practical significance.

A general model describing permeance as a function of external relative humidity and temperature was developed. The model satisfactorily predicted the permeance of the three films.

CHAPTER 4
KINETICS OF DETERIORATIVE REACTIONS IN DRIED FOODS

4.1 INTRODUCTION

The quantitative approach to shelf life prediction requires that the deteriorative mechanisms limiting the shelf life of the specific food be identified and that an index of the deteriorative reactions be measured as a function of time. It is assumed that the deteriorative mechanisms and their dependence on environmental parameters (i.e water activity, temperature and oxygen pressure) can be described by a mathematical, although not necessarily analytical, function.

The objectives of this study were:

a. to determine the kinetics of quality deterioration in dried onion flakes, green beans and apricot halves
b. to develop models describing the deteriorative reactions as functions of water activity and temperature.

4.2 LITERATURE REVIEW

4.2.1 Background

Chemical kinetics is the study of rates and rates of change of chemical reactions under various conditions. Since the chemical reactions in a food system can be very complex, it is usually easier to examine a reaction from a purely mathematical or semi-empirical approach based on chemical laws rather than on a mechanistic approach in which each step must be known (Labuza and Kamman, 1983).

The loss of quality for most foods can be presented by a mathematical equation of the following form:

$$\pm \frac{\delta A}{\delta \Theta} = kA^n \qquad (4\text{-}1)$$

where:

A = the quality factor measured

Θ = time

k = a constant which depends on temperature and water activity

n = a power factor called order of the reaction which defines whether the rate is dependent on the amount of A present

$\pm \frac{\delta A}{\delta \Theta}$ = the rate of change of A with time. A negative sign is used if the deterioration is a loss of A and a positive sign is used if it is for production of an undesirable end product.

For quality changes in foods, the reaction order has generally been shown to be either 0 or 1, depending on the reaction involved (Pope, 1980; Labuza, 1982b).

When n = 0, the reaction is said to be zero-order with respect to A. This implies that the rate of loss of A is constant with time and independent of the concentration of A. Zero-order kinetics have been reported to be applicable to nonenzymic browning in dried products and lipid oxidation in snacks and dry foods. Reference?

Many foods that do not deteriorate by zero-order kinetics follow a pattern where n=1 which results in an exponential decrease in the rate of loss as quality decreases. Thus the rate of loss of quality is directly dependent on the

amount of A left. The types of deterioration that follow first-order reactions include vitamin losses and loss of protein quality in dried foods, and rancidity in dried vegetables.

As was mentioned earlier, foods generally deteriorate following a zero- or first-order reaction. However, the reaction order n can range over any fractional value from 0 to 2 for different reactions (Singh et al., 1976; Lin and Agalloco, 1979). In certain studies, reactions were best described by nonlinear equations such as polynomial equations (Smoot and Nagy, 1980).

Reviews on determining reaction order models and on statistical analysis of food deterioration data have been made by Saguy and Karel (1980), Lenz and Lund (1980), Hill and Grieger-Block (1980), Labuza and Kamman (1983), Lund (1983) and Arabhashi and Lund (1985).

4.2.2 Factors Affecting the Kinetics of Reactions

Several factors such as temperature, water activity, oxygen availability and food composition affect the kinetics of deteriorative reactions in food. In the following sections, the first three factors mentioned, which are the most relevant to dried fruits and vegetables, are discussed.

4.2.2.1 Temperature

Increases in temperature are known to accelerate deteriorative reactions in food and thus reduce product shelf life.

The most common and generally valid assumption is that temperature dependence of the rate of deterioration will follow the Arrhenius equation:

$$k = k_o \exp(-E_a/RT) \qquad (4\text{-}2)$$

where:

k = rate constant
k_o = pre-exponential constant
E_a = activation energy
R = gas constant
T = absolute temperature

The use of the Arrhenius equation was considered by Saguy and Karel (1980) to be the soundest approach to modelling temperature dependence. The Arrhenius model, unlike other possible expressions of temperature dependence, has a thermodynamic basis (Kwolek and Bookwalter, 1971: Saguy and Karel, ibid.; Labuza and Kamman, 1983).

The activation energy is generally derived from the slope of a plot of the natural logarithm of rate constant (k) versus the inverse of absolute temperature (Arrhenius plot) and depends on compositional factors such as water activity, moisture content and solids concentration. Furthermore, when the reaction mechanism changes with temperature, the activation energy may vary substantially. Thus, the Arrhenius equation has limited applicability and the range of validity and the influence of other factors on activation energy must be considered when using such a model (Tannenbaum, 1975).

Large statistical errors are commonly associated with the calculation of the temperature dependence of reactions. Arabshahi and Lund (1985), Haralampu et al. (1985) and Cohen and Saguy (1985) suggested methods of analysing

kinetic data which provide statistically more reliable final results.

The Arrhenius plot can also be used to establish shelf life plots of specific products based on a known end-point quality deterioration value (Labuza and Kamman, 1983). An Arrhenius type plot known as the shelf life plot is often used in shelf life studies. Here, instead of plotting the rate of the deteriorative reaction, the time to end of shelf life at a specific temperature is plotted.

There could be many limitation besides statistical errors in using either the Arrhenius or shelf life plots to predict shelf life at some lower temperature. Generally the problems exist because some reactions which predominate at higher temperatures do not predominate at lower temperatures (Labuza and Riboh, 1982). Some of the limitations of using the Arrhenius model have been discussed by Labuza (1984b).

4.2.2.2 Water Activity

Water, a major constituent of foods, is an important factor influencing the rates of deteriorative reactions in foods. Water content by itself is not regarded as the best parameter to express the effects of water on reaction rates; water activity is more useful:

$$a_w = \frac{p}{p_o} \qquad (4\text{-}3)$$

where:

a_w = water activity

p = partial pressure of water in the food

p_o = vapour pressure of water

Although water activity is considered to be a far better indicator of food stability than water content, it must be emphasized that a_w is only one parameter defining the reactivity of water molecules within solid food systems (Gilbert, 1986). Other factors such as oxygen concentration, pH, water mobility, and the type of solute present, can, in some instances have strong influences on the rate of degradation (Fennema, 1985; Duckworth, 1981). Nonetheless, water activity correlates sufficiently well with the rates of many degradative reactions to make it worthwhile, in many situations, to measure and use as one indicator of the condition of the water present in the food system. It must be noted, however, that only when the water component is the rate-limiting factor, which in fact is often the case, can a_w be expected to have a direct influence on the rate of the degradative reaction (van den Berg and Bruin, 1981).

A figure showing the generalized deteriorative reaction rates in foods as a function of water activity was presented by Labuza (1980) and is shown in Figure 4.1. Since all food systems possess their own special features, chemically and physically, with respect to deteriorative reactions, the information in Figure 4.1 gives only a generalised insight into the rates of deteriorative reactions as a function of a_w. Starting from a_w=1, a decrease in water activity slows down all types of chemical deterioration and microbial growth until, at a certain level, all reactions are almost completely inhibited except for chemical oxidation of lipids, which is strongly favoured by a further decrease in a_w.

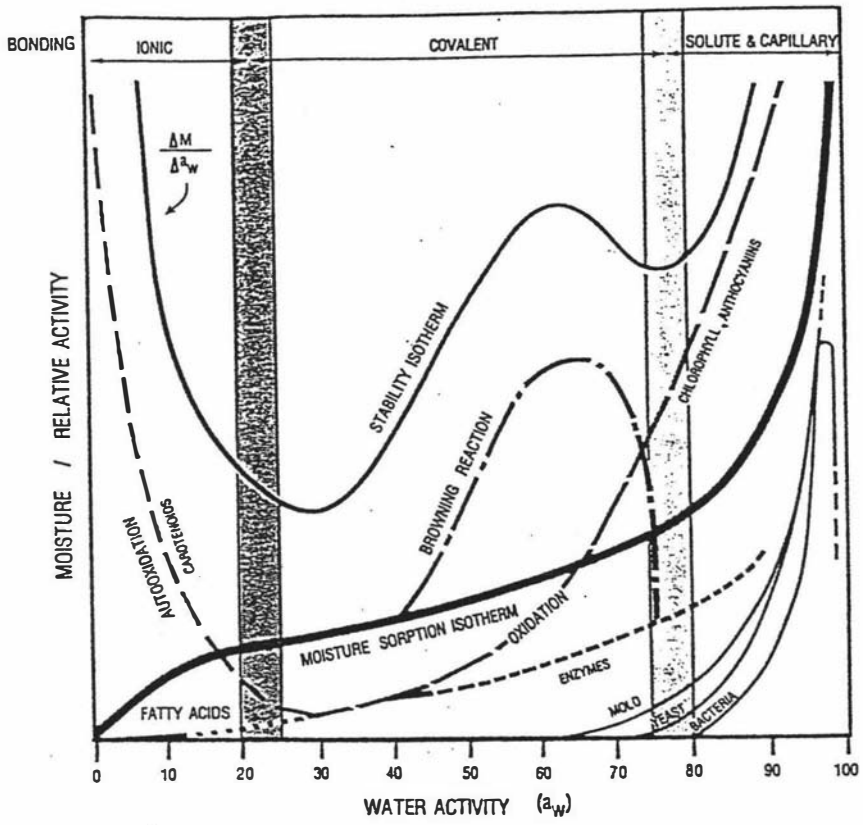


Fig. 4.1. Diagramatic representation of the influence of water activity on chemical, enzymatic, and microbiological changes.

Iglesias and Chirife (1982) summarized the main types of changes in foods affected by water activity. Studies on the influence of water activity on the rate of nonenzymic browning reactions in foods were reported by a number of workers (Labuza et al., 1970; Karel and Labuza, 1968; Eichner, 1975; Resnik and Chirife, 1979; Rockland and Nishi, 1980; Labuza and Saltmarch, 1981; Leung, 1987). The influence of water activity on pigment stability in food products was reported by von Elbe (1987).

With reference to the kinetic equations given in Section 4.2.1, Labuza (1980) discussed the effect of water activity on rate constants (k), concentration of reactant species (A) and reaction order (n).

A number of relationships have been suggested to describe the dependence of reaction rates on water activity and moisture content. Several authors who studied browning in vegetables reported an exponential relationship between the browning rate and moisture content (Legault et al., 1951; Ross, 1948). Mizrahi et al. (1970) proposed a more complicated equation correlating the browning rates for dried cabbage with moisture content.

Quast and Karel (1972) reported that oxidation in potato chips was inversely related to the square root of water activity. A linear relationship between moisture content or a_w and reaction rate has been described for nutrient retention in dry foods (Beetner et al., 1974, 1976). Several equations were suggested by different authors to describe the relationship between ascorbic acid retention and water activity (Labuza, 1972; Wanninger, 1972).

A complex functional relationship was reported between the rate of food quality deterioration and moisture content (Saguy et al., 1979a, b; 1980).

It should be noted that a deteriorative reaction in a food system is inevitably a multifactorial process of which a_w is only one factor. It is only when the water component is the rate-limiting factor that a_w can be expected to have a direct influence (van den Berg and Bruin, 1981).

One problem that is encountered when determining the effect of a_w on the rate of deteriorative reactions is that a_w itself may be affected by other factors, in particular temperature. For a dried product, a change in temperature may not only directly affect the rate of the reaction but also indirectly affect it through a change in a_w. This makes the interpretation of kinetic data much more complicated. Some studies on the prediction of shelf life

have considered a_w and temperature simultaneously in the development of models (Mizrahi et al., 1970, 1977b).

Aside from affecting modes of deterioration and their rates, water activity also affects moisture transfer through certain packaging materials (Labuza, 1982b). This will be discussed further in the next chapter. Thus, the role of water activity in shelf life prediction is of great importance particularly in dried food products sensitive to moisture gain or loss which are packaged in materials which are permeable to water vapour.

4.2.2.3 Oxygen

Many foods deteriorate due to reaction with oxygen. Some of the deteriorative reactions that are caused or accelerated by the presence of oxygen are lipid oxidation, aerobic degradation of ascorbic acid and other nutrients, nonenzymic browning, and the development of off-flavours and off-odours.

For some dried foods which are susceptible to oxidative deterioration, the influence of oxygen is of major importance particularly when dealing with flexible packaging materials which are permeable to oxygen.

The effect of oxygen is often simply a question of the total amount available for reaction with food components (Saguy and Karel, 1980). If this amount is limited to a level that causes no significant effect in the food and there is no potential for additional oxygen coming into contact with the food, then the reaction rate is irrelevant. In other cases, the total amount of oxygen potentially able to react with nutrients is, in fact, significant and the effect of oxygen concentration (or partial pressure) on the rate must be considered.

The effect of oxygen on reactions occurring in dried food products during storage is dependent on the moisture content or water activity of the product (Stadtman et al., 1946b; Legault et al., 1949). Legault et al. (ibid.) reported that the effect of oxygen on browning appeared to be confined to fruit and vegetables with moisture contents of about 13% or higher. Dutton et al. (1943) and Lajolo et al. (1971) observed that chlorophyll conversion to pheophytins in dried spinach was not significantly influenced by the presence of oxygen. The rate of browning in dried apricots was affected by the moisture content of the product, oxygen having no effect when the moisture content was 10 to 15%, but causing an increase in browning at 20-25% moisture content (Stadtman et al., ibid.). Bishov et al. (1971) found that the presence of oxygen had a deleterious effect on the flavour properties of freeze-dried foods, including green beans stored at 38°C.

4.2.3 Modes of Deterioration

The key to the application of kinetics to the prediction of quality loss is selection of the major mode of deterioration, measurement of some quality factor related to this mode, and then application of mathematical models to make the needed predictions.

A review of the studies made on the deterioration of quality in dried onion, green beans and apricots is presented in this section.

4.2.3.1 Onion

The main method of processing onions is by dehydration and it is important that the dried product has a high pungency. It is both a vegetable and a condiment, when dehydrated.

A considerable amount of work has been carried out on onion volatiles and this was summarised by Whitaker (1976). The majority of the studies conducted on onions and its products have been on isolating and determining its flavour components, and on the methods of measuring its pungency, flavour and aroma. Among these were the studies of Schwimmer and co-workers (1961, 1962, 1964) on the pyruvic acid test as an indicator of onion pungency. Few literature reports could be found on the storage stability of dried onions.

The Continental Can Company (1944) studied the effect of storage time, temperature and gas-packing on onion flakes. When packed in an atmosphere essentially free of oxygen (in cans) and stored at a temperature of 27°C or less, the onion flakes retained the greater portion of their initial flavour and vitamin C content for a period of about one year. The product deteriorated very rapidly when stored at temperatures above 27°C. They were no longer acceptable in flavour after three months at 37°C. Flavour loss was accompanied by a darkening in colour. Legault et al. (1954) also observed that the shelf life of dried onion was limited by browning and a deterioration in flavour.

In the study of Peleg et al. (1970), dried kibbled onions of the Egyptian variety (4 to 5% moisture content) were packed in different packaging materials and stored at different temperatures (15 to 35°C) at 44%RH for 39 weeks. Browning increased significantly with storage temperature and to a smaller extent with different packaging materials. Products in polyethylene deteriorated most, but the difference between Saran- and can-packed products was small. All products stored at 15°C and those in cans at 25°C were found to be of good organoleptic quality after the 39 week storage period.

Peleg et al. (1970) reported that the pyruvic acid test used by Schwimmer et al. (1961, 1962, 1964) did not correlate with the odour threshold values of the dehydrated kibbled onions. This was explained by the formation of carbonyls, other than pyruvic acid, during storage which interfered with the test.

4.2.3.2 Green Beans

Dried vegetables deteriorate primarily through lipid oxidation reactions which cause rancid or "hay-like" off-flavours; nonenzymic browning reactions which cause darkening, hardness and loss of available protein; oxidation which results in loss of vitamins such as vitamin C and thiamine; and oxidation of pigments such as chlorophyll and carotene, leading to unacceptable colours (Labuza, 1982).

Chlorophyll degradation can occur during processing and storage and depends on temperature, pH, time, enzyme action, oxygen, and light (Lajolo and Marquez, 1982). There has been a large amount of work done aimed at preserving the green colour of heat processed green vegetables (Clydesdale et al., 1970). However, although most of the processes that have been developed result in an attractive product after processing, the beneficial effects are quickly lost during storage (Tan and Francis, 1962; Luh et al., 1964; Gupte et al. 1964; Buckle and Edwards, 1970).

The most common mechanism of chlorophyll degradation seems to be its acid catalysed transformation into pheophytin which has a dull olivegreen colour, although oxidation through the conjugated cation of lipoxygenase and subsequent bleaching was observed in some foods (Buckle and Edwards, 1970). The formation of chlorophyllides during blanching has also been reported (Jones et al., 1963).

Although many studies have been made on green colour changes during processing and storage, little is known on the pigment behaviour in low and intermediate moisture systems. Chlorophyll degradation in dried foods is likely to occur either at relatively high water activity (water available for chemical reaction) or low a_w (mechanism linked to free radicals or lipid oxidation).

Several workers have observed the conversion of chlorophyll to pheophytin in dried vegetables, this conversion being related to the degree of blanching which the products had undergone before dehydration (Dutton et al., 1943; Foda et al., 1968).

Chlorophyll degradation in blanched, freeze-dried spinach puree was studied in model systems as a function of water activity, pH and temperature, and also in the presence of glycerol, a water binding agent (Lajolo et al., 1971; Lajolo and Marquez, 1982). They reported that for a_ws greater than 0.32, the most important mechanism of chlorophyll degradation was the transformation to pheophytin. At lower a_ws, the degradation rate was slower and other compounds in addition to pheophytin were formed. The reaction was found to have a first-order dependence on pH, water activity and pigment concentration. The addition of glycerol increased the rate of degradation of chlorophyll.

Kapsalis et al. (1967) studied the effect of a_w and temperature on the quality of freeze-dried peas during storage with respect to thiamin and carotene retention, chlorophyll stability, and oxygen uptake (a measure of lipid oxidation resulting in hay-like off-flavours). Chlorophyll was observed to be stable at 21.1°C at all relative humidities (0 to 50 %RH) and at 43.3°C at low a_w. However, at 43.3°C and a_ws above 0.23, progressively

greater amounts of chlorophyll were lost in 84 days of storage. The rate of oxygen uptake also increased with the a_w of the product and was greater than the rates of thiamine and carotene loss.

Bishov et al. (1971) studied the influence of oxygen on the flavour of freeze-dried foods, including green beans, at 38°C. The sensory panel detected an oxidised flavour and considered the dried green beans unacceptable after 5 months storage in 25% oxygen packs. The fresh green bean flavour was retained even after 12 months storage in "zero" oxygen headspace.

Although the studies mentioned above were conducted using spinach and other green vegetables, it is likely that the same general reactions of chlorophyll degradation would also apply to dried green beans.

4.2.3.3 Apricot

Apricot products have been observed to gradually darken during storage. This darkening has been attributed to a combination of at least two different reactions. The greatest effect is undoubtedly from the nonenzymic Maillard-type browning reaction, which occurs between amino acids and sugars and results in the production of dark-coloured compounds (Song and Chichester, 1967; Bolin and Stafford, 1974). The other reaction involves the breakdown of carotenoid pigments.

Both reactions were reported by Baurnfiend et al. (1947) to occur in canned apricots stored for a few months at 21°C. The darkening of the fruit colour eventually resulted in the product becomimg unacceptable to consumers. Consumer preference was based mainly on attractive appearance (i.e. attractive colour).

Colour is thus an important factor governing the quality of apricot products. Stadtman et al. (1946a) defined the edible shelf life as the time required for the apricot to darken to such an extent that it was no longer generally acceptable.

However, flavour changes associated with browning have also been shown to be important. For example, in a study by Dalal and Salunkhe (1964), canned apricots in 40% sugar solution stored at different temperatures (4.5 to 49°C) were analysed at weekly intervals for 16 weeks for colour and other chemical parameters. The brown colour was observed to increase with time and temperature. After 16 weeks storage, the fruits stored at 38 and 49°C were condidered to be unacceptable due to the development of a "burnt" flavour.

Salem and Hegazi (1973) observed the development of brown colour during the production and storage of sun-dried apricot juice (apricot sheets). They also reported the chemical changes occurring in the product.

Stadman et al. (1946 a,b,c) studied the many factors which influenced the rate of darkening of dried apricots during storage. They showed the importance of SO_2 level, moisture content, temperature and oxygen availability. Most of their experiments were done under carefully controlled conditions, but at high temperatures (40 to 50°C). The shelf life, which was based on the degree of darkness of dried fruit samples, was found to be inversely proportional to the initial sulfur dioxide concentration. The influence of moisture content on the rate of deterioration of apricots at moisture contents greater than 10% was dependent upon the quantity of oxygen available to the fruit. In the presence of oxygen, the rate of darkening was increased at high relative to low moisture contents by

amounts which varied with the quantity of oxygen available to the fruit. This was attributed to the increased loss of sulphur dioxide with increase in oxygen uptake. Browning was observed to follow a first-order reaction model.

Anet and Reynolds (1957) studied the chemistry of nonenzymic browning in freeze-dried apricots and Lee et al. (1979) the kinetics of the production of biologically active Maillard browned products in apricots.

In the studies which were reviewed in this section, different apricot products were used and carotene was determined using a variety of methods, as was browning. Thus, the results cannot be compared directly. However, the studies all show that the major factor leading to the unacceptability of apricots is the change in colour, reported either as carotene loss or brown pigment production on storage. No attempt was made in the above studies to determine the actual rates of change or the kinetics of quality deterioration in apricot products.

4.3 MATERIALS AND METHODS

4.3.1 Moisture Content

The moisture content of the dried products was determined using the AOAC (1985) method. Around three grams of finely cut or ground sample were spread over the bottom of a previously dried and tared metal dish provided with a tight-fitting cover. The sample in the dish was then dried for 7 hours at 70^{o}C under pressure not greater than 100 mm Hg. After drying the cover was replaced, the dish was cooled in a desiccator, and then weighed accurately.

For the dried apricot, a bent glass rod was weighed together with the metal dish. A small amount of distilled water was added to the sample and it was allowed to rehydrate for a few minutes. The sample was then mashed with the glass rod to allow a more even spread of the sample in the metal dish. The sample in the dish (plus glass rod) was dried and then weighed as above.

4.3.2 Onion

4.3.2.1 Material

The dried onion flakes were prepared commercially in the U.S.A. and generously supplied by Unilever (N.Z.) Ltd, Hastings. The onion flakes were uniform cream in colour with an initial moisture content of 4.4% (wet basis). They were unsulphited. The sample was considered to be highly pungent, based on pyruvic acid content.

4.3.2.2 Thiolsulphinate Determination

The method used for determining the amount of thiolsulphinate in dried onion was a modification of the method developed by Freeman and McBreen (1973).

Established methods of appraisal of onion flavour depend upon determination of unstable intermediates or relatively stable end-products of enzymic action on flavour precursors. These hydrolytic reactions occur when the tissues are disintegrated.

On disintegration of onion tissue, two molecules of flavour precursor (S-alkyl-L-cysteine sulphoxide) undergo hydrolysis, yielding two molecules of pyruvate and one molecule of thiolsulphinate:

$2R\text{-}S(O)\text{-}CH_2\text{-}CH(NH_2)\text{-}CO_2H$ ——————> $R\text{-}S\text{-}S(O)\text{-}R$ +
s-alkyl-L-cysteine sulphoxide
thiolsulphinate

$2CH_3\text{-}CO\text{-}CO_2H + 2NH_3$
pyruvic acid

Schwimmer and co-workers (Schwimmer and Weston, 1961; Schwimmer and Guadagni, 1962, 1968; Schwimmer et al., 1964) reported that the pyruvate formed was highly correlated (r=0.97) to the olfactory threshold of onion and thus could be used as an indicator of the pungency of fresh and dried onion products. Taste-panel pungency tests, compared with analyses for pyruvic acid, in dried onion lead to the conclusion that 25 micromoles of enzymatically produced pyruvates/g represent a highly pungent onion, while 10 micromoles/g or lower represent a mild onion. Thus, the acceptability level for dried onion flakes was set at 10 µm/g pyruvic acid or 5 µm/g thiolsulphinate. Commercial production by American dehydrators is usually in the 20 to 35 micromole range (Hart and Fischer, 1971).

However, Peleg et al. (1970) found that the pyruvic acid method could not be used as a sensitive indicator of dried onion quality during storage due to the formation of other carbonyl compounds which interfered with the test.

This problem does not apply to thiolsulphinate measurement. Freeman and McBreen (1973) reported a good correlation between thiolsulphinate and pyruvate concentration in dried onion (r=0.89) suggesting the usefulness of thiolsuphinate content as an indicator of pungency in dried onion during storage.

The method of Freeman and McBreen (ibid.) is based on the extraction of thiolsulphinate into hexane and the

measurement of the extinction of the solution at 254 ηm. The method is rapid and simple to conduct.

4.3.2.2.1 Procedure

Sample Preparation

The dried onion flakes were ground to a fine powder (20 mesh) using a domestic coffee mill immediately prior to analysis.

Extraction

A 0.50g sample of onion powder was weighed into a centrifuge tube. Twentyfive mL of distilled water was added and the powder reconstituted for 5 min. The mixture was then centrifuged for 5 min at 2600 rpm. Five mL of the clear supernatant was measured into a 100 mL Erlenmeyer flask. Thiolsulphinate was extracted by adding 10 mL hexane and swirling the mixture gently. The hexane layer was separated by passing the mixture through Whatman phase separation paper (No.1PS). The aqueous layer was returned back to the flask and the remaining thiolsulphinate was extracted with 5 mL hexane. The first and second extracts were combined and the absorbance of the solution was determined immediately at 254 ηm.

4.3.2.2.2 Calculation

*
The pyruvic acid contents of dried onion samples were determined and correlated with the amount of thiolsulphinate based on the relationship:

2 mol. of pyruvate = 1 mol. of thiolsuphinate

---

* A standard curve was prepared with varying concentrations of pyruvate.

The molar absorptivity of thiolsulphinate solution at 254 ηm was determined and was found to be:

$\varepsilon = A/bc = 0.014$ g/μmole.cm

where A = absorbance
b = path length (cm)
c = concentration of the solution (μmole/g)

From this the thiolsulphinate content of the hexane solution was determined using the equation:

$c = A/\varepsilon b = A/0.014 \times 1cm$

4.3.2.2.3 Reliability of the Method

The reliability of the method was determined and the results are presented in Table 4.1.

Table 4.1. Thiolsulphinate content of dried onion.

Sample No.	Thiolsulphinate Content (μm/g)
1	11.21
2	11.07
3	10.86
4	11.00
5	11.07
6	11.28
X ± sd	11.08 ± 0.15
% precision	1.35%

4.3.2.3 Browning Measurement

The measurement of the optical index is primarily a measure of the nonenzymic browning that may occur during processing and storage. It is an official method of the American Dehydrated Onion and Garlic Association (ADOGA, 1976).

The maximum optical index established by ADOGA for white onion (fancy powdered onion and granulated onion/onion piece sizes) is 105.

4.3.2.3.1 Procedure

A 2.00 g sample of onion powder was weighed into a beaker and mixed with 0.5 g of filter-aid (Celite). One hundred mL of 10% NaCl solution was then added to the dry sample, first adding 5 to 10 mL and stirring to form a slurry, then adding the remainder of the NaCl solution. The mixture was allowed to stand for 15 min with occasional stirring. It was then filtered through Whatman No.50 filter paper (glazed filter paper). The set-up was not moved and the rehydrated onion and filter-aid was allowed to settle in the bottom of the filter paper. This helped in the filtration process. The clear filtrate was collected separately after 25 min of filtration. The absorbance of the filtrate was determined at 420 ηm. The spectrophotometer was standardised with filtered 10% NaCl solution.

4.3.2.3.2 Calculation

The absorbance was calculated on the basis of a 1% solution, 420 ηm wavelength and 5 cm cell length:

$$\text{optical index} = \frac{\text{absorbance} \times 5 \times 1000}{1 \text{ cm cell path} \times \text{sample weight (g)}}$$

4.3.2.3.2 Reliability of the Method

The reliability of the above method was determined and the results are presented in Table 4.2.

Table 4.2. Optical Index of dried onion.[1]

Sample No.	Optical Index
1	61.88
2	62.50
3	64.04
4	66.50
5	64.36
6	67.16
X ± sd	64.41 ± 2.10
% precision	3.26%

[1] The possible time dependence of the optical index was not explored further.

4.3.3 Green Beans

4.3.3.1 Material

The dried sliced green beans were produced commercially and supplied by Unilever (N.Z.) Ltd, Hastings. The green beans had an attractive green colour with an initial moisture content of 3.7% (wet basis). The samples used for the reliability test had a mean sulphur dioxide content of 824.9 while those that were used in the storage tests had a mean SO_2 content of 463.6 mg/kg.

4.3.3.2 Chlorophyll Content Determination

A spectrophotometric method was used to determine quantitatively chorophylls a and b and total chlorophyll based on the equations developed by Vernon (1960). The method makes use of specific absorptivities and changes in specific absorptivity for the different components at appropriate wavelengths in 80% acetone.

The method was used by Lajolo et al.(1971) and Lajolo and Marquez (1982) in their studies on dried spinach puree.

The dried green beans was considered unacceptable when more than 30% loss of chlorophyll a was observed based on sensory tests and the report of Lajolo et al. (1971).

4.3.3.2.1 Procedure

Sample Preparation

The dried sliced green beans were ground to a fine powder (20 mesh) using a domestic coffee mill.

Pigment Extraction

A 1.50g green bean sample was weighed and rehydrated with 10 mL H_2O and 0.1g $MgCO_3$ for 10 min in an MSE flask. Forty mL of 100% acetone (to make the actual concentration 80%) was added and the mixture blended for 5 min using an MSE blender. It was then filtered under vacuum through Whatman No.1 filter paper. The residue was blended again with 40 mL of 80% acetone for another 5 min and filtered. Twenty mL 80% acetone was added to the residue and blended for 2 min and then filtered. The filtrate was transferred into a 100 mL volumetric flask and made up to volume with 80% acetone.

The whole procedure was conducted under subdued lighting conditions.

Determination

From this solution, a control and a converted sample were obtained for spectrophotometric measurements. The control was prepared by adding 0.3 mL of 80% acetone to 9.7 mL of the filtered extract. The conversion sample was prepared by adding 0.3 mL of saturated oxalic acid in 80% acetone to 9.7 mL of the same filtered extract. Both were stoppered and kept in the dark at room temperature for 3 hours, after which the absorbance of both samples was determined at 645, 655, 662, 666, and 700 ηm.

4.3.3.2.2 Calculations

The chlorophyll concentrations were calculated using the following equations:

Eqn 1:

chph a present (mg/L) = 25.38 (A662) + 3.64 (A645)

total chph a with no conversion (mg/L) = 20.65 (A666) - 6.02 (A655)

Eqn 2:

chph b present (mg/L) = 30.38 (A645) - 6.58 (A662)

total chph b with no conversion (mg/L) = 32.74 (A655) - 13.75 (A666)

Eqn 3:

chph present (mg/L) = 18.80 (A662) + 34.02 (A645)

total chph with no
conversion (mg/L) = 6.90 (A666) + 26.72 (A655)

4.3.3.2.3 Reliability of the Method

The reliability of the above method was determined and the results are presented in Table 4.3.

Table 4.3. Chlorophyll content of dried greenbeans.

Sample No.	Chlorophyll Content (mg/kg)		
	a	b	total
1	422.67	160.67	584.00
2	425.33	161.33	586.00
3	422.00	157.33	579.33
4	424.00	161.33	586.00
5	423.33	162.00	585.00
6	417.33	156.67	574.67
7	422.00	157.33	579.33
X ± sd	422.38±2.52	159.52±2.30	582.05±4.34
% precision	0.60	1.44	0.74

4.3.3.3 Sulphur Dioxide Determination

The method used was a modification of the procedures developed by Paul (1954), Burroughs and Sparks (1963) and Tanner (1963). The sample is acidified with phosphoric acid and is subjected at room temperature to a stream of air. The SO_2 stripped off is then oxidised in a hydrogen peroxide solution. The H^+ formed is titrated with dilute

standard alkali. The reaction gives a net gain of $2H^+$ for each SO_2 stripped out of the gas:

$$SO_2 + H_2O_2 \longrightarrow SO_3 + H_2O$$

$$H_2O + SO_3 \longrightarrow 2H^+ + SO_4^{-2}$$

4.3.3.3.1 Procedure

Determination of Free SO_2

The apparatus that was used is shown in Figure 4.2.

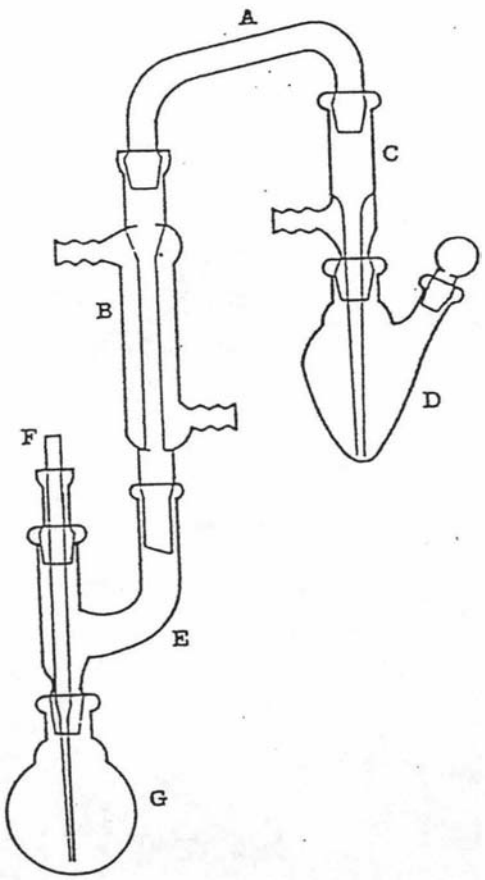


Fig. 4.2. Semimicro apparatus for SO_2 determination by aeration-oxidation : A, connecting adapter; B, condenser; C, vacuum adapter; D, 50-mL pear-shaped flask; E, Claissen adapter; F, Pasteur pipet sealed with 'o' ring; G, 50-mL round-bottom flask.

Ten mL of 0.3% hydrogen peroxide was pipetted into the 50-mL pear shaped flask (D). Three drops of methyl red indicator was added to turn the solution to yellow. The vacuum line was connected to adapter C. Three grams of green bean sample was weighed into a round-bottom flask (G) and rehydrated with 15 mL H_2O for 10 min to form a puree. Ten mL of 25% phosphoric acid (by volume) was then added to the sample. The flow of the water in the condenser (B) was started to restrain volatile organic acids from distilling over. The vacuum was turned on and air was drawn through the system for 10 min. The flask (D) was then removed and the acid formed was titrated with the 0.01 N sodium hydroxide back to the yellow endpoint.

Determination of Bound SO_2

The procedure given above was followed, but the sample in the flask was heated to a gentle boil and aspirated for another 10 min before titrating with 0.01 N sodium hydroxide.

4.3.3.3.2 Calculation

$$\text{Sulphur Dioxide content (mg/kg)} = \frac{N \times V \times 32 \times 1000}{Q}$$

where:

N = normality of sodium hydroxide solution
V = volume (mL) of sodium hydroxide
Q = weight of sample in g or volume of sample in mL

Total SO_2 = Free SO_2 + Bound SO_2

4.3.3.3.3 Reliability of the Method

The reliability of the method as applied to dried green beans was determined. The results are given in Table 4.4.

Table 4.4. Sulfur dioxide content of dried green beans.

Sample No.	NaOH (mL)			Total SO_2 (mg/kg)
	Free	Bound	Total	
1	1.80	5.85	7.65	816.00
2	2.05	5.60	7.65	816.00
3	2.60	4.95	7.55	805.33
4	1.70	5.90	7.60	810.67
5	2.40	5.50	7.90	842.67
6	2.40	5.65	8.05	858.67
X ± sd			824.89 ±	20.98
% precision			2.5%	

4.3.4 Apricot

4.3.4.1 Material

The dried apricot halves were produced commercially in Alexandra, N.Z. by Charlie and Marie Harrex. The apricot sample was graded as "Choice" and was sized 32 mm to 39 mm in diameter. The initial moisture content was 25.6% (wet basis) and the mean SO_2 content was 1572 mg/kg.

4.3.4.2 Browning Measurement

Numerous methods to measure the extent of browning in dried apricots have been reported in previous studies (Nury and Brekke, 1963; Salem and Hegazi, 1973; and Bolin and Stafford, 1974; Lee et al., 1979). The methods differed in the solvents used and their concentrations, and on the spectrophotometric or colourimetric procedure.

The different spectrophotometric methods were tested for their applicability in this study. However, they were all found inadequate for one reason or another (e.g. poor clarity of the extracted solution; time consuming method). Modifications were done and the following procedure was developed which was found to result in better extraction of the brown pigments and better clarity of the final solution. The results were also found to be more reproducible.

4.3.4.2.1 Sample Preparation

The apricot was cut into small pieces using a domestic coffee mill and then rehydrated with distilled water at a ratio of 1 part apricot to two parts water by weight, for 20 minutes. The mixture was blended for three minutes to form a smooth slurry, using a high-speed MSE blender.

4.3.4.2.2 Procedure

Fifteen grams of apricot slurry was weighed into a 150 mL Erlenmeyer flask. Fifty mL of an ethanol solution, prepared by mixing 1 part 95% ethanol : 1 part H_2O, was added to the sample. The mixture was continously shaken for 60 min. It was then centrifuged at 2500 rpm for 20 min. Ten mL of 95% ethanol was added to 10 mL of the supernatant, and after mixing it was filtered through Whatman No.4 filter paper to remove the gelatinous precipitate. The filtrate was refiltered through Whatman No.42 filter paper to produce a clear solution.

The absorbance of the solution was measured at 420 ηm with a Varian Series 634 spectrophotometer.

4.3.4.2.3 Reliability of the Method

The method was used to measure the extent of browning in an initial sample of dried apricot and a sample that had been stored at 40°C for 10 days. The results are given in Table 4.5. The reliability of the method was determined based on the data obtained.

Table 4.5. Browning measurements (absorbance at 420 ηm) for dried apricot.

Sample No.	Initial Sample	Stored Sample (10 days at 40°C)
1	0.072	0.074
2	0.066	0.077
3	0.067	0.074
4	0.070	0.075
5	0.069	0.070
6	0.066	0.075
X ± sd	0.068 ± .002	0.074 ± .002
% precision	3.5%	3.1%

To determine if the absorbance readings reflected the actual amount of brown pigment formed in the apricot samples, and to confirm that efficient extraction was occurring, the absorbance of the solutions extracted from apricot samples of different browning intensities was measured.

Dried apricot was temperature abused until a very brown sample was obtained. It was cut into small pieces and made into a slurry following the procedure given in Section 4.3.4.2.1 . The same procedure was followed with an apricot sample which had no indications of browning. The two slurries were mixed in differing proportions. Extraction and spectrophotometry were conducted following the procedure given above.

The results are given in Table 4.6. The absorbance readings at 420 nm were found to be highly correlated (r=0.99) to the browning intensity (i.e. amount of brown pigment) of the samples. Thus, this spectrophotometric method could be considered suitable as a measure of the extent of nonenzymic browning in dried apricot.

Table 4.6. Browning measurements (average of two readings) of apricot samples of varying browning intensities.

Sample No.	Sample Ratio (g) (Brown : Initial)	Absorbance (420 ηm)
1	0 : 15	0.060
2	2 : 13	0.084
3	4 : 11	0.114
4	6 : 9	0.149
5	8 : 7	0.210
6	10 : 5	0.260
7	12 : 3	0.316
8	15 : 0	0.388

4.3.4.3 Sensory Evaluation

Sensory evaluation was conducted to determine the unacceptable level of browning in dried apricot.

The Quantitative Descriptive Analysis (QDA) technique (Gatchalian, 1981; Stone et al., 1974) was used to determine the relative browning intensities of a series of apricot samples by a panel of judges. Browning, of the same samples, was also measured objectively following the procedure in the preceding section. The sensory results were then correlated with the objective measurements. The absorbance reading at 420 ηm corresponding to an unacceptable level of browning, as perceived by the panelists, was determined.

4.3.4.3.1 Procedure

The dried apricot samples were cut to small, regular sized pieces and spread evenly to completely cover the bottom part of glass petri dishes. Each dish was provided with an opaque white cover.

The sensory panel consisted of 12 students and staff members from the Faculty of Technology at Massey University. The panelists were given a briefing prior to actual testing. The procedure was explained and it was emphasized that samples should be evaluated on the intensity of the brown colour or the amount/level of brown in the sample, and not on whether the colour was yellow, orange or brown. Apricot samples with extreme intensities of brownness (i.e. one very brown and one without a trace of brown colour) were shown to the panelists as references so as to minimise variation among the panelists and to encourage them to use the whole range of the linear scale. Two test trials were conducted.

Sensory evaluation was conducted following standard methods (Gatchalian, 1981). An example of the scoresheet used is given in Appendix 4.1. The unstructured scale is of specific length with anchor points at the middle and at each end of the scale. The panelist had the task of placing a vertical mark across the line at that point which best reflected the magnitude of his or her perceived intensity of browning. The marked scales were then translated into quantitative scores which were used in the statistical analyses.

4.3.4.3.2 Results

A summary of the results of the sensory evaluation is given in Appendix 4.2. The sensory scores for browning were found to be exponentially related to the absorbance readings. A high correlation (r=0.99) between the sensory scores and the natural logarithm of the absorbance readings was observed. An absorbance reading of around 0.250 at 420 ηm corresponded to the browning level that was considered unacceptable by the sensory panel. This value is comparable to the level of 0.300 at 400 ηm set by Nury et al. (1960) as a limit for the acceptability of the colour of dried apricots.

4.3.4.3 Sulphur Dioxide (SO_2) Determination

The procedure given in Section 4.3.3.3 was followed to determine the SO_2 content of the apricot samples.

4.3.4.3.1 Reliability of the Method

The method was used to determine the sulfur dioxide content of the slurry of a dried apricot sample. The results are

given in Table 4.7. The reliability of the method was determined using the data obtained.

Table 4.7. Sulphur dioxide content of dried apricot.

Sample No.	NaOH (mL)			Total SO_2 (mg/kg)
	Free	Bound	Total	
1	1.70	13.90	15.60	1439.14
2	0.80	15.30	16.10	1485.26
3	1.05	15.05	16.10	1485.26
4	0.60	15.40	16.00	1476.04
5	0.60	15.90	16.50	1522.16
6	0.55	15.80	16.35	1508.32
7	0.30	15.85	16.15	1489.87
X ± sd				1486.58 ± 26.19
% precision				1.76%

Although there was high variability with the free SO_2, the total SO_2 value had high precision. For dried apricot, much of the absorbed SO_2 is lost during drying and of that which remains, 80 to 90% is in a combined form (McBean, 1967). Thus, it was decided to measure and report sulphur dioxide content of the apricot samples as total SO_2.

4.4 EXPERIMENTAL

The dried onion flakes, sliced green beans, and apricot halves were stored in white pigmented, rigid high density polyethylene containers at controlled temperatures and relative humidities.

Photographs of the container set-up are shown in Figure 4.3. The base of the containers were filled with different saturated salt solutions to a depth of 1.5 to 2.0 cm to give different RH conditions within the sealed containers. The different salts used and their corresponding RH values at the three temperatures used are given in Table 4.8. The products were spread onto slotted plastic trays allowing a headspace of at least 3 cm for air and moisture circulation. The trays were covered with a No.16 plastic mesh screen to avoid the samples falling into the salt solution while still allowing moisture transfer to occur unimpeded. The trays were supported by plastic stands such that there was a 2 cm distance between the surface of the salt solution and the bottom of the trays. The containers were fitted with a tight cover and sealed with adhesive tape.

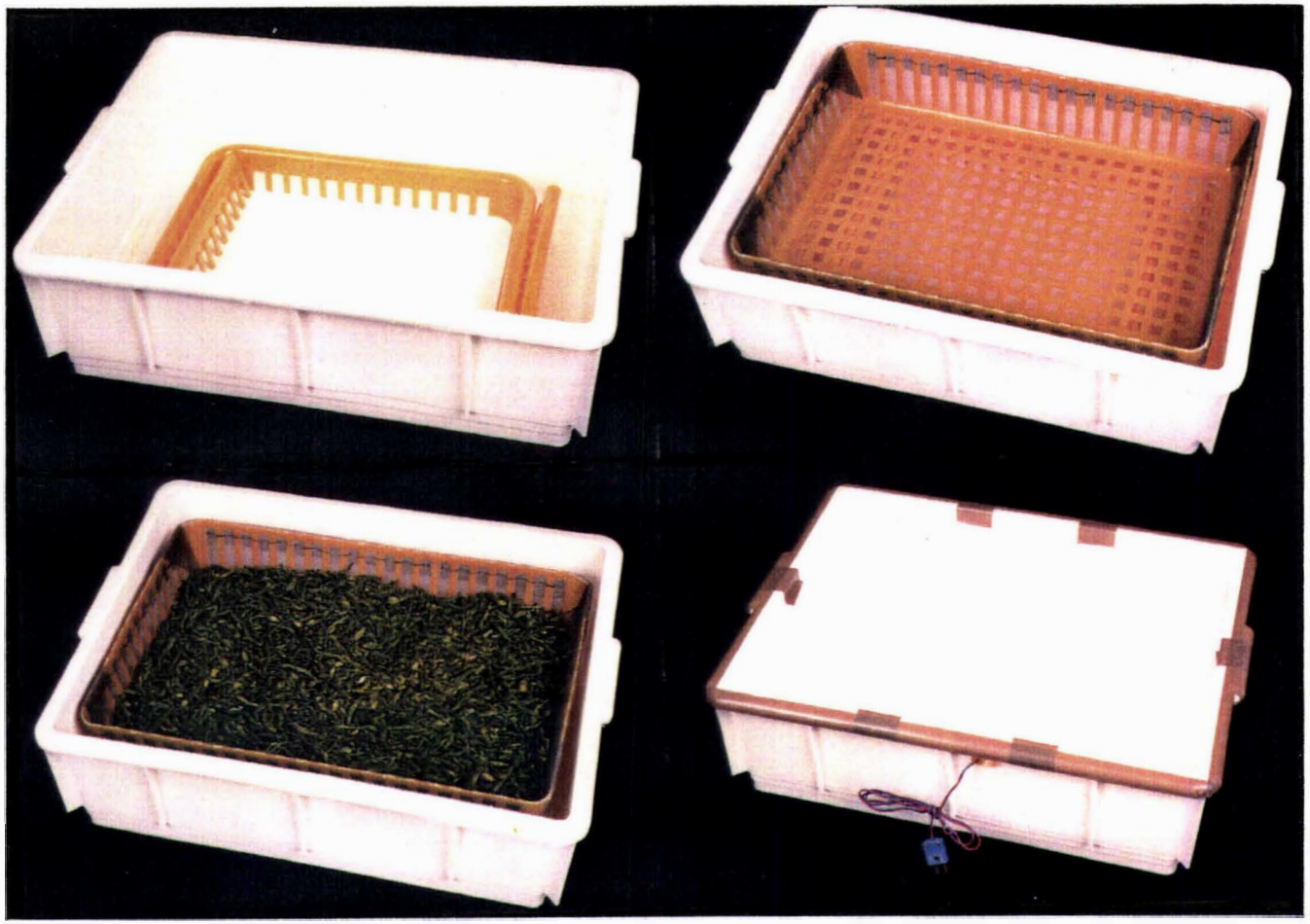
Table 4.8. The salts used in preparing the saturated salt slurries and their corresponding relative humidities (%).[1]

Salt	Temperature (°C)		
	20	30	40
Magnesium Chloride	33	32	32
Potassium Carbonate	43	43	43
Sodium Bromide	59	56	53
Potassium Iodide	70	68	66
Ammonium Sulphate	81	81	80

[1] From Greenspan (1977)

The containers were stored in their respective controlled temperature rooms (1.5 m x 2 m x 2.53 m), the temperatures used being 20 ± 0.5, 30 ± 0.5, and 40 ± 1.0°C. The

A



B

C

D

Fig. 4.3. The container set-up used in the storage trials showing: A - rigid plastic container with plastic stands, B - slotted plastic tray covered with mesh screen, C - tray with samples, and D - sealed container with thermocouple wires.

containers were fitted with thermocouple wires for monitoring the sample temperatures.

Sampling of the products was done at different time periods for the different temperatures: every four weeks at 20°C, every two weeks at 30°C, and every four days at 40°C. The sampling frequency was adjusted depending on the observed extent of quality deterioration. Duplicate samples were obtained per treatment per sampling period. Remaining samples in the container were mixed every sampling period.

The saturated salt slurries were mixed and adjusted, if necessary, for loss of water due to product adsorption every sampling period.

The samples were analysed for the quality parameters listed below, using the methods discussed above:

a. onion flakes - moisture content, browning, thiolsulphinate content
b. green beans - moisture content, SO_2 content, chlorophyll content
c. apricot halves - moisture content, SO_2 content, browning

The effect of oxygen on the kinetics of deteriorative reactions in dried onion flakes and green beans was not investigated in the present study because it was not expected to have a significant effect on the rate of reaction at the a_w range tested, based on reports of previous studies. Legault et al. (1954) did not find any advantage in nitrogen-gas packing of dried onion products as opposed to that with air. Dutton et al. (1943) noted that the presence or absence of oxygen did not influence pheophytinisation in dried spinach. Lajolo et al. (1971) came to a similar conclusion. The effect of oxygen on browning appeared to be confined to fruit and vegetables

with moisture contents of about 13% or higher (Legault, 1949).

Kinetic and Statistical Analysis

Kinetic and statistical analyses of the data were performed using the computer packages Minitab (Ryan et al., 1976) and BMDP (Dixon, 1985).

4.5 RESULTS AND DISCUSSION

4.5.1 Onion

The results of the storage trials for dried onion flakes are given in Appendix 4.3.to 4.11.

Moisture content equilibrium was generally reached by the first sampling period (Figure 4.4). The data at time zero were excluded in the kinetic calculations, when necessary, to account for the equilibration period following the recommendation of Arabshahi and Lund (1985). The average equilibrium moisture contents compared very well with the values obtained from the sorption isotherms discussed in the previous chapter, with a difference of ±0.5 (% dry basis). This further supports the assumption that equilibrium had been attained at the different RH conditions and that the onion samples could be assumed to have the corresponding water activities.

4.5.1.1 Browning

Browning, as measured by the optical index, increased with an increase in time, temperature, and water storage

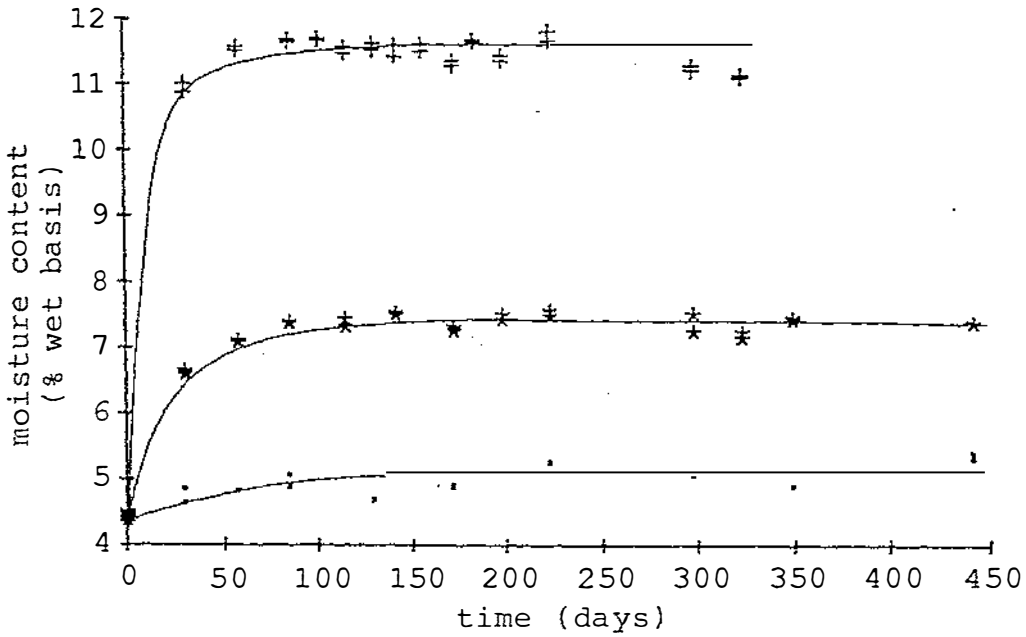


Fig. 4.4. Increase in moisture content of dried onion flakes stored at 20°C and 33%RH (·), 43%RH (*) and 59%RH (+).

activity. The colour of the onion flakes changed during storage from a uniform cream colour to golden brown and then to brown (Figure 4.5).

Zero- and first-order reaction models were fitted to the data and the results of the regression analyses are given in Tables 4.9 and 4.10. Browning fitted a zero-order model better, as evidenced by the higher R^2 values, and can be described with the equation:

$$C = C_o + kt \qquad (4\text{-}4)$$

where C = browning concentration measured as optical index
C_o = initial optical index
k = reaction rate constant ($time^{-1}$)
t = time (days)

It must be noted that this equation is a mathematical model that does not represent the actual mechanism of the

Fig. 4.5. Change in colour of dried onion flakes, packaged in LDPE film, during storage at 40°C/90%RH.

Fig. 4.6. Change in colour of dried green beans, packaged in LDPE film, during storage at 40°C/90%RH.

Table 4.9. Results of the regression analysis for browning in onion flakes based on a zero-order reaction model.

Temp. (°C)	a_w	C_o (optical index)	k (oi.day^{-1})	R^2 (%)
20	.33	62.0	.005	5.3
	.43	54.6	.093	94.5
	.59	62.0	.268	98.1
30	.32	62.5	.078	89.6
	.43	64.3	.464	96.6
	.56	65.5	1.12	99.2
40	.32	57.4	.841	95.5
	.43	27.5	3.39	98.5
	.53	6.1	6.04	98.9

Table 4.10. Results of the regression analysis for browning in onion flakes based on a first-order reaction model.

Temp. (°C)	a_w	ln C_o (optical index)	k (day^{-1}) (x 10^{-2})	R^2 (%)
20	.33	4.13	0.008	5.3
	.43	4.05	0.11	94.7
	.59	4.23	0.25	97.2
30	.32	4.15	0.10	91.2
	.43	4.19	0.51	96.0
	.56	4.22	1.04	96.5
40	.32	4.09	0.95	94.8
	.43	3.91	2.91	96.7
	.53	3.97	3.80	95.1

reaction. The plot of the optical index versus time for the different storage conditions are shown in Figures 4.7 to 4.9. The R^2 value for the regression equation at 20°C and a_w = 0.33 was very low due to the very low reaction rate (i.e. very little browning was observed over a storage period of 631 days or around 1 year and 9 months). All other samples deteriorated to an unacceptable level (optical index = 105) within this time period.

As was mentioned earlier, the equilibration period was taken into account in the calculations for the reaction rate constants. Data at time zero were excluded in the regression analyses. For the samples where equilibrium was not reached by the first sampling period (i.e. samples at 40°C) a stepwise regression was conducted to determine if the inclusion of the corresponding data would affect the reaction rate constants obtained. In most cases it was found that the reaction rate constants were not significantly affected.

The precision of the reaction rate constants is dependent on the analytical precision of the method used to measure the reactant concentration, and on the extent of reaction that has ocurred (Benson, 1960). Benson (ibid.) presented a table (reproduced here as Table 4.11) which summarised what precision in analytical capability was required to measure k to a given degree of accuracy.

The analytical precision of the method for measuring browning was ± 3.26% (refer to Table 4.2). The extent of the reaction was greater than 50% for almost all of the samples. Thus, from Benson's table, the error in calculated rate constants caused by analytical errors would be around 6%. A ±5 to 10% error is considered acceptable for complex food systems (Labuza, 1984b).

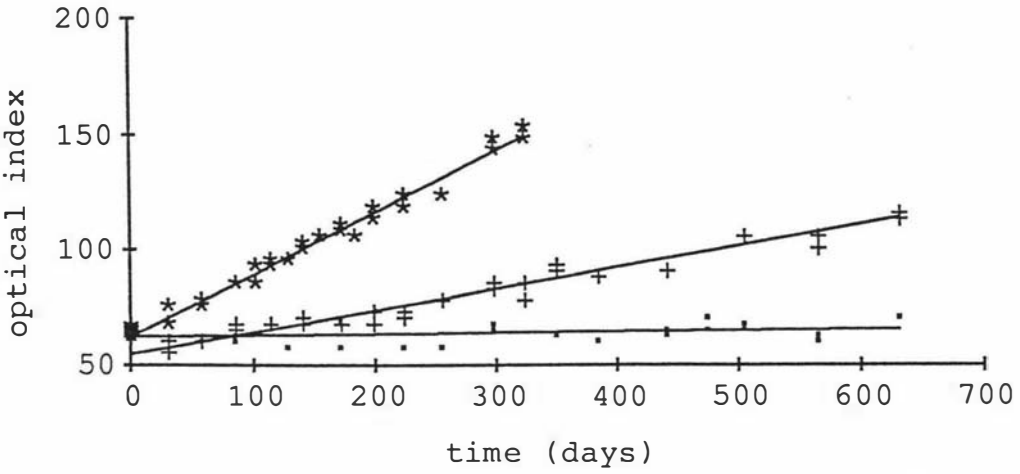


Fig. 4.7. Nonenzymic browning in onion flakes with a_w = .33 (·), .43 (+) and .59 (*) during storage at 20°C.

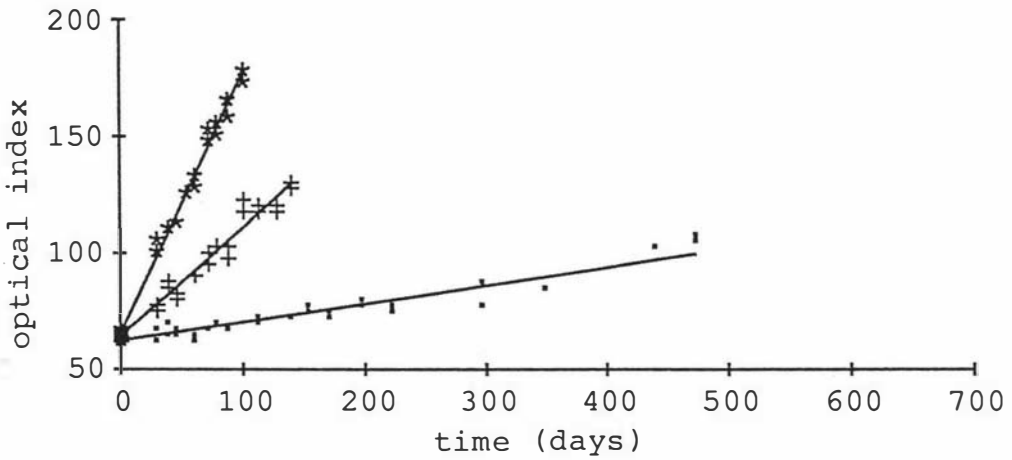


Fig. 4.8. Nonenzymic browning in onion flakes with a_w = .32 (·), .43 (+), and .56 (*) during storage at 30°C.

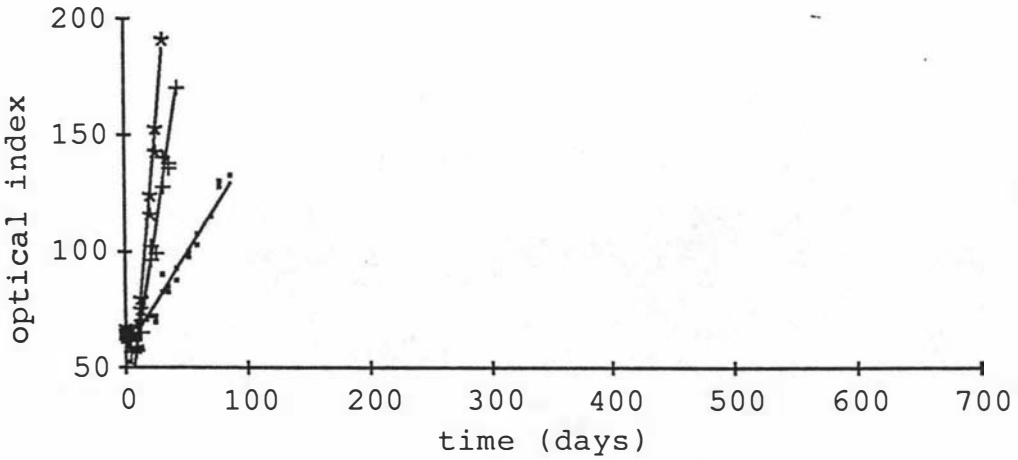


Fig. 4.9. Nonenzymic browning in onion flakes with a_w = .32 (·), .43 (+), and .53 (*) during storage at 40°C.

Table 4.11. Errors in calculated rate constants caused by analytical errors.[1,2]

Analytical Precision (%)	Percent error in reaction rate k at the following percent change in reactant species monitored:						
	1%	5%	10%	20%	30%	40%	50%
± 0.1	14	2.8	1.4	0.7	0.5	0.4	0.3
± 0.5	70	14	7	3.5	2.5	2	1.5
± 1.0	>100	28	14	7	5	4	3
± 2.0	>100	56	28	14	10	8	6

[1] From Benson (1960)

[2] Valid for a rate expression of the form

$$\frac{\delta C}{\delta t} = kC^n \quad (n = 0, 1/2, 1 \ldots, 4)$$

If higher precision of k values is desired, much higher analytical precision must be obtained, and higher degrees of conversion used (Hill and Grieger-Block, 1980).

The reaction rate constants (k) for browning increased with an increase in water activity at all three temperatures. A plot of the k values against a_w (Figure 4.10) shows that a linear relationship exists between the two. Linear equations of the form:

$$k = \alpha + \beta a_w \qquad (4\text{-}5)$$

were calculated and are given in Table 4.12. Beetner et al. (1974, 1976) reported the same relationship between k and a_w for nutrient retention in dry foods.

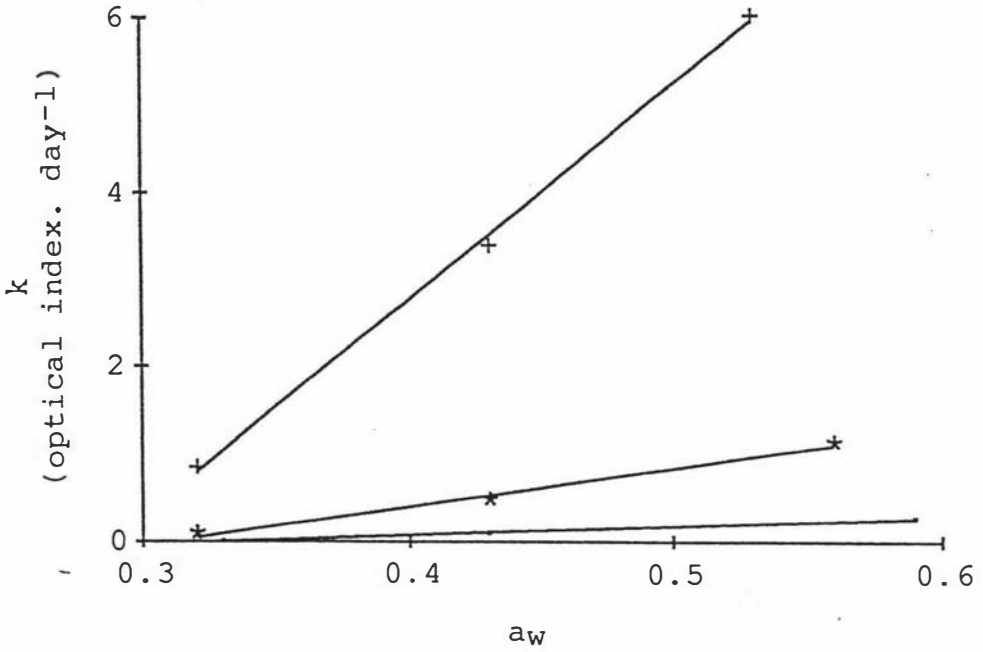


Fig. 4.10. Relationship between rate constant (k) and a_w for browning in onion flakes at 20°C (·), 30°C (*) and 40°C (+).

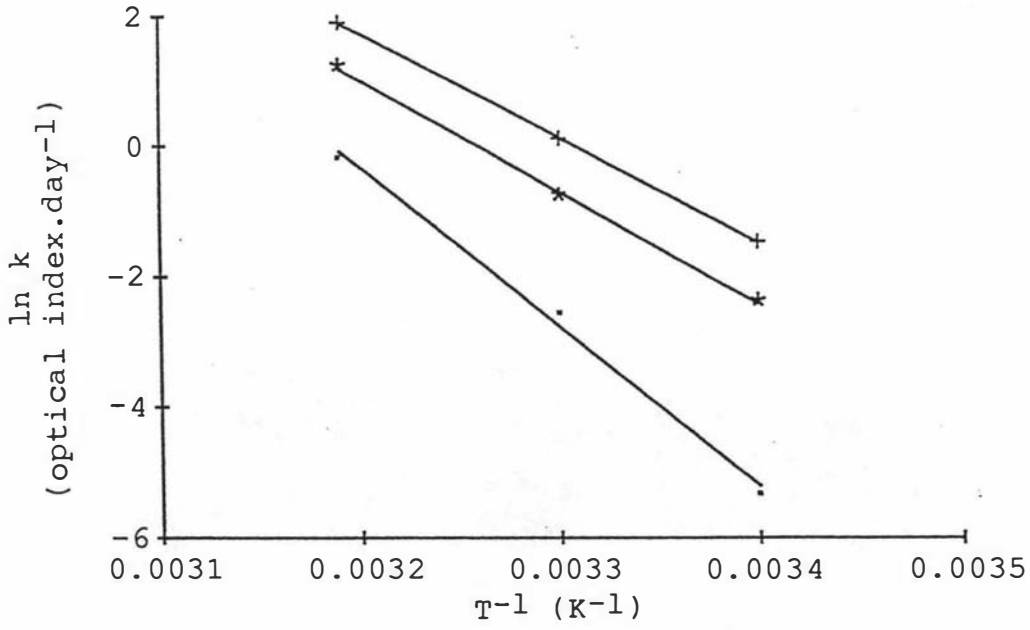


Fig. 4.11. Arrhenius relationship between k and T for browning in onion flakes with a_w = .32 (·), .43 (*) and .56 (+).

Table 4.12. Equations describing the relationship between rate constant (k) and a_w for browning in dried onion flakes.

Temp. (^oC)	Equation	R^2 (%)
20	$k = -0.34 + 1.02\ a_w$	99.7
30	$k = -1.35 + 4.36\ a_w$	99.0
40	$k = -7.13 + 24.73\ a_w$	99.9

This behaviour can be explained by the binding of water and the mobility of the reaction species. At low a_w water is tightly bound to surface polar sites by chemisorption and is generally unavailable for reaction and solution. The upper limit of this region is the monolayer value, which occurs at a_w = 0.2 to 0.3 for most foods. Above the monolayer (a_w = 0.32 to 0.43 for onion), increasing moisture contents result in faster mobility of the reaction species. This leads to a greater browning rate.

Using the equations given in Table 4.12, rate constant values were interpolated for a_w = 0.56 to be able to determine the temperature effect at constant a_w. The Arrhenius equation (eqn 4-3) was found to satisfactorily describe the relationship between reaction rate constants and temperature over the investigated temperature range (Figure 4.11).

A two-step regression method was used in determining the activation energies. In this method the first regression was used to derive the rate constant which was then regressed versus the reciprocal of the absolute temperature to obtain the estimates for Ea and k_o. When the ln k is plotted against the reciprocal of the absolute temperature

(1/T) the slope of the curve is equivalent to E_a/R where E_a is the activation energy (kJ mol^{-1}) and R is the universal gas constant (8.317 J mol^{-1}).

This method results in a high standard deviation in E_a and a large confidence interval making the activation energy statistically meaningless (Arabshahi and Lund, 1985; Haralampu et al., 1985 ; Cohen and Saguy, 1985). This is due to the low number of temperatures (i.e. degrees of freedom) and unnecessary parameters estimated. The derived wide confidence interval reduces the applicability of the model and hampers its utilisation.

To avoid the abovementioned drawbacks nonlinear regression was suggested (Haralampu et al., 1985; Cohen and Saguy, 1985). To increase the degrees of freedom, thus narrowing the confidence interval, the following procedure was derived to calculate activation energy directly from the original data in one step.

Equation 4-4 describes a zero-order model:

$$C = C_o + kt \qquad (4\text{-}4)$$

Substituting the Arrhenius model in Equation 4-4 results to:

$$C = C_o + k_o t \exp(-E_a/RT) \qquad (4\text{-}6)$$

Equation 4-6 is not easily regressed directly, since the parameters are highly collinear (interdependent). A reparametisation of the equation improves this situation (Himmelblau, 1970), and improves the convergence of the program (Arabshahi and Lund, 1985). Equation 4-6 may be rewritten:

$$C = C_o + A\, t \exp(-E_a/R\ (1/T - \lambda)) \qquad (4\text{-}7)$$

where: $A = ko \exp(-Ea/R\ \lambda)$

$\lambda = 1/N \sum 1/T$

The initial concentrations (C_o) used were obtained from the regression equations used to derive the rate constants and are given in Table 4.9.

This nonlinear regression was performed using the SHAZAM computer program (White, 1982). The results of the two methods for determining activation energy are given in Table 4.13. The nonlinear method could only be used for the samples with a_w = 0.32 and 0.43 for which actual browning data were available at constant water activity at the three temperatures.

Table 4.13. Results of the Arrhenius equations and Q_{10} values for browning in dried onion flakes. E_as were calculated using the two-step regression method and the nonlinear regression method (shown in parenthesis).

a_w	ln k_o ± 95% c.i.	E_a ± 95% c.i. ($kJ.mol^{-1}$)	R^2 (%)	Q_{10} 20-30°C	Q_{10} 30-40°C
0.32	75.5 ± 40.7 (72.9 ± 3.27)	196.90 ± 102.40 (190.43 ± 7.75)	99.9	16.0	10.8
0.43	53.8 ± 55.6 (55.7 ± 1.11)	137.06 ± 140.06 (141.85 ± 3.57)	99.4	5.0	7.3
0.56	51.0 ± 37.4	128.03 ± 94.30	99.7	4.2	5.4

The results show that using the nonlinear method greatly improved the accuracy of the E_a values by giving a more acceptable confidence interval. The activation energies

calculated by the two methods were not significantly different from each other. The confidence interval for the sample with a_w = 0.56 would be expected to be within the same range as for the two other a_ws. Thus, all subsequent calculations for E_a were done, when possible, using the nonlinear regression method.

The E_a values obtained for the different water activities (128 to 190 $kJmol^{-1}$) are comparable to those reported by other authors for browning in dried vegetables (Mizrahi et al., 1970; Hendel et al., 1955).

Another way that temperature effects on the browning reaction at various water activities can be measured is through the use of the term Q_{10}, defined as the increase in rate for every 10°C increase in temperature and related to activation energy by:

$$\ln Q_{10} = \frac{E_a}{(T)(T+10)} \qquad (4\text{-}8)$$

Legault et al. (1954) reported that the Q_{10} value for the browning reactions in dried onion was between 5 and 8. This range of Q_{10} agrees well with the values obtained in the present study (Table 4.13).

Activation energy was observed to decrease with an increase in water activity of the samples. This trend was also reported by Mizrahi et al. (1970) for nonenzymic browning in freeze dried cabbage, by Hendel et al. (1955) in dried potatoes, and by Singh et al. (1983) in intermediate moisture apples. The effect of water seems to be to decrease the temperature sensitivity of the reaction with increasing levels of water present. The mechanism by which this occurs has not been elucidated. However, since from kinetic theory the E_a is an overall measure of the limiting

E_a for each step in the reaction scheme, a lower E_a suggests that as water content increases, those previously limiting steps proceed with greater ease. This may be due to better diffusion to and from the reaction site, increased proton and electron mobility at the site, or some other factor (Labuza and Saltmarch, 1981).

An attempt was made to derive a simple empirical equation that could satisfactorily describe the relationship between E_a and a_w. The correlations of the different transformations of the two variables were determined using the SP123 computer program (Walonick, 1987). The highest correlation was obtained between the reciprocal of E_a and the reciprocal of a_w.

The equation was tested using the linear regression analysis, and the resulting equation was found acceptable (Figure 4.12):

$$E_a^{-1} = \alpha - \beta a_w^{-1} \qquad (4\text{-}9)$$

$$E_a = \frac{1}{0.0114 - 0.00194\ a_w^{-1}} \qquad R^2 = 98.6\%$$

4.5.1.2 Thiolsulphinate Loss

The quantity of thiolsulphinate, an indicator of pungency, decreased with an increase in time, temperature and water activity. A level of 5.0 µm/g correlates with an onion product with mild pungency. Thus, this level was set as the minimum amount below which the onion was considered unacceptable.

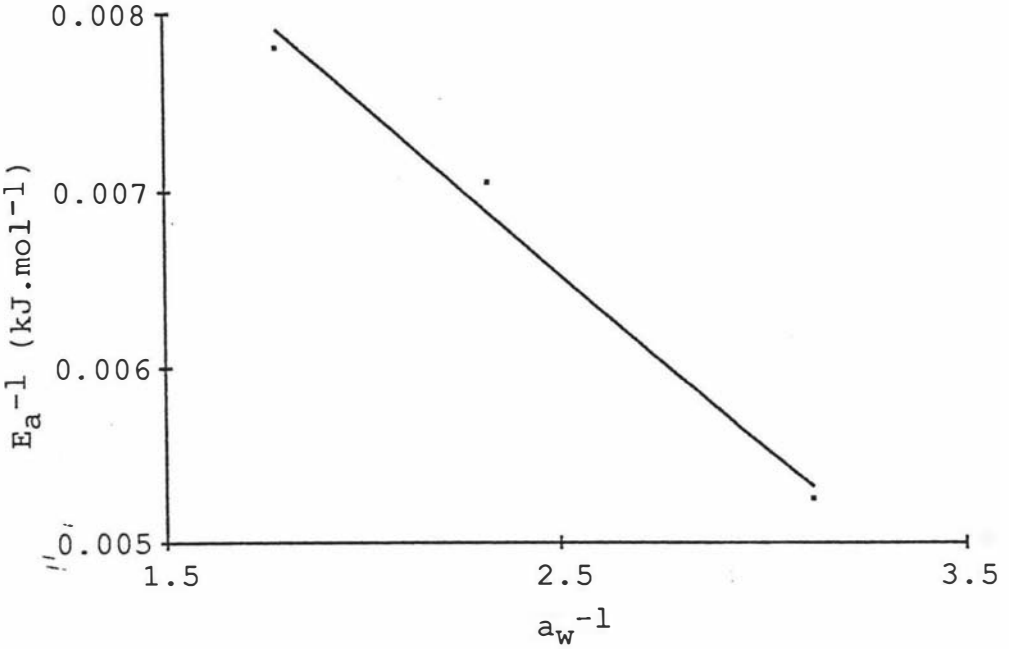


Fig. 4.12. Relationship between E_a and a_w for browning in onion flakes.

Kinetics of Thiolsulphinate loss

The results of the regression analyses for zero- and first-order models are given in Tables 4.14 and 4.15. Thiolsulphinate loss in dried onion flakes fitted a first-order model better than a zero-order model. The reaction can be expressed with the following equation:

$$C = C_o \exp(-kt) \qquad (4\text{-}10)$$

where: C = thiolsulphinate concentration (μm/g)
C_o= initial thiolsulphinate concentration

Plots of the logarithm of thiolsuphinate concentration versus time are shown in Figures 4.13 to 4.15.

Based on Table 4.11 from Benson (1960), the errors associated with the calculated rate constants would be around 3%. The precision of the k values for thiolsulphinate loss was higher than that for browning due

Table 4.14. Results of the regression analysis for thiosulphinate loss in onion flakes based on a zero-order reaction model.

Temp. (^{o}C)	a_w	C_o (μm/g)	k ($\mu m.g^{-1}.day^{-1}$) ($\times 10^{-2}$)	R^2 (%)
20	.33	12.8	0.79	90.7
	.43	11.7	1.21	89.9
	.59	10.9	2.10	94.9
30	.32	11.5	1.94	91.4
	.43	11.8	5.63	96.8
	.56	11.6	8.15	95.2
40	.32	12.0	10.2	96.5
	.43	11.9	16.9	93.9
	.53	11.6	20.7	93.2

Table 4.15. Results of the regression analysis for thiosulphinate loss in onion flakes based on a first-order reaction model.

Temp. (^{o}C)	a_w	ln C_o (μm/g)	k (day^{-1}) ($\times 10^{-3}$)	R^2 (%)
20	.33	2.56	0.74	92.7
	.43	2.50	1.50	95.1
	.59	2.48	3.02	95.0
30	.32	2.47	2.43	96.6
	.43	2.50	7.01	98.5
	.56	2.48	10.38	98.4
40	.32	2.53	13.44	98.3
	.43	2.55	23.40	96.5
	.53	2.63	36.04	98.5

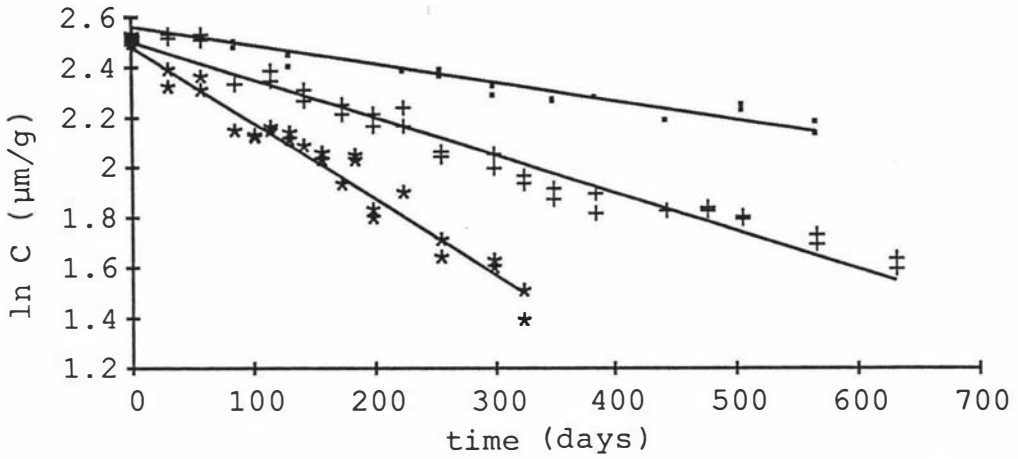


Fig. 4.13. Thiolsulphinate loss in onion flakes with a_w = .33 (·), .43 (+) and .59 (*) during storage at 20°C.

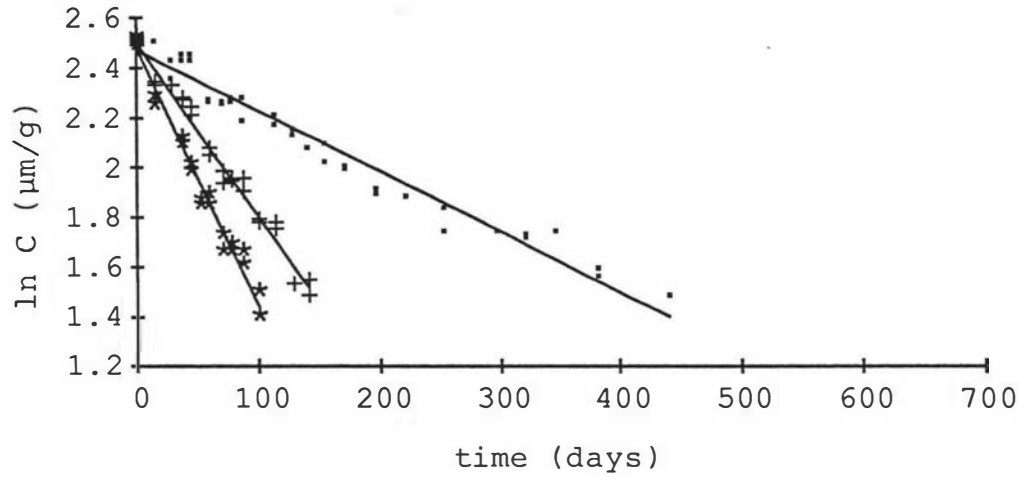


Fig. 4.14. Thiosulphinate loss in onion flakes with a_w = .32 (·), .43 (+) and .56 (*) during storage at 30°C.

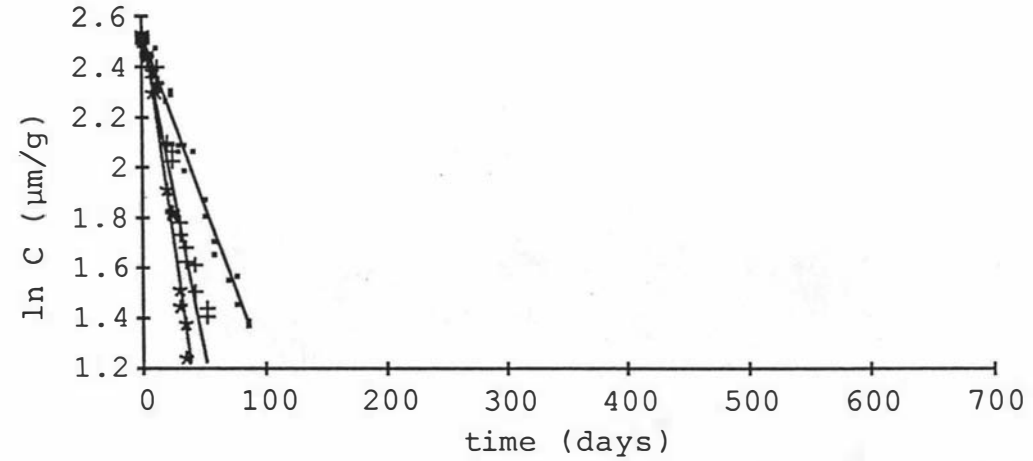


Fig. 4.15. Thiolsulphinate loss in onion flakes with a_w = .32 (·), .43 (+) and .53 (*) during storage at 40°C.

to the higher analytical precision in measuring the thiolsulphinate content (±1.35%) of the onion flakes.

A linear relationship between reaction rate constant and water activity (eqn 4-5) was also observed for thiolsulphinate loss. This relationship is shown in Figure 4.16 and the linear equations fitted to the data are given in Table 4.16.

Table 4.16. Equations describing the relationship between rate constant (k) and a_w for thiolsulphinate loss in dried onion flakes.

Temp. (^oC)	Equation	R^2 (%)
20	$k = -0.002 + 0.009\ a_w$	99.7
30	$k = -0.008 + 0.033\ a_w$	98.2
40	$k = -0.021 + 0.107\ a_w$	99.1

The Arrhenius equation was fitted to the temperature data for thiolsulphinate loss at a_w = 0.32, 0.43 and 0.56 (Figure 4.17 and Table 4.17). The E_a values obtained were 101 to 117 kJ mol^{-1} which is a typical range for flavour and enzyme reactions in food (Saguy and Karel, 1980). Activation energy was also found to decrease with an increase in water activity similar to the results for nonenzymic browning in onion flakes.

Equation 4-9 was found to be applicable to the data for thiolsulphinate loss. The following equation was obtained using linear regression analysis:

$$E_a = \frac{1}{.012 - .0010\ a_w^{-1}} \qquad R^2 = 97.7\%$$

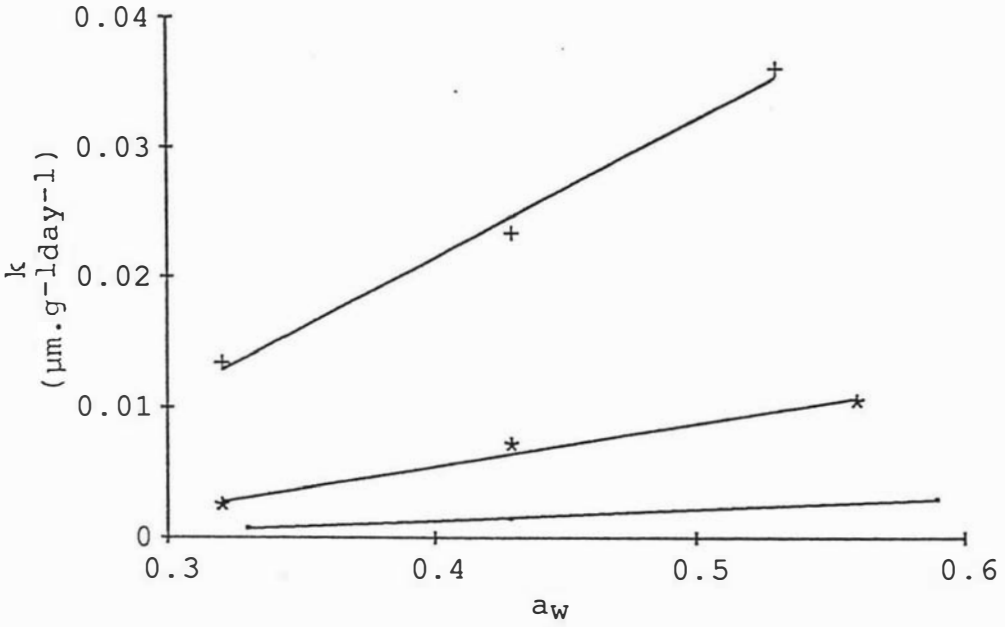


Fig. 4.16. Relationship between k and a_w for thiolsulphinate loss in onion flakes at 20°C (·), 30°C (*) and 40°C (+).

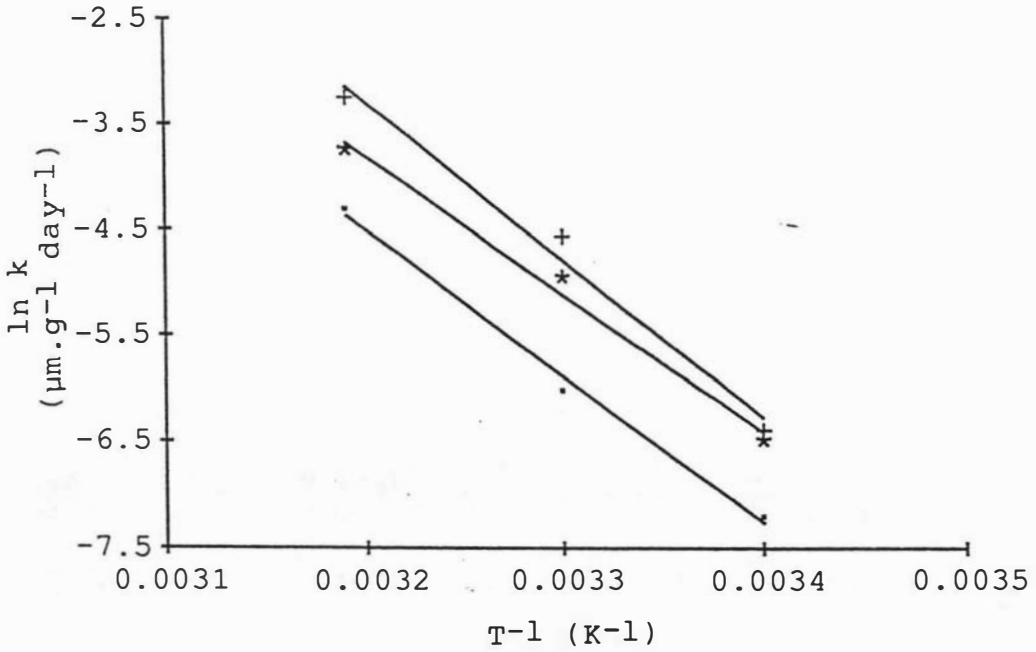


Fig. 4.17. Arrhenius relationship between k and T for thiolsulphinate loss in onion flakes with a_w = .32 (·), .43 (*) and .56 (+).

Table 4.17. Results of the Arrhenius equations and Q_{10} values for thiolsulphinate loss in dried onion flakes.

a_w	ln k_o	E_a ± 95% c.i. ($kJ.mol^{-1}$)	Q_{10} 20-30°C	Q_{10} 30-40°C
0.32	40.45	116.81 ± 5.19[a]	3.3	5.5
0.43	36.57	104.94 ± 2.98[a]	4.7	3.3
0.56	35.60	101.23 ± 17.3[b] (R^2 = 100.0)	3.4	3.5

[a] Calculated using a nonlinear regression method.
[b] Calculated using a two-step regression method.

4.5.1.3 Shelf Life of the Dried Onion Flakes

The shelf life of dried onion flakes under different storage conditions, based on nonenzymic browning and thiolsuphinate loss, is given in Table 4.18. It can be seen that the predominant deteriorative reaction determining unacceptability of the product is dependent on the water activity and temperature. This is more clearly shown in Figures 4.18 to 4.20. At a constant temperature of 20°C, below an a_w of around 0.43, thiolsulphinate loss is the predominant reaction while above this a_w, browning is the predominant reaction determining the shelf life of dried onion flakes. With a constant a_w of 0.32 , above a temperature of around 35°C, browning is the shelf life-limiting reaction, while below this temperature it is thiolsuphinate loss. This result demonstrates the importance of determining and monitoring at least two major

Table 4.18. Shelf life of dried onion flakes based on browning and thiolsulphinate loss.[1]

Temperature (°C)	a_w	Shelf life (days)	
		Browning	Thiolsulphinate
20	.33	>631	>631
	.43	505	631
	.59	172	298
30	.32	474	383
	.43	100	128
	.56	38	87
40	.32	59	70
	.43	24	42
	.53	<20	30

[1] Unacceptable levels:
Browning - $\geq$ 105 optical index
Thiolsulphinate - $\leq$ 5 µm/g

modes of deterioration in foods which exhibit more than one major deteriorative mechanism.

The higher Q_{10} values for browning also confirm that at high temperatures, browning would be the predominant deteriorative reaction. In practical terms this information would be important when comparing or determining the shelf life of products, similar to dried onion flakes, that are to be stored under tropical and temperate conditions. Using dried onion flakes as an example, under normal temperate conditions unacceptability of the product would be based on loss of pungency. However, under tropical conditions where temperatures would

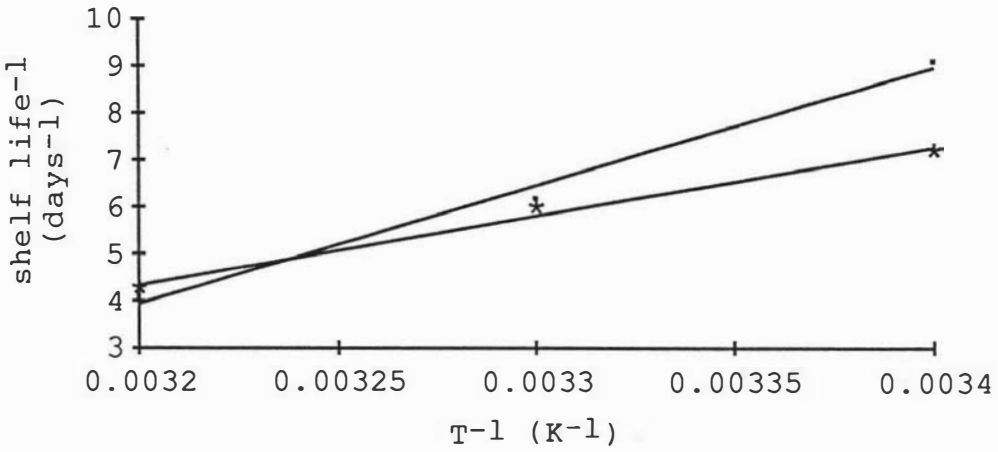


Fig. 4.18. Shelf life plots for dried onion flakes with a_w = 0.32 based on browning (·) and thiolsulphinate loss (*).

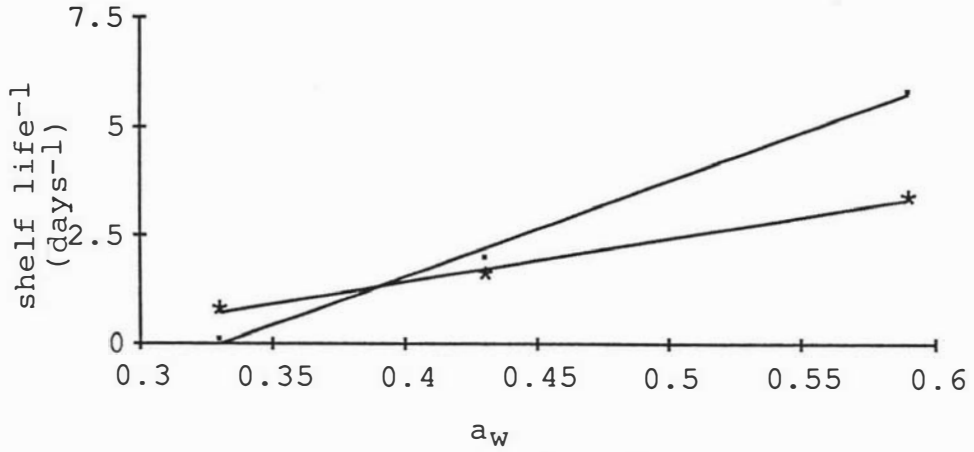


Fig. 4.19. Plot of the reciprocal of shelf life ($days^{-1}$) at 20°C based on browning (·) and thiolsulphinate loss (*).

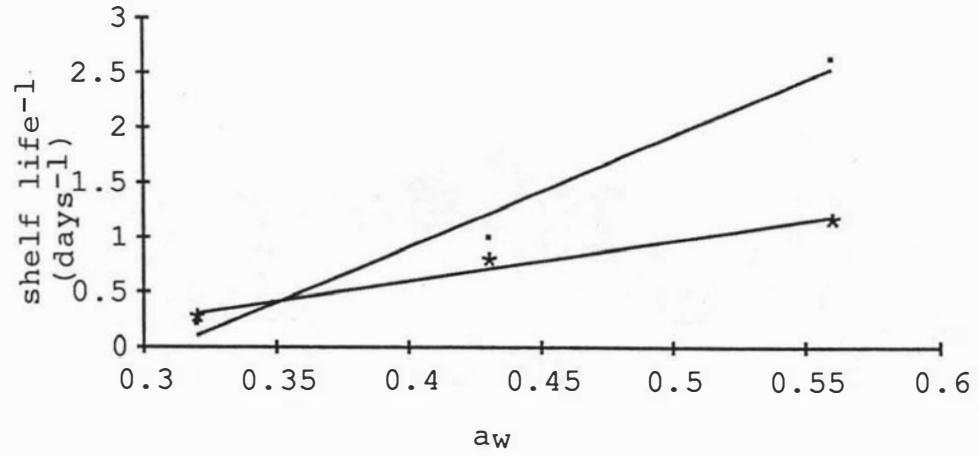


Fig. 4.20. Plot of the reciprocal of shelf life ($days^{-1}$) at 30°C based on browning (·) and thiolsulphinate loss (*).

be higher than 35°C, the browning reaction would determine unacceptability.

4.5.2 Green Beans

The results of the change in the quality parameters of dried green beans are given in Appendices 4.12 to 4.20.

Moisture content equilibrium was generally attained by the first sampling period. The equilibration period was taken into account in the kinetic calculations. The equilbrium moisture contents compared closely with those obtained from the sorption isotherms discussed in Chapter 2.

4.5.2.1 Chlorophyll Loss

The average chlorophyll contents of the initial samples of dried green beans were: chlorophyll *a* (chph *a*) = 263.6 ± 5.6 mg/kg, chlorophyll *b* (chph *b*) = 82.7 ± 2.7 mg/kg and total chlorophyll = 345.0 ± 8.3 mg/kg. The average ratio between the amount of chph *a* and chph *b* was 3.17. This supports the observation that chph *a* and chph *b* occur in plants at the ratio of about 3 to 1, respectively (Francis and Clydesdale, 1975).

The colour of the green bean samples changed during storage from green to olivegreen and then to brown, indicative of pheophytinisation (Figure 4.6). In food processing and storage, the most common change in chlorophyll is the replacement of magnesium by hydrogen in the molecule and the consequent formation of the dull, olive-brown pheophytins. Lajolo *et al*. (1971) reported that during the storage of dried spinach puree at 37°C and a_w higher than 0.32 (as is the case in the present study) the most

important mechanism of chlorophyll degradation is conversion to pheophytin.

Chlorophyll loss was found to better fit a zero-order model rather than a first-order model (Tables 4.19 to 4.24). This was more clearly observed for the samples which had undergone greater than or equal to 50% chlorophyll loss. Lajolo and Marquez (1982) reported a first-order reaction for chlorophyll loss in dried spinach puree. A poorer fit, as evidenced by the lower R^2 values, was observed for chlorophyll *b* loss. This is partly due to the lower destruction rates of chph *b* (<30% loss).

The reaction rates were determined for the different storage conditions and are given in Tables 4.19 to 4.24. Based on Table 4.11 from Benson (1960) the errors associated with the calculated rate constants would be around 3-7% depending on the extent of the reaction. The plots of chph *a* concentration versus time are shown in Figures 4.21 to 4.23.

The rate of reaction for chph *a* loss was 3.9 to 5.9 times faster (except for the samples at a_w = 0.33 and 0.43 at 20°C which were higher) than for chph *b*. This factor is comparable to that which was previously reported for acetone-water systems (Schanderl *et al.*, 1962) of 5.5 and higher than those observed by Lajolo *et al.* (1971) of 2.5 to 3 for dried spinach puree.

Since the rate of chph *a* loss was much higher than for chph *b*, and also because of the higher content of the former in dried greenbeans (3.2 times more), it is reasonable to suggest that the destruction of chph *a* is the principal factor responsible for colour loss in dried green beans. The studies of Sweeney and Martin (1961) and Lajolo and Marquez (1982) on green vegetables arrived at a similar conclusion.

Table 4.19. Results of the regression analysis for chlorophyll a loss in green beans based on a zero-order reaction model.

Temp. (^{o}C)	a_w	C_o (mg/kg)	k ($mg.kg^{-1}.day^{-1}$)	R^2 (%)
20	.33	262	0.09	83.5
	.43	265	0.16	96.4
	.59	264	0.56	95.1
30	.32	274	0.32	92.9
	.43	280	0.68	96.0
	.56	271	1.41	97.4
40	.32	281	1.19	95.0
	.43	268	1.89	95.5
	.53	294	4.30	98.5

Table 4.20. Results of the regression analysis for chlorophyll a loss in green beans based on a first-order reaction model.

Temp. (^{o}C)	a_w	ln C_o (mg/kg)	k (day^{-1}) (x 10^{-3})	R^2 (%)
20	.33	5.57	0.37	84.6
	.43	5.59	0.76	96.3
	.59	5.62	2.98	93.0
30	.32	5.63	1.49	94.8
	.43	5.66	3.14	94.9
	.56	5.66	7.49	96.6
40	.32	5.66	5.55	92.3
	.43	5.61	9.20	93.8
	.53	5.86	29.9	94.3

Table 4.21. Results of the regression analysis for chlorophyll b loss in green beans based on a zero-order reaction model.

Temp. (°C)	a_w	C_o (mg/kg)	k ($mg.kg^{-1}.day^{-1}$) ($\times 10^{-1}$)	R^2 (%)
20	.33	78.7	0.09	12.7
	.43	76.6	0.22	54.7
	.59	78.6	1.13	89.9
30	.32	83.7	0.76	74.0
	.43	86.3	1.76	76.0
	.56	84.5	3.17	80.8
40	.32	83.5	2.03	61.5
	.43	80.9	3.23	80.0
	.53	85.7	8.68	94.1

Table 4.22. Results of the regression analysis for chlorophyll b loss in green beans based on a first-order reaction model.

Temp. (°C)	a_w	ln C_o (mg/kg)	k (day^{-1}) ($\times 10^{-3}$)	R^2 (%)
20	.33	4.37	0.11	12.7
	.43	4.34	0.28	55.3
	.59	4.39	1.81	87.0
30	.32	4.43	1.08	77.2
	.43	4.47	2.49	76.3
	.56	4.46	4.76	80.5
40	.32	4.43	2.90	60.1
	.43	4.40	4.53	79.7
	.53	4.50	15.0	91.3

Table 4.23. Results of the regression analysis for total chlorophyll loss in green beans based on a zero-order reaction model.

Temp. (°C)	a_w	C_o (mg/kg)	k ($mg.kg^{-1}.day^{-1}$)	R^2 (%)
20	.33	342	0.09	81.1
	.43	341	0.18	94.9
	.59	341	0.67	93.1
30	.32	359	0.41	90.7
	.43	367	0.87	94.1
	.56	356	1.73	96.2
40	.32	364	1.39	91.9
	.43	346	2.16	96.2
	.53	379	5.11	98.4

Table 4.24. Results of the regression analysis for total chlorophyll loss in green beans based on a first-order reaction model.

Temp. (°C)	a_w	ln C_o (mg/kg)	k (day^{-1}) (x 10^{-3})	R^2 (%)
20	.33	5.84	0.30	81.7
	.43	5.84	0.64	94.8
	.59	5.88	2.72	90.4
30	.32	5.90	1.43	93.2
	.43	5.93	3.01	93.2
	.56	5.92	6.78	95.6
40	.32	5.92	4.89	89.0
	.43	5.86	7.79	94.8
	.53	6.07	25.0	94.7

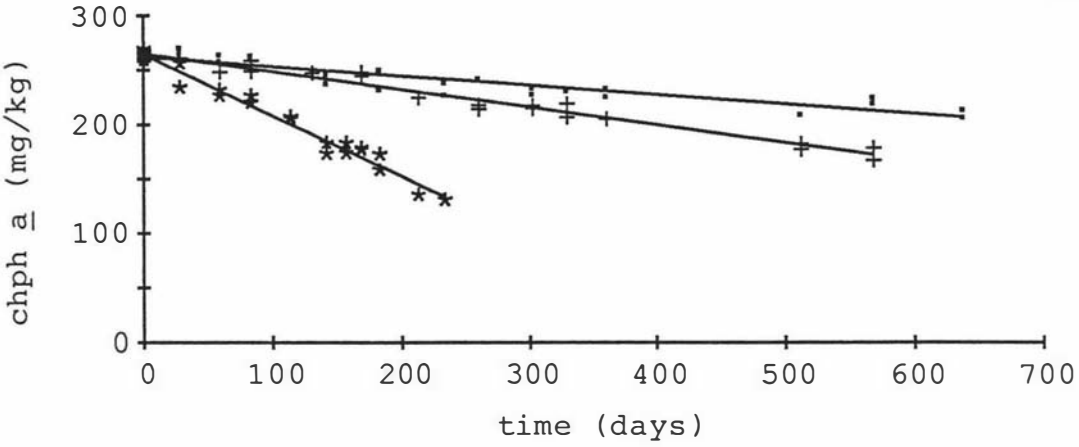


Fig. 4.21. Chlorophyll a loss in dried green beans with a_w = .33 (·), .43 (+) and .59 (*) during storage at 20°C.

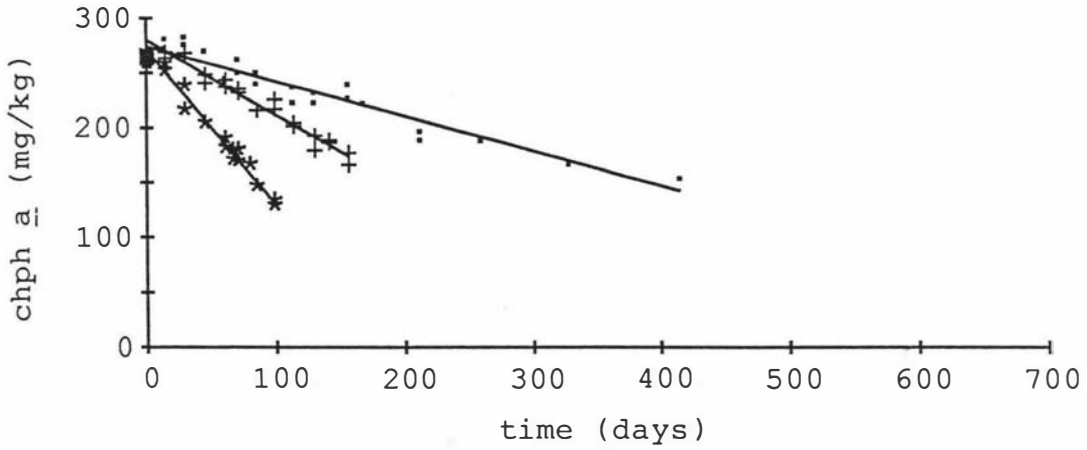


Fig. 4.22. Chlorophyll a loss in dried green beans with a_w = .32 (·), .43 (+) and .56 (*) during storage at 30°C.

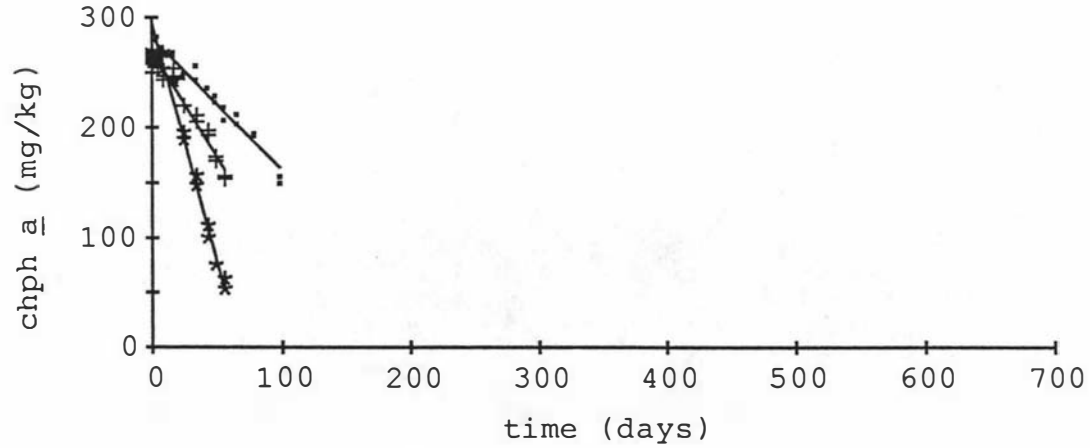


Fig. 4.23. Chlorophyll a loss in dried green beans with a_w = .32 (·), .43 (+) and .53 (*) during storage at 40°C.

Thus, the remainder of the kinetic study on the quality degradation in the dried green beans will concentrate on the loss of chlorophyll *a*.

Since the conversion of chlorophyll into pheophytin is an acid-catalysed reaction, the availability of water is essential, and it is to be expected that water activity will influence the rate of chlorophyll loss. The rate constant was found to be exponentially related to water activity for all three temperatures (Figure 4.24):

$$k = \alpha \exp(\beta a_w) \qquad (4\text{-}11)$$

The equations describing the relationship are given in Table 4.25. Chlorophyll loss (Lajolo *et al.*, 1971; Lajolo and Marquez, 1982) and other degradative reactions in food have been reported to exhibit an exponential relationship between k and a_w (Singh *et al.*, 1983; Labuza, 1972).

Table 4.25. Equations describing the relationship between rate constant (k) and a_w for chlorophyll *a* loss in dried green beans.

Temp. (°C)	Equation	R^2 (%)
20	$\ln k = -4.86 + 7.21\ a_w$	99.7
30	$\ln k = -3.10 + 6.19\ a_w$	99.6
40	$\ln k = -1.84 + 6.09\ a_w$	96.5

Using the equations given in Table 4.25, the k values for a_w = 0.56 at 20 and 40°C were interpolated. The relationship between reaction rate and temperature was determined at constant a_w = 0.32, 0.43 and 0.56. The

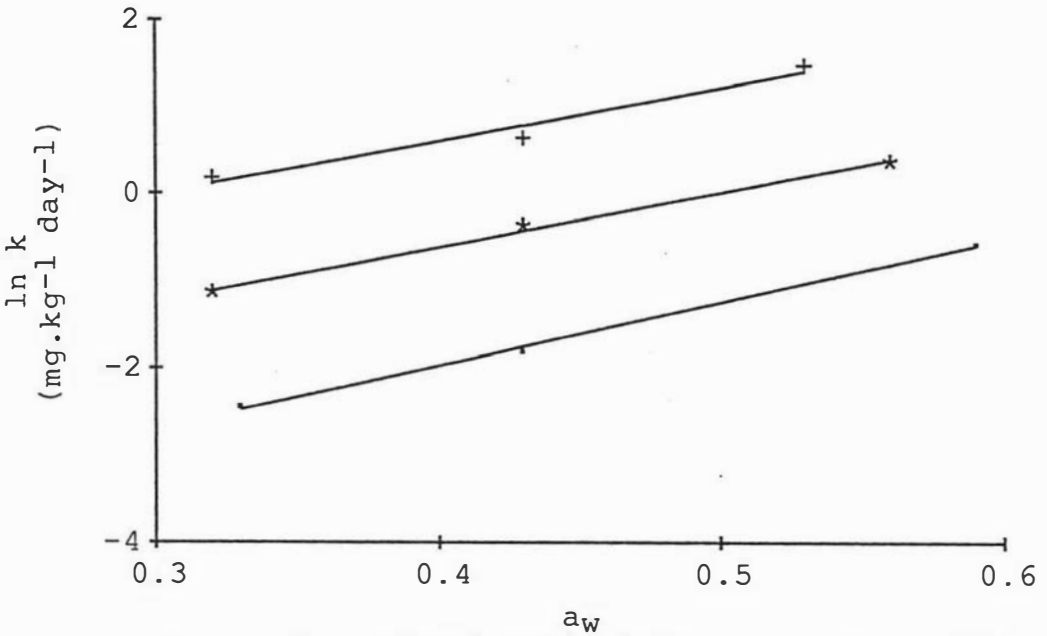


Fig. 4.24. Relationship between k and a_w for chlorophyll a loss in dried green beans at 20°C (·), 30°C (*) and 40°C (+).

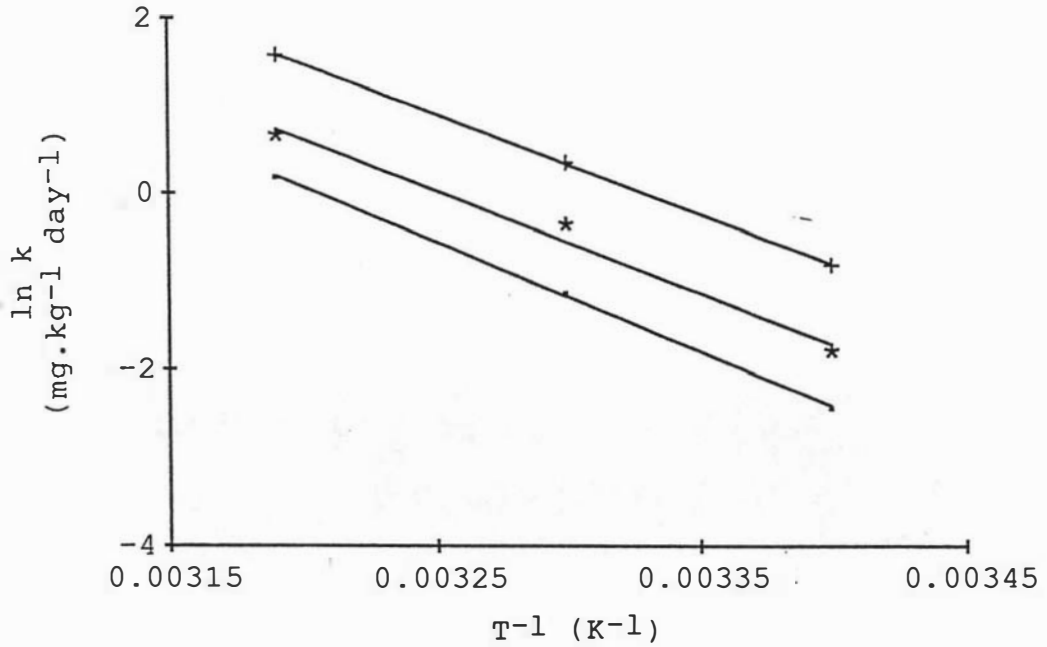


Fig. 4.25. Arrhenius plot for chlorophyll a loss in dried green beans with a_w = .32 (·), .43 (*) and .56 (+).

Arrhenius equation satisfactorily described the relationship (Figure 4.25). The calculated activation energies are given in Table 4.26. These E_a values (91 to 100 $kJ.mol^{-1}$) are comparable to those obtained by Lajolo *et al*. (1971).

Table 4.26. Results of the Arrhenius equations and Q_{10} values for chlorophyll *a* loss in dried green beans.

a_w	ln k_o	$E_a \pm$ 95% c.i. ($kJ.mol^{-1}$)	Q_{10} 20-30°C	Q_{10} 30-40°C
0.32	38.79	100.64 ± 5.80[a]	3.7	3.7
0.43	36.50	93.24 ± 3.64[a]	4.2	2.8
0.56	36.50	91.15 ± 38.4[b] (R^2) = 99.9)	3.2	3.4

[a] Calculated using a nonlinear regression method.
[b] Calculated using a two-step regression method.

The activation energies for chlorophyll *a* loss decreased with an increase in water activity, suggesting that as water content increases, the sensitivity of the reaction to temperature decreases. This trend was also observed by Lajolo *et al*. (1971) and Lajolo and Marquez (1982) in their studies. The applicability of equation 4-9 to describe the relationship between E_a and a_w was tested using the linear regression analysis, and a good fit was obtained:

$$E_a = \frac{1}{.0123 - .00073\ a_w^{-1}} \qquad R^2 = 99.0\%$$

Equation 4-9 satisfactorily expressed the relationship between activation energy and water activity for browning

and thiolsulphinate loss in dried onion flakes, and chlorophyll a loss in dried green beans. It is suggested that equation 4-9 can serve as a generalized model describing the relationship between E_a and a_w for deteriorative reactions in dried vegetables. Its applicability to other reactions and other dried vegetables has yet to be verified.

4.5.2.2 Sulphur Dioxide Loss

The sulphur dioxide loss in dried green beans followed a first-order model better than a zero-order model (Figure 4.26 to 4.28). The reaction rate constants are given in Tables 4.27 to 4.28.

The rate of SO_2 loss was linearly related to water activity at all three temperatures (Figure 4.29 and Table 4.29). This differs from the exponential relationship observed for chlorophyll loss, indicating that the reactions resulting in chlorophyll and SO_2 loss are independent of each other. Sulphur dioxide loss would be expected to correlate with browning in dried green beans.

Table 4.29. Equations describing the relationship between rate constant (k) and a_w for SO_2 loss in dried green beans.

Temp. (^oC)	Equation	R^2 (%)
20	$k = -0.0075 + 0.022\ a_w$	99.5
30	$k = -0.0304 + 0.099\ a_w$	99.5
40	$k = -0.0493 + 0.211\ a_w$	100.0

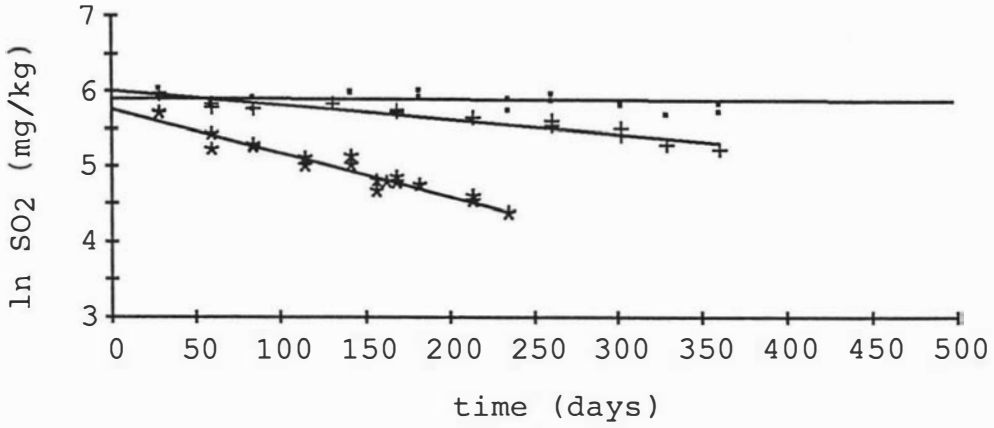


Fig. 4.26. Sulphur dioxide loss in dried green beans with a_w = .33 (·), .43 (+) and .59(*) during storage at 20°C.

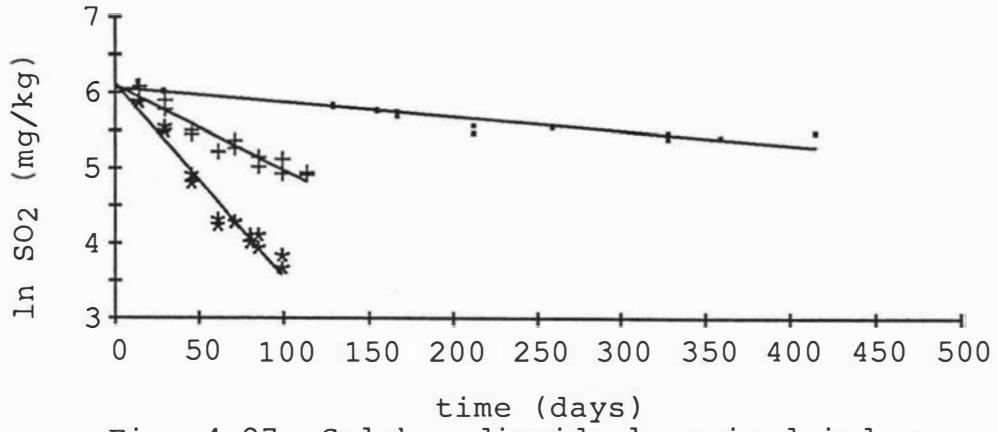


Fig. 4.27. Sulphur dioxide loss in dried green beans with a_w = .32 (·), .43 (+) and .56 (*) during storage at 30°C.

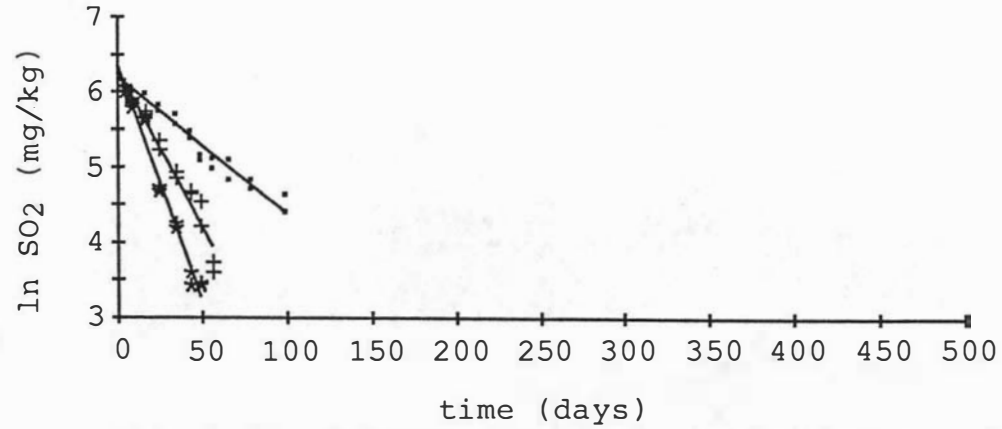


Fig. 4.28. Sulphur dioxide loss in dried green beans with a_w = .32 (·), .43 (+) and .53 (*) during storage at 40 °C

Table 4.27. Results of the regression analysis for SO_2 loss in green beans based on a zero-order reaction model.

Temp. (^oC)	a_w	C_o (mg/kg)	k ($mg.kg^{-1}.day^{-1}$)	R^2 (%)
20	.33	368	0.03	2.8
	.43	388	0.53	93.1
	.59	278	0.92	88.2
30	.32	421	0.59	86.8
	.43	410	2.78	84.1
	.56	339	3.51	85.5
40	.32	433	4.13	90.5
	.43	411	7.07	95.7
	.53	396	8.57	90.4

Table 4.28. Results of the regression analysis for SO_2 loss in green beans based on a first-order reaction model.

Temp. (^oC)	a_w	ln C_o (mg/kg)	k (day^{-1}) (x 10^{-2})	R^2 (%)
20	.33	5.90	0.008	2.5
	.43	6.00	0.19	91.2
	.59	5.75	0.58	94.0
30	.32	6.06	0.19	89.2
	.43	6.10	1.13	90.9
	.56	6.11	2.56	95.8
40	.32	6.19	1.81	96.1
	.43	6.28	4.18	96.1
	.53	6.33	6.24	97.6

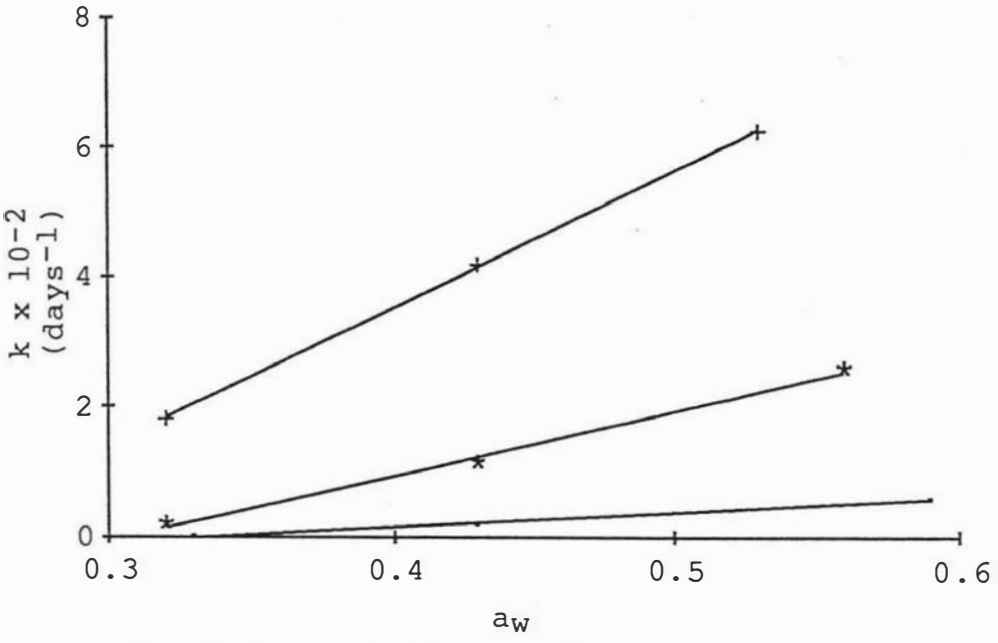


Fig. 4.29. Relationship between k and a_w for SO_2 loss in dried green beans at 20°C (·), 30°C (*) and 40°C (+).

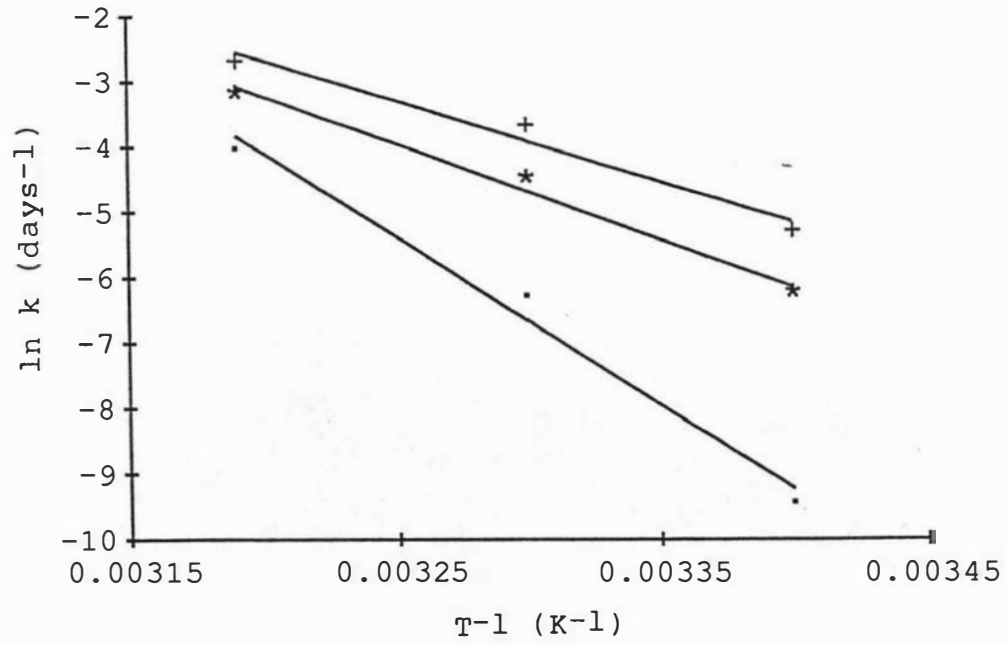


Fig. 4.30. Arrhenius plot for SO_2 loss in dried green beans with a_w = .32 (·), .43 (*) and .56 (+).

The Arrhenius relationship was fitted to the rate of reaction and temperature at the three water activity levels (Figure 4.30). The calculated activation energies (100 to 170 kJ mol^{-1}) presented in Table 4.30, compare well with literature values. Legault et al. (1949) reported E_a values of 138 to 180 $kJmol^{-1}$ for loss of SO_2 in dried vegetables, their values decreasing with increasing moisture content over the range studied (3 to 8%). A similar trend was observed in the present study.

Table 4.30. Results of the Arrhenius equations and Q_{10} values for SO_2 loss in dried green beans.

a_w	ln k_o	E_a ± 95% c.i. ($kJ.mol^{-1}$)	Q_{10} 20-30°C	Q_{10} 30-40°C
0.32	61.40	170.31 ± 6.55[a]	23.8	9.5
0.43	41.31	115.76 ± 5.74[a]	5.9	3.7
0.56	35.70	99.76 ± 151.5[b] (R^2 = 98.6)	4.4	2.4

[a] Calculated using a nonlinear regression method.
[b] Calculated using a two-step regression method.

4.5.3 Apricot

The results of the storage trials for apricot halves are given in Appendices 4.21 to 4.29.

Moisture content equilibrium was generally reached by the first sampling period. The data at time zero were excluded in the kinetic calculations to account for the initial equilibration period (Arabshahi and Lund, 1985). The

samples with a_w = 0.56 and 0.68 followed a desorption process, while those with a_w = 0.81 followed an adsorption process.

4.5.3.1 Nonenzymic Browning

Nonenzymic browning increased with time and temperature. The colour of the dried apricot samples changed from yellow orange to brownish orange to brown (Figures 4.31 and 4.32).

A lag period, where the browning measurement remained almost constant, was observed for the apricot samples at 20°C. The lag period was found to be approximately 59 days. During this initial stage of nonenzymic browning, colourless precursors are formed (Eichner, 1975). The existence of the lag period was reported by Karel and Nickerson (1964) in dehydrated orange juice, and Singh et al. (1983) in intermediate moisture apples. No lag period was observed at 30 and 40°C, probably due to the faster rate of browning. The reaction rates for the apricot samples at 20°C were calculated excluding the lag period (Arabshahi and Lund, 1985).

A zero- and first-order model were fitted to the data. The results of the regression analyses giving the reaction rate constants are given in Tables 4.31 and 4.32. The browning reaction fitted the first-order model better than the zero-order model, as indicated by the higher R^2 values, at all water activities and temperatures. Stadtman (1946a) and Davis et al.(1973) reported a similar observation in their studies on the browning of dried apricot during storage.

Plots of the natural logarithm of the reaction rates (ln k) against storage time at the different storage conditions are shown in Figures 4.33 to 4.35. The error associated

Fig. 4.31 . Change in colour of dried apricot halves, packaged in LDPE film, during storage at 30°C/75%RH.

Fig. 4.32 . Change in colour of dried apricot halves, packaged in LDPE film, during storage at 40°C/90%RH.

Table 4.31. Results of the regression analysis for browning in dried apricot based on a zero-order reaction model.

Temp. (°C)	a_w	C_o (absorbance)	k (abs.day^{-1}) (x 10^{-3})	R^2 (%)
20	.59	-0.015	0.73	93.1
	.70	-0.011	1.08	88.6
	.81	-0.004	0.66	84.4
30	.56	-0.030	3.31	90.8
	.68	0.030	3.45	93.3
	.81	-0.003	2.31	96.5
40	.53	0.007	16.9	90.7
	.66	0.042	14.9	95.9
	.80	0.038	12.4	91.1

Table 4.32. Results of the regression analysis for browning in dried apricot based on a first-order reaction model.[1]

Temp. (°C)	a_w	ln C_o (absorbance)	k (day^{-1}) (x 10^{-2})	R^2 (%)
20	.59	-3.37	0.60	96.3
	.70	-3.16	0.80	90.0
	.81	-3.24	0.54	94.6
30	.56	-3.16	2.04	98.4
	.68	-2.96	2.18	98.0
	.81	-3.22	1.85	98.4
40	.53	-2.93	10.9	97.2
	.66	-2.93	11.7	97.8
	.80	-3.00	10.7	98.5

[1] Samples stored at 20°C exhibited a lag period of around 59 days.

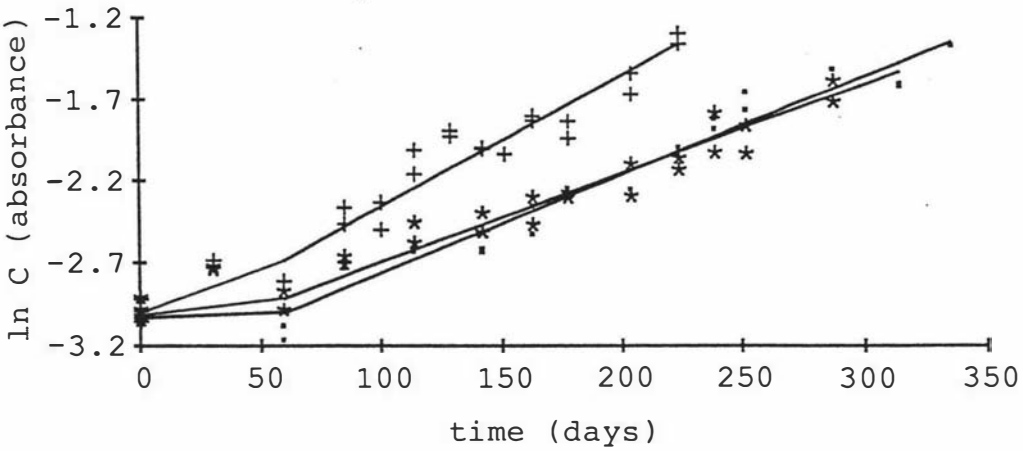


Fig. 4.33. Nonenzymic browning in dried apricots with a_w = .59 (·), .70 (+) and .81 (*) during storage at 20°C.

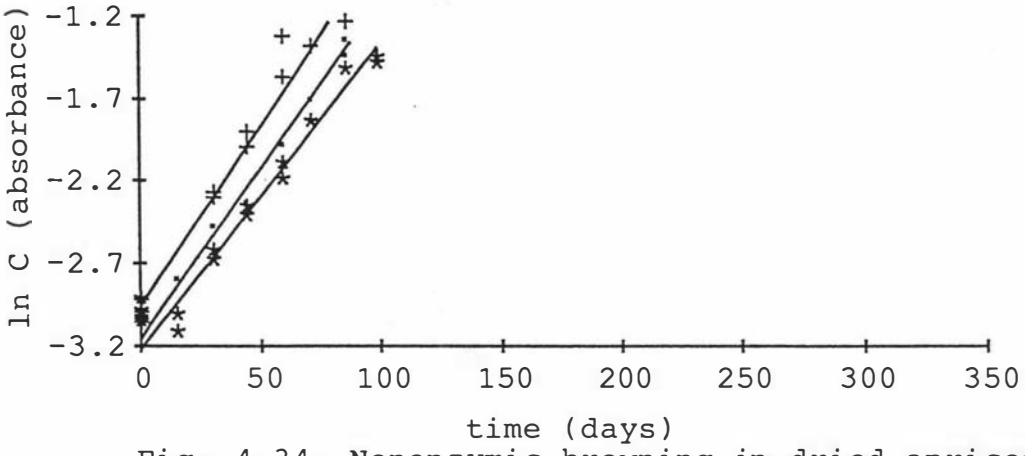


Fig. 4.34. Nonenzymic browning in dried apricots with a_w = .56 (·), .68 (+) and .81 (*) during storage at 30°C.

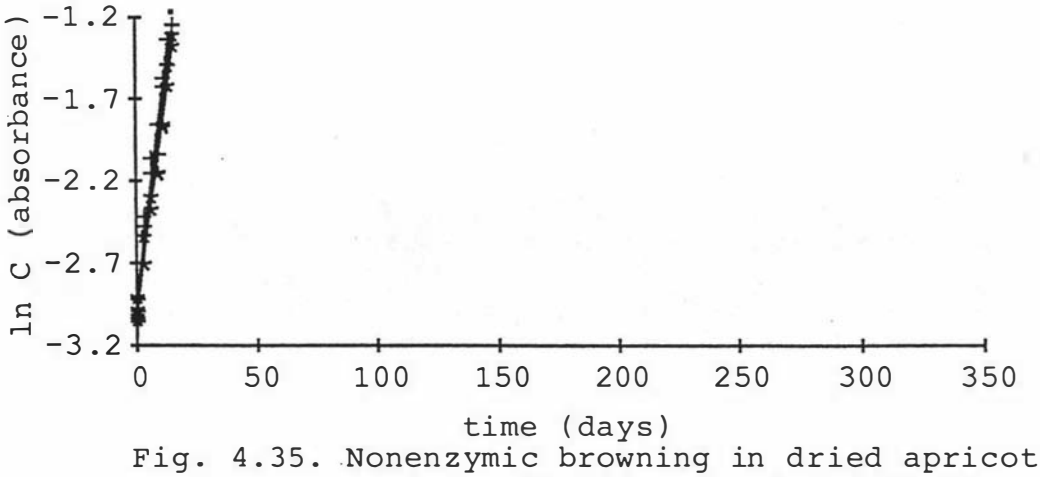


Fig. 4.35. Nonenzymic browning in dried apricots with a_w = .53 (·), .66 (+) and .80 (*) during storage at 40°C.

with the calculated rate constants would be ≤ 9% based on Benson's table given in Table 4.11.

A higher rate constant (k) was obtained for the samples with a_ws of around 0.68 at all three temperatures. With only three k values, a quadratic equation seemed to be the most appropriate model that could be used to describe the relationship between a_w and k (Figure 4.36):

$$k = \alpha + \beta a_w + \gamma a_w^2 \qquad (4\text{-}12)$$

The equations that were obtained are given in Table 4.33.

Table 4.33. Equations describing the relationship between rate constant (k) and a_w for browning in dried apricot.

Temp. (°C)	Equation	a_w maxima
20	$k = -0.082 + 0.261a_w - 0.188a_w^2$	0.69
30	$k = -0.043 + 0.195a_w - 0.148a_w^2$	0.66
40	$k = -0.096 + 0.648a_w - 0.492a_w^2$	0.66

It was reasonable to assume a parabolic or quadratic relationship between k and a_w considering there were only three k values and a narrow a_w range. Studies have shown this relationship to exist at a limited a_w range (±0.15 of the a_w maxima) (Labuza and Saltmarch, 1981). Extrapolation should not be made outside the a_ws tested because deviation in the trend would be expected as was observed in the studies of Loncin *et al*. (1968), Eichner (1975) and Warmbier *et al*. (1976). More complex equations have been proposed by other authors over a wider a_w range (Toribio *et al*., 1984).

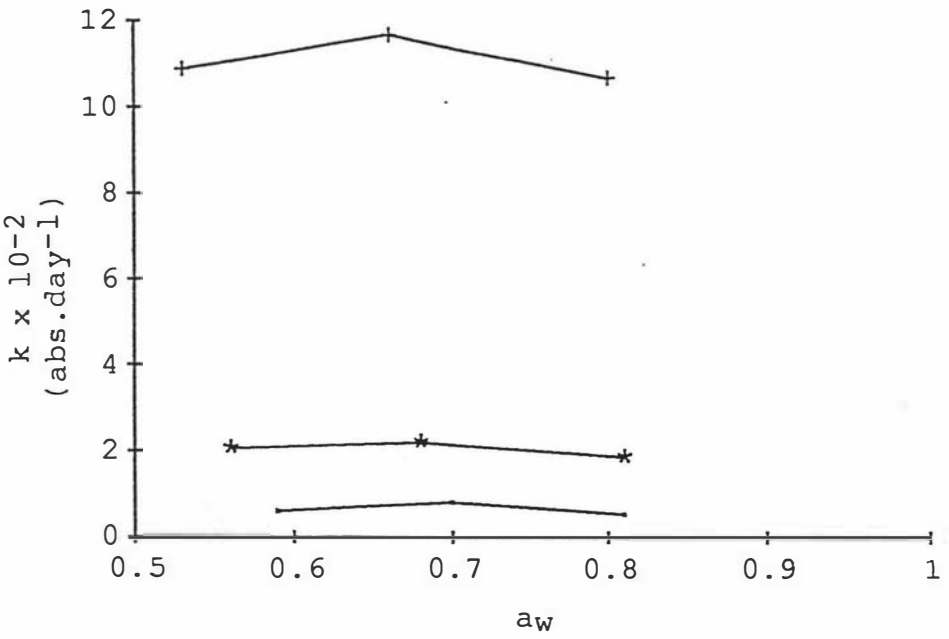


Fig. 4.36. Relationship between k and a_w for browning in dried apricots at 20°C (·), 30°C (*) and 40°C (+).

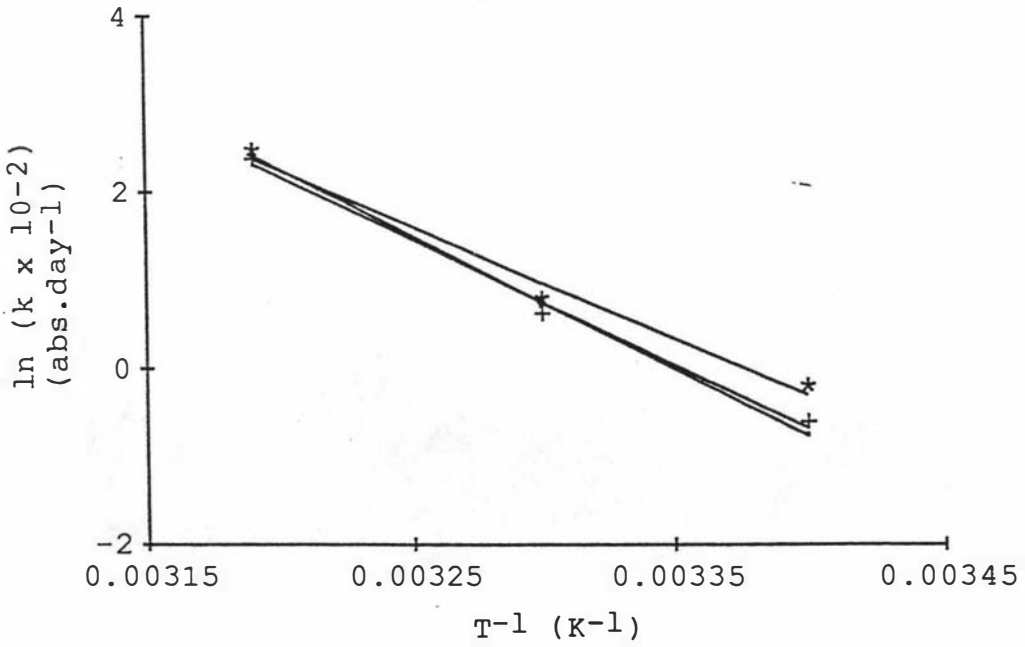


Fig. 4.37. Arrhenius plot for browning in dried apricots with a_w = .59 (·), .68 (*) and .81 (+).

In general, nonenzymic browning follows the observed pattern, in which a maxima is present. This phenomenon can be partly explained by the binding of water and the mobility of the reaction species.

At low water activity the limiting factor is inadequate mobility; therefore, addition of water, which solubilises or plasticises the system, promotes the reaction. At high water activity, however, water strongly inhibits browning because it dilutes the reactants. Besides the mobility and dilution factors, water may affect nonenzymic browning by inhibiting or enhancing some of the intermediate reactions (Labuza and Saltmarch, 1981).

With respect to browning, water can retard the rate of the initial glycosylamine reaction in which water is a product. This results in product inhibition. Eichner and Karel (1972) found this to be the case in studies of browning reaction between glucose and glycine in glycerol/water mixtures. Other reactions in the sequence may also be inhibited since three moles of water are produced per mole of carbohydrate used. On the other hand, water may enhance deamination reactions in the browning reaction sequence as observed by Reynolds (1963) for the production of furfural or hydroxymethylfurfural.

Stadtman et al. (1946 a,b,c) reported that the rate constant for browning reactions in dried apricots increased with increasing moisture content over a range of 10 to 25%. A browning maxima was not observed. It is probable that the maxima for the specific lot of dried apricots would coincide with a higher moisture content. A similar assumption was made by Singh et al. (1983) in their study on intermediate moisture apples wherein a maxima was not observed over an a_w range of 0.62 to 0.89.

Many studies of browning have analysed the specific a_w at which the maximum rate of browning occurs. Labuza (1970), Labuza et al. (1972), Loncin et al. (1968) and Karel and Labuza (1968) have all reported an a_w between 0.65 and 0.70 for the browning rate maxima. The values obtained in this study fall within this range.

The variations in a_w or water content rate maxima for browning can be attributed to the physical and/or chemical nature of the food itself (Karel and Labuza, 1968).

The fact that many workers have reported a maxima for browning in the a_w = 0.60 to 0.80 range makes this reaction a significant one with respect to intermediate moisture foods that are in the a_w = 0.60 to 0.85 range (Labuza, 1975).

Figure 4.36 shows the effect of temperature on the reaction rate constant of nonenzymic browning. The rate constants at 40°C are considerably higher than those at 20 and 30°C. The effect of changes in water activity on the rate of the reaction appears insignificant when compared to the effect of changes in temperature.

From the quadratic equations that were obtained, the reaction rates at constant a_w for the different temperatures were calculated. This was done to enable the determination of the relationship of reaction rate and temperature at constant a_w.

The Arrhenius plot for browning in apricot is presented in Figure 4.37. The E_a values were calculated from the Arrhenius equation and are given in Table 4.34. The calculated activation energies and Q_{10} values are comparable to published results. Stadtman et al. (1946a) reported an E_a of 109 kJ mol^{-1} and a Q_{10} of 3.9 for dried

apricots and Nury and Brekke (1963) reported E_a values of 100 to 109 kJ mol^{-1} for raisins.

Table 4.34. Results of the Arrhenius equations and Q_{10} values for browning in dried apricots.

a_w	ln k_o	E_a ± 95% c.i. ($kJ.mol^{-1}$)	R^2 (%)	Q_{10} 20-30°C	Q_{10} 30-40°C
0.59	40.9	112.44 ± 156.66[a]	99.9	3.5	5.5
0.68	36.9	102.07 ± 213.74[a]	99.5	2.7	5.4
0.81	41.0	112.93 ± 172.20[a] 105.18 ± 10.34[b]	98.5	3.4	5.8

[a] Calculated using a two-step regression method.
[b] Calculated using a nonlinear regression method.

The trend observed for dried onion flakes and green beans toward lower E_a and Q_{10} values with higher water activity was not observed for dried apricot. The E_a value at a_w = 0.68 was lower than those at a_w = 0.56 and 0.81. This was due to the relatively small difference in reaction rates between the samples at the three a_w levels at 40°C (i.e. the change in reaction rates with temperature at 0.56 and 0.81 was bigger than that at 0.68).

A quadratic equation was fitted to the data and the following equation describing E_a as a function of a_w was obtained:

$$E_a = x + ya_w + za_w^2$$

$$E_a = 542.89 - 1262.61\ a_w + 903.46\ a_w^2 \qquad (4\text{-}13)$$

Equation 4-13 is an empirical equation that may be used for prediction purposes over the a_w range tested.

Other factors that could have affected the rate of the browning reaction are the amount of oxygen that is absorbed by the product and the sulphur dioxide content. This will be further discussed in the next section.

4.5.3.2 Sulphur Dioxide Loss

The sulphur dioxide content of the dried apricot samples decreased with time and temperature.

The results of the regression analyses for a first- and zero-order reaction models are given in Tables 4.35 and 4.36. Sulphur dioxide loss in the dried apricot was found to better fit a first-order reaction model. This agrees with the results of Stadtman et al. (1946b) and Davis et al. (1973). The plots of the logarithm of the SO_2 concentration versus storage time at the different RHs and temperatures are shown in Figures 4.38 to 4.40.

A similar relationship between k and a_w for browning was found to be the case for SO_2 loss with a maximum being observed at around a_w = 0.70 (Figure 4.41). A quadratic equation was fitted to the data and the results are presented in Table 4.37.

The Arrhenius plot for SO_2 loss in apricots is presented in Figure 4.42. The E_a values corresponding to the different a_w levels were calculated based on the Arrhenius equation and the results are given in Table 4.38. The E_a and Q_{10} values obtained in the present study agree with published results. Stadtman et al. (1946a) reported an E_a of 109 $kJ.mol^{-1}$ and a Q_{10} of 4.

Table 4.35 Results of the regression analysis for SO_2 loss in dried apricot based on a zero-order reaction model.

Temp. (^oC)	a_w	C_o (mg/kg)	k ($mg.kg^{-1}.day^{-1}$)	R^2 (%)
20	.59	2015	3.90	89.7
	.70	1307	6.14	93.9
	.81	1546	5.04	96.9
30	.56	2223	16.29	96.3
	.68	1083	11.28	82.2
	.81	1383	13.57	90.6
40	.53	1538	54.12	94.5
	.66	1434	89.63	92.2
	.80	1517	96.54	96.4

Table 4.36. Results of the regression analysis for SO_2 loss in dried apricot based on a first-order reaction model.

Temp. (^oC)	a_w	ln C_o (mg/kg)	k (day^{-1}) (x 10^{-2})	R^2 (%)
20	.59	7.71	0.32	88.9
	.70	7.48	1.07	96.6
	.81	7.50	0.69	93.3
30	.56	7.97	1.50	93.7
	.68	7.57	3.19	93.3
	.81	7.54	2.25	96.8
40	.53	7.35	4.74	95.5
	.66	7.32	11.95	98.9
	.80	7.38	12.21	98.8

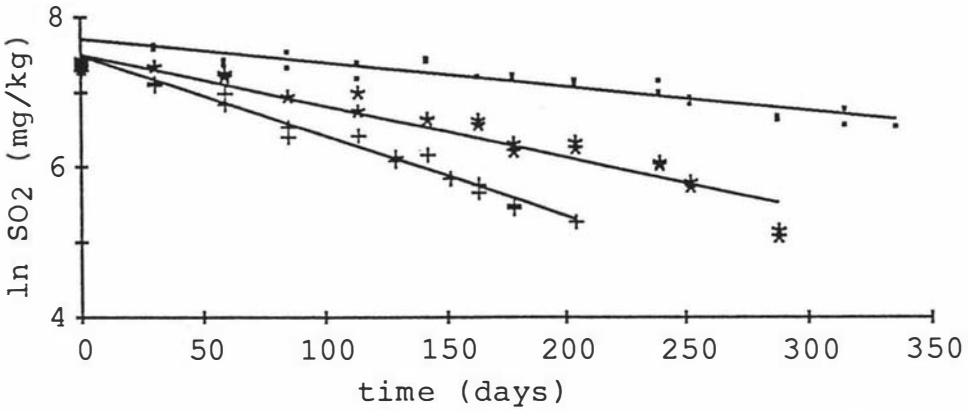


Fig. 4.38. Sulphur dioxide loss in dried apricots with a_w = .59 (·), .70 (+) and .81 (*) during storage at 20°C.

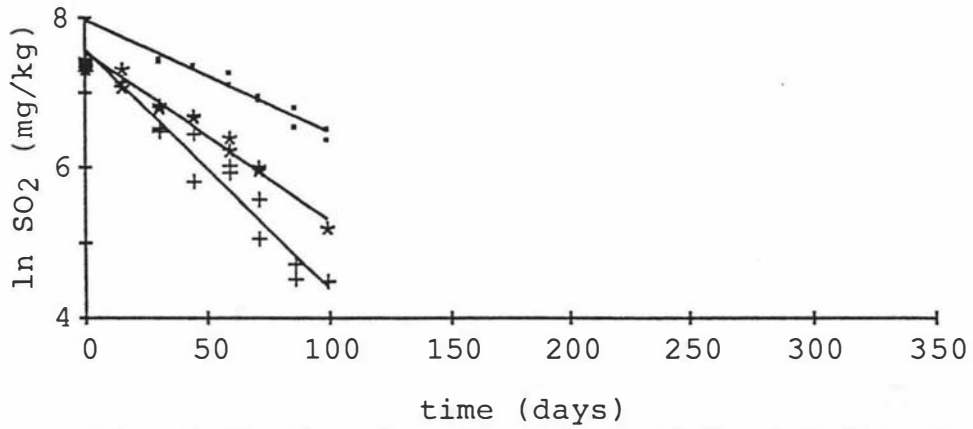


Fig. 4.39. Sulphur dioxide loss in dried apricots with a_w = .56 (·), .68 (+) and .81 (*) during storage at 30°C.

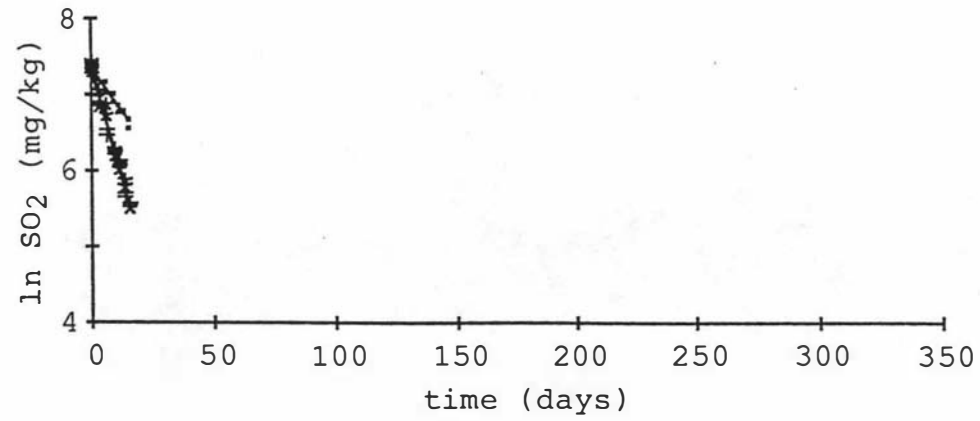


Fig. 4.40. Sulphur dioxide loss in dried apricots with a_w = .53 (·), .66 (+) and .80 (*) during storage at 40°C.

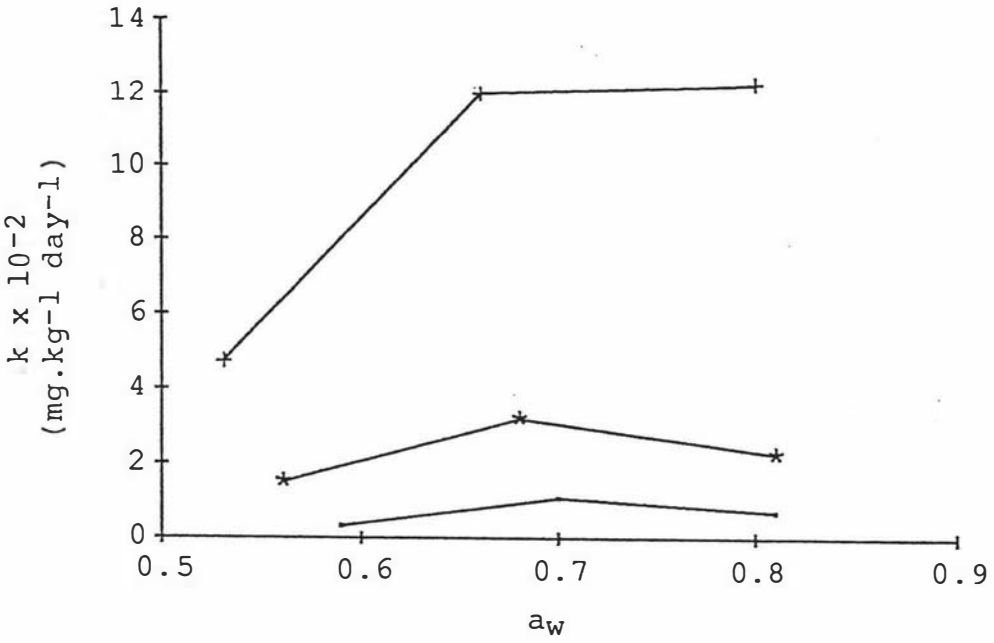


Fig. 4.41. Relationship between k and a_w for SO_2 loss in dried apricots at 20°C (·), 30°C (*) and 40°C (+).

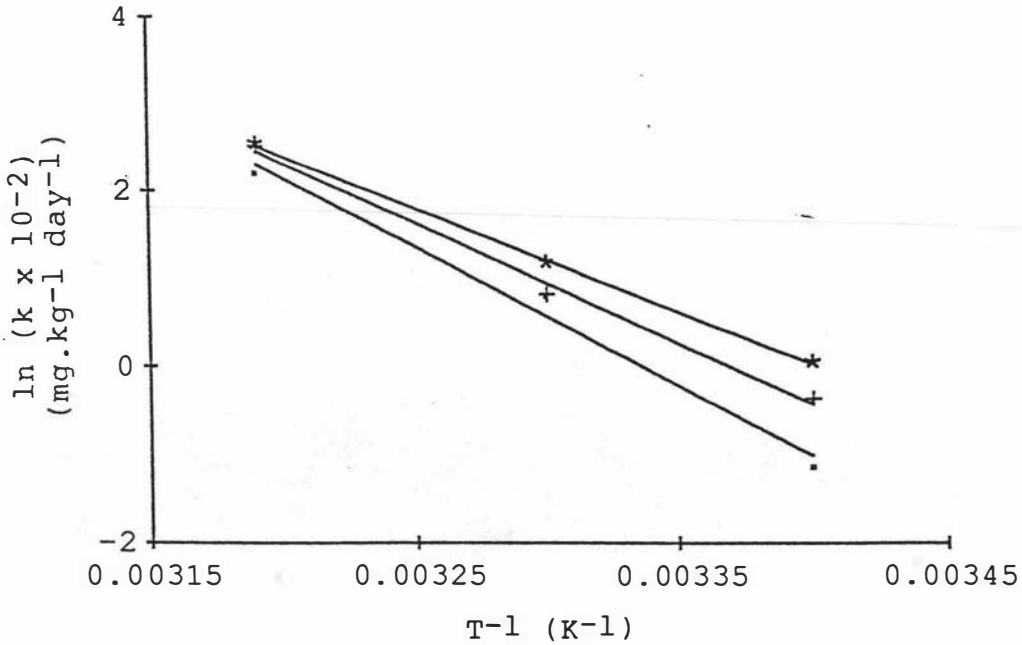


Fig. 4.42. Arrhenius plot for SO_2 loss in dried apricots with a_w = .59 (·), .68 (*) and .81 (+).

Table 4.37. Equations describing the relationship between rate constant (k) and a_w for SO_2 loss in dried apricot.

Temp. (^oC)	Equation	a_w maxima
20	$k = -0.230 + 0.671\ a_w - 0.467\ a_w^2$	0.72
30	$k = -0.389 + 1.20\ a_w - 0.853\ a_w^2$	0.70
40	$k = -0.941 + 2.92\ a_w - 1.99\ a_w^2$	0.73

Table 4.38. Results of the Arrhenius equations and Q_{10} values for SO_2 loss in dried apricots.

a_w	ln k_o	$E_a \pm$ 95% c.i. ($kJ.mol^{-1}$)	R^2 (%)	Q_{10} 20-30^oC	Q_{10} 30-40^oC
0.59	46.4	131.61 ± 146.68[a]	99.8	6.4	4.3
0.68	34.5	95.41 ± 63.93[a]	99.5	3.1	3.9
0.81	39.8	109.44 ± 134.22[a]	98.5	3.3	5.4
		105.34 ± 9.65[b]			

[a] Calculated using a two-step regression method.
[b] Calculated using a nonlinear regression method.

Under aerobic conditions, SO_2 loss in dried apricot has been attributed to the oxidation of SO_2 to sulphate and its irreversible reaction with fruit constituents (Stadtman et al., 1946b; Davis et al., 1973).

The rate of SO_2 loss is dependent on the rate of oxygen adsorption of the fruit. The rate of oxygen consumption

increases with an increase in moisture content (Stadtman et al., 1946a). Hence, the rate of SO_2 loss is expected to increase with moisture content.

Sulphur dioxide is also lost through its reaction with the intermediates or products of the browning reaction as shown in Figure 4.43 (McWeeny et al., 1974).

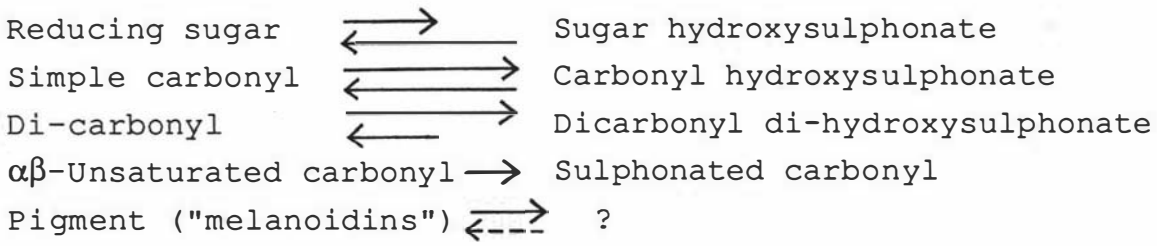


Figure 4.43. Sulphite effects on nonenzymic browning.

Thus, the rate of browning is influenced by the rate of SO_2 loss. A plot of the rate constants of SO_2 loss against moisture content or water activity of the fruit is expected to show a maxima as was observed for browning.

It is the combined effects of these two reactions on SO_2 loss which results in the trend that was observed between the rate of SO_2 loss and a_w. At low a_w, the oxidation and browning reactions are both slow, resulting in a low rate of SO_2 loss. With an increase in a_w to 0.68, both reaction rates increase and so does the rate of SO_2 loss. With a further increase in a_w to 0.81, the rate of oxidation is increased but the rate of browning decreases. The net result is a rate of SO_2 loss slightly lower than that at 0.68, but significantly higher than at 0.53.

Stadtman et al. (1946a) suggested that the end of the shelf life of dried apricots was reached when 65% of the initial SO_2 content was lost. The results of the study of Davis et al. (1973) supported this suggestion. The present study,

however, clearly shows that this generalisation is not applicable to dried apricots exposed to different RH and temperature conditions due to the complexity of the reactions taking place during storage which are affected by several interrelated factors.

In this case where there is an undefined supply of oxygen, the effects of the different variables (i.e. water activity, temperature, SO_2) cannot be isolated, since browning and SO_2 loss are affected by oxygen consumption which in turn is dependent on a_w and temperature. Caution must be taken in interpreting the kinetic results that have been obtained for dried apricots due to the aforementioned limitations.

It is suggested that in order to be able to obtain more meaningful kinetic results, more than three water activity levels should be tested and the effect of oxygen on the reactions should be investigated.

One problem associated with determining oxygen effects on foods is the difficulty in determining rates of oxygen uptake, especially at low oxygen levels. Another problem is the fact that water content seriously affects oxidation rates (Labuza et al., 1970).

4.6 CONCLUSION

Storage trials were conducted on dried onion flakes, green beans and apricot halves. The rates of the various deteriorative reactions occurring during storage at different relative humidities and temperatures were determined.

For onion flakes and green beans, the rates of reactions were found to increase with an increase in the water activity of the products. The Arrhenius equation satisfactorily described the relationship between rate constants and temperatures. Mathematical models were developed expressing the rate constants as functions of water activity and temperature, and the activation energies as functions of water activity.

Nonenzymic browning and sulphur dioxide loss in dried apricots exhibited a trend wherein the rate increased with water activity until a maximum was reached and then decreased with a further increase in water activity. The reactions followed the Arrhenius equation at all three water activity levels. The present study did not investigate the effects of oxygen on the kinetics of the different reactions. This was considered a limitation to the interpretation of the kinetic data on dried apricots.

CHAPTER 5
DEVELOPMENT AND EVALUATION OF SHELF LIFE PREDICTION MODELS

5.1 INTRODUCTION

This chapter is concerned with the development of mathematical models to describe the deteriorative reactions discussed in Chapter 4, and the use of these models to predict the shelf lives of the dried food products.

Mathematical modelling is a procedure leading to the description of a process or phenomena by one or more mathematical equations. In the previous chapter, equations were developed expressing the concentration (C) of the index of deterioration, the reaction rate constant (k) and the activation energy (E_a) as functions of temperature and water activity. The dependent variables (C, k, E_a) were expressed as functions of individual independent variables (a_w, temperature). An alternative approach to shelf life prediction is the development of a single mathematical model to fit all of the experimental data as a function of the combined effects of the different independent variables.

The first objective of this study was to develop models describing the quality deterioration occurring during storage of the dried onion flakes, green beans and apricot, as influenced by the factors time, temperature and water activity.

The accomplishment of the first objective would satisfy the first four assumptions mentioned in Chapter 1 which form the basis of shelf life prediction techniques:

a. The deteriorative mechanisms limiting shelf life and their dependence on environmental parameters can be described by a mathematical function.

$$C = f(a_w, t, T)$$

b. Maximum acceptable deterioration can be determined by correlating objective tests of deterioration with organoleptic parameters.

c. The internal environment depends on the conditions of the food. The moisture sorption isotherms describe the water activity of the food which determines the vapour pressure inside the package.

d. Barrier properties of the package can be related to the internal and external environments.

$$P/X = f(RH, T)$$

The first two assumptions were discussed in Chapter 4, the third assumption in Chapter 2 and the fourth assumption in Chapter 3.

The final step towards shelf life prediction is to fulfill the fifth assumption, namely that the different equations can be combined and solved with the aid of a computer.

A review of the studies that have been conducted to develop techniques to predict the shelf life of packaged foods was given in Chapter 1.

The second objective of this chapter was to predict (using a computer-aided technique) the moisture transfer into and the shelf life of dried onion flakes and green beans packaged in low density polyethylene film and the laminate

of polyethylene and polyester.

5.2 EXPERIMENTAL

5.2.1 Calculation and Program Development

Nonlinear regression analysis was used for the evaluation of the more complex models developed in the study. This analysis was performed on a PRIME 750 computer with the BMDP AR program (Dixon, 1985).

The BASIC language was used to prepare the computer iteration program for the prediction of shelf life. An IBM compatible microcomputer was used to run the program.

5.2.2 Storage Trials

Polyethylene (LDPE, 60 μm) and the laminate (30 μm LDPE and 12 μm PET) films were made into bags using a controlled temperature heat sealer. Care was taken in the sealing process to ensure that uniform and integral seals were obtained.

The dried onion flakes and sliced green beans were obtained from the same sources as the samples used in the storage experiments in Chapter 4. Approximately 25 g of onion flakes and 30 g of green beans were packaged in the prepared LDPE and laminate bags. The use of such small amounts of sample per bag made it possible to spread the samples in a thin layer inside the bags. This was to avoid the occurrence of a moisture gradient within the product inside the bags. The resulting packages had areas of 120

mm x 100 mm for the onion flakes and 120 mm x 135 mm for the green beans.

The packaged dried products were stored in the controlled RH plastic containers described in Section 4.4 of the previous chapter. The bags were arranged in the slotted trays in such a way that none of them overlapped (i.e. all areas of the package were exposed to the controlled atmosphere). The products were stored at controlled conditions: 30°C/75%RH and 40°C/90%RH. Controlled relative humidities were maintained with the use of saturated salt slurries: NaCl for 75% RH and K_2CO_3 for 90% RH. The plastic containers were stored in controlled temperature rooms at 30±0.5°C and 40±1.0°C.

Sampling was done at different time periods during storage until the unacceptable level of the index of deterioration was reached. Samples from duplicate bags per treatment were analysed each sampling period. The onion flakes were analysed for nonenzymic browning and thiolsulphinate content and the green beans for chlorophyll a content. The methods for determining the different quality indices, discussed in Section 4.3, were followed in the analyses.

5.3 DEVELOPMENT OF MODELS FOR QUALITY DETERIORATION IN DRIED FOODS

The order of reaction describes the concentration of the reactant or product as a function of time, with all other variables constant.

$$C = C_o - kt \qquad \text{(zero-order)} \qquad (5\text{-}1)$$

$$C = C_o \exp(-kt) \qquad \text{(first-order)} \qquad (5\text{-}2)$$

Nonenzymic browning in onion flakes and chlorophyll a loss in green beans were found to best fit the zero-order model. Thiolsulphinate loss in onion flakes, browning in apricots and SO_2 loss in greenbeans and apricots were better described by the first-order model.

The Arrhenius equation (5-3) was found to adequately describe the effect of temperature on the rates of the deteriorative reactions occurring in the three dried products.

$$k = k_o \exp(-E_a/RT) \qquad (5\text{-}3)$$

By substituting k into equations 5-1 and 5-2 an expression of concentration as a function of both time and temperature was derived:

$$C = C_o - k_o \exp(-E_a/RT)\ t \qquad \text{(zero-order)} \quad (5\text{-}4)$$

$$C = C_o \exp-[k_o \exp(-E_a/RT)\ t] \qquad \text{(first-order)} \quad (5\text{-}5)$$

In the previous chapter, equations 5-4 and 5-5 were used to calculate the activation energies. It resulted in a good fit and statistically meaningful E_a values.

The rate constants at constant temperature and the E_a values were observed to be highly dependent on water activity. The following empirical equations for the three products (determined in the previous chapter), satisfactorily described the relationship:

<u>onion flakes</u> (nonenzymic browning and thiolsulphinate loss)

$$k_o = \alpha + \beta a_w \qquad (5\text{-}6)$$

$$E_a = \frac{1}{\gamma - \delta a_w^{-1}} \qquad (5\text{-}7)$$

green beans (chlorophyll a loss)

$$k_o = \alpha \exp \beta a_w \qquad (5\text{-}8)$$

$$E_a = \frac{1}{\gamma - \delta a_w^{-1}} \qquad (5\text{-}9)$$

apricot (nonenzymic browning)

$$k_o = \alpha + \beta a_w + \gamma a_w^2 \qquad (5\text{-}10)$$

$$E_a = x + y a_w + z a_w^2 \qquad (5\text{-}11)$$

Parameters k_o and Ea were then substituted into equations 5-4 or 5-5 depending on the reaction order giving the equations:

nonenzymic browning in onion flakes:

$$C = C_o + (\alpha + \beta a_w) \exp [-(1/\gamma - \delta a_w^{-1}) /RT] t \qquad (5\text{-}12)$$

thiolsulphinate loss:

$$C = C_o \exp -[(\alpha + \beta a_w) \exp((- 1/\gamma - \delta a_w^{-1}) /RT) t] \qquad (5\text{-}13)$$

chlorophyll a loss:

$$C = C_o - (\alpha \exp \beta a_w) \exp((- 1/\gamma - \delta a_w^{-1}) /RT) t \qquad (5\text{-}14)$$

nonenzymic browning in apricots:

$$C = C_o \exp[(\alpha + \beta a_w + \gamma a_w^2) \exp (-(x + y + z a_w^2) /RT) t] \qquad (5\text{-}15)$$

Equations 5-12 to 5-15 are mathematical models expressing C as a function of a_w, time and temperature. Since previous studies have shown that oxygen has negligible effects on dried onion flakes and green beans, these equations serve as the overall quality deterioration model for these two products. For dried apricots, the effect of oxygen on the deteriorative reactions has not been isolated; its effect would have been combined in the observed effects of temperature and water activity (i.e. oxygen absorption is influenced by temperature and water activity).

Analysis of equations 5-12 to 5-15 using the BMDP AR program showed that a high correlation existed between the coefficients of the equations. This was not unexpected since nonlinear regression applied to models with the Arrhenius-type relationship generates very highly correlated parameter estimates (Himmelblau, 1970). To overcome this problem, and in order to preserve the theoretical consideration and at the same time simplify the model, the following approach was considered.

The development of a new model using the 'reference' approach, in which the rate of reaction at any given temperature is related to a 'reference' temperature (T_1) was considered. In this approach the use of k_o is eliminated:

$$k_{t2} = k_{t1} \cdot \exp\left[\frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] \qquad (5\text{-}16)$$

where:

k_{T2} = reaction rate at investigated temperature T_2

k_{T1} = reaction rate at reference temperature T_1

In the present study, the reference temperature used was 30°C.

Both k_t and E_a are dependent on a_w according to equations 5-6 to 5-11.

The value of k is thus given by the following equations:

nonenzymic browning in onion flakes:

$$k = (\alpha + \beta a_w) \exp\left[-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{303.15}\right)\right] \qquad (5\text{-}17)$$

thiolsulphinate loss:

$$k = (\alpha + \beta a_w) \exp\left[-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{303.15}\right)\right] \qquad (5\text{-}18)$$

chlorophyll a loss:

$$k = (\alpha \exp\beta a_w) \exp\left[-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{303.15}\right)\right] \qquad (5\text{-}19)$$

nonenzymic browning in apricots:

$$k = (\alpha + \beta a_w + \gamma a_w^2) \exp\left[-\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{303.15}\right)\right] \qquad (5\text{-}20)$$

Therefore, the new models can be written:

nonenzymic browning in onion flakes (eqn 5-21):

$$C = C_o + (\alpha + \beta a_w) \exp\left[- \frac{1}{(\gamma - \delta a_w)} \left(\frac{1}{R}\right)\left(\frac{1}{T} - \frac{1}{303.15}\right)\right] t$$

thiolsulphinate loss in onion flakes (eqn 5-22):

$$C = C_o \exp - \left[(\alpha + \beta a_w) \exp \left(- \frac{1}{(\gamma - \delta a_w)} \left(\frac{1}{R}\right)\left(\frac{1}{T} - \frac{1}{303.15}\right)\right) t \right]$$

chlorophyll <u>a</u> loss in green beans (eqn 5-23):

$$C = C_o - (\alpha \exp \beta a_w) \exp\left[- \frac{1}{(\gamma - \delta a_w)} \left(\frac{1}{R}\right)\left(\frac{1}{T} - \frac{1}{303.15}\right)\right] t$$

nonenzymic browning in apricots (eqn 5-24):

$$C = C_o \exp\left[(\alpha + \beta a_w + \gamma a_w^2) \exp\left[- (x + y a_w + z a_w^2) \left(\frac{1}{R}\right)\left(\frac{1}{T} - \frac{1}{303.15}\right)\right] t\right]$$

The above models were tested for the different deteriorative reactions, and the estimates of the coefficients α, β, γ, and δ were determined with the use of the BMDP AR program. The calculated values of the coefficients of the kinetic equations in Chapter 4 were used as initial estimates in the calculation of the nonlinear equations. The results giving the values of the

coefficients and the standard errors of estimate are presented in Tables 5.1 to 5.4.

To verify the validity of the deterioration models to describe the deteriorative reactions during storage, a comparison of actual and predicted values for the three products stored under various conditions was made. The actual values were the observed results from the kinetic studies in the previous chapter. Plots comparing the actual and predicted results are shown in Figures 5.1 to 5.4. They show a relatively good overall fit for the three products. The residual values were relatively small and randomly scattered indicating an acceptable fit with the model exhibiting no bias. The residual plots are shown in Appendices 5.1 to 5.4.

Equations 5-20 to 5-23 were used to predict the shelf life of unpackaged dried onion flakes, green beans and apricots stored under simulated conditions identical to the temperatures and RHs tested in the previous chapter. The shelf lives were determined based on the acceptability levels established in the Chapter 4* which were:

a. nonenzymic browning in onion flakes ≤ 105 optical index
b. thiolsulphinate loss in onion flakes ≥ 5 µm/g
c. chlorophyll a loss in green beans ≤ 30% loss
d. nonenzymic browning in apricot ≤ .250 absorbance

* Refer to:
  a. Section 4.3.2.3 (p.104)
  b. Section 4.3.2.2 (p.101)
  c. Section 4.3.3.2 (p.106)
  d. Section 4.3.4.3.2 (p.116)

8% of the actual values. In practical terms, this means a maximum difference of one month between actual and predicted shelf life for a sample with an actual shelf life of one year. The predicted values are thus of practical

Table 5.1. Results of the nonlinear regression analysis of the deterioration model for nonenzymic browning in onion flakes.[1]

Coefficient	Estimate	Standard Error
α	-1.373	0.023
β	4.571	0.064
γ	0.010	0.0003
δ	0.001	0.0001

[1] EMS = 62.46 no. of data points = 218

Table 5.2. Results of the nonlinear regression analysis of the deterioration model for thiolsulphinate loss in onion flakes.[1]

Coefficient	Estimate	Standard Error
α	-0.008	0.0002
β	0.033	0.0007
γ	0.012	0.0004
δ	0.001	0.0002

[1] EMS = 0.272 no. of data points = 224

Table 5.3. Results of the nonlinear regression analysis of the deterioration model for chlorophyll a loss in onion flakes.[1]

Coefficient	Estimate	Standard Error
α	0.038	0.002
β	6.581	0.106
γ	0.012	0.0005
δ	0.001	0.0002

[1] EMS = 85.73 no. of data points = 177

Table 5.4. Results of the nonlinear regression analysis of the deterioration model for browning in dried apricots.[1]

Coefficient	Estimate	Standard Error
α	-0.012	0.017
β	0.105	0.051
γ	-0.080	0.038
x	901.778	107.321
y	-2355.469	325.191
z	1689.766	241.576

[1] EMS = .001 no. of data points = 140

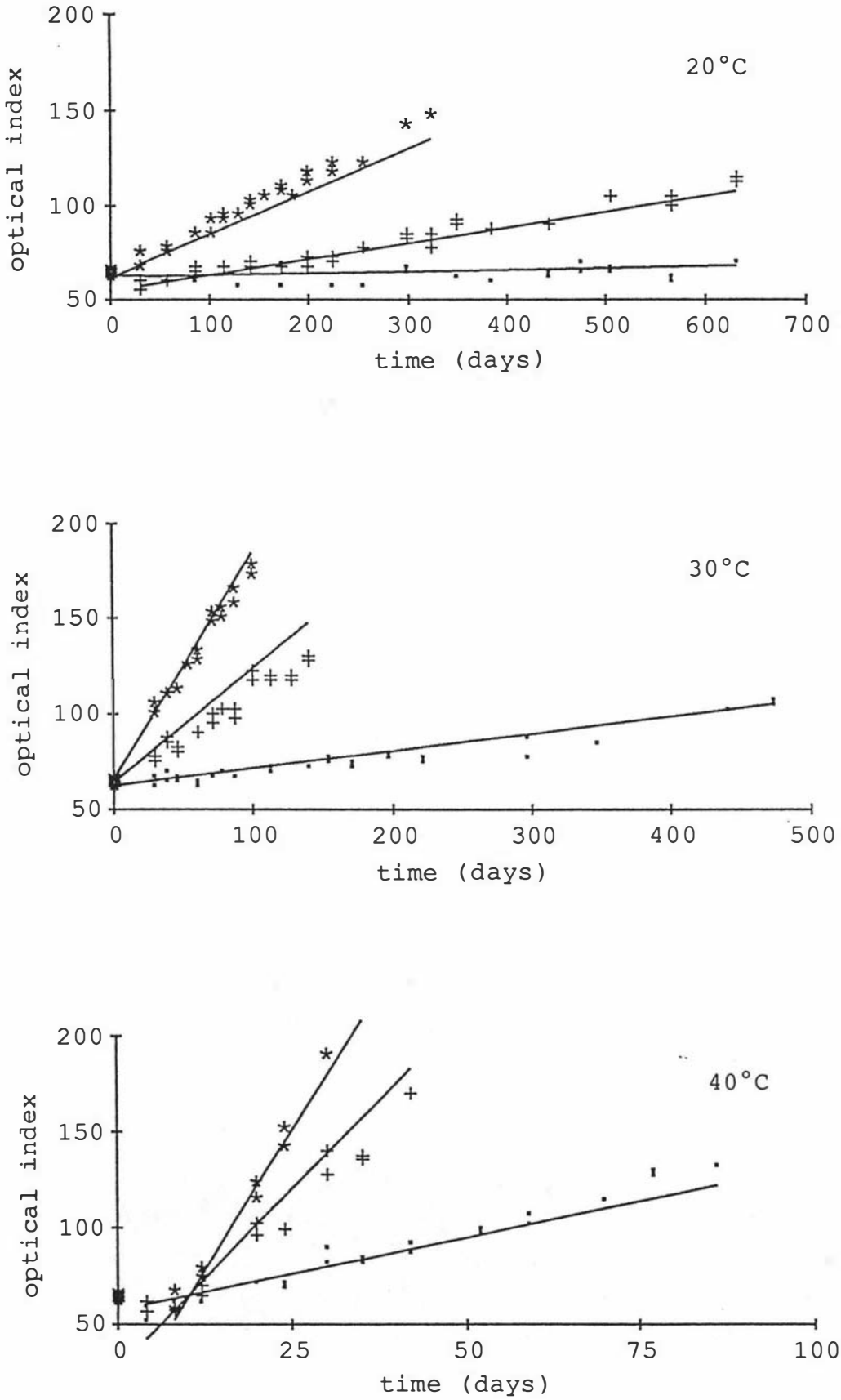


Fig. 5.1. Comparison of the actual (point symbols) and predicted (solid lines) values for nonenzymic browning in onion flakes with a_w = .32 (·), .43 (+) and .56 (*) at 20, 30 and 40°C.

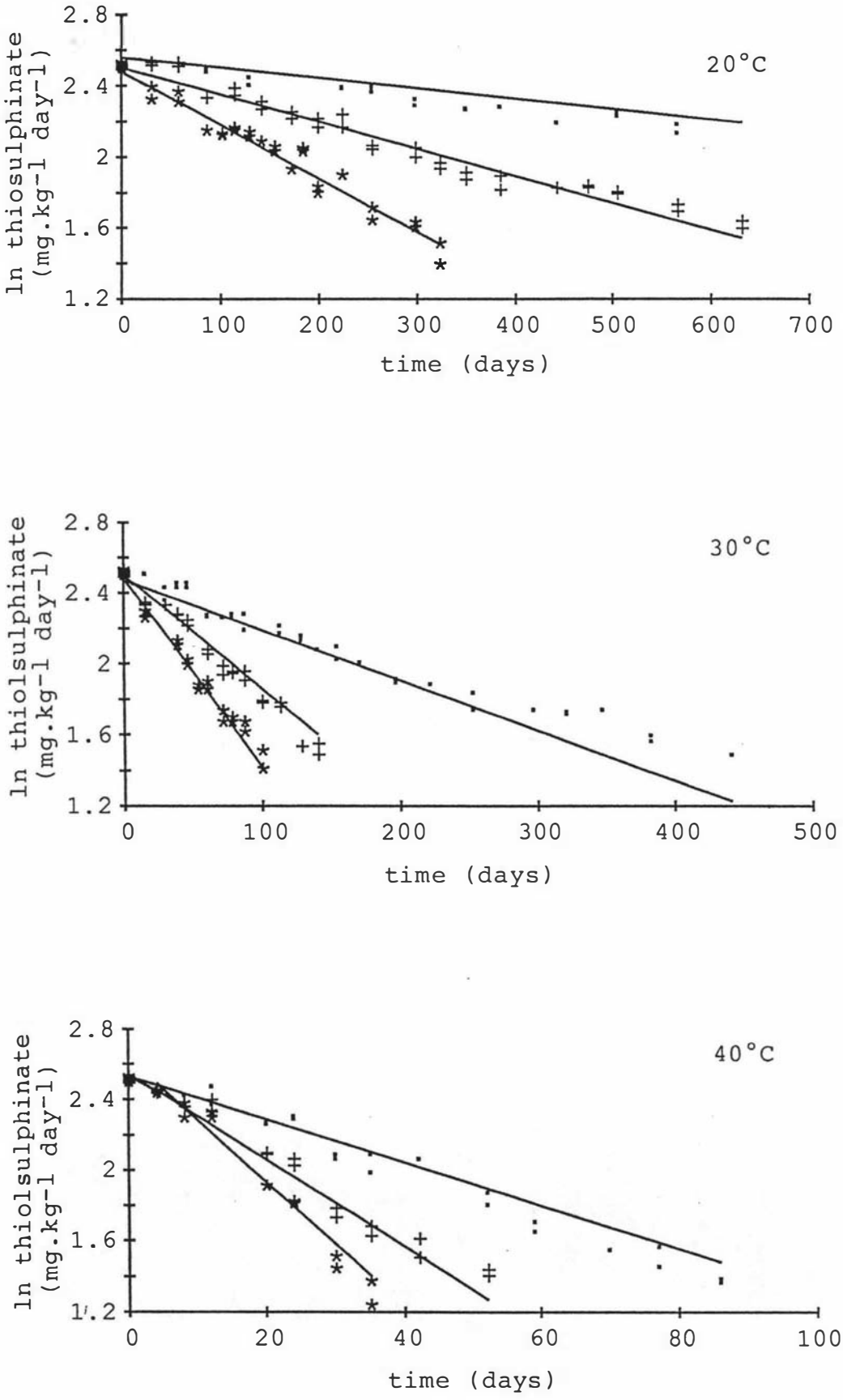


Fig. 5.2. Comparison of the actual (point symbols) and predicted (solid lines) values for thiolsulphinate loss in onion flakes with a_w = .32 (·), .43 (+) and .56 (*) at 20, 30 and 40°C.

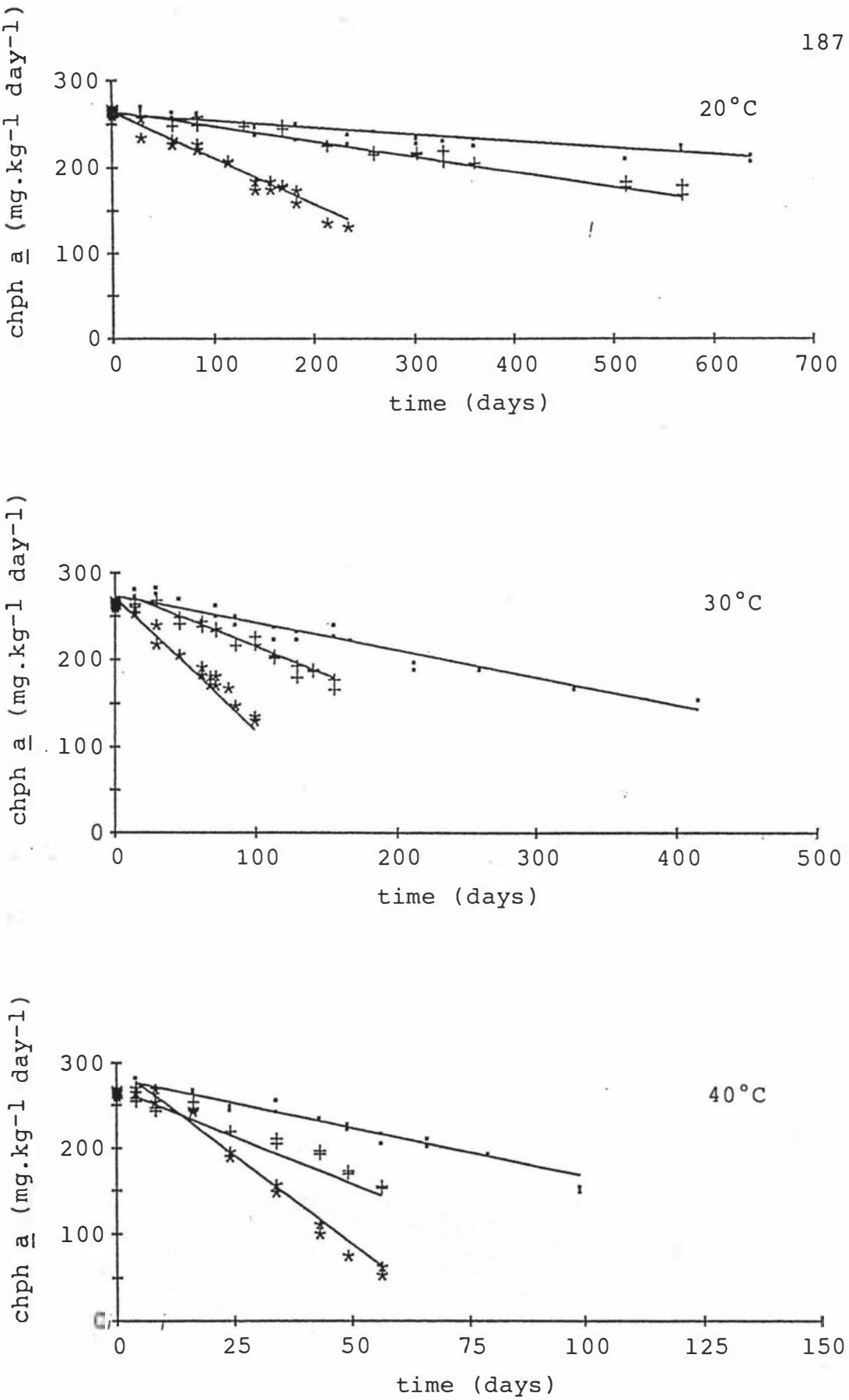


Fig. 5.3. Comparison of the actual (point symbols) and predicted (solid lines) values for chlorophyll a loss in green beans with a_w = .32 (·), .43 (+) and .56 (*) at 20, 30 and 40°C.

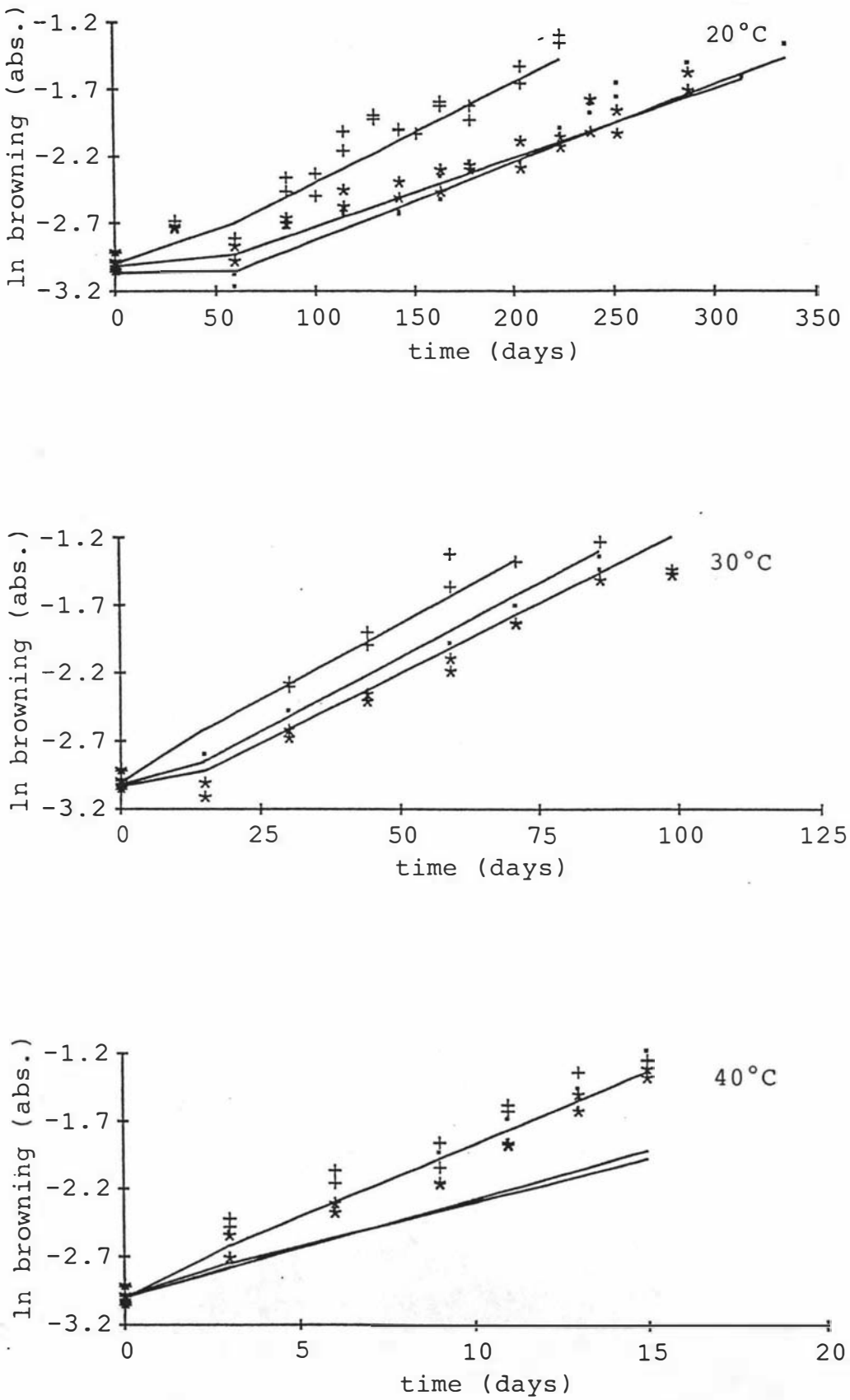


Fig. 5.4. Comparison of actual (point symbols) and predicted (solid lines) values for browning in apricots with a_w = .56 (·), .68(+) and .81 (*) at 20, 30 and 40°C.

Table 5.5. Actual and (predicted) shelf life (days) of dried onion flakes based on browning.[1]

a_w	Temperature (°C)		
	20	30	40
0.32	>631 (4778)	474 (472)	59 (63)
0.43	593 (600)	83 (69)	22 (21)
0.56	183 (190)	31 (33)	17 (17)

[1] Unacceptable level ≥ 105 optical index

Table 5.6. Actual and (predicted) shelf life (days) of dried onion flakes based on thiolsulphinate loss.[1]

a_w	Temperature (°C)		
	20	30	40
0.32	>631 (1619)	369 (306)	66 (75)
0.43	631 (585)	136 (139)	40 (38)
0.56	298 (288)	84 (82)	27 (29)

[1] Unacceptable level ≤ 5 μm/g

Table 5.7. Actual and (predicted) shelf life (days) of dried green beans based on chlorophyll a loss.[1]

a_w	Temperature (°C) 20	30	40
0.32	>637 (962)	273 (282)	86 (84)
0.43	478 (452)	143 (146)	45 (38)
0.56	150 (148)	61 (56)	25 (26)

[1] Unacceptable level ≤ 185 mg/kg

Table 5.8. Actual and (predicted) shelf life (days) of dried apricot halves based on browning.[1]

a_w	Temperature (°C) 20	30	40
0.56	336 (349)	86 (82)	14 (14)
0.68	224 (239)	71 (70)	14 (24)
0.80	315 (363)	103 (90)	15 (22)

[1] Unacceptable level ≥ .250 absorbance

utility considering the complexity of the deteriorative reactions and the inherent variability in any particular food product.

A comparison of the actual and predicted shelf lives for apricot (Table 5.8) shows that a good agreement (5% difference) was obtained for the samples with a water activity of around 0.56 at the three temperatures, and for the samples with an a_w of around 0.68 stored at 20 and 30°C. However, a poor agreement was observed for the samples stored at the highest temperature and RH. This indicates the inadequacy of the deterioration model to describe the browning reaction in dried apricot over the whole range of temperatures and humidities investigated. This limitation of the model is likely due to the fact that the influence of oxygen on the browning reaction and on SO_2 loss was not isolated in the kinetic study in the previous chapter and hence, its effect was not fully expressed in the deterioration model.

Therefore the dried apricot was not considered any further in the subsequent study on packaged dried foods due to the inadequacy of the deterioration model for browning.

5.4 PREDICTION OF MOISTURE TRANSFER AND SHELF LIFE OF PACKAGED DRIED FOODS

The shelf life prediction of dried foods packaged in permeable films requires accurate knowledge of the rate of transport of water vapour across the film barrier. The moisture transfer equation was derived from equations 3-1 and 3-2 of Chapter 3 to give the following:

$$\frac{Q}{t} = \frac{P}{X}(p_1 - p_2) = \frac{P}{X}\Delta p \qquad (5\text{-}24)$$

where Q/t = amount of water vapour permeating through a film at time (mL/s)

A = area (cm^2)

p_1, p_2 = vapour pressure of water on each side of the film (cm Hg)

$\Delta p = p_1 - p_2$ = driving force for vapour flow

P/X = film permeance (mL cm^{-2} s^{-1} cm Hg^{-1})

The prediction of moisture transfer to a packaged food requires the analysis of equation 5-24 given certain boundary conditions. The simplest analysis requires the assumptions that P/X is constant, that the external environment is at constant temperature and RH, and that p_2, the vapour pressure of the water in the food follows some simple function of the moisture content.

A further assumption is that the moisture gradient inside the package is negligible, i.e. the package should be the major resistance to vapour transport. This is the case whenever P/X is less than about 1.4×10^{-5} mL cm^{-2} s^{-1} cm Hg^{-1}, which is the case for most films under high humdity conditions.

The critical point about equation 5-24 is that the internal vapour pressure is not constant but varies with the moisture content of the food at any time. Thus the rate of gain or loss of moisture is not constant but falls as Δp gets smaller. Thus some function of p_2, the internal vapour pressure as a function of the moisture content, must be inserted into the equation to be able to make proper predictions. If a constant rate is assumed, the product will be overprotected.

In low and intermediate moisture foods, the internal vapour pressure is determined by the water activity of the food which is a function of the food's moisture content and is described by the sorption isotherm. Several functions can be applied to describe the moisture sorption isotherm. The most simple and commonly used is the linear function. This has been extensively tested for foods and found to give good predictions of actual weight gain or loss over a limited water activity range (Taoukis et al., 1988).

In the present study, the GAB isotherm equation, which successfully defined the whole isotherm (see Chapter 2), was used to predict the moisture transfer to the packaged dried foods.

The equations obtained describing the kinetic reactions and moisture sorption isotherms of the dried vegetables, the permeability characteristics of the packaging films, and moisture transfer were combined in a mathematical model for prediction of moisture content, extent of deteriorative reaction, and shelf life of the products.

An iteration procedure over time intervals of 0.5 day was developed with the aid of a microcomputer. A program to perform the calculations was written in the BASIC language and is presented in Appendix 5.5. The iteration procedure is shown as a flow sheet in Figure 5.5 and is summarised below.

The following are the required inputs of the program:

RH = external RH to which the package will be exposed
T = storage temperature
m_1 = initial moisture content of the sample (%dry basis)
p_o = vapour pressure of pure water at storage temperature
Δt = time interval
A = surface area of the packaging film exposed to the

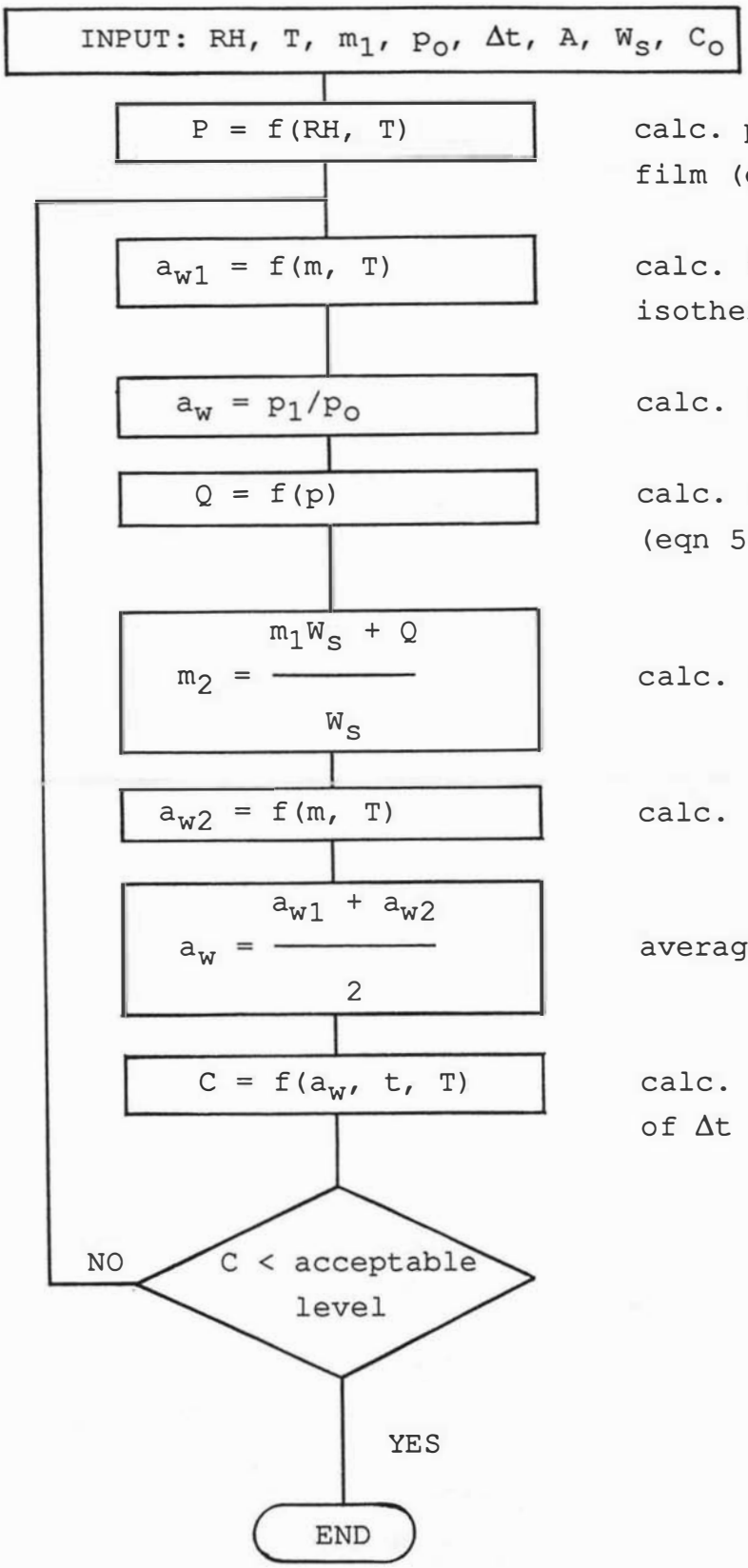


Fig. 5.5. Flow diagram of computer iteration.

storage atmosphere
W_s = dry weight of sample (g)
C_o = initial concentration or level of the index of deterioration

Iteration steps:

1. The permeance (P/X) of the packaging film used is determined at a specific RH and temperature using equation 3-12.

2. The water activity (a_w) at the beginning of the interval Δt is calculated using the GAB isotherm equation eqn 2-3.

3. The internal vapour pressure (p_1) inside the package is determined .

4. The moisture content increase due to water vapour permeation for Δt is calculated using equation (5-24).

5. The moisture content increase from step 4 is added to the initial moisture content (m_i) to obtain the moisture content at the end of the interval Δt.

6. The water activity at the end of the interval is determined using the GAB equation.

7. The average water activity for the time interval is calculated.

8. The average a_w is used to determine the extent of the deteriorative reaction using the deterioration models for each product (eqn 5-20 to 5-23).

The process is repeated to calculate changes occurring in the next time interval. An endpoint value, corresponding to the unacceptability level, was set in the program to

terminate computation when the concentration of the index of deterioration exceeded the specified level.

Figure 5.6 presents an example of the output giving the predicted moisture content and water activity, concentration of the index and the shelf life of the dried food at specific time intervals.

To verify the validity of the mathematical model and the iteration procedure for shelf life prediction, actual storage trials on the dried products packaged in polyethylene (60 μm) and the laminate film (12 μm polyester and 30 μm polyethylene) were conducted under test conditions. The experimental procedure for the storage trials are given in Section 5.2.2. The storage conditions simulated were 30°C/75% RH and 40°C/90% RH.

It would be ideal to have conducted storage trials at lower temperature and RH conditions (e.g. 20°C/55%RH) to be able to confirm the adequacy of the models over a wider range of storage conditions. However, an actual test on packaged dried onion flakes and green beans at such low temperatures would involve time periods of more than one year. Considering the time limitation of the present study (due to a finite funding period) it was deemed impractical to conduct actual tests at 20°C. It is also reasonable to assume, based on the good fit of the deterioration models discussed in Section 5.3 over the whole temperature range, that if the models were to be found acceptable in describing the quality deterioration at higher temperatures (i.e. 30 and 40°C) and RHs, then the models would apply just as well to lower temperature and RH conditions.

Tables 5.9 to 5.16 present a comparison of the results of the computer simulation and the actual storage trials giving the moisture contents and the levels of the index of

```
SHLIFE >start of run

 Title : Shelf life prediction of dehydrated foods
 Food sample ..............  ONIONS
 Packaging material .......  LDPE
 Temperature ..............  30  deg.C
 Rh .......................  75
 Initial Moisture Content..  5.72  gm/100gm
 Time interval ............  .5  day(s)
 Water vapour pressure ....  31.82  mm Hg
 Area .....................  240  sq.cm
 Dry solid weight .........  23.65  gm

  Checkpoint at:  14  days
  Moisture Content (M2)...   7.324 gm/100gm
  Water Activity (Aw).....   0.405
  Concentration (I).......  58.537

  Checkpoint at:  35  days
  Moisture Content (M2)...   9.376 gm/100gm
  Water Activity (Aw).....   0.483
  Concentration (I).......  72.680

  Checkpoint at:  43  days
  Moisture Content (M2)...  10.072 gm/100gm
  Water Activity (Aw).....   0.506
  Concentration (I).......  79.833

  Checkpoint at:  54  days
  Moisture Content (M2)...  10.968 gm/100gm
  Water Activity (Aw).....   0.534
  Concentration (I).......  90.936

  Checkpoint at:  62  days
  Moisture Content (M2)...  11.580 gm/100gm
  Water Activity (Aw).....   0.551
  Concentration (I).......  99.816

 Results: --------------------
  Shelf life of ONIONS =  66.5  day(s)
  Final Moisture Content (M2)...  11.912 gm/100gm
  Final Water Activity (Aw).....   0.560
  Final Concentration (I)....... 105.077

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end of run
```

Fig. 5.6 Sample of the computer program output.

Table 5.9. Actual and predicted results for dried onion flakes packaged in LDPE and stored at 30°C/75%RH.[1,2]

Time (days)	moisture content (% dry basis)			optical index			thiolsulphinate (μm/g)		
	Actual	Predicted		Actual	Predicted		Actual	Predicted	
		uc	c		uc	c		uc	c
0	5.72			54.0			11.64		
14	7.34	7.26	7.25	62.5	58.46	58.54	11.50	10.94	10.93
	7.18			60.0			11.57		
35	9.61	9.14	9.38	80.0	72.09	72.68	8.93	9.48	9.44
	9.47			80.0			9.50		
43	10.35	9.75	10.08	80.0	78.9	79.83	8.36	8.87	8.81
	9.90			80.0			8.6		
54	10.93	10.52	10.97	92.5	89.40	90.94	7.14	8.04	7.95
	10.90			87.5			7.07		
62	11.51	11.03	11.58	107.5	97.75	99.82	6.86	7.44	7.33
	---			102.5			6.07		
80	12.22	12.07	12.87	117.5	119.43	121.89	5.00	6.17	6.02
	11.98			115.0			5.00		

[1] Blanks represent excluded results due to error.

[2] uc = results calculated based on uncorrected moisture contents

c = results calculated based on corrected moisture contents

Table 5.10. Actual and predicted results for dried onion flakes packaged in laminate film and stored at 30°C/75%RH.[1,2]

Time (days)	moisture content (% dry basis)			optical index			thiolsulphnate (µm/g)		
	Actual	Predicted		Actual	Predicted		Actual	Predicted	
		uc	c		uc	c		uc	c
0	5.72			54.0			11.64		
14	7.98	7.88	7.96	57.5	59.39	59.47	11.28	10.86	10.86
	7.98			62.5			11.14		
35	11.20	10.31	10.59	85.0	76.23	76.86	8.36	9.20	9.16
	10.91			85.0			7.43		
43	11.59	11.07	11.45	90.0	84.48	85.47	7.50	8.53	8.46
	11.46			92.5			7.43		
54	12.57	11.99	12.52	102.5	97.05	98.63	6.50	7.61	7.52
	---			102.5			6.36		
62	13.21	12.60	13.23	120.0	---	109.02	5.78	6.97	6.86
	13.15			120.0			5.86		
80	13.87	13.79	14.68	130.0	---	---	4.21	5.64	---
	13.80			125.0			4.50		

[1] Blanks represent excluded results due to error.

[2] uc = results calculated based on uncorrected moisture contents

c = results calculated based on corrected moisture contents

Table 5.11. Actual and predicted results for dried onion flakes packaged in LDPE film and stored at 40°C/90%RH.[1]

Time (days)	moisture content (% dry basis)			optical index			thiolsulphinate (µm/g)		
	Actual	Predicted		Actual	Predicted		Actual	Predicted	
		uc	c		uc	c		uc	c
0	5.72			54.0			11.64		
6	8.27	7.64	7.91	67.5	72.14	72.75	9.07	10.52	10.49
	8.48			70.0			9.36		
13	9.95	9.55	10.26	90.0	105.0	107.85	7.71	8.86	8.73
	10.22			102.5			7.43		
20	11.77	11.19	12.46	110.0	148.6	152.29	5.43	7.16	6.92
	12.07			122.5			4.43		

[1] uc = results calculated based on uncorrected moisture contents

c = results calculated based on corrected moisture contents

Table 5.12. Actual and predicted results for dried onion flakes packaged in laminate film and stored at 40°C/90%RH.[1,2]

Time (days)	moisture content (% dry basis)			optical index			thiolsulphinate (μm/g)		
	Actual	Predicted		Actual	Predicted		Actual	Predicted	
		uc	c		uc	c		uc	c
0	5.72			54.0			11.64		
6	9.32	8.30	8.59	65.0	74.13	74.72	8.78	10.43	10.40
	9.48			67.5			8.50		
13	11.99	11.74	11.52	110.0	113.52	114.14	7.07	8.59	8.46
	11.84			112.5			7.14		
20	14.34	13.78	14.15	140.0	159.35	163.37	4.57	6.75	6.53
	14.46			125.0			4.07		

[1] uc = results calculated based on uncorrected moisture contents

c = results calculated based on corrected moisture contents

Table 5.13. Actual and predicted values for dried green beans packaged in LDPE film and stored at 30°C/75%RH.

Time (days)	moisture content (%dry basis)		chlorophyll a (mg/kg)		SO_2 (mg/kg)
	Actual	Predicted	Actual	Predicted	Actual
0	5.66		467.0		549.0
14	7.31	7.28	461.36	459.68	484.8
	7.46		462.58		458.4
36	9.12	9.26	447.29	440.37	200.7
	9.44		403.28		241.6
57	10.94	10.73	391.20	412.95	73.7
	11.22		389.75		72.0
70	11.52	11.50	338.98	391.80	74.2
	11.66		353.73		78.2
78	12.03	11.93	342.85	377.28	62.5
	11.97		348.65		78.9
85	12.31	12.28	315.60	363.69	21.1
	11.88		317.95		51.2

Table 5.14. Actual and predicted values for dried green beans packaged in laminate film and stored at 30°C/75%RH.

Time (days)	moisture content (%dry basis)		chlorophyll a (mg/kg)		SO_2 (mg/kg)
	Actual	Predicted	Actual	Predicted	Actual
0	5.66		467.0		549.0
14	7.86	7.92	461.36	458.81	474.8
	7.83		462.58		471.6
36	11.08	10.44	429.64	434.50	156.0
	10.74		434.48		196.3
57	12.54	12.18	357.11	398.82	70.0
	12.51		369.44		72.5
70	13.20	13.04	314.16	371.30	58.3
	13.17		323.06		62.34
78	13.30	13.52	280.23	352.51	63.8
	13.22		273.94		57.9

Table 5.15. Actual and predicted values for dried green beans packaged in LDPE film and stored at 40°C/90%RH.

Time (days)	moisture content (%dry basis)		chlorophyll *a* (mg/kg)		SO_2 (mg/kg)
	Actual	Predicted	Actual	Predicted	Actual
0	5.66		467.0		549.0
10	9.16	8.86	414.65	440.03	169.0
	8.90		442.41		214.7
18	11.59	10.86	379.97	401.68	68.4
	11.35		353.31		83.7
24	12.85	12.16	302.48	362.95	41.3
	12.04		334.39		47.37

Table 5.16. Actual and predicted values for dried green beans packaged in laminate film and stored at 40°C/90%RH.

Time (days)	moisture content (%dry basis)		chlorophyll a (mg/kg)		SO_2 (mg/kg)
	Actual	Predicted	Actual	Predicted	Actual
0	5.66		467.0		549.0
10	10.40	9.87	422.72	435.59	141.6
	10.18		390.96		125.9
18	13.33	12.34	325.44	387.03	52.5
	12.65		319.15		42.2
24	14.17	13.90	243.80	337.30	26.5
	13.75		244.69		26.5

deterioration at various storage time periods for the two products.

The plots of the moisture content against storage time are shown in Figures 5.7 to 5.10. It can be seen that the predicted moisture contents for green beans compare well with the actual values, at both storage conditions and using the two packaging films. However for onion flakes, the predicted moisture contents were consistently lower than the actual values and more so for the samples stored at the higher temperature and RH condition.

This can be explained by the fact that water is produced during the browning reaction. Nonenzymic browning occurs during the storage of dried onion flakes and this would lead to an increase in the moisture content of the product. This phenomenon was also observed by Mizrahi et al. (1970) as a result of the browning reaction in dried cabbage.

The differences between the predicted and actual moisture content values for onion flakes were observed to increase with storage time, and generally in proportion to the increase in browning in the onion flakes. This proportion was found to be around 0.015 (i.e. for every 1 point increase in optical index, moisture content difference increased by 0.015). This factor is purely an empirical value and should be used with caution.

The correction factor was incorporated in the computer iteration procedure (after step 5) for dried onion flakes. Mizrahi et al. (1970) also used a correction factor for moisture content in their study. As shown in Figures 5.7 and 5.8, the corrected moisture contents are much closer to the actual values.

There was no significant difference at $p=0.05$ using the Students's t-test for all cases except for onion flakes

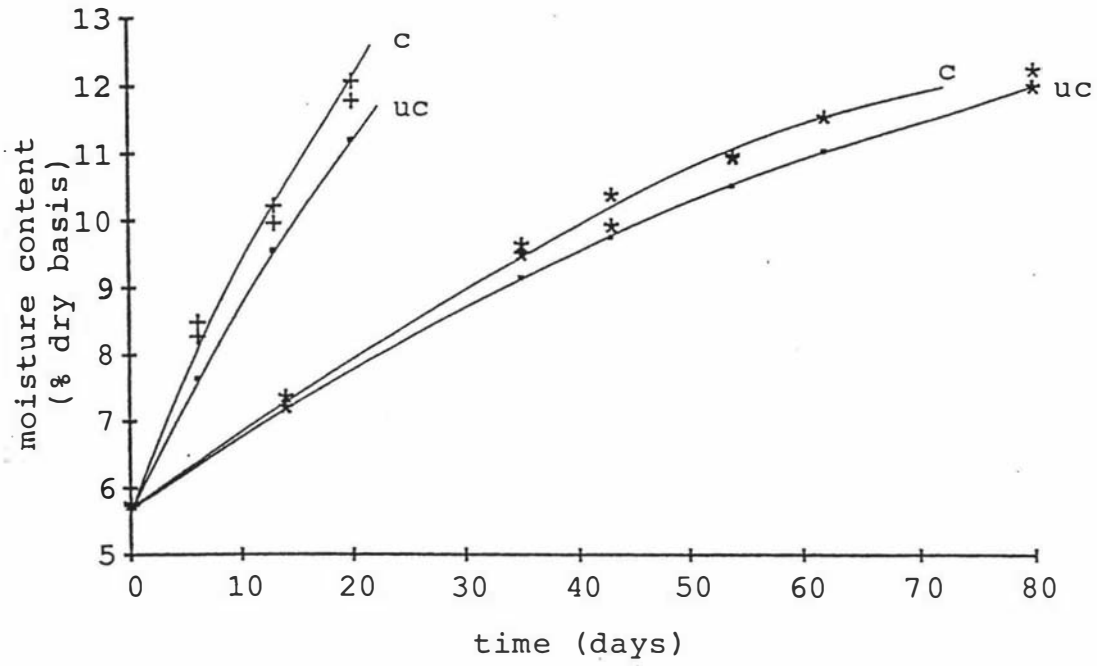

Fig. 5.7. Corrected (c) and uncorrected (uc) moisture contents for onion flakes packaged in LDPE film and stored at 30°C/75%RH (*) and 40°C/90%RH (+).

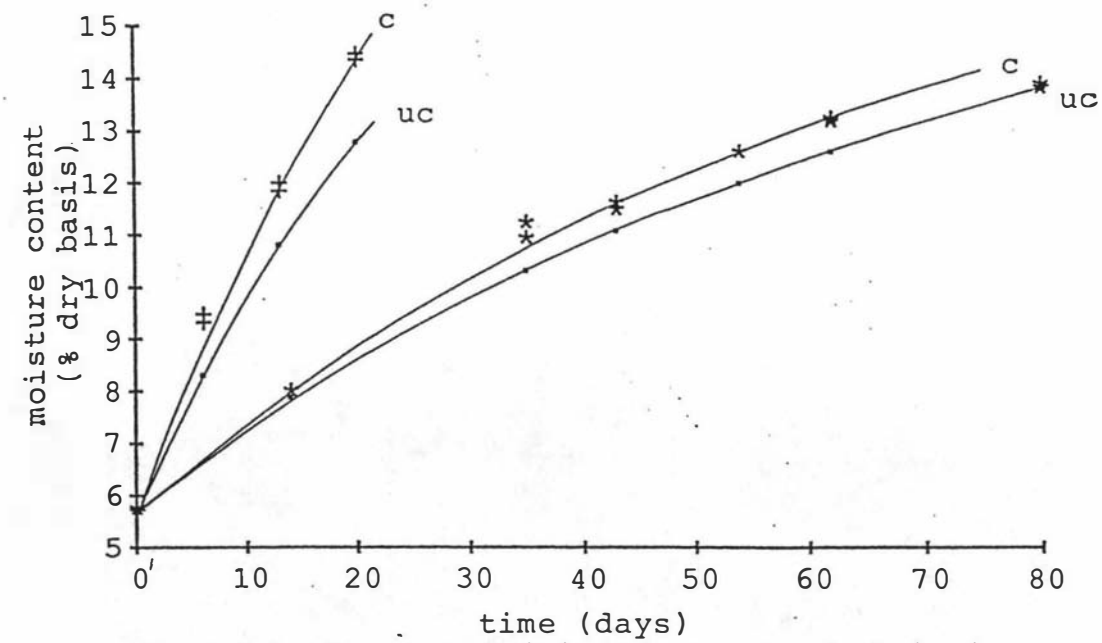

Fig. 5.8. Corrected (c) and uncorrected (uc) moisture contents for onion flakes packaged in laminate film and stored at 30°C/75%RH (*) and 40°C/90%RH.

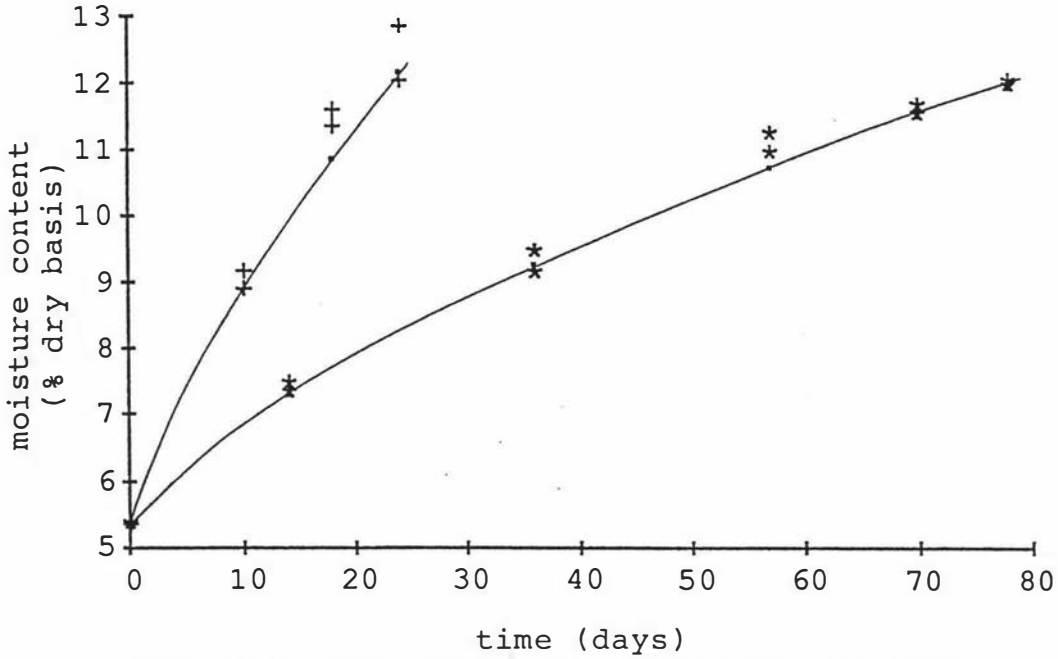

Fig. 5.9. Moisture contents for green beans packaged in LDPE film during storage at 30°C/75%RH (*) and 40°C/90%RH (+).

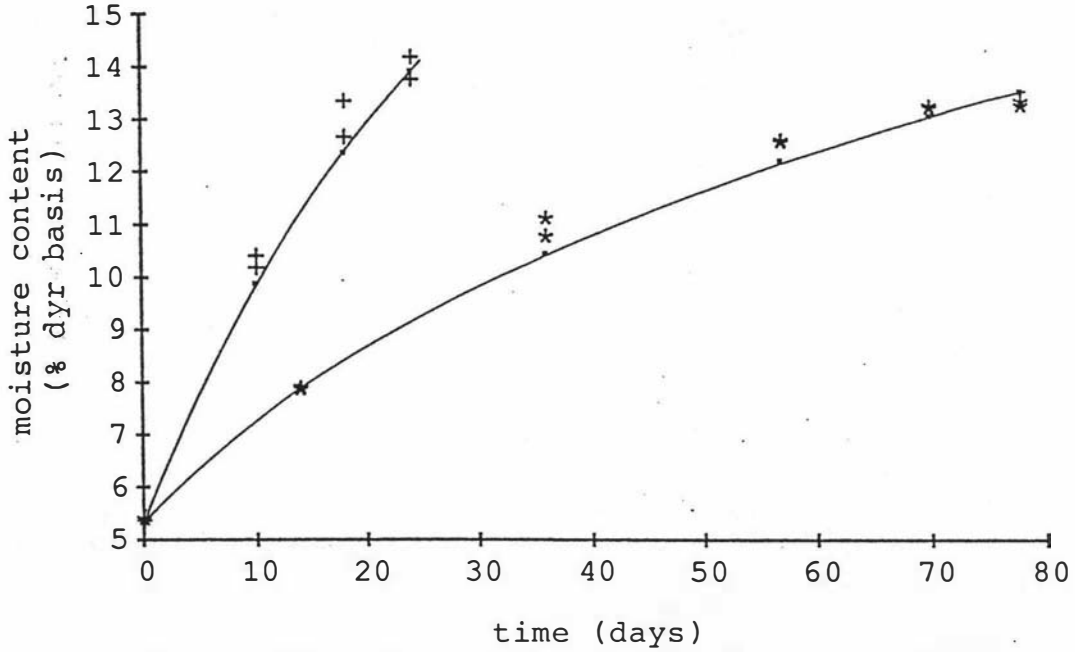

Fig. 5.10. Moisture contents for green beans packaged in laminate film during storage at 30°C/75%RH (*) and 40°C/90%RH (+).

packaged in laminate film and stored at 40°C and 90%RH which was not significant at p=0.01. This indicates that the moisture transport prediction model (described by steps 1 to 5 in the computer iteration) used in this study satisfactorily predicts the moisture content changes in dried green beans and onion flakes packaged in flexible films, and the program could be applied to most dried products whenever the variable storage conditions are known. This information may be used to determine the end of shelf life of a dried food product if unacceptability is solely dependent on moisture content or water activity (e.g. loss of crispness in biscuits). For such cases, the iteration procedure can be terminated at this point.

This part of the study demonstrates that the principles and assumptions involved in the derivation of the mathematical model are valid and that good simulations of moisture content changes in packaged dried products can be made by using a computer iterative technique.

Tables 5.9 to 5.12 show that the predicted and actual results for browning in onion flakes agree reasonably well for both packaging films at the two storage conditions. The effect of the correction for the increase of moisture content due to browning was evaluated by comparing the predicted values with and without this correction. The correction for moisture generated in browning improved the prediction, but the error due to ignoring this correction is not large. Predictions at a lower temperature and humidity such as at 20°C and 55% RH (Table 5.17) show that the errors due to omission of this correction remain relatively small. However, there may be other conditions in which disregard of the correction may have greater significance.

The corrected moisture content was also used in the calculation of thiolsulphinate loss in dried onion flakes.

Table 5.17. Predicted results for browning in dried onion flakes stored at 20°C/55%RH based on uncorrected (uc) and corrected (c) moisture contents.[1,2]

Time (days)	LDPE				Laminate			
	Moisture Content (%db)		Optical Index		Moisture Content (%db)		Optical Index	
	uc	c	uc	c	uc	c	uc	c
100	8.11	8.16	57.94	57.99	8.68	8.74	59.03	59.10
200	9.50	9.64	67.48	67.83	10.15	10.31	70.51	70.91
300	10.36	10.62	80.38	81.33	10.95	11.23	85.22	86.26
400	10.93	11.30	95.31	97.16	11.42	11.78	101.67	103.57
end of shelf life	11.17	11.54	105.01	105.07	11.48	11.82	105.01	105.01

[1] Initial moisture content = 5.72%
Initial optical index = 54

[2] End of shelf life:
LDPE uncorrected = 460.5 days
LDPE corrected = 446.5 days
Laminate uncorrected = 419.5 days
Laminate corrected = 408.0 days

It can be seen in Tables 5.9 to 5.12 that the agreement between the actual and predicted thiolsulphinate results was not as good as that for nonenzymic browning. At 30°C, for both packaging films, the agreement was reasonable up to an a_w of around 0.53. Above this a_w, the difference between the actual and predicted values became greater with an increase in a_w. This would be partly due to the cumulative error effect as a result of the iteration technique (i.e. the errors from each time interval add up).

Because of the complexity of the systems being modelled there are a number of possible reasons that could have contributed to this observed discrepancy. The moisture transfer model could have affected the results but this is unlikely since the same model when applied to the prediction of browning in onion flakes, gave good results. This suggests that the possible reason has to do with the characteristics of the product. A different batch of samples from those that were used for the kinetic experiments in Chapter 4 was used in the present study. The sorption characteristics of the product could be different but once again this is unlikely. If the sorption characteristics had been changed then it would be expected that the browning results for the same set of samples would also have been adversely affected, but such was not the case.

Since the differences between the actual and predicted values seemed to increase with an increase in the a_w of the product, it is more likely that the sensitivity of the reaction leading to thiolsulphinate loss as a function of changes in water activity of the onion flakes was higher for this particular batch of onion flakes. This speculation needs to be investigated further to be able improve the present model for thiolsulphinate loss in onion flakes.

Nonenzymic browning is the predominant reaction determining the shelf life of onion flakes at the high temperatures used in the present study. Thus, the browning results served as the basis for calculating the shelf life of the onion flakes stored at the conditions tested. A comparison of the actual and predicted shelf lives given in Table 5.18 shows a good agreement between them for all simulated variables. This indicates the adequacy of the iterative technique for the successful prediction of the shelf life of dried onion flakes based on nonenzymic browning.

At low temperatures (e.g. 20^{o}C) and low water activities however, the predominant deteriorative reaction occurring in onion flakes is the loss of pungency which is indicated by thiolsulphinate loss. Thus, if the prediction of the shelf life of onion flakes at 20^{o}C was based on the thiolsulphinate model then the result would be overestimated.

The results for chlorophyll a loss in dried green beans during storage are presented in Tables 5.13 to 5.16. A similar problem to that of thiolsulphinate loss, was observed for chlorophyll a loss. Acceptable agreement between predicted and actual results were obtained for greenbeans up to an a_w of around 0.60. Above this a_w, the rate of the actual reaction was faster resulting in significantly lower actual values. A similar explanation as was given for thiolsulphinate loss in onion flakes is suggested.

The actual and predicted shelf lives of green beans based on chlorophyll a loss are given in Table 5.19. The agreement between the results was not as good as was observed for onion flakes based on browning. However, the prediction technique can still be considered of practical value in giving shelf life estimates. The prediction

Table 5.18. Actual and predicted shelf lives for dried onion flakes based on nonenzymic browning (days).

Film	30°C/75%RH		40°C/90%RH		20°C/55%RH
	Actual	Predicted	Actual	Predicted	Predicted
LDPE	63	66	15	13	446 403[a]
Laminate	58	59	12	12	408 378[a]

[a] Predicted shelf life based on thiolsulphinate loss.

Table 5.19. Actual and predicted shelf lives for dried green beans based on chlorophyll *a* loss (days).

Film	30°C/75%RH		40°C/90%RH		20°C/55%RH
	Actual	Predicted	Actual	Predicted	Predicted
LDPE	84	102	25	29	556
Laminate	70	88	18	25	516

models may need to be modified to account for the observed discrepancy in the results.

The predicted shelf lives of the two products at 20°C and 55%RH are presented in Tables 5.18 and 5.19. This demonstrates the use of accelerated testing methods and kinetic principles to predict shelf life at lower levels of experimental variables (i.e. in this case temperature and humidity) in considerably shorter time periods.

Aside from predicting the shelf life of dried foods, the moisture transport prediction model can also be used to determine the optimum package system to keep the product within certain a_w limits for its shelf life. Different overall permeances or permeability equations can be substituted into the prediction model to determine the best combination.

Results of the storage trials and the computer simulations show that if the desired shelf life of the dried onion flakes and green beans was one year, and if the products were to be stored in conditions similar to that tested (i.e. tropical conditions) then both the LDPE and laminate films used would provide inadequate protection against moisture gain and quality deterioration. However, for a sample stored at 20°C and 55%RH, the moisture content prediction would show that if the objective was to keep the dried vegetable below an a_w of 0.60 for one year, then both films would adequately provide the required protection.

The models can also be used to predict the effect of changes in parameters like external RH, area of package to foods weight ratio (A/W_s) and temperature, on the quality and shelf life of dried foods packaged in a particular film.

The computer iteration technique is applicable as well to prediction under simulated variable storage and distribution conditions. If the variable conditions which the products would undergo during distribution and storage are known then it would be easy to simulate these conditions to get workable initial estimates of shelf life. Not having to conduct numerous actual tests would greatly reduce testing time and costs.

5.5 CONCLUSION

Mathematical models were developed which described the quality deterioration in dried onion flakes, green beans and apricots as functions of time, water activity and temperature. The models successfully predicted the shelf lives of the unpackaged dried foods stored at different temperature and RH conditions.

A computer iteration procedure was developed based on the equations obtained describing the kinetic reactions and moisture isotherms of the dried vegetables, the permeability characteristics of the packaging films, and the moisture transfer through the packaging films. Acceptable results on moisture content, extent of deteriorative reaction and shelf life were predicted for dried onion flakes and green beans.

The results of this study demonstrate that the principles and assumptions involved in the derivation of the mathematical models are valid and that good simulations of quality change and shelf life can be made by using a computer iterative technique.

CHAPTER 6
SUMMARY AND CONCLUSIONS

The development of a quantitive approach to the shelf life prediction of packaged dried foods, specifically onion flakes, sliced green beans, and apricot halves, involved the mathematical modelling of product and package characteristics as functions of environmental conditions, i.e. temperature and humidity.

The WVTR and permeability constants of LDPE (60 μm), PET (12 μm) and a laminate of both films (30 μm LDPE and 12 μm PET) were determined at different temperatures and humidities. A general model was developed which satisfactorily predicted permeances of the three films as a function of external relative humidity and temperature. It is suggested that models of similar form may be applied to other flexible films for prediction purposes.

The moisture sorption isotherms of the three products were determined at 20, 30, and 40°C. The GAB model adequately described the isotherms of the dried foods over a wide range of water activities (a_w = 0.20 to 0.90) and temperatures. This supports the current view that the GAB iostherm model can be considered to provide the best equation for the description and interpretation of food isotherms. A weighted, direct nonlinear regression anaylsis of sorption data is recommended for the development of GAB equations.

The kinetics of the different deteriorative reactions limiting the shelf life of the three dried products and their acceptable limits were determined. Storage trials were conducted on the three products under different relative humidity and temperature conditions.

Nonenzymic browning in onion flakes and chlorophyll a loss in green beans were better described by a zero-order reaction model. Thiolsulphinate loss in onion flakes, nonenzymic browning in apricot, and SO_2 loss in both greenbeans and apricots followed a first-order reaction model better. For onion flakes and green beans, the rates of reactions were found to increase with an increase in the water activity of the products. Empirical equations were derived describing the relationship between rates of reactions and water activity. The Arrhenius equation satisfactorily described the relationship between rate constants and temperature.

Nonenzymic browning and sulphur dioxide loss in dried apricots exhibited a trend wherein the rate increased with water activity until a maximum was reached and then decreased with a further increase in water activity. The reactions followed the Arrhenius equation at all three water activity levels.

Mathematical models of quality deterioration in the dried foods were developed based on the theoretical and empirical equations obtained from the kinetics of the deteriorative reactions as functions of storage time, water activity and temperature. There was close agreement between the actual and predicted shelf lives of the unpackaged dried foods stored under different temperature (20 to 40^{o}C) and RH (32% to 59% RH for onion flakes and green beans; 59% to 81% RH for apricot) conditions.

This demonstrates the validity of using mathematical models based on kinetic principles for the prediction of quality deterioration over a range of environmental conditions. It is expected that other dried foods could be described by similar kinetic expressions and hence the basic assumptions of the shelf life models could have a general application

to dried food products, specifically dried fruits and vegetables. It is suggested that improvements in the prediction model for dried apricots could be made by investigating and isolating the effect of oxygen on quality deterioration.

In order to predict the shelf life of the dried products packaged in the polymeric films, a computer iterative technique was developed which combined the models describing the permeability characteristics of the packaging films, the sorption properties of the product, the kinetics of deterioration in the products and the mass transport equation. By solving these equations numerically with the aid of a computer, moisture gain, quality loss and shelf life of the products were predicted under various storage conditions. There was reasonable agreement between experimental results and those predicted by the computer simulation program.

This further demonstrates that the principles and assumptions involved in the derivation of the mathematical models are valid and that good simulations of moisture content and quality changes in packaged dried products can be made by using a computer iterative technique.

With the use of this technique, the effect of changes in parameters such as environmental conditions, packaging material, and package surface area to foods weight ratio on product quality and shelf life could easily be predicted without having to conduct laborious and expensive actual tests. The use of iterative simulation is a very versatile method and can lead towards product and process optimisation.

The results of the present study show the great potential in using a quantitative approach to food quality deterioration and shelf life prediction. It is foreseen

that future developments in the areas of accelerated tests, analytical methods, and an understanding of the mechanisms of quality deterioration in foods would lead to more accurate prediction and greater utilisation of the quantitative approach in shelf life prediction.

Having demonstrated the validity and utility of this approach, it is now over to the food industry to make wider use of what is a very valuable yet comparatively inexpensive tool.

In 1979, Marcus Karel, one of the leaders in the field of food product and process optimisation, stated that the major stumbling blocks to the rapid development of quantitative procedures are:

a. There are relatively few practising food technologists with a thorough background in mathematics, physical chemistry, and engineering, the disciplines required for the quantitative analysis of optimisation problems.
b. Relatively little is known about many important aspects of foods. Information on physical properties, kinetic behavior of reacting species, and interactions among food components is still scarce.

Karel believed that one of the major tasks for the present generation of food technologists is to overcome this stumbling blocks.

I hope that this study has contributed towards the achievement of this objective.

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Appendix 2.1. Adsorption isotherm data for Microcrystalline cellulose (MCC) at 25°C.[1]

a_w	Mean Moisture Content (% dry basis)		Standard Deviation	
	Reference[2] ($X_o \pm D_{cr}$)	Actual (X)	Reference (s_r)[3]	Actual (s)
0.11	2.02 ± 0.50	1.62	.04	.04
0.23	3.19 ± 0.44	2.80	.04	.04
0.33	4.06 ± 0.51	3.77	.04	.04
0.44	5.04 ± 0.37	4.56	.05	.08
0.53	5.82 ± 0.54	5.89	.08	.02
0.58	6.48 ± 0.43	6.17	.02	.05
0.71	8.21 ± 0.38	----	.08	---
0.75	8.83 ± 0.62	8.24	.07	.05
0.83	10.95 ± 0.59	10.14	.08	.06
0.90	12.96 ± 0.60	----	.09	---
0.94	----	13.11	---	.11
Mean	± 0.498	---	.06	.06

[1]Reference values from Wolf et al. (1984).

[2] $$D_{cr} = \frac{1}{\sqrt{2}} \sqrt{R^2 - r^2 \left(\frac{n - 1}{n} \right)}$$

where R = reproducibility
r = repeatability

[3] $s_r = \frac{r}{2.83}$ at the 95% probability level

Appendix 3.1. Change in absorbance at 690 ηm of the detector film, for LDPE (60 μm) exposed to different external RHs at 20°C.[1]

External RH (%)	Time (hr)	Replicate 1	2	3
59.1	0.0	.000	.000	.000
	1.5	.010	.015	.012
	3.0	.017	.021	.017
	4.5	.031	.033	.030
	6.0	.039	.039	.038
	7.5	.049	.049	.044
	9.0	.057	.056	.051
75.5	0.0	.000	.000	.000
	1.5	.009	---	.010
	3.0	.018	.017	.024
	4.7	.033	.038	.036
	6.0	.052	.046	.049
	7.5	.057	.063	.063
	9.0	---	.073	---
94.6	0.0	.000	.000	.000
	1.5	.017	.015	.015
	3.0	.041	.027	.034
	4.7	.052	.038	.050
	6.0	.064	.062	.071
	7.5	.088	.098	.101

[1]Blanks represent excluded results due to error.

Appendix 3.2. Change in absorbance at 690 ηm of the detector film, for LDPE (60 μm) exposed to different external RHs at 30°C.[1]

External RH (%)	Time (hr)	Replicate 1	2	3
56.0	0.0	.000	.000	.000
	1.0	.020	.017	.017
	2.0	.029	.023	.025
	3.0	.036	.036	.031
	4.0	.051	.041	.049
	7.0	.081	.077	.083
	8.0	.092	.092	.092
75.1	0.0	.000	.000	.000
	1.0	.021	.023	.025
	2.0	.034	.041	.038
	3.0	.048	.053	---
	4.0	.067	.069	.072
	7.0	.117	.120	.124
	8.0	.134	.137	.150
92.3	0.0	.000	.000	.000
	1.0	.028	.020	.033
	2.0	.049	.038	.039
	3.0	.069	.071	.061
	4.0	.090	.086	.075
	7.0	.175	.163	.148
	8.0	.214	.187	.195

[1]Blanks represent excluded results due to error.

Appendix 3.3. Change in absorbance at 690 ηm of the detector film, for LDPE (60 μm) exposed to different external RHs at 40°C.[1]

External RH (%)	Time (hr)	Replicate 1	2	3
53.2	0.0	.000	.000	.000
	1.0	.019	.017	---
	2.0	.040	.035	.037
	3.25	.058	.057	.055
	4.0	.075	.075	.069
	5.0	.097	.085	.091
	6.0	.119	.114	.113
74.7	0.0	.000	.000	.000
	1.0	.026	.023	.025
	2.0	.062	.057	.066
	3.25	.098	.092	.103
	4.0	.128	.120	.140
	5.0	.166	.158	.175
	6.0	.202	.197	.217
89.0	0.0	.000	.000	.000
	1.0	.034	.035	.027
	2.0	.078	.071	.075
	3.25	.132	.125	.127
	4.0	.174	.166	.168
	5.0	.234	.228	.237
	6.0	.316	.308	.328

[1]Blanks represent excluded results due to error.

Appendix 3.4. Change in absorbance at 690 ηm of the detector film, for polyester (12 μm) exposed to different external RHs at 20°C.[1]

External RH (%)	Time (hr)	Replicate 1	2	3
59.1	0.0	.000	.000	.000
	1.5	.069	.089	.059
	2.5	.116	.130	.113
	3.5	.173	.184	.156
	4.5	.224	.254	.227
	5.5	.276	.299	.272
	6.5	.324	.356	.336
75.5	0.0	.000	.000	.000
	1.5	.117	.111	.094
	2.5	.207	.193	.175
	3.5	.297	.278	.254
	4.5	.402	.385	.354
	5.5	.477	.459	.428
	6.5	.554	.535	.516
94.6	0.00	.000	.000	.000
	1.17	.121	.132	.127	.140
	1.67	.175	.192	.186	.201
	2.17	.227	.249	.240	.260
	3.17	.342	.381	.356	.391
	4.17	.468	.507	.492	.511
	5.17	.575	.615	.603	.620
	6.17	.677	.717	.715	.720

[1]Blanks represent excluded results due to error.

Appendix 3.5. Change in absorbance at 690 ηm of the detector film, for polyester (12 μm) exposed to different external RHs at 30°C.[1]

External RH (%)	Time (hr)	Replicate 1	2	3
56.0	0.0	.000	.000	.000
	1.58	.102	.096	.090
	2.58	.200	.193	.182
	3.58	.299	.294	.275
	4.58	.400	.400	.390
	5.58	.500	.495	.491
	6.58	.601	.601	.600
75.1	0.0	.000	.000	.000
	1.42	.127	.145	.132
	2.42	.263	.315	.281
	3.42	.431	.486	.445
	4.42	.612	.654	.624
	5.42	.755	.757	.770
92.3	0.00	.000	.000	.000
	1.25	.187	.213	.179	.192
	2.25	.422	.462	.418	.430
	3.25	.663	.652	.656	.650

[1]Blanks represent excluded results due to error.

Appendix 3.6. Change in absorbance at 690 ηm of the detector film, for polyester (12 μm) exposed to different external RHs at 40°C.[1]

External RH (%)	Time (hr)	Replicate 1	2	3
53.2	0.0	.000	.000	.000
	1.0	.102	.085	.097
	1.5	.179	.156	.170
	2.0	.258	.231	.261
	2.5	.328	.301	.336
	3.0	.407	.373	.409
	3.5	.465	.437	.474
74.7	0.00	.000	.000	.000
	1.42	.221	.229	.241
	1.92	.373	.390	.391
	2.42	.522	.542	.531
	2.92	.646	.672	.659
	3.42	.746	.775	.760
89.0	0.0	.000	.000	.000
	1.0	.190	.202	.201
	1.5	.346	.364	.358
	2.0	.540	.545	.544
	2.5	.700	.707	.719

[1]Blanks represent excluded results due to error.

Appendix 3.7. Change in absorbance at 690 ηm of the detector film, for the laminate film exposed to different external RHs at 20°C.[1]

External RH (%)	Time (hr)	Replicate 1	2	3
59.1	0.0	.000	.000	.000
	1.5	.014	.016	.018
	3.0	.021	.022	.027
	4.5	.034	.036	.037
	6.0	.043	.046	.052
	7.5	.055	.059	.064
	9.0	.071	.076	.083
75.5	0.0	.000	.000	.000
	1.32	.016	.012	.020
	2.82	.037	.031	.043
	4.32	.053	.048	.066
	5.82	.073	.062	.089
	7.32	.095	.081	.111
	8.82	.119	.100	.134
94.6	0.00	.000	.000 .000	.000
	1.0	.012	.017 .019	.017
	2.5	.039	.044 .040	.044
	4.0	.062	.071 .078	.069
	5.5	.085	.099 .105	.096
	7.1	.116	.129 .140	.128
	8.5	.137	.157 .160	.149

[1]Blanks represent excluded results due to error.

Appendix 3.8. Change in absorbance at 690 ηm of the detector film, for the laminate film exposed to different external RHs at 30°C.[1]

External RH (%)	Time (hr)	Replicate 1	2	3
56.0	0.0	.000	.000	.000
	1.67	.023	.028	.028
	3.00	.044	.047	.048
	4.50	.070	.075	.076
	6.00	.085	.089	.096
	7.50	.105	.113	.122
75.1	0.0	.000	.000	.000
	1.50	.013	.017	.015
	2.92	.052	.056	.045
	4.50	.093	.094	.088
	6.00	.128	.132	.122
	7.50	.166	.169	.164
92.3	0.00	.000	.000 .000	.000
	2.00	.028	.025 .030	.029
	3.67	.083	.072 .079	.072
	5.00	.123	.112 .114	.108
	6.50	.188	.176 .165	.157
	7.50	.235	.232 .205	.193
	8.50	---	--- .256	.243
	9.50	---	--- .315	.302

[1]Blanks represent excluded results due to error.

Appendix 3.9. Change in absorbance at 690 ηm of the detector film, for the laminate film exposed to different external RHs at 40°C.[1]

External RH (%)	Time (hr)	Replicate 1	2	3
53.2	0.0	.000	.000	.000
	1.72	.002	.006	.005
	2.72	.040	.038	.030
	3.72	.059	.061	.058
	4.72	.089	.084	.086
	5.72	.122	.117	.118
	6.72	.152	.144	.151
	7.72	.184	.172	.186
	8.72	.212	.199	.211
74.7	0.0	.000	.000	.000
	1.48	.013	.030	.022
	2.48	.068	.084	.066
	3.48	.118	.133	.111
	4.48	.180	.184	.164
	5.48	.231	.237	.221
	6.48	.293	.292	.277
	7.48	.341	.338	.315
89.0	0.00	.000	.000	.000
	1.18	.008	.023	.031
	2.18	.057	.068	.082
	3.18	.108	.126	.135
	4.18	.172	.196	.204
	5.18	.254	.275	.283
	6.18	.337	.363	.361
	7.18	.426	.437	.435
	8.18	.507	.513	.486

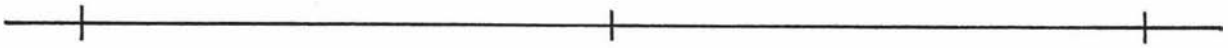
[1]Blanks represent excluded results due to error.

Appendix 4.1. Sample of the sensory score sheet.

Name: Set No.
Date:

A. Please evaluate the samples of dried apricot for the intensity of the brown colour. Remove the cover, one sample at a time, evaluate the sample, answer the question in Part B, and replace the cover after each evaluation.

Place a vertical mark across the line and indicate the code number of the sample at that point which best describes the intensity of the brown colour.



imperceptible moderate high

B. Do you consider the dried apricot sample acceptable in terms of colour? Place a check mark under the appropriate answer.

Sample	Acceptable	Not Acceptable
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

Thank you.

Appendix 4.2. Results of the sensory evaluation and objective measurements (absorbance) for browning in dried apricot.[1]

Sample No.	Trial 1		Trial 2	
	Absorbance	Sensory Scores	Absorbance	Sensory Scores
1	0.060	1.34	0.053	1.35
2	0.076	2.80	0.078	3.48
3	0.115	5.78	0.144	5.82
4	0.195	7.17	0.192	8.28
5	0.258[u]	10.91	0.255[u]	10.85
6	0.506[u]	13.40	0.370[u]	12.52

[u] considered unacceptable by the panelists

[1]Mean scores for 12 panelists.
Pooled estimate of the standard deviation = 0.61.

Appendix 4.3. Changes in the quality parameters of dried onion flakes during storage at 20°C and 33% RH.

Time (days)	Moisture Content (%wb)	Browning (optical index)	Thiolsulphinate (µm/g)
0	4.46	61.88	12.43
0	4.48	62.50	12.50
0	4.35	64.04	12.07
0	4.44	66.50	12.21
0	4.46	64.36	12.28
30	4.64	---	12.71
30	4.86	---	12.93
57	4.82	---	13.14
57	4.83	60.00	13.36
85	4.87	60.00	12.21
85	5.06	62.50	11.93
129	4.68	57.50	11.57
129	4.69	57.50	11.07
172	4.86	69.00	---
223	5.25	57.50	10.85
223	5.26	57.50	10.93
254	--	57.50	10.64
254	--	57.50	10.93
298	5.06	67.50	9.86
298	5.06	65.00	10.21
349	--	62.50	9.71
349	4.90	62.50	9.64
384	--	60.00	---
384	--	---	9.78
442	5.31	65.00	8.93
442	5.40	62.50	---
475	--	65.00	---
475	--	70.00	---
505	5.29	65.00	9.50
505	5.31	67.50	9.28
566	5.11	62.50	8.43
566	5.05	60.00	8.86
631	5.17	70.00	---
631	5.14	70.00	---

[1] Blanks represent excluded results due to error.

Appendix 4.4. Changes in the quality parameters of dried onion flakes during storage at 20°C and 43% RH.

Time (days)	Moisture Content (%wb)	Browning (optical index)	Thiolsulphinate (µm/g)
0	4.46	61.88	12.43
0	4.48	62.50	12.50
0	4.35	64.04	12.07
0	4.44	66.50	12.21
0	4.46	64.36	12.28
30	6.61	60.00	12.36
30	6.55	55.00	12.57
57	7.04	60.00	12.28
57	7.07	60.00	12.57
85	7.36	67.50	10.28
85	7.33	65.00	---
114	7.28	67.50	10.43
114	7.40	67.50	10.86
141	7.46	70.00	9.64
172	7.22	67.50	9.50
172	7.28	67.50	9.14
198	7.39	72.50	9.14
198	7.47	67.50	8.71
223	7.53	72.50	8.71
223	7.45	70.00	9.36
254	--	77.50	7.86
254	--	77.50	7.71
298	7.48	85.00	7.78
298	7.21	82.50	7.36
323	7.20	85.00	7.14
323	7.11	77.50	6.92
349	7.38	90.00	6.60
349	7.42	92.50	6.78
384	--	87.50	6.14
384	--	---	6.64
442	7.34	90.00	6.21
442	7.70	90.00	---
475	--	107.50	6.21
475	--	107.50	6.28
505	7.59	105.00	6.00
505	7.56	105.00	6.07
566	7.36	100.00	5.64
566	7.43	105.00	5.43
631	7.31	115.00	4.93
631	7.34	112.50	5.14

[1] Blanks represent excluded results due to error.

Appendix 4.5. Changes in the quality parameters of dried onion flakes during storage at 20°C and 59% RH.

Time (days)	Moisture Content (%wb)	Browning (optical index)	Thiolsulphinate (µm/g)
0	4.46	61.88	12.43
0	4.48	62.50	12.50
0	4.35	64.04	12.07
0	4.44	66.50	12.21
0	4.46	64.36	12.28
30	11.01	67.50	10.14
30	10.87	75.00	10.86
57	11.56	77.50	10.00
57	11.51	75.00	10.57
85	11.64	85.00	8.50
85	11.69	85.00	---
101	11.67	85.00	8.28
101	11.71	92.50	8.36
114	11.57	92.50	8.50
114	11.49	95.00	8.64
129	11.54	95.00	8.21
129	11.63	---	8.43
141	11.43	100.00	8.00
141	11.60	102.50	8.00
155	11.52	105.00	7.78
155	11.62	105.00	7.57
172	11.28	110.00	---
172	11.36	107.50	6.86
183	11.67	---	7.71
183	11.64	105.00	7.57
198	11.35	112.50	6.21
198	11.44	117.50	6.00
223	11.81	117.50	---
223	11.65	122.50	6.64
254	---	122.50	5.14
254	---	---	5.50
298	11.28	142.50	4.93
298	11.21	147.50	5.07
323	11.14	152.50	4.50
323	11.10	147.50	4.00

[1] Blanks represent excluded results due to error.

Appendix 4.6. Changes in the quality parameters of dried onion flakes during storage at 30°C and 32% RH.

Time (days)	Moisture Content (%wb)	Browning (optical index)	Thiolsulphinate (µm/g)
0	4.46	61.88	12.43
0	4.48	62.50	12.50
0	4.35	64.04	12.07
0	4.44	66.50	12.21
0	4.46	64.36	12.28
15	4.68	---	12.28
15	4.80	---	---
29	4.83	62.50	11.36
29	4.66	67.50	10.57
38	4.75	70.00	11.64
38	4.65	65.00	11.36
45	4.85	67.50	11.36
45	4.81	65.00	11.64
60	5.03	62.50	9.64
60	5.01	65.00	9.71
71	4.79	67.50	9.57
71	4.79	67.50	9.64
78	5.02	70.00	9.64
78	5.13	70.00	9.78
87	4.45	67.50	8.93
87	4.73	67.50	9.78
113	4.85	70.00	9.14
113	4.77	72.50	8.78
128	4.69	---	8.64
128	4.79	---	8.43
140	4.88	72.50	8.00
140	4.92	72.50	8.00
154	4.68	77.50	7.57
154	4.70	75.00	3.14
171	4.63	72.50	7.36
171	4.66	75.00	7.43
197	5.02	77.50	6.78
197	4.95	80.00	6.64
222	5.15	75.00	6.57
222	5.08	77.50	6.57
253	---	---	5.71
253	---	---	6.28
297	4.89	87.50	5.71
297	4.91	77.50	5.71
322	4.56	---	5.64
322	4.66	---	5.57
348	4.82	85.00	5.71
348	4.78	---	---
383	---	82.50	4.93
383	---	---	4.78
441	5.11	102.50	4.43
474	---	107.50	---
474	---	105.00	---

Appendix 4.7. Changes in the quality parameters of dried onion flakes during storage at 30°C and 43% RH.

Time (days)	Moisture Content (%wb)	Browning (optical index)	Thiolsulphinate (µm/g)
0	4.46	61.88	12.43
0	4.48	62.50	12.50
0	4.35	64.04	12.07
0	4.44	66.50	12.21
0	4.46	64.36	12.28
15	6.60	---	10.43
15	6.70	---	10.28
29	7.20	77.50	---
29	7.21	75.00	10.28
38	6.99	87.50	9.71
38	7.17	85.00	9.78
45	7.28	82.50	9.43
45	7.17	80.00	9.14
60	7.37	90.00	8.00
60	7.43	90.00	7.78
71	7.26	100.00	6.93
71	7.20	95.00	7.28
78	7.43	102.50	7.07
78	7.47	102.50	7.00
87	6.94	97.50	6.71
87	7.14	102.50	7.07
100	7.08	117.50	5.93
100	7.21	122.50	6.00
113	7.21	120.00	5.78
113	7.21	117.50	5.93
128	7.19	117.50	4.64
128	6.99	120.00	---
140	7.19	127.50	4.71
140	7.24	130.00	4.43

[1] Blanks represent excluded results due to error.

Appendix 4.8 Changes in the quality parameters of dried onion flakes during storage at 30°C and 56% RH.

Time (days)	Moisture Content (%wb)	Browning (optical index)	Thiolsulphinate (µm/g)
0	4.46	61.88	12.43
0	4.48	62.50	12.50
0	4.35	64.04	12.07
0	4.44	66.50	12.21
0	4.46	64.36	12.28
15	9.99	---	9.86
15	10.25	---	9.50
29	10.40	105.00	---
29	10.30	100.00	---
38	10.48	110.00	8.36
38	10.43	110.00	8.14
45	10.30	112.50	7.28
45	10.36	112.50	7.50
53	10.45	125.00	6.50
53	10.30	125.00	6.36
60	10.50	127.50	6.64
60	10.57	132.50	6.36
71	10.47	147.50	5.64
71	10.65	152.50	5.28
78	10.61	150.00	5.43
78	10.65	155.00	5.28
87	10.26	157.50	5.28
87	10.22	165.00	5.00
100	10.50	172.50	4.07
100	10.41	177.50	4.50

[1] Blanks represent excluded results due to error.

Appendix 4.9. Changes in the quality parameters of dried onion flakes during storage at 40°C and 32% RH.

Time (days)	Moisture Content (%wb)	Browning (optical index)	Thiolsulphinate (µm/g)
0	4.46	61.88	12.43
0	4.48	62.50	12.50
0	4.35	64.04	12.07
0	4.44	66.50	12.21
0	4.46	64.36	12.28
4	4.40	59.70	11.71
4	4.53	52.24	11.64
8	---	61.88	10.78
8	---	57.97	11.28
12	4.33	61.88	10.71
12	4.46	62.50	11.86
20	4.48	72.11	9.57
20	4.54	72.00	9.64
24	4.55	69.65	10.00
24	4.74	72.14	9.86
30	4.39	82.50	7.86
30	4.43	90.00	8.07
35	4.59	85.00	8.07
35	4.61	82.50	7.28
42	4.49	87.50	---
42	4.53	92.50	7.86
52	4.60	100.00	6.07
52	4.55	97.50	6.50
59	4.72	107.50	5.50
59	4.68	102.50	5.21
70	4.49	115.00	4.71
70	4.49	115.00	---
77	4.61	130.00	4.78
77	4.68	127.50	4.28
86	4.43	132.50	4.00
86	4.14	132.50	3.93

[1] Blanks represent excluded results due to error.

Appendix 4.10. Changes in the quality parameters of dried onion flakes during storage at 40°C and 43% RH.

Time (days)	Moisture Content (%wb)	Browning (optical index)	Thiolsulphinate (µm/g)
0	4.46	61.88	12.43
0	4.48	62.50	12.50
0	4.35	64.04	12.07
0	4.44	66.50	12.21
0	4.46	64.36	12.28
4	5.38	61.88	11.43
4	5.44	56.65	11.50
8	---	57.21	10.57
8	5.31	57.69	10.57
12	6.78	65.00	11.00
12	6.68	70.00	10.28
20	6.81	96.15	8.07
20	6.99	101.99	8.14
24	6.88	99.01	7.86
24	6.82	----	7.57
30	7.06	127.50	5.64
30	6.84	140.00	5.93
35	7.02	135.50	5.36
35	7.00	137.50	5.07
42	6.84	170.00	4.50
42	7.00	170.00	5.00
52	7.03	207.50	4.21
52	7.02	210.00	4.07

[1] Blanks represent excluded results due to error.

Appendix 4.11. Changes in the quality parameters of dried onion flakes during storage at 40°C and 53% RH.

Time (days)	Moisture Content (%wb)	Browning (optical index)	Thiolsulphinate (µm/g)
0	4.46	61.88	12.43
0	4.48	62.50	12.50
0	4.35	64.04	12.07
0	4.44	66.50	12.21
0	4.46	64.36	12.28
4	6.76	---	11.50
4	6.80	---	11.36
8	7.33	57.69	10.71
8	7.38	67.16	9.86
12	9.42	74.26	10.21
12	9.46	78.82	9.86
20	9.57	123.19	6.71
20	9.79	115.02	6.71
24	9.39	151.74	6.07
24	9.81	141.79	6.14
30	9.26	210.00	4.50
30	9.48	190.00	4.21
35	9.36	210.00	3.93
35	9.57	207.50	3.43
42	9.55	257.50	---
42	9.58	252.50	3.00
52	9.49	320.00	2.21
52	9.50	332.50	2.28

[1] Blanks represent excluded results due to error.

Appendix 4.12. Changes in the quality parameters of dried green beans stored at 20°C and 33% RH.[1]

Time (days)	Moisture Content (%wb)	SO_2 (mg/kg)	Chph *a*	Chph *b* (mg/kg)	total chph
0	3.59	465.9	268.4	82.9	351.3
0	3.57	461.4	266.8	81.4	348.1
0	3.65	472.0	257.6	80.8	337.8
0	3.67	463.2	261.7	82.5	344.2
0	3.66	458.9	259.6	82.1	341.7
0	3.58	489.5	258.9	80.1	339.1
28	4.46	373.0	270.1	84.5	354.6
28	4.56	419.6	264.6	80.9	345.6
59	4.42	340.0	263.9	75.8	339.7
59	4.34	361.1	257.8	79.5	337.6
84	4.57	316.0	260.4	76.6	337.0
84	4.55	372.0	262.3	78.2	340.5
141	4.52	402.6	246.5	73.3	319.8
141	4.49	396.1	237.4	74.2	311.6
182	4.60	407.2	232.1	78.1	320.2
182	4.71	375.6	250.3	78.2	238.5
234	5.03	367.6	238.3	79.3	317.6
234	5.05	310.7	227.3	76.8	304.9
260	4.88	388.2	---	---	---
260	4.67	356.2	241.3	77.4	318.6
302	4.59	333.8	227.8	80.9	308.6
302	4.74	344.7	233.2	80.6	313.8
329	4.65	---	---	---	---
329	4.73	294.5	230.3	71.0	301.3
360	4.60	340.1	225.1	73.2	298.3
360	4.69	302.9	232.6	77.5	298.3
512	5.14	---	---	---	---
512	5.18	---	209.1	71.1	280.2
568	4.81	368.4	219.1	81.0	300.1
568	4.82	385.7	224.1	79.7	303.8
637	---	345.1	205.8	69.0	274.9
637	---	375.9	213.0	74.2	287.3

[1] Blanks represent excluded results due to error.

Appendix 4.13. Changes in the quality parameters of dried green beans stored at 20°C and 43% RH.[1]

Time (days)	Moisture Content (%wb)	SO_2 (mg/kg)	Chph a	Chph b (mg/kg)	total chph
0	3.59	465.9	268.4	82.9	351.3
0	3.57	461.4	266.8	81.4	348.1
0	3.65	472.0	257.6	80.8	337.8
0	3.67	463.2	261.7	82.5	344.2
0	3.66	458.9	259.6	82.1	341.7
0	3.58	489.5	258.9	80.1	339.1
28	6.04	385.9	260.6	77.6	338.2
28	5.92	391.1	259.1	80.1	339.2
59	6.42	339.7	248.0	70.0	317.9
59	6.39	324.2	247.9	71.7	319.6
84	6.61	---	248.3	77.6	325.9
84	6.57	315.9	258.4	74.1	332.5
130	6.43	338.8	247.6	71.5	319.1
168	6.62	311.5	248.1	75.6	323.7
168	6.62	305.0	244.7	76.5	321.2
213	---	281.4	224.8	71.2	296.0
213	---	283.0	---	---	---
260	6.51	269.3	217.6	66.0	283.6
260	6.48	254.5	214.5	71.8	286.2
302	6.54	244.0	217.4	75.5	292.9
302	6.55	224.8	214.7	73.8	288.5
329	6.65	198.3	206.3	73.0	279.4
329	6.63	---	218.6	71.1	289.7
360	6.32	185.1	---	---	---
360	6.44	184.7	205.0	65.9	270.9
512	6.90	---	182.3	65.5	247.8
512	6.85	---	176.7	62.8	239.5
568	6.63	---	178.0	67.9	245.9
568	6.57	---	167.2	64.5	231.7

[1] Blanks represent excluded results due to error.

Appendix 4.14. Changes in the quality parameters of dried green beans stored at 20°C and 59% RH.[1]

Time (days)	Moisture Content (%wb)	SO_2 (mg/kg)	Chph a	Chph b (mg/kg)	total chph
0	3.59	465.9	268.4	82.9	351.3
0	3.57	461.4	266.8	81.4	348.1
0	3.65	472.0	257.6	80.8	337.8
0	3.67	463.2	261.7	82.5	344.2
0	3.66	458.9	259.6	82.1	341.7
0	3.58	489.5	258.9	80.1	339.1
28	10.03	296.2	255.1	75.9	330.9
28	9.98	295.2	232.6	73.6	306.3
59	10.41	181.7	225.2	69.4	294.6
59	10.35	222.9	230.6	73.0	303.6
84	10.22	185.6	225.2	69.4	294.6
84	10.29	192.6	219.0	66.4	285.5
114	10.37	161.0	206.2	68.1	274.3
114	10.38	145.4	204.0	64.6	268.6
141	9.60	165.7	172.0	66.4	228.4
141	9.99	147.4	182.0	63.4	245.4
156	10.10	103.6	182.1	63.5	245.5
156	10.31	118.7	173.1	61.6	234.7
168	10.14	116.5	176.1	61.5	237.6
168	9.98	125.1	177.5	63.9	241.4
182	9.95	117.4	156.9	57.5	214.4
182	10.02	112.5	171.7	59.2	230.9
213	---	96.8	---	---	---
213	---	90.6	134.1	49.3	183.4
234	10.23	78.2	---	---	---
234	10.25	77.7	129.0	49.5	178.5

[1] Blanks represent excluded results due to error.

Appendix 4.15. Changes in the quality parameters of dried green beans stored at 30°C and 32% RH.[1]

Time (days)	Moisture Content (%wb)	SO_2 (mg/kg)	Chph a	Chph b (mg/kg)	total chph
0	3.59	465.9	268.4	82.9	351.3
0	3.57	461.4	266.8	81.4	348.1
0	3.65	472.0	257.6	80.8	337.8
0	3.67	463.2	261.7	82.5	344.2
0	3.66	458.9	259.6	82.1	341.7
0	3.58	489.5	258.9	80.1	339.1
14	3.82	464.0	272.4	88.2	360.5
14	3.86	435.8	281.3	92.0	373.3
29	4.16	413.8	282.6	87.5	370.2
29	4.42	408.8	275.6	87.2	362.9
45	4.53	---	269.9	82.6	352.5
45	4.53	---	249.2	78.0	327.2
61	4.55	---	240.4	74.2	314.6
61	4.46	---	244.9	72.8	317.7
71	4.46	---	262.2	76.3	338.5
71	4.47	---	250.3	75.4	325.8
85	4.32	---	250.0	76.2	326.3
85	4.43	---	240.6	71.3	311.8
113	4.64	---	222.9	66.7	289.6
113	4.61	---	237.4	74.2	311.6
129	4.35	333.1	232.2	72.6	304.8
129	4.44	346.2	223.1	68.7	291.8
155	4.72	318.0	239.8	79.8	319.7
155	4.62	322.1	226.8	72.8	299.6
167	4.22	297.4	222.4	74.2	296.6
167	4.48	313.7	222.1	72.2	294.4
212	---	236.1	196.6	68.1	264.6
212	---	260.7	188.8	61.7	250.6
259	4.52	260.6	187.9	68.2	256.1
259	4.66	255.2	190.9	60.4	251.4
328	4.85	236.1	166.2	56.5	222.7
328	4.80	217.9	166.4	58.5	224.9
359	4.52	224.4	---	---	---
415	4.79	---	153.5	58.3	211.9
415	4.91	237.3	---	---	---

[1] Blanks represent excluded results due to error.

Appendix 4.16. Changes in the quality parameters of dried green beans stored at 30°C and 43% RH.[1]

Time (days)	Moisture Content (%wb)	SO_2 (mg/kg)	Chph a	Chph b (mg/kg)	total chph
0	3.59	465.9	268.4	82.9	351.3
0	3.57	461.4	266.8	81.4	348.1
0	3.65	472.0	257.6	80.8	337.8
0	3.67	463.2	261.7	82.5	344.2
0	3.66	458.9	259.6	82.1	341.7
0	3.58	489.5	258.9	80.1	339.1
14	5.42	435.7	263.9	87.1	351.0
14	5.05	420.1	268.9	88.1	357.0
29	6.37	323.2	---	---	---
29	6.41	362.5	268.1	82.9	351.1
45	6.41	231.6	240.8	73.3	314.1
45	6.36	245.0	248.4	74.8	323.2
61	6.48	182.4	243.7	77.2	320.9
61	6.46	185.0	237.4	77.0	314.4
71	6.48	192.8	236.0	72.8	308.7
71	6.51	212.3	232.2	72.6	304.8
85	6.21	171.6	215.7	64.4	280.1
85	6.38	150.5	216.2	68.4	284.6
99	6.68	137.1	217.1	76.5	293.6
99	6.60	166.5	225.8	79.3	305.1
113	6.41	139.4	201.6	66.8	268.4
113	6.33	134.6	204.1	72.4	276.4
129	6.40	---	192.6	60.0	252.6
129	6.30	---	179.2	58.6	237.8
140	6.09	---	186.1	63.8	249.9
140	6.20	---	188.6	59.7	248.3
1	6.76	---	177.0	59.9	236.9
155	6.65	---	165.6	57.3	222.9

[1] Blanks represent excluded results due to error.

Appendix 4.17. Changes in the quality parameters of dried green beans stored at 30°C and 56% RH.[1]

Time (days)	Moisture Content (%wb)	SO_2 (mg/kg)	Chph a	Chph b (mg/kg)	total chph
0	3.59	465.9	268.4	82.9	351.3
0	3.57	461.4	266.8	81.4	348.1
0	3.65	472.0	257.6	80.8	337.8
0	3.67	463.2	261.7	82.5	344.2
0	3.66	458.9	259.6	82.1	341.7
0	3.58	489.5	258.9	80.1	339.1
14	8.16	349.7	257.9	83.6	341.4
14	8.24	344.2	251.6	84.1	336.3
29	9.36	249.8	237.8	75.3	313.0
29	9.09	236.6	215.7	67.3	283.0
45	9.02	119.5	203.8	66.4	270.2
45	9.04	133.3	---	---	---
61	9.16	68.2	189.6	61.9	251.5
61	9.24	73.7	180.9	63.1	243.9
67	9.04	---	169.7	62.5	232.2
67	9.09	---	179.4	70.4	249.8
71	9.32	70.7	178.9	61.5	240.4
71	9.10	70.9	168.6	62.1	230.7
80	9.17	53.8	---	---	---
80	9.25	59.4	165.7	67.0	232.7
85	9.20	50.0	---	---	---
85	9.13	59.3	146.3	56.0	202.3
99	9.52	45.3	133.2	49.0	182.2
99	9.24	38.4	128.6	54.4	183.0

[1] Blanks represent excluded results due to error.

Appendix 4.18. Changes in the quality parameters of dried green beans stored at 40°C and 32% RH.[1]

Time (days)	Moisture Content (%wb)	SO_2 (mg/kg)	Chph a	Chph b (mg/kg)	total chph
0	3.59	465.9	268.4	82.9	351.3
0	3.57	461.4	266.8	81.4	348.1
0	3.65	472.0	257.6	80.8	337.8
0	3.67	463.2	261.7	82.5	344.2
0	3.66	458.9	259.6	82.1	341.7
0	3.58	489.5	258.9	80.1	339.1
4	4.08	467.4	282.4	86.5	368.9
4	3.97	454.8	264.4	80.8	345.2
8	4.16	421.5	262.3	76.4	338.7
8	4.18	419.6	261.2	80.8	341.9
16	4.03	395.0	264.5	81.8	346.3
16	3.97	395.6	268.4	85.0	353.4
24	4.47	339.1	244.8	73.7	318.5
24	4.46	310.9	249.3	70.2	319.5
34	4.34	264.0	243.4	77.0	320.4
34	4.25	298.2	256.0	81.0	337.0
43	4.26	218.2	---	---	---
43	4.17	239.0	236.0	72.8	308.7
49	4.32	175.5	222.8	75.3	298.1
49	4.38	162.5	228.9	73.4	302.3
56	4.26	166.2	206.7	69.2	276.0
56	4.32	145.9	218.3	77.6	296.0
66	4.37	125.5	203.0	73.9	276.9
66	4.44	164.6	212.1	74.8	287.0
79	4.50	111.4	194.3	74.1	268.4
79	4.55	125.1	192.4	72.5	264.9
99	4.44	81.9	147.7	53.6	201.3
99	4.46	102.6	155.2	57.9	213.1

[1] Blanks represent excluded results due to error.

Appendix 4.19. Changes in the quality parameters of dried green beans stored at 40°C and 43% RH.[1]

Time (days)	Moisture Content (%wb)	SO_2 (mg/kg)	Chph a	Chph b (mg/kg)	total chph
0	3.59	465.9	268.4	82.9	351.3
0	3.57	461.4	266.8	81.4	348.1
0	3.65	472.0	257.6	80.8	337.8
0	3.67	463.2	261.7	82.5	344.2
0	3.66	458.9	259.6	82.1	341.7
0	3.58	489.5	258.9	80.1	339.1
4	5.65	403.5	257.7	81.6	339.2
4	5.51	428.4	254.3	81.5	335.8
8	5.87	346.1	246.5	74.2	320.6
8	6.01	369.3	243.1	75.0	318.2
16	5.96	309.3	253.9	80.4	324.2
16	5.84	297.2	246.7	77.1	323.8
24	6.59	187.7	220.0	68.7	288.7
24	6.41	210.5	---	---	---
34	6.30	139.0	211.1	72.7	283.7
34	6.30	127.4	205.3	71.7	276.9
43	6.19	103.9	193.3	66.0	259.4
43	6.25	106.7	197.2	69.2	266.4
49	6.22	67.5	170.0	59.6	229.7
49	6.27	92.6	173.5	63.5	237.0
56	6.30	36.5	153.8	63.9	217.6
56	6.37	41.8	155.7	65.4	221.1

[1] Blanks represent excluded results due to error.

Appendix 4.20. Changes in the quality parameters of dried green beans stored at 40°C and 53% RH.[1]

Time (days)	Moisture Content (%wb)	SO_2 (mg/kg)	Chph a	Chph b (mg/kg)	total chph
0	3.59	465.9	268.4	82.9	351.3
0	3.57	461.4	266.8	81.4	348.1
0	3.65	472.0	257.6	80.8	337.8
0	3.67	463.2	261.7	82.5	344.2
0	3.66	458.9	259.6	82.1	341.7
0	3.58	489.5	258.9	80.1	339.1
4	6.26	392.4	268.1	82.0	350.2
4	6.05	419.9	262.6	79.3	342.0
8	7.58	342.9	266.8	84.4	351.3
8	7.45	316.7	252.0	75.9	327.9
16	7.74	282.8	241.0	75.3	316.4
16	7.81	271.2	244.1	68.6	312.7
24	8.88	110.4	194.5	61.6	256.1
24	8.72	104.9	188.0	60.5	248.5
34	8.20	64.6	155.6	62.7	218.3
34	8.24	68.3	146.8	60.1	206.9
43	8.28	35.4	98.7	49.2	147.9
43	8.22	30.1	109.8	50.9	160.6
49	8.61	30.1	---	---	---
49	8.46	30.7	73.7	40.6	114.4
56	8.44	---	61.3	46.8	108.1
56	8.35	---	51.6	33.4	85.0

[1] Blanks represent excluded results due to error.

Appendix 4.21. Changes in the quality parameters of dried apricots during storage at 20°C and 59% RH.

Time (days)	Moisture Content (%wb)	Browning (absorbance)	SO_2 (mg/kg)
0	25.62	0.050	1457.3
0	25.96	0.048	1553.2
0	25.40	0.050	1557.0
0	25.49	0.054	1661.3
0	25.38	0.047	1611.2
30	15.84	---	---
30	18.33	---	---
59	---	0.042	1560.2
59	---	0.046	1685.6
85	13.02	0.065	1858.0
85	12.56	0.065	1508.9
114	12.77	0.072	1307.8
114	12.73	0.074	1616.1
142	10.35	0.073	1638.3
142	10.06	0.072	1694.8
163	12.33	0.095	1328.7
163	13.13	0.080	1346.7
178	13.37	0.106	1361.7
178	12.88	0.100	1276.8
204	12.74	0.105	1273.1
204	11.02	---	1186.9
224	---	0.130	---
224	---	0.136	---
239	15.15	0.162	1086.8
239	14.53	0.152	1265.8
252	13.46	0.171	1020.1
252	12.83	0.190	928.7
288	12.78	---	748.4
288	13.64	0.220	987.7
315	12.34	0.199	699.1
315	12.52	0.201	864.0
336	11.16	0.255	680.4
336	11.20	0.254	680.4

[1] Blanks represent excluded results due to error.

Appendix 4.22. Changes in the quality parameters of dried apricots during storage at 20°C and 70% RH.

Time (days)	Moisture Content (%wb)	Browning (absorbance)	SO_2 (mg/kg)
0	25.62	0.050	1457.3
0	25.96	0.048	1553.2
0	25.40	0.050	1557.0
0	25.49	0.054	1661.3
0	25.38	0.047	1611.2
30	20.87	0.068	1188.4
30	20.92	0.068	1230.01
59	---	---	1069.3
59	20.30	0.060	922.5
85	19.21	0.094	680.3
85	18.89	0.085	596.6
100	17.99	0.097	---
100	18.26	0.082	---
114	19.07	0.115	---
114	17.84	0.133	607.6
129	---	0.145	433.8
129	---	0.150	457.5
142	18.42	0.135	466.7
142	17.60	0.134	466.9
151	18.33	0.130	343.5
151	17.42	0.130	343.2
163	19.37	0.160	284.7
163	19.10	0.165	315.0
178	19.17	0.144	240.9
178	18.26	0.160	229.7
204	17.35	0.189	192.6
204	18.40	0.215	---
224	---	0.257	---
224	---	0.273	---

[1] Blanks represent excluded results due to error.

Appendix 4.23. Changes in the quality parameters of dried apricots during storage at 20°C and 81% RH.

Time (days)	Moisture Content (%wb)	Browning (absorbance)	SO_2 (mg/kg)
0	25.62	0.050	1457.3
0	25.96	0.048	1553.2
0	25.40	0.050	1557.0
0	25.49	0.054	1661.3
0	25.38	0.047	1611.2
30	23.50	0.064	---
30	24.40	0.065	1501.1
59	---	0.050	1364.5
59	27.30	0.056	1309.1
85	27.33	0.066	1006.0
85	27.56	0.069	1009.9
114	28.11	0.085	829.5
114	28.41	0.075	1057.6
142	25.64	0.090	745.1
142	27.01	0.080	737.4
163	26.75	0.099	729.2
163	27.32	0.084	688.4
178	28.91	0.102	480.5
178	28.52	0.099	535.4
204	27.63	0.122	546.4
204	27.30	0.100	500.1
224	---	0.126	---
224	---	0.117	---
239	28.72	0.166	415.9
239	30.54	0.130	400.4
252	30.70	0.129	302.7
252	29.66	0.153	320.6
288	29.80	0.203	168.1
288	28.56	0.178	154.1
315	28.06	0.254	---
315	29.25	0.251	---

[1] Blanks represent excluded results due to error.

Appendix 4.24. Changes in the quality parameters of dried apricots during storage at 30°C and 56% RH.

Time (days)	Moisture Content (%wb)	Browning (absorbance)	SO_2 (mg/kg)
0	25.62	0.050	1457.3
0	25.96	0.048	1553.2
0	25.40	0.050	1557.0
0	25.49	0.054	1661.3
0	25.38	0.047	1611.2
15	23.64	---	---
15	23.04	0.061	---
30	11.17	0.084	1672.4
30	13.19	0.084	1708.3
44	10.27	0.097	1567.0
44	10.00	0.092	1530.1
59	10.39	0.138	1418.2
59	9.56	---	1226.4
71	9.43	0.182	1044.8
71	10.26	0.160	993.7
86	11.43	0.237	897.8
86	11.83	0.261	687.2
99	9.30	0.327	683.1
99	8.91	0.347	673.8

[1] Blanks represent excluded results due to error.

Appendix 4.25. Changes in the quality parameters of dried apricots during storage at 30°C and 68% RH.

Time (days)	Moisture Content (%wb)	Browning (absorbance)	SO_2 (mg/kg)
0	25.62	0.050	1457.3
0	25.96	0.048	1553.2
0	25.40	0.050	1557.0
0	25.49	0.054	1661.3
0	25.38	0.047	1611.2
15	20.61	---	---
15	19.61	---	1259.0
30	18.27	0.103	678.3
30	18.36	0.100	649.3
44	17.13	0.136	627.8
44	16.47	0.149	334.1
59	17.20	0.208	410.8
59	16.66	0.266	375.9
71	15.60	---	262.3
71	15.66	0.251	156.0
86	15.91	0.290	111.1
86	16.88	0.317	91.1
99	14.57	0.450	88.0
99	14.10	0.400	88.2

[1] Blanks represent excluded results due to error.

Appendix 4.26. Changes in the quality parameters of dried apricots during storage at 30°C and 81% RH.

Time (days)	Moisture Content (%wb)	Browning (absorbance)	SO_2 (mg/kg)
0	25.62	0.050	1457.3
0	25.96	0.048	1553.2
0	25.40	0.050	1557.0
0	25.49	0.054	1661.3
0	25.38	0.047	1611.2
15	25.80	0.054	1459.6
15	26.72	0.049	1143.0
30	25.30	0.072	894.8
30	25.55	0.068	864.5
44	24.86	0.094	776.8
44	24.32	0.089	764.2
59	24.80	0.122	582.3
59	---	0.111	491.0
71	23.95	0.157	380.0
71	25.23	0.158	394.2
86	26.62	0.217	---
99	26.22	0.233	176.2
99	27.58	0.225	---

[1] Blanks represent excluded results due to error.

Appendix 4.27. Changes in the quality parameters of dried apricots during storage at 40°C and 53% RH.

Time (days)	Moisture Content (%wb)	Browning (absorbance)	SO_2 (mg/kg)
0	25.62	0.050	1457.3
0	25.96	0.048	1553.2
0	25.40	0.050	1557.0
0	25.49	0.054	1661.3
0	25.38	0.047	1611.2
3	17.50	0.078	1231.3
3	15.85	0.081	1344.0
6	13.59	0.095	1292.6
6	12.54	0.093	1113.8
9	11.18	---	989.2
9	11.58	0.146	1100.2
11	11.09	0.159	863.4
11	15.58	0.187	945.5
13	10.34	0.234	881.0
13	10.83	0.203	872.7
15	10.32	0.310	699.9
15	10.68	0.266	788.6

[1] Blanks represent excluded results due to error.

Appendix 4.28. Changes in the quality parameters of dried apricots during storage at 40°C and 66% RH.

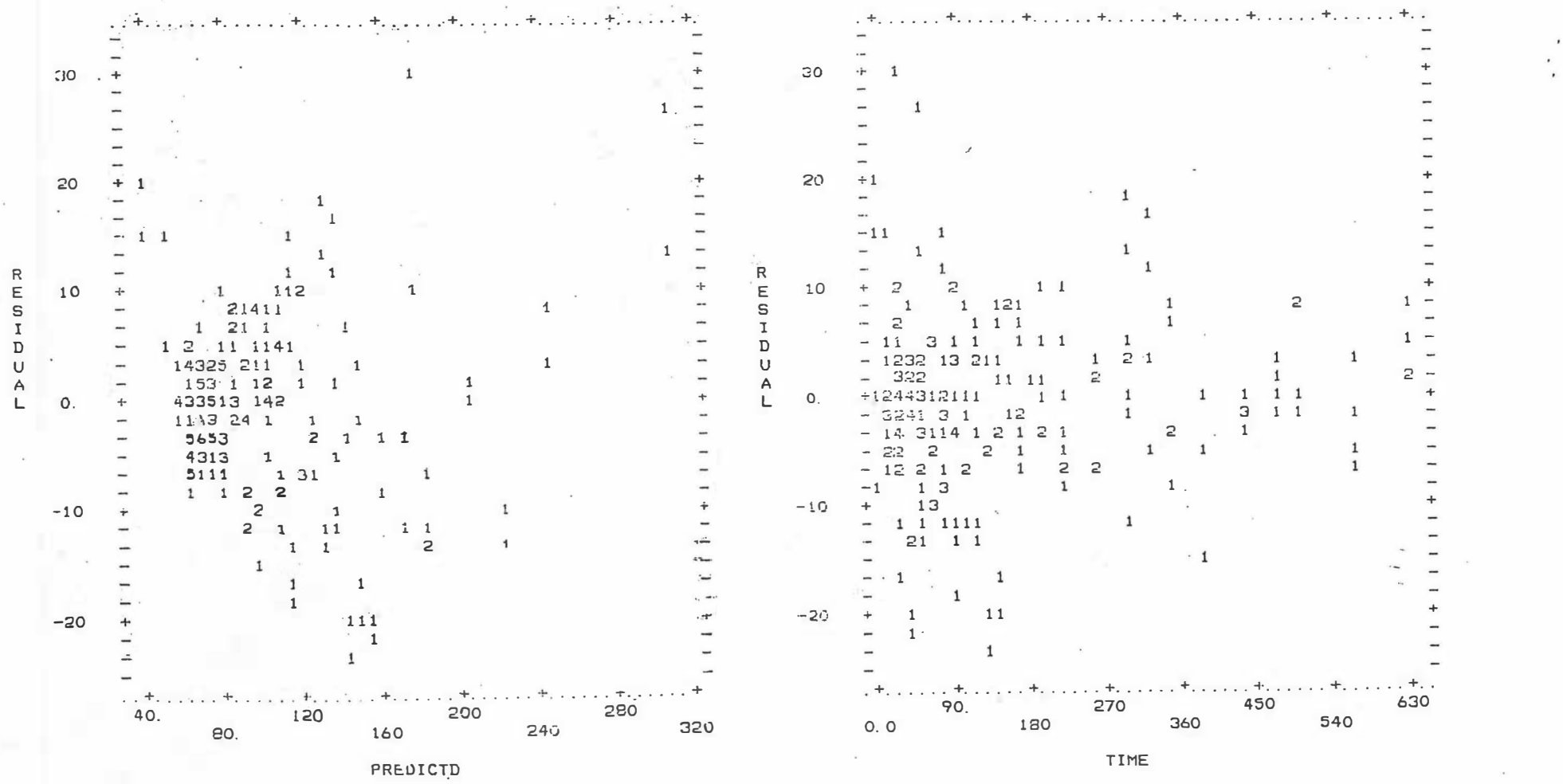
Time (days)	Moisture Content (%wb)	Browning (absorbance)	SO_2 (mg/kg)
0	25.62	0.050	1457.3
0	25.96	0.048	1553.2
0	25.40	0.050	1557.0
0	25.49	0.054	1661.3
0	25.38	0.047	1611.2
3	20.61	0.089	999.9
3	20.89	0.084	983.3
6	16.71	0.127	687.1
6	18.40	0.116	636.5
9	15.85	0.130	524.2
9	16.31	0.156	521.8
11	16.05	0.207	458.0
11	16.16	0.197	435.9
13	16.90	0.263	285.8
13	15.41	0.225	301.9
15	16.57	0.287	260.7
15	15.52	0.286	262.0

[1] Blanks represent excluded results due to error.

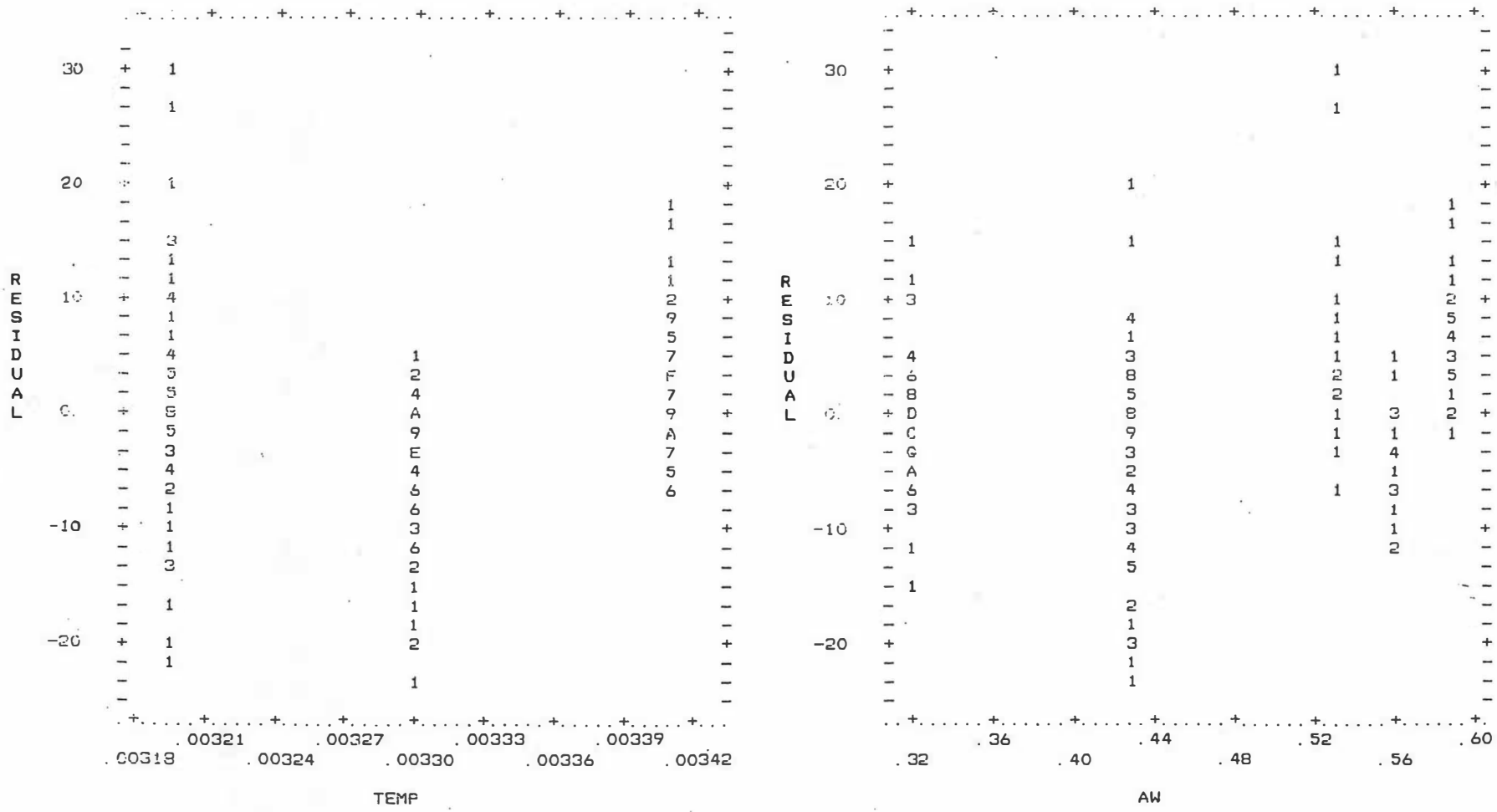
Appendix 4.29. Changes in the quality parameters of dried apricots during storage at 40°C and 80% RH.

Time (days)	Moisture Content (%wb)	Browning (absorbance)	SO_2 (mg/kg)
0	25.62	0.050	1457.3
0	25.96	0.048	1553.2
0	25.40	0.050	1557.0
0	25.49	0.054	1661.3
0	25.38	0.047	1611.2
3	25.61	0.066	---
3	25.63	0.078	1123.7
6	25.49	0.092	942.8
6	25.15	0.099	813.2
9	26.20	0.115	522.6
9	26.31	0.114	477.9
11	26.48	0.154	435.5
11	26.83	0.152	405.9
13	26.80	0.221	347.2
13	27.39	0.196	322.3
15	25.20	0.267	---
15	27.32	0.250	241.8

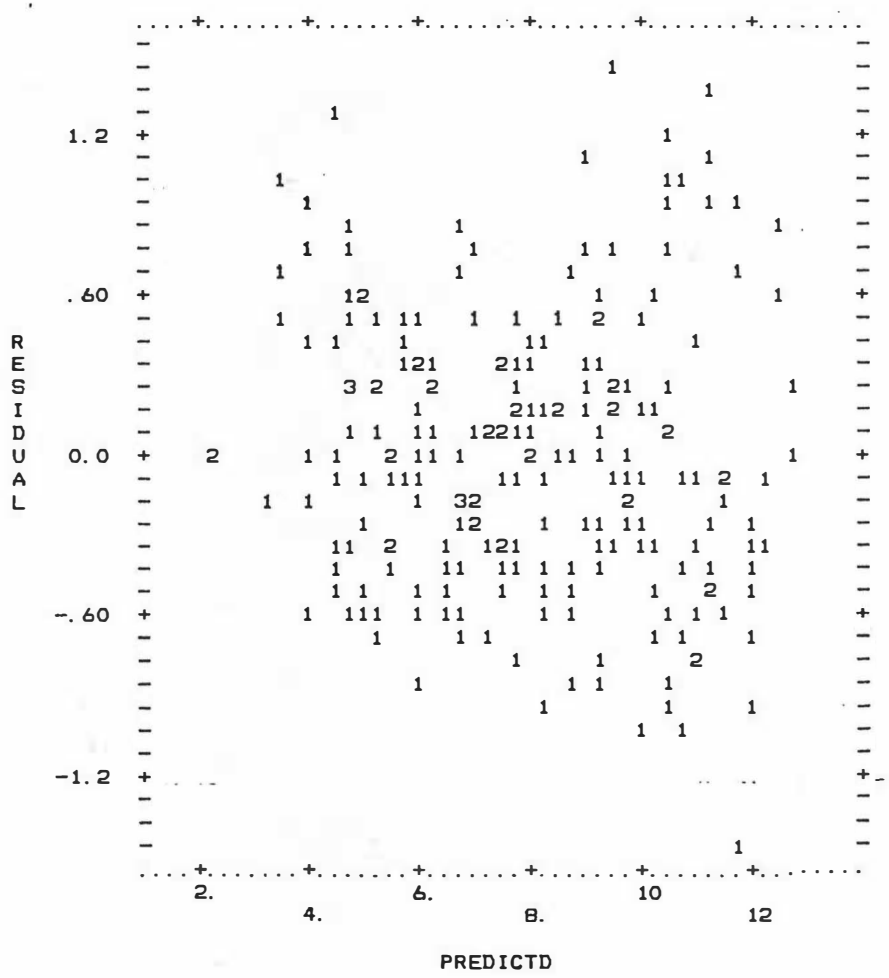
[1] Blanks represent excluded results due to error.

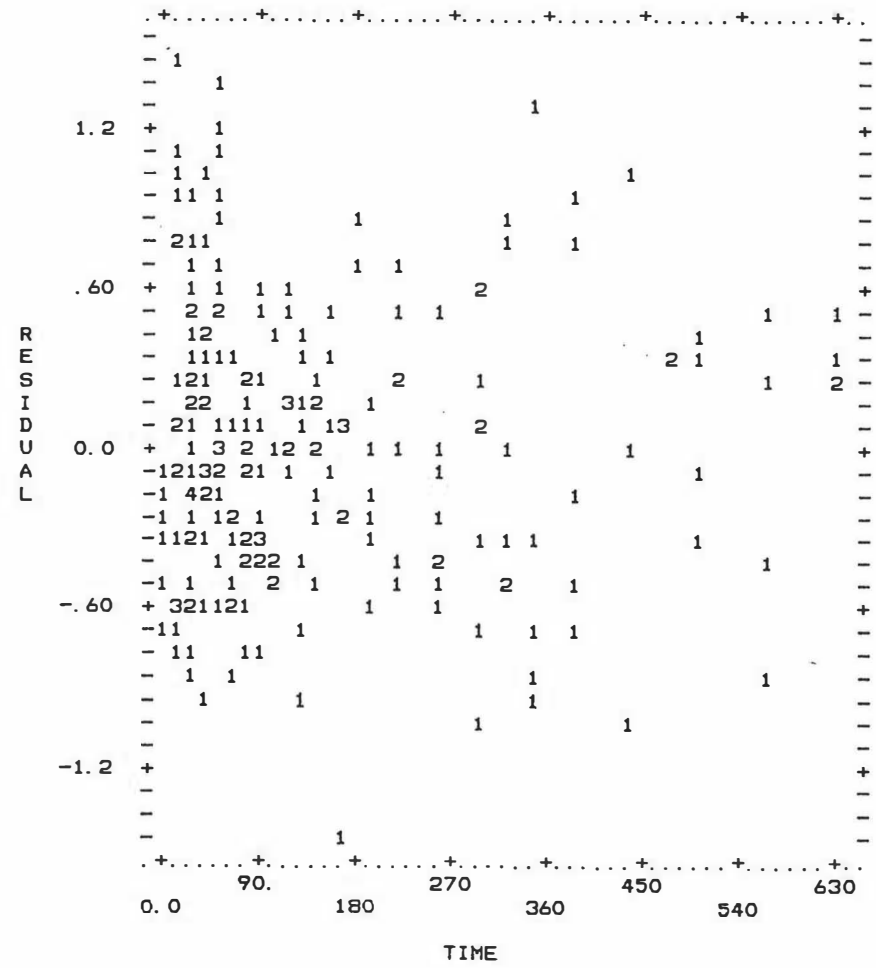


Appendix 5.1. Residual plots for the deterioration model for browning in dried onion flakes.

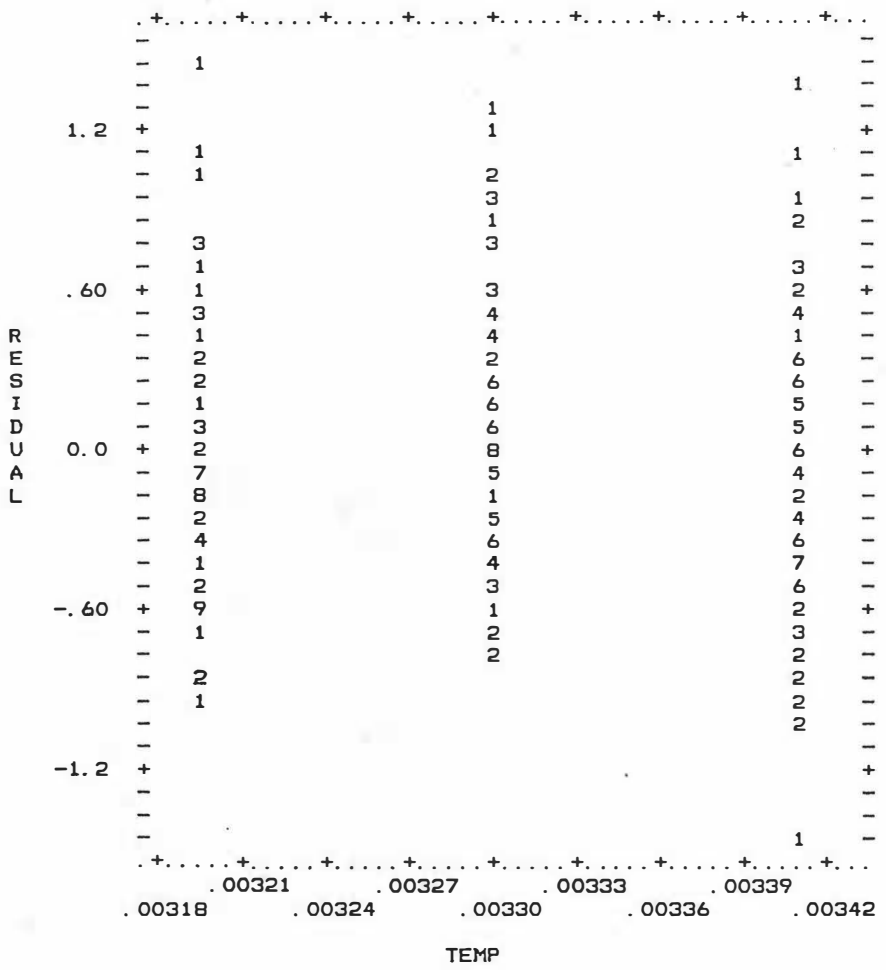


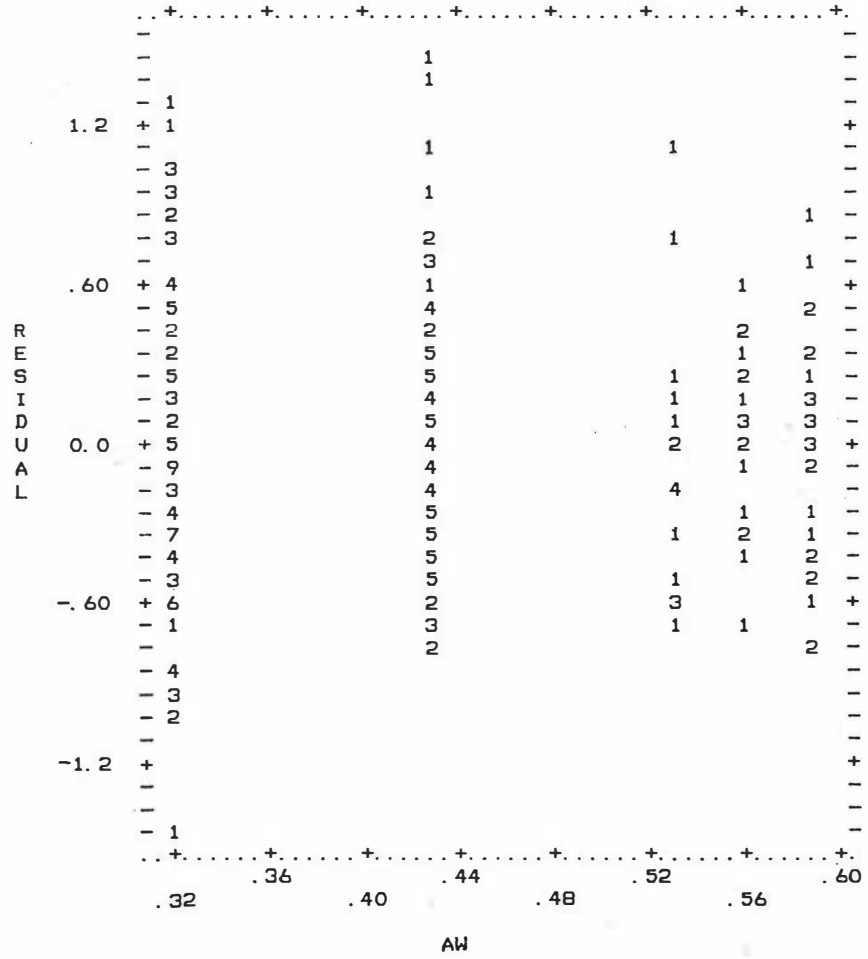
Appendix 5.1. continued



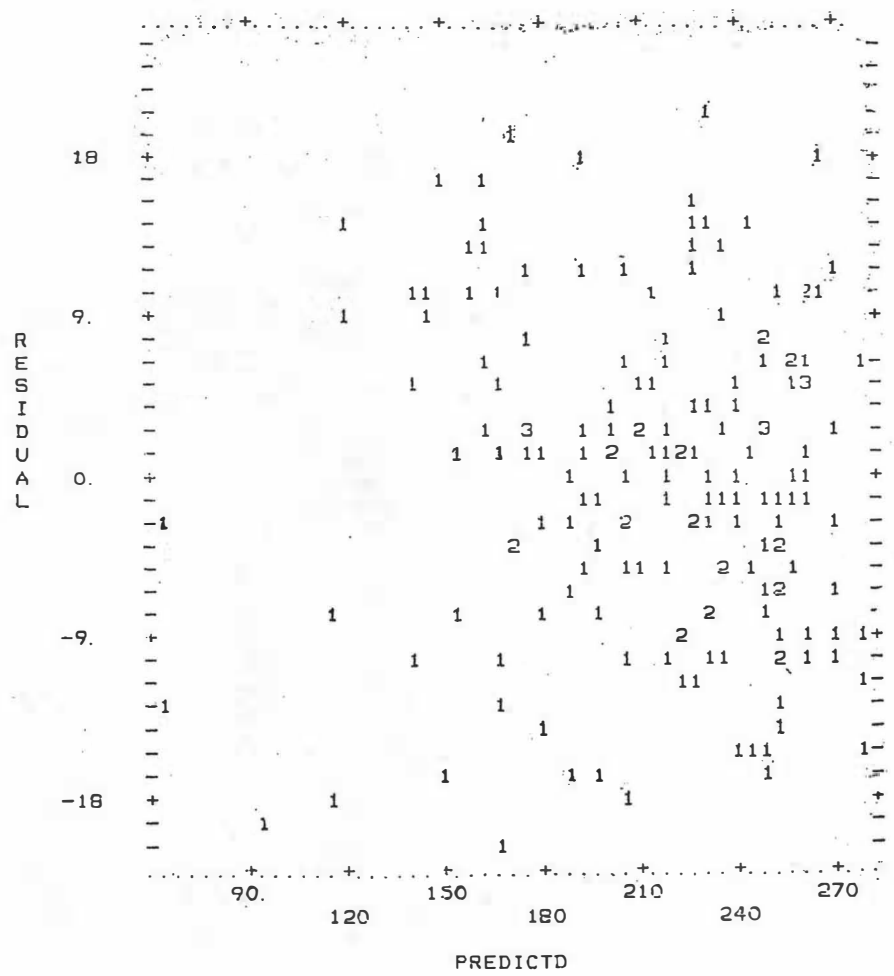


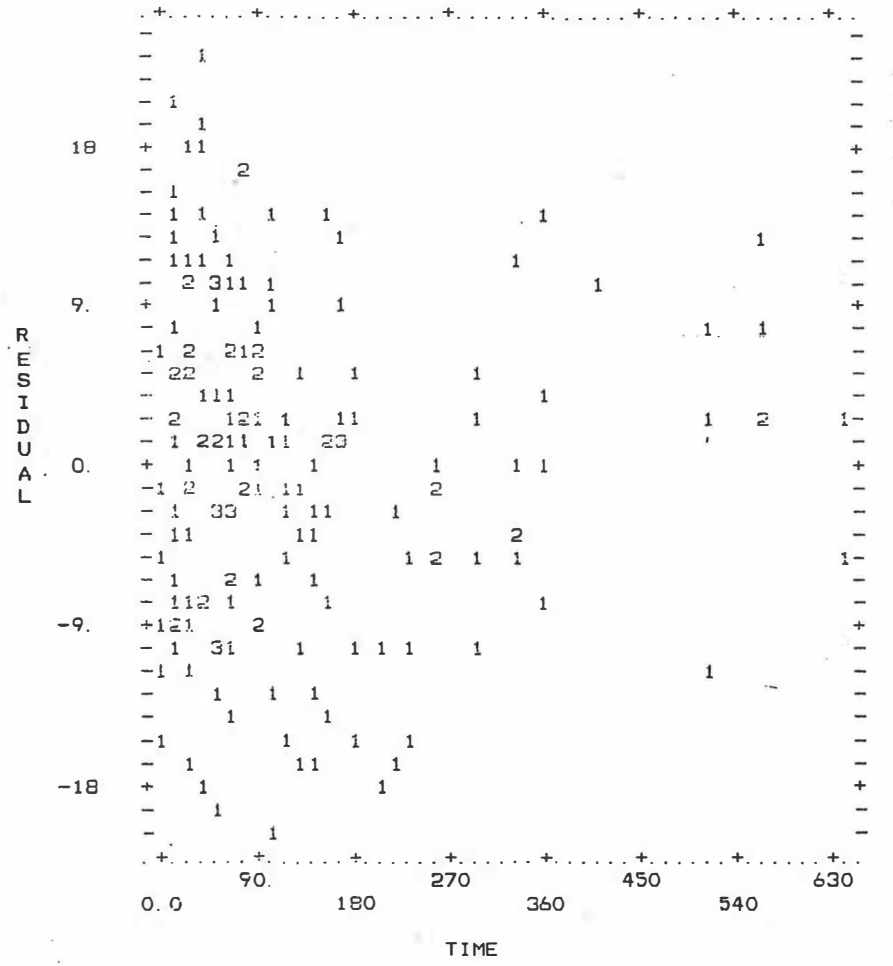
Appendix 5.2. Residual plots for the deterioration model for thiolsulphinate loss in dried onion flakes.



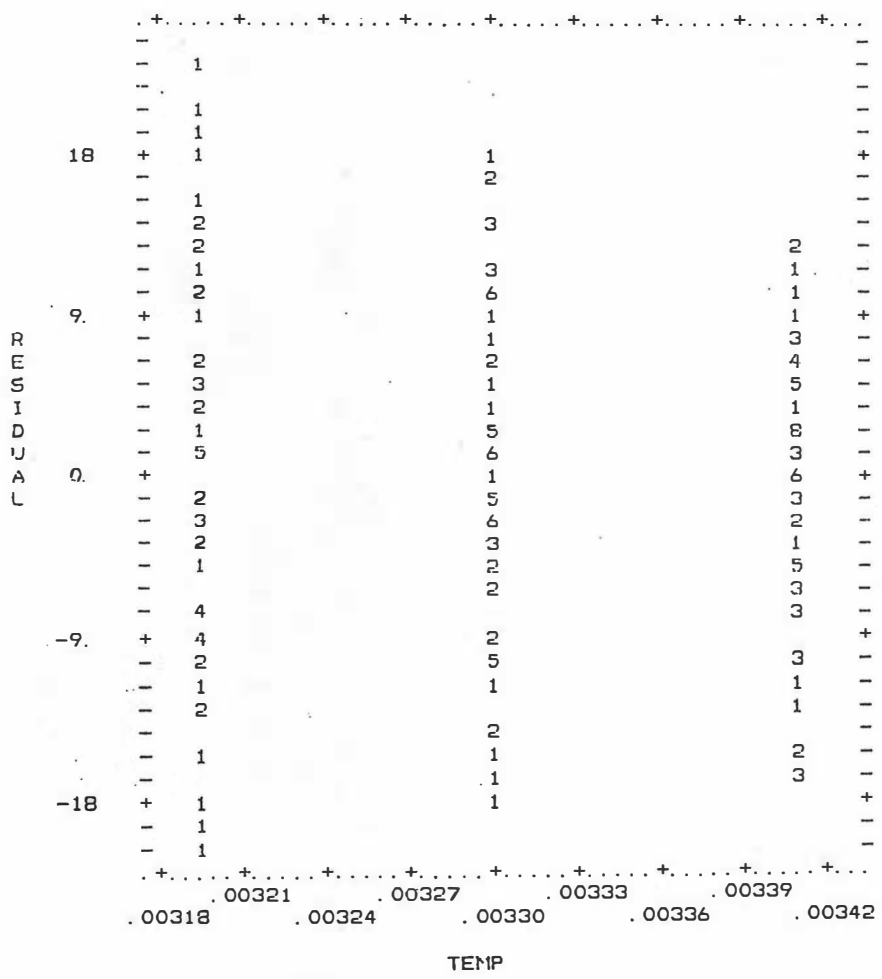


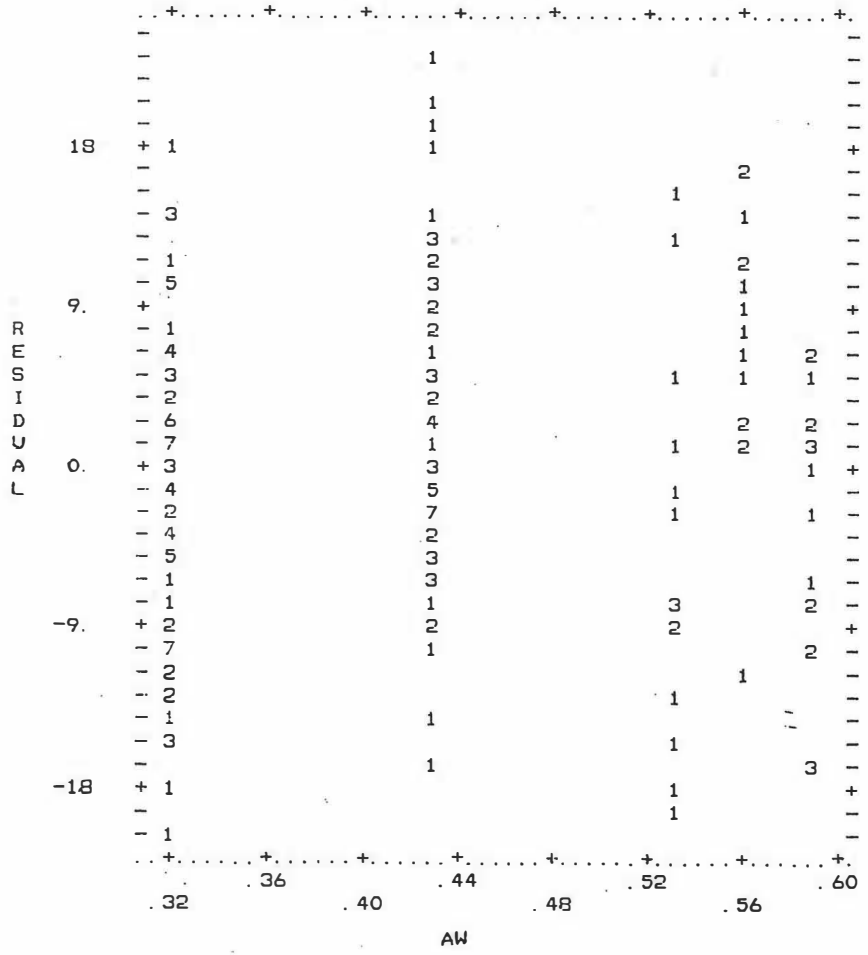
Appendix 5.2. continued



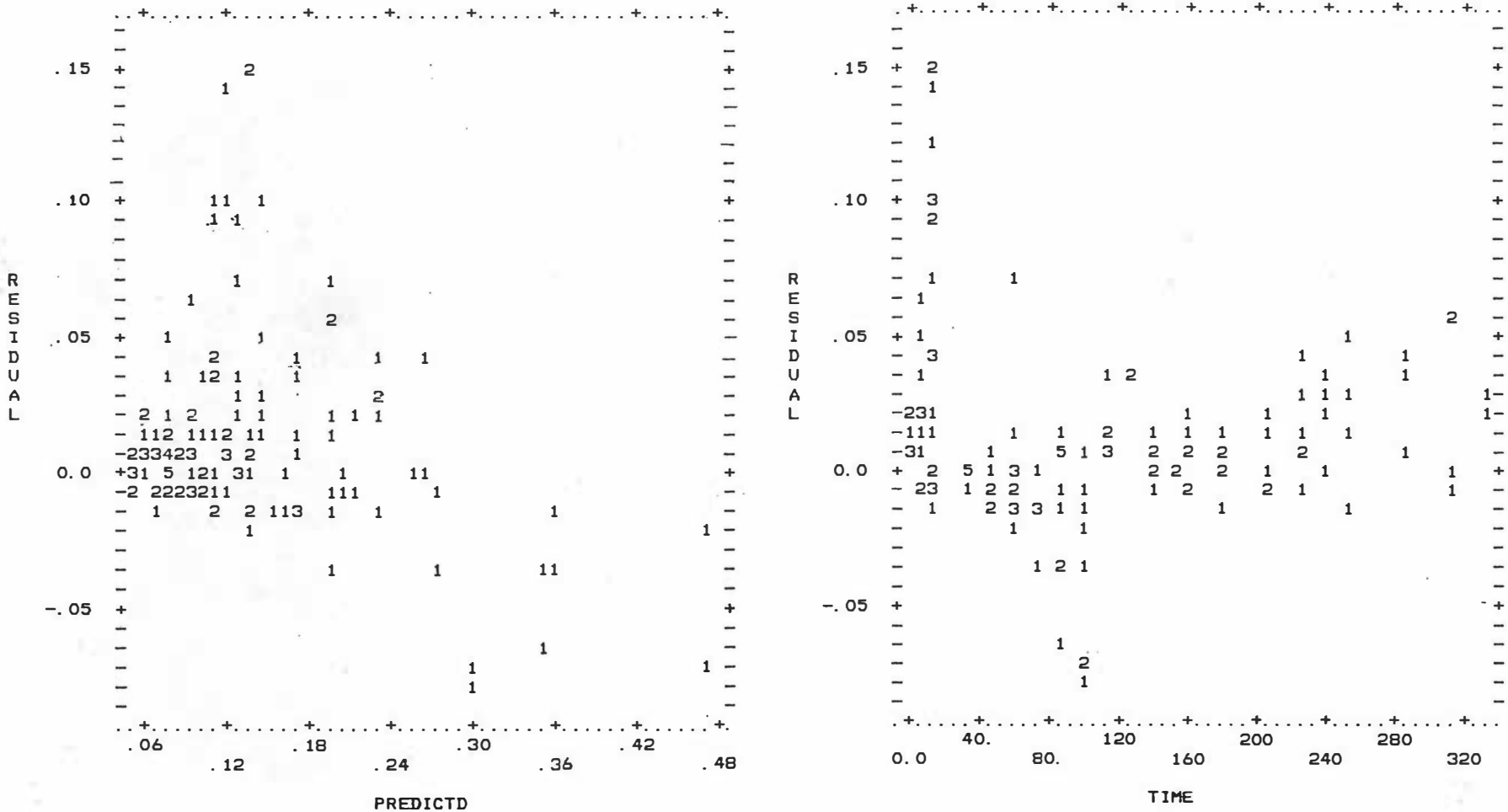


Appendix 5.3. Residual plots for the deterioration model for chlorophyll a loss in dried green beans.

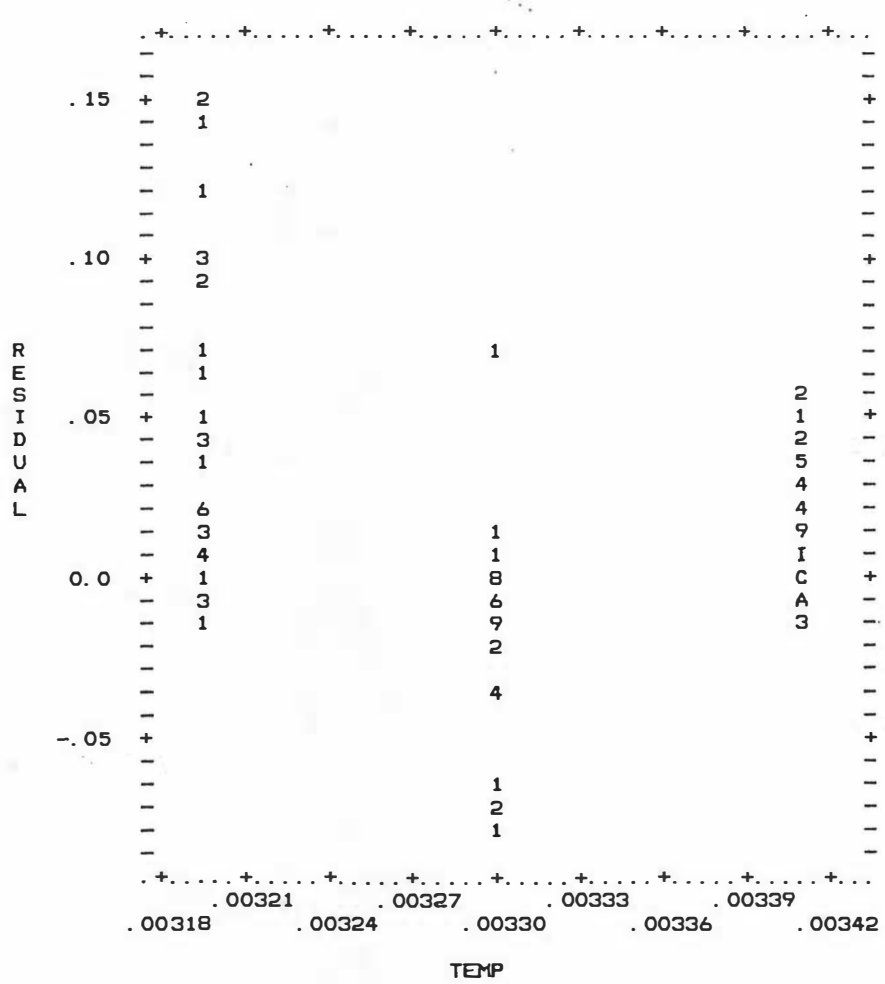


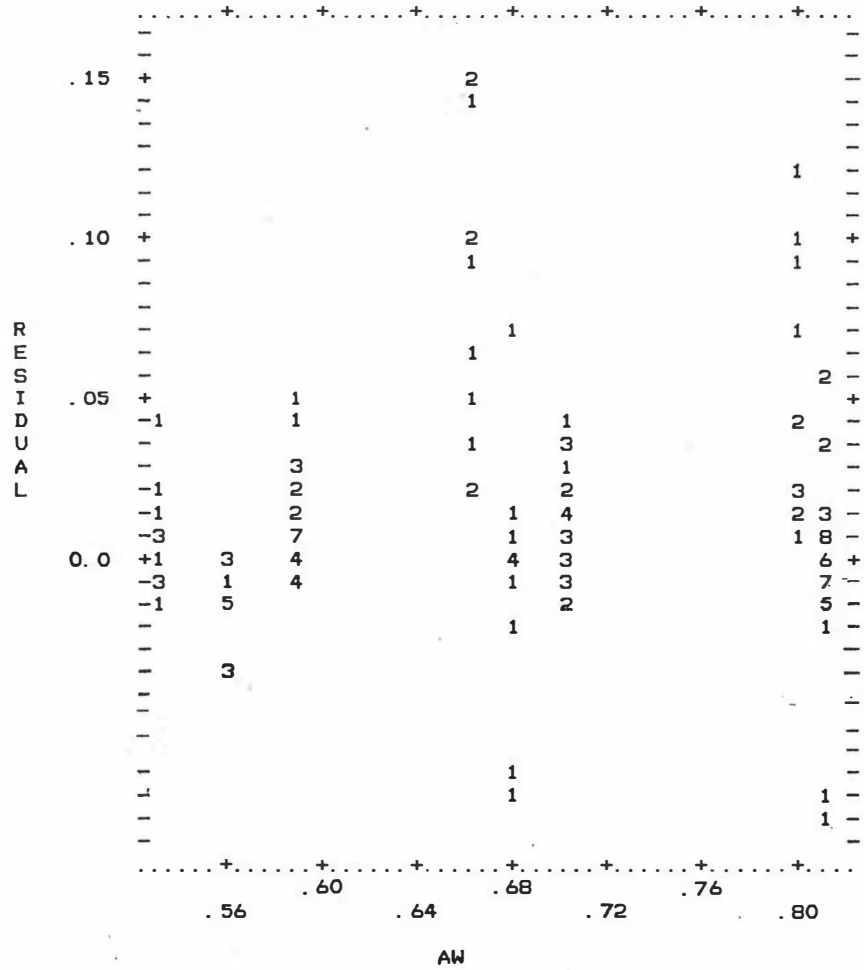


Appendix 5.3. continued



Appendix 5.4. Residual plots for the deterioration model for browning in dried apricots.





Appendix 5.4. continued

```
10  REM ---------------------
20  REM Program-Id.  SHLIFE.
30  REM ---------------------
40  REM
100 DEFINT X
110 CLEAR 5000
120 OPEN "I" , #1 , "A:SHLIFE.DAT"
130 OPEN "I" , #2 , "A:SHLIFE.TBL"
500 REM
510 DIM M0(5), C(5), K(5), I0(5)
520 DIM D1(5), D2(5), E1(5), E2(5)
530 DIM A1(5), A2(5), B1(5), B2(5)
560 DIM X5(20), X5$(20), XP(10)
570 DIM SA$(5), PA$(5), ER$(20)
600 X5$(1)="SAMPLES" : X5$(2)="PACKAGING" : X5$(3)="D1" : X5$(4)="D2"
610 X5$(5)="E1" : X5$(6)="E2" : X5$(7)="A1" : X5$(8)="A2"
620 X5$(9)="B1" : X5$(10)="B2" : X5$(11)="I0"
630 FM$ = "####.###"
640 X7 = 0 : REM results printing indicator
700 REM
701 REM Error Messages
702 REM --------------
710 ER$(1) = "DATA READ ERROR"
720 ER$(2) = "TABLE READ ERROR"
730 ER$(3) = "NO DEFINITION "
740 ER$(4) = "UNRECOGNIZABLE INPUT"
750 ER$(5) = "ALREADY DEFINED"
760 ER$(6) = "INVALID MATERIAL"
770 ER$(7) = "INVALID PACKAGING MATERIAL"
900 REM
901 REM Prompt for output device
902 REM ------------------------
950 PRINT "Direct output to (P)rinter or (S)creen? "
960 L$ = INPUT$(1)
965 X1 = 0
970 IF L$ = "P" OR L$ = "p"  THEN  X1 = 1
975 IF L$ = "S" OR L$ = "s"  THEN  X1 = 2
980 IF X1 = 0 THEN 960
1000 REM
1001 REM Read in Constants table
1002 REM ------------------------
1050 LINE INPUT# 2, L$
1070 IF LEFT$(L$,1) = "*"   THEN 1050
1080 IF LEFT$(L$,1) <> ":"  THEN XR = 3 : GOTO 30000
1090 LA$ = "" : LA$ = MID$(L$,2,4)
1100 IF LA$ = "SAMP"  THEN GOSUB 10000 : GOTO 1070
1110 IF LA$ = "PACK"  THEN GOSUB 11000 : GOTO 1070
1125 IF X2=0 THEN LA$="SAMPLES"     : XR=3 : GOTO 30000
1126 IF X3=0 THEN LA$="PACKAGING"   : XR=3 : GOTO 30000
1130 LA$ = "" : LA$ = MID$(L$,2,2)
1140 IF LA$ = "D1"    THEN GOSUB 13000 : GOTO 1050
1150 IF LA$ = "D2"    THEN GOSUB 13500 : GOTO 1050
1160 IF LA$ = "E1"    THEN GOSUB 14000 : GOTO 1050
1170 IF LA$ = "E2"    THEN GOSUB 14500 : GOTO 1050
1180 IF LA$ = "A1"    THEN GOSUB 15000 : GOTO 1050
1190 IF LA$ = "A2"    THEN GOSUB 15500 : GOTO 1050
1200 IF LA$ = "B1"    THEN GOSUB 16000 : GOTO 1050
1210 IF LA$ = "B2"    THEN GOSUB 16500 : GOTO 1050
1245 IF LA$ = "I0"    THEN GOSUB 18500 : GOTO 1050
1250 LA$ = "" : LA$ = MID$(L$,2,3)
1260 IF LA$ = "END"   THEN GOSUB 19000 : GOTO 2000
1270 XR = 4 : GOTO 30000
2000 REM
2001 REM Read in data
2002 REM ------------
2050 INPUT# 1, T$
2060 INPUT# 1, M$
2070 INPUT# 1, PK$
2080 INPUT# 1, T1
2090 INPUT# 1, RH
2100 INPUT# 1, M1
2110 INPUT# 1, TD, DD$
2115 INPUT# 1, P0
2120 INPUT# 1, AR
2130 INPUT# 1, WS
2140 INPUT# 1, XP(1),XP(2),XP(3),XP(4),XP(5),XP(6),XP(7),XP(8),XP(9)
2200 REM
2208  GOSUB 6800   : REM get max checkpoint
2210  GOSUB 7000   : REM validate MATERIAL (M$) input
2220  GOSUB 7300   : REM validate PACKAGING (PK$) input
2240  GOSUB 8000   : REM print input data
2250  GOSUB 4500   : REM compute all other variables
2260  GOSUB 5000   : REM compute Permeance (P) for given Rh & temp
2300  REM start of loop
2302  REM -------------
2400  GOSUB 5300   : REM compute water activity (AW)
2410  GOSUB 5900   : REM Compute P1 & Q
2420  GOSUB 6500   : REM Compute AW at T2...
2450  GOSUB 5600   : REM compute concentration (I) for T2
2500  REM
2501  REM test condition for iteration
2502  REM ----------------------------
2550  IF X2 = 1 THEN 3000
2552  IF X2 = 3 THEN 3200
2560  REM onions:
2570  IF I > 105.0  THEN GOSUB 6000
2575  IF I > 105.0 AND XP(9) <> 999 THEN 40000
2580  M1 = M2 + ( 0.015 * ( I - I0 ))
2581  REM M1 = M2
2582  I0 = I
2585  GOSUB 8700
2586  IF T2 => XP(10) THEN 40000
2590  GOTO 2300
3000  REM green beans:
3050  IF I < 327.0  THEN GOSUB 6000
3055  IF I < 327.0 AND XP(9) <> 999 THEN 40000
3060  I0 = I : M1 = M2
3065  GOSUB 8700
3066  IF T2 => XP(10) THEN 40000
3070  GOTO 2300
```

Appendix 5.5. Computer iteration program.

```
3200  REM onions (Thiolsulphinate)
3210  IF I < 5.0  THEN GOSUB 6000
3215  IF I < 5.0 AND XP(9) <> 999 THEN 40000
3220  M1 = M2
3224  I0 = I : I4 = I3
3230  GOSUB 8700
3235  IF T2 => XP(10) THEN 40000
3240  GOTO 2300
4500  REM
4501  REM Compute all other variables
4502  REM ----------------------------
4540  I0 = I0(X2) : I4 = I0(2)
4545  R = 8.317
4550  TMP = T1 + 273.15
4555  PE = P0 * RH / 100.0
4570  IF X2 = 1  THEN 4650
4580  REM onions
4590  M0 = 4.134 * EXP( 176.286 / TMP )
4600  C  = 0.015 * EXP(1524.840 / TMP )
4610  K  = 1.252 * EXP( -76.574 / TMP )
4620  RETURN
4650  REM green beans
4660  M0 = 1.678 * EXP( 432.589 / TMP )
4670  C  = 0.062 * EXP(1093.148 / TMP )
4680  K  = 1.137 * EXP( -54.132 / TMP )
4690  RETURN
5000  REM
5001  REM Compute Permeance
5002  REM -----------------
5050  A = A1(X3) * ( EXP(A2(X3) / RH ) )
5060  B = B1(X3) + ( B2(X3) / RH )
5070  P = A * ( EXP( (-B*1000.0) / (R*TMP) ))
5080  P = P * 6.95
5081  REM PRINT "P=";P
5130  RETURN
5300  REM
5301  REM Compute Water Activity
5302  REM ----------------------
5360  Z1 = M0 * C * K
5370  Z2 = C * K - ( 2.0*K )
5380  Z3 = ( C*(K*K) ) - ( K*K )
5390  Z4 = ( Z1/M1 ) - Z2
5500  AW = ( -Z4 + SQR( Z4*Z4 + 4*Z3 ) ) / (2*Z3)
5501  REM PRINT " AW= " ;AW
5510  RETURN
5600  REM
5601  REM Compute Concentration (I)
5602  REM -------------------------
5650  IF X2 = 1 THEN 5800
5652  IF X2 = 3 THEN 5750
5660  REM onions:
5670  D  = D1(X2) + ( D2(X2) * AW )
5680  E  = 1.0 / ( E1(X2) - ( E2(X2) / AW ))
5690  Z1 = ( 1.0/TMP ) - ( 1.0/303.15 )
5700  Z2 = -(E*1000.0) / 8.317
5710  Z1 = EXP( Z2*Z1 )
5720  I  = I0 + ( D*TD*Z1 )
5730  T2 = T2 + TD
5740  RETURN
5750  REM onions (Thiolsulphinate)
5751  GOSUB 6600
5752  D  = D1(X2) + ( D2(X2) * AW )
5754  E  = 1.0 / ( E1(X2) - ( E2(X2) * AW ))
5756  Z1 = ( 1.0/TMP ) - ( 1.0/303.15 )
5758  Z2 = -(E*1000.0) / 8.317
5760  Z1 = EXP( Z2*Z1 )
5762  I  = I0 * EXP( -D*TD*Z1 )
5764  T2 = T2 + TD
5766  RETURN
5800  REM green beans:
5810  D  = D1(X2) * EXP( D2(X2) * AW )
5820  E  = 1.0 / ( E1(X2) - ( E2(X2) / AW ))
5830  Z1 = ( 1.0/TMP ) - ( 1.0/303.15 )
5840  Z2 = -( E*1000.0 ) / 8.317
5850  Z1 = EXP( Z2*Z1 )
5860  I  = I0 - ( D*TD*Z1 )
5870  T2 = T2 + TD
5880  RETURN
5900  REM
5901  REM Compute P1 & Q
5902  REM ---------------
5910  P1 = AW * P0
5920  Q  = ( P*AR ) * ( PE-P1 ) * TD
5930  M2 = ( (M1/100.0)*WS + Q ) / WS * 100.0
5931  REM PRINT "P1=";P1," Q=";Q
5940  RETURN
6000  REM
6001  REM Print Out result
6002  REM ----------------
6005  IF X7 = 1 THEN RETURN
6006  X7 = 1
6050  IF X1 = 2  THEN 6300
6100  LPRINT : LPRINT "  Results: ---------- "
6110  LPRINT "   Shelf life of "; M$; " = "; T2 ;" day(s)"
6130  LPRINT "   Final Moisture Content (M2)...";
6132  LPRINT USING FM$ ; M2; : LPRINT " gm/100gm"
6140  LPRINT "   Final Water Activity (Aw).....";
6142  LPRINT USING FM$ ; AW
6150  LPRINT "   Final Concentration (I).......";
6152  LPRINT USING FM$ ; I
6160  LPRINT : LPRINT "  ---------- "
6170  RETURN
6300  PRINT : PRINT   "  Results: ---------- "
6310  PRINT "   Shelf life of "; M$; " = "; T2 ;" day(s)"
6330  PRINT "   Final Moisture Content (M2)...";
6332  PRINT USING FM$ ; M2; : PRINT " gm/100gm"
6340  PRINT "   Final Water Activity (Aw).....";
6342  PRINT USING FM$ ; AW
6350  PRINT "   Final Concentration (I).......";
6352  PRINT USING FM$ ; I
```

Appendix 5.5. continued

```
6360  PRINT : PRINT   "  ------------------------------ "
6370  RETURN
6500  REM
6501  REM Compute Water Activity at T2
6502  REM -----------------------------
6510  Z1 = M0 * C * K
6520  Z2 = C * K - ( 2.0*K )
6530  Z3 = ( C*(K*K) ) - ( K*K )
6540  Z4 = ( Z1/M2 ) - Z2
6580  AY = ( -Z4 + SQR( Z4*Z4 + 4*Z3 ) ) / (2*Z3)
6581  AZ = AW
6585  AW = ( AW+AY ) / 2
6590  RETURN
6600  REM
6601  REM Browning part for Thiolsulphinate
6602  REM --------------------------------
6610  D  = D1(2) + ( D2(2) * AW )
6620  E  = 1.0 / ( E1(2) - ( E2(2) / AW ))
6630  Z1 = ( 1.0/TMP ) - ( 1.0/303.15 )
6640  Z2 = -(E*1000.0) / 8.317
6650  Z1 = EXP( Z2*Z1 )
6660  I3 = I4 + ( D*TD*Z1 )
6670  M2 = M2 + ( 0.015 * ( I3 - I4 ))
6680  Z1 = M0 * C * K
6690  Z2 = C * K - ( 2.0*K )
6700  Z3 = ( C*(K*K) ) - ( K*K )
6710  Z4 = ( Z1/M2 ) - Z2
6720  AY = ( -Z4 + SQR( Z4*Z4 + 4*Z3 ) ) / (2*Z3)
6730  AW = ( AZ+AY ) / 2
6740  RETURN
6800  REM
6810  REM get max checkpoint
6820  REM --------------------
6830  XP(10) = XP(1)
6840  FOR X6 = 2 TO 8
6850  IF XP(X6) > XP(10)  THEN XP(10) = XP(X6)
6860  NEXT X6
6870  RETURN
7000  REM
7001  REM Material validation
7002  REM --------------------
7050  FOR X6 = 1 TO X2
7060  IF M$ = SA$(X6) THEN X2 = X6 : RETURN
7070  NEXT X6
7080  XR = 6
7090  GOTO 30000
7300  REM
7301  REM Packaging material validation
7302  REM -----------------------------
7350  FOR X6 = 1 TO X3
7360  IF PK$ = PA$(X6) THEN X3 = X6 : RETURN
7370  NEXT X6
7380  XR = 7
7390  GOTO 30000
8000  REM
```

Appendix 5.5. continued

```
8001  REM Print Input data
8002  REM ----------------
8010  IF X1 = 2  THEN 8300
8040  LPRINT : LPRINT " SHLIFE >start of run  "
8050  LPRINT : LPRINT "  "; T$
8060  LPRINT "  Food sample ..............  "; M$
8070  LPRINT "  Packaging material .......  "; PK$
8080  LPRINT "  Temperature ..............."; T1 ;" deg.C"
8090  LPRINT "  Rh ........................"; RH
8100  LPRINT "  Initial Moisture Content.."; M1 ;" gm/100gm"
8110  LPRINT "  Time interval ............."; TD; " day(s)"
8115  LPRINT "  Water vapour pressure ...."; P0 ;" mm Hg"
8120  LPRINT "  Area ......................"; AR ;" sq.cm"
8130  LPRINT "  Dry solid weight ........."; WS ;" gm"
8140  RETURN
8300  REM
8305  PRINT : PRINT " SHLIFE >start of run  "
8310  PRINT : PRINT "  "; T$
8320  PRINT "  Food sample ..............  "; M$
8330  PRINT "  Packaging material .......  "; PK$
8340  PRINT "  Temperature ..............."; T1 ;" deg.C"
8350  PRINT "  Rh ........................"; RH
8360  PRINT "  Initial Moisture Content.."; M1 ;" gm/100gm"
8370  PRINT "  Time interval ............."; TD; " day(s)"
8375  PRINT "  Water vapour pressure ...."; P0 ;" mm Hg"
8380  PRINT "  Area ......................"; AR ;" sq.cm"
8390  PRINT "  Dry solid weight ........."; WS ;" gm"
8400  RETURN
8700  REM
8701  REM print checkpoints
8702  REM ------------------
8710  FOR X6 = 1 TO 8
8720  IF T2 = XP(X6) THEN 8800
8730  NEXT X6
8740  RETURN
8800   IF X1 = 2 THEN 8900
8820   LPRINT : LPRINT "   Checkpoint at: "; T2; " days"
8830   LPRINT "   Moisture Content (M2)...";
8832   LPRINT USING FM$ ; M2; : LPRINT " gm/100gm"
8840   LPRINT "   Water Activity (Aw).....";
8842   LPRINT USING FM$ ; AW
8850   LPRINT "   Concentration (I).......";
8852   LPRINT USING FM$ ; I
8860   RETURN
8900   REM screen display
8920   PRINT : PRINT "   Checkpoint at: "; T2; " days"
8930   PRINT "   Moisture Content (M2)...";
8932   PRINT USING FM$ ; M2; : PRINT " gm/100gm"
8940   PRINT "   Water Activity (Aw).....";
8942   PRINT USING FM$ ; AW
8950   PRINT "   Concentration (I).......";
8952   PRINT USING FM$ ; I
8960   RETURN
10000 REM
10001 REM Read Samples (MAX 5)
```

```
10002 REM ----------------------
10050 IF X2 <> 0  THEN XR = 5 : GOTO 30000
10100 FOR X6 = 1 TO 50
10110 INPUT# 2, L$
10120 IF LEFT$(L$,1) = "*"    THEN 10200
10130 IF LEFT$(L$,1) = ":"    THEN RETURN
10140 X2 = X2 + 1 : X5(1) = X5(1) + 1
10150 IF X2 < 6  THEN SA$(X2) = L$
10200 NEXT X6
10210 RETURN
11000 REM
11001 REM Read Packaging (MAX 5)
11002 REM ----------------------
11050 IF X3 <> 0  THEN XR = 5 : GOTO 30000
11100 FOR X6 = 1 TO 50
11110 INPUT# 2, L$
11120 IF LEFT$(L$,1) = "*"    THEN 11200
11130 IF LEFT$(L$,1) = ":"    THEN RETURN
11140 X3 = X3 + 1 : X5(2) = X5(2) + 1
11150 IF X3 < 6  THEN PA$(X3) = L$
11200 NEXT X6
11210 RETURN
13000 REM
13001 REM D1, indexed by samples
13002 REM ----------------------
13050 IF X5(3) <> 0  THEN XR = 5 : GOTO 30000
13060 INPUT# 2, D1(1),D1(2),D1(3),D1(4),D1(5)
13070 X5(3) = 1
13080 RETURN
13500 REM
13501 REM D2, indexed by samples
13502 REM ----------------------
13550 IF X5(4) <> 0  THEN XR = 5 : GOTO 30000
13560 INPUT# 2, D2(1),D2(2),D2(3),D2(4),D2(5)
13570 X5(4) = 1
13580 RETURN
14000 REM
14001 REM E1, indexed by samples
14002 REM ----------------------
14050 IF X5(5) <> 0  THEN XR = 5 : GOTO 30000
14060 INPUT# 2, E1(1),E1(2),E1(3),E1(4),E1(5)
14070 X5(5) = 1
14080 RETURN
14500 REM
14501 REM E2, indexed by samples
14502 REM ----------------------
14550 IF X5(6) <> 0  THEN XR = 5 : GOTO 30000
14560 INPUT# 2, E2(1),E2(2),E2(3),E2(4),E2(5)
14570 X5(6) = 1
14580 RETURN
15000 REM
15001 REM A1, indexed by packaging
15002 REM -------------------------
15050 IF X5(7) <> 0  THEN XR = 5 : GOTO 30000
15060 INPUT# 2, A1(1),A1(2),A1(3),A1(4),A1(5)
```

Appendix 5.5. continued

```
15070 X5(7) = 1
15080 RETURN
15500 REM
15501 REM A2, indexed by packaging
15502 REM -------------------------
15550 IF X5(8) <> 0  THEN XR = 5 : GOTO 30000
15560 INPUT# 2, A2(1),A2(2),A2(3),A2(4),A2(5)
15570 X5(8) = 1
15580 RETURN
16000 REM
16001 REM B1, indexed by packaging
16002 REM -------------------------
16050 IF X5(9) <> 0  THEN XR = 5 : GOTO 30000
16060 INPUT# 2, B1(1),B1(2),B1(3),B1(4),B1(5)
16070 X5(9) = 1
16080 RETURN
16500 REM
16501 REM B2, indexed by packaging
16502 REM -------------------------
16550 IF X5(10) <> 0  THEN XR = 5 : GOTO 30000
16560 INPUT# 2, B2(1),B2(2),B2(3),B2(4),B2(5)
16570 X5(10) = 1
16580 RETURN
18500 REM
18501 REM I0, indexed by samples
18502 REM ----------------------
18550 IF X5(11) <> 0  THEN XR = 5 : GOTO 30000
18560 INPUT# 2, I0(1),I0(2),I0(3),I0(4),I0(5)
18570 X5(11) = 1
18580 RETURN
19000 REM
19001 REM Check for missing data in table
19002 REM -------------------------------
19050 FOR X6 = 1 TO 11
19060 IF X5(X6) = 0 THEN PRINT "MISSING DATA: ";X5$(X6) : X5(16) = 1
19070 NEXT X6
19080 IF X5(16) = 1 THEN 40000
19090 RETURN
30000 REM
30001 REM Error Routine
37002 REM -------------
37010 IF X1 = 1  THEN 37500
37020 IF XR > 100  THEN 37200
37025 IF XR = 3 OR 4 OR 5  THEN PRINT LA$;" ";
37030 PRINT ER$(XR)
37040 GOTO 40000
37200 XR = XR - 100
37210 IF XR = 3 OR 4 OR 5  THEN PRINT LA$;" ";
37220 PRINT ER$(XR)
37230 RETURN
37500 REM
37520 IF XR > 100  THEN 37700
37525 IF XR = 3 OR 4 OR 5  THEN LPRINT LA$;" ";
37530 LPRINT ER$(XR)
37540 GOTO 40000
```

```
37700 XR = XR - 100
37710 IF XR = 3 OR 4 OR 5  THEN LPRINT LA$;" ";
37720 LPRINT ER$(XR)
37730 RETURN
40000 REM
40001 REM End routine
49002 REM ------------
49005 PRINT : PRINT "Do you want to display the constants? "
49006 L$ = INPUT$(1)
49007 IF L$ = "N" OR L$ = "n"  THEN 49500
49010 PRINT X2,X3
49020 FOR X6 = 1 TO 5
49030 PRINT SA$(X6),PA$(X6)
49040 NEXT X6
49045 PRINT : PRINT "D1","D2","E1","E2"
49050 FOR X6 = 1 TO 5
49060 PRINT D1(X6),D2(X6),E1(X6),E2(X6)
49070 NEXT X6
49080 REM PRINT "Press any key to continue "
49090 REM L$ = INPUT$(1)
49100 PRINT : PRINT "A1","A2","B1","B2","I0"
49110 FOR X6 = 1 TO 5
49120 PRINT A1(X6),A2(X6),B1(X6),B2(X6),I0(X6)
49130 NEXT X6
49500 REM
49600 IF X1 = 1 THEN LPRINT : LPRINT " end of run " : GOTO 49900
49650 PRINT : PRINT " end of run "
49900 CLOSE
49910 END
```

```
* TABLE OF CONSTANTS USED IN SHLIFE PROGRAM
:SAMPLES
 "GREEN BEANS" , ONIONS , "ONIONS THIO"
:PACKAGING
 LDPE , LAMINATE
:D1
  0.038340 , -1.372683 , -0.007646  ,,
:D2
  6.581393 , 4.571451  , 0.032694   ,,
:E1
  0.011912 , 0.009658  , 0.011696   ,,
:E2
  0.000654 , 0.001179  , 0.000982   ,,
:A1
  0.089848 , 0.000089  ,,,
:A2
  -438.630087 , 66.021357 ,,,
:B1
  27.524750 , 9.097196  ,,,
:B2
  -1061.488775 , 214.328817 ,,,
:I0
  481.00 , 54.00 , 12.05 ,,
:END
```

Appendix 5.5. continued