# SHELF LIFE EVALUATION OF FOODS

Edited by
C.M.D. Man
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SPRINGER-SCIENCE+BUSINESS MEDIA, B.V



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SPRINGER-SCIENCE+BUSINESS MEDIA, B.V

First edition 1994

© 1994 Springer Science+Business Media Dordrecht
Originally published by Chapman & Hall in 1994
**Softcover reprint of the hardcover 1st edition 1994**

Typeset in 10/12pt Times by Acorn Bookwork, Salisbury, Wiltshire

Suffolk
ISBN 978-1-4613-5871-8 ISBN 978-1-4615-2095-5 (eBook)
DOI 10.1007/978-1-4615-2095-5
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A catalogue record for this book is available from the British Library
Library of Congress Catalog Card Number: 94-70985

Printed on acid-free text paper, manufactured in accordance with ANSI/NISO Z39.48-1992 (Permanence of Paper)

# Preface

The subject of shelf life of foods is not a new one. Increasing consumer interest in food safety, quality and date marking, competitive pressures from retailers and extensive legislative changes, however, have combined to give the subject a new significance. The proper and correct determination of shelf life is of course fundamental to Good Manufacturing Practice (GMP) for the food and drink industry. Manufacturers who aim to produce safe, wholesome and attractive food products 'right the first time' and 'right every time' will already know the importance of proper shelf life evaluation. Incorrect shelf lives can potentially bring about dire legal, safety or financial consequences. This is not to belittle the difficulty of failing to meet consumer expectations consistently as a result of shelf lives that have been arrived at unreliably.

A proper evaluation of shelf life must be grounded on sound scientific principles, supported by up-to-date techniques in food science and technology. This book, therefore, begins with five chapters reviewing the principles of shelf life evaluation. These are followed by ten chapters on a number of selected food products. All the authors either have first hand experience on the practice of shelf life evaluation or are involved in research of the subject. Because of the diversity and complexity of food products now available, no attempt has been made to cover every product group, let alone every product conceivable. It is our belief that sufficient practical information has been included for the beginner as well as for those who are more experienced in shelf life evaluation. It has been our intention to include the most up-to-date practice. Readers will have to decide for themselves whether or not it is the best practice. Constructive criticism is very much welcome. Either through quiet reflection or active discussion and exchange of views, it is very much hoped that new ideas for refinement and improvement in existing techniques will emerge, as will ideas for future research and development in this important area of food technology.

We dedicate this volume to those working in the food industry worldwide, for whom the evaluation of shelf life, directly or indirectly, is a major part of their livelihood, and whose care and diligence have helped to ensure the supply of safe, wholesome and quality food products. We dedicate it too, to our authors who, despite heavy workloads, have contributed to make this book a reality. We would like to thank the publishers for their understanding, patience, enthusiasm and support, particularly

at times when it looked as if the project was never going to finish. Last but not least, we would dearly love to thank our families for their forbearance in their bewilderment at the fuss the subject of shelf life of foods has caused.

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# Part 1 – The principles

# 1 Scientific principles of shelf life evaluation

R.P. SINGH

## 1.1 Introduction

Foods are perishable by nature. Numerous changes take place in foods during processing and storage. It is well known that conditions used to process and store foods may adversely influence the quality attributes in foods. Upon storage for a certain period, one or more quality attributes of a food may reach an undesirable state. At that instant, the food is considered unsuitable for consumption and it is said to have reached the end of its shelf life. In this chapter, certain major modes of food deterioration will be examined. These modes of deterioration will be expressed mathematically as rate equations. Reaction kinetics and various models that are used in practice to express quality changes in foods will be discussed. At the end of the chapter, a brief discussion of sensors that indicate time and temperature exposures of foods and their use in monitoring shelf life of foods will be presented.

## 1.2 Major modes of food deterioration

During storage and distribution, foods are exposed to a wide range of environmental conditions. Environmental factors such as temperature, humidity, oxygen and light can trigger several reaction mechanisms that may lead to food degradation. As a consequence of these mechanisms, foods may be altered to such an extent that they are either rejected by the consumer, or they may become harmful to the person consuming them. It is therefore imperative that a good understanding of different reactions that cause food deterioration is gained prior to developing specific procedures for the evaluation of the shelf life of foods. Chemical, physical and microbiological changes are the leading causes of food deterioration. A brief discussion of these changes is presented in this section. For more extended coverage of these topics, the reader is referred to books by Coultate (1989), Fennema (1985) and Labuza (1982) as well as later chapters of this book.

### *1.2.1 Physical changes*

Physical changes are caused by mishandling of foods during harvesting, processing and distribution; these changes lead to a reduced shelf life of foods. Bruising of fruits and vegetables during harvesting and post-harvest handling leads to the development of rot. Crushing of dried snack foods during distribution seriously affects their quality. Tuberous and leafy vegetables lose water when kept in atmospheres with low humidity and they subsequently wilt. Dried foods when kept in high humidity may pick up moisture and become soggy. In the case of frozen foods, fluctuating temperatures are often destructive, for example, fluctuating temperatures cause recrystalization of ice cream leading to an undesirable sandy texture. Freezer burn is a major quality defect in frozen foods that is induced from the exposure of frozen foods to fluctuating temperatures. If the fluctuations are large and the food undergoes a phase change then there are more prominent undesirable changes, for example changes caused by thawing and refreezing of foods. Similarly, phase changes involving melting and solidifying of fats are detrimental to the quality of candies and other lipid containing confectionery items.

### *1.2.2 Chemical changes*

During the processing and storage of foods, several chemical changes occur that involve the internal food components and the external environmental factors. These changes may cause food deterioration and reduce the shelf life. The most important chemical changes are associated with enzymic action, oxidative reactions, particularly lipid oxidation that alters the flavour of many lipid containing foods, and non-enzymic browning that causes changes in appearance.

At favorable temperatures, such as room temperature, many enzymic reactions proceed at rapid rates altering the quality attributes of foods. For example, fruits upon cutting tend to brown rapidly at room temperature due to the reaction of phenolase with the cell constituents that are released upon cutting of the tissue in the presence of oxygen. Enzymes such as lipoxygenase, if not denatured during the blanching process, can influence food quality even at sub-freezing temperatures. In addition to temperature, other environmental factors such as oxygen, water and pH induce deleterious changes in foods that are catalyzed by enzymes.

The presence of unsaturated fatty acids in foods is a prime reason for the development of rancidity during storage as long as oxygen is available. While development of off-flavors is markedly noticeable in rancid foods, the generation of free radicals during the autocatalytic process leads to other undesirable reactions, for example, loss of vitamins, alteration of color, and degradation of proteins.

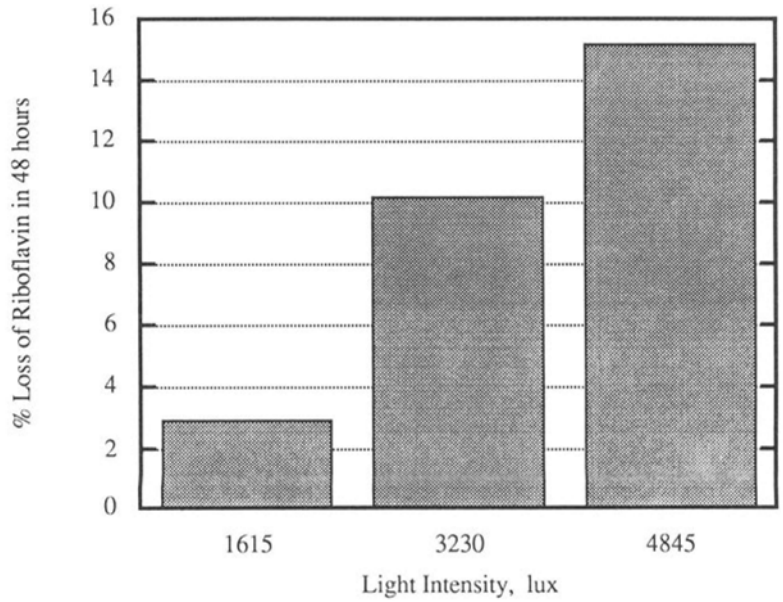



**Figure 1.1** Loss of riboflavin in whole milk stored in blow molded high density polyethylene bottles under light at 4.4°C.

The rates of lipid oxidation are influenced by several factors. As indicated previously in this chapter, the environmental temperature is an important variable. The presence of oxygen in the immediate vicinity of the food leads to increased rates of oxidation. Similarly, water plays an important role; lipid oxidation occurs at high rates at very low water activities. In determining the shelf life of foods that contain lipids, the important reaction mechanisms and their rates of reactions must be known. In addition to lipid oxidation, there are other chemical reactions that are induced by light such as loss of vitamins, and browning of meats. The influence of light on riboflavin loss in milk stored in high density polyethylene bottles is shown in Figure 1.1 (Singh *et al.*, 1976).

Non-enzymic browning is a major cause of quality change and degradation of nutritional content in many foods. This type of browning reaction occurs due to the interaction between reducing sugars and amino acids. These reactions result in the loss of protein solubility, darkening of lightly colored dried products and the development of bitter flavors. Environmental factors such as temperature, water activity and pH have an influence on non-enzymic browning.

### *1.2.3 Microbiological changes*

In determining the influence of microorganisms on the shelf life of foods, the rates of microbial growth as a function of various environmental factors must be known. Microbes have the ability to multiply at high rates when favorable conditions are present. Prior to harvest, fruits and vegetables have generally good defense mechanisms against microbial attacks, however after separation from the plant, they can easily succumb to microbial proliferation. Similarly, meat upon slaughter is unable to resist rapidly growing microbes. Microbial proliferation in cottage cheese stored at three temperatures is shown in Figure 1.2 (Shellhammer and Singh, 1991). Microbial growth in foods results in food spoilage with the development of undesirable sensory characteristics and in certain cases the food may become unsafe for consumption.

The pathogenicity of certain microorganisms is a major safety concern in processing and handling of foods. Upon ingestion, microorganisms such as *Salmonella* species and *Escherichia coli* strains cause infection while others such as *Aspergillus flavus*, *Clostridium botulinum* and *Staphylococcus aureus* produce chemicals in foods that are toxic to humans. Botulism is a well known food poisoning because of the high potency of the toxin and the high rates of fatality associated with it. Food poisoning

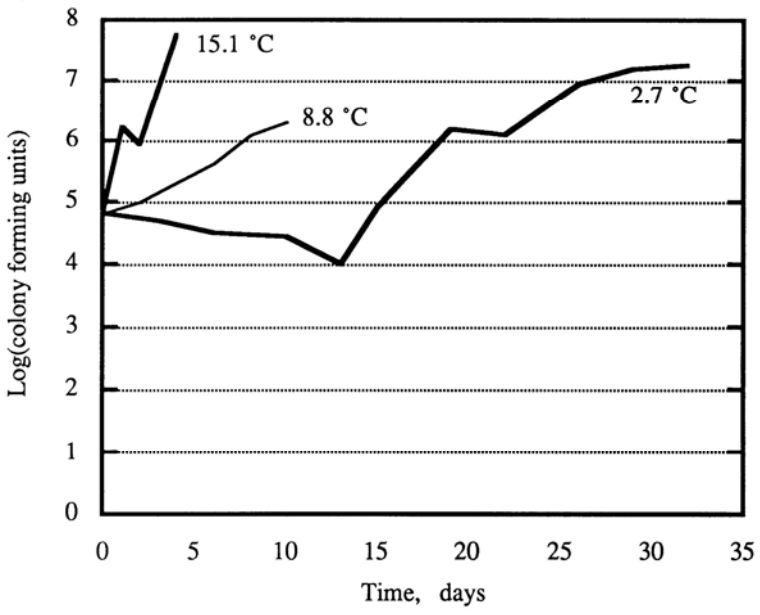



**Figure 1.2** Standard plate count for cottage cheese stored at three constant temperatures.

due to *Staphylococcus* is more frequent although it is not as severe as botulism. The presence of molds and their growth on a food product may result in undesirable appearance and off-flavors. Under certain favorable conditions mold spores may also produce chemicals that are toxic to humans. During food processing and storage, special procedures are employed to minimize or prevent the occurrence of pathogenic and spoilage microorganisms.

Various measures commonly used to minimize or prevent microbial growth in foods include altering the environmental temperature, such as either lowering the temperature to slow the growth processes, or raising temperature to destroy the microbes; removing water such that it is unavailable to the growing microbes; controlling the environmental gases such as lowering oxygen or increasing carbon dioxide concentration; reducing or stopping the microbial growth by adding acid; and promoting fermentation thus lowering the pH.

## 1.3 Evaluation of food quality

A common practice employed to evaluate the shelf life of a given food product is to determine changes in selected quality characteristics over a period of time. One may consider quality of a food as a gross measure of the food deterioration occurring in a food item. However, it should be recognized that the term quality is meant to encompass several quality attributes or characteristics. From a consumer's standpoint, the sensory expectations derived from the presence (or absence) of desirable (or undesirable) characteristics of a given food determine the quality of a product. Therefore a food product noted for its high quality has more of the desirable characteristics.

Empirical or analytical techniques may be used to quantify the quality attributes of food. For example, enumeration of microbes or determination of chemical components of a product are analytical techniques, whereas the use of human subjects to monitor changes in the magnitudes of quality characteristics constitute empirical techniques. Considerable research has been conducted on quality evaluation of foods with an aim to determine their shelf life (Jul, 1984; Van Arsdel *et al.*, 1969; Singh *et al.*, 1986; Labuza, 1982).

In the case of frozen foods, shelf life has been described by the use of various terms. For example, practical storage life (PSL) is defined as 'the period of frozen storage after freezing of an initially high quality product during which the organoleptic quality remains suitable for consumption or the process intended' (IIR, 1986). This definition requires the use of a number of sensory evaluation procedures and statistical analysis techniques. Most of these procedures rely on the use of sensory difference tests

(discrimination methods), and the shelf life failure is determined with strict statistical criteria. Shelf life failure is often identified by 'Just Noticeable Difference' (JND). JND is the 'earliest time when a difference between the quality of test and control samples can be detected by trained sensory panels' (Van Arsdel *et al.*, 1969). The use of this criterion is not restricted to one specific quality attribute or characteristic, rather it represents the overall quality of a product.

Using statistical analysis, the degree of difference between the test product and the control may be assessed at any predetermined confidence level. It may even be related to the noticeable difference between the test and the control sample that may be of commercial significance. The use of a difference test, such as JND, provides information on how long a product may be stored, for example, the PSL of a product. Readers are referred to Table 15.1 (Chapter 15) for PSL values of some common foods. While this is useful information on shelf life of different foods, it fails to provide a measure of the rate at which the quality attribute is changing.

There is considerable evidence in the literature that temperature plays a major role in causing changes in food quality during storage. Higher storage temperatures generally lead to increased quality deterioration. In the past, there have been several attempts to use mathematical techniques and models to describe changes in food quality as influenced by storage temperature. Some of the earlier interest in this area was stimulated by observations that fluctuating storage temperatures caused more detrimental change in frozen foods than storage at constant temperature. Hicks (1944) modeled the changes in food quality by assuming an exponential relationship between the rate of quality change and temperature. He used an *effective mean temperature* to represent a diurnal temperature fluctuation. The *effective mean temperature* was a constant value that produced the same change in quality as a regular sinusoidal temperature change. Other temperature functions, such as square and sawtooth functions, were modeled by Schwimmer *et al.* (1955). Using mixed linear and exponential relationships between temperature and rate of quality change, Schubert (1977) also developed an effective mean temperature for the periodic temperature fluctuations. He used an empirical function containing three experimentally derived parameters to describe the effect of temperature on the rate of quality change. Employing chemical kinetic theory, Labuza (1979) used random variable temperature conditions to obtain effective temperature. These approaches have simplified the incorporation of fluctuating temperatures in calculating quality changes in foods.

Use of the chemical kinetic approach to model changes in food quality was suggested by Kwolek and Bookwalter (1971). The kinetic approach and the Arrhenius relationship that describes the influence of temperature

on the reaction rate constants was also promoted by Saguy and Karel (1980). Lai and Heldman (1982) developed methods to determine the value of the activation energy of food quality losses from shelf life data at known temperatures. A computer-aided method to simulate changes in food quality during storage of frozen foods was used by Singh (1976). Wells *et al.* (1987) provided a graphical representation of the temperature history and food quality relationships.

### *1.3.1 Reaction kinetics*

Chemical kinetics involves the study of the rates and mechanisms by which one chemical species converts to another. The rate of a chemical reaction is determined by the mass of a product produced or the reactant consumed per unit time. In general, the rates of reactions may be determined by monitoring the concentration of either the reactants or the products of the reactions. The mechanism of a reaction, on the other hand, is more difficult to determine since it involves the sequence of steps that produce the overall result. Mechanisms of reactions are determined only in simple systems.

A general form of kinetic model may be obtained by considering the following chemical reaction

$$aA + bB \underset{k_b}{\overset{k_f}{\leftrightarrow}} cC + dD \tag{1.1}$$

where A and B are reactants, C and D are the products, and $a$, $b$, $c$ and $d$ are stoichiometric coefficients for the reactants and products, and $k_f$ and $k_b$ are forward and backward reaction rate constants. The rate at which a reactant, for example reactant A, changes would be given by

$$-\frac{d[A]}{dt} = k_f[A]^{\alpha}[B]^{\beta} - k_b[C]^{\gamma}[D]^{\delta} \tag{1.2}$$

where [A], [B], [C] and [D] are the concentrations of reactants (mass per unit volume); $\alpha$, $\beta$, $\gamma$ and $\delta$ are the reaction orders with respect to each product or reactant; and $t$ is time. Equations (1.1) and (1.2) are for a general case, since these equations are unsolvable because of too many unknowns, therefore simplifying procedures are used. For example, the reaction conditions may be chosen such that either the forward or the backward reaction is predominant. If the concentration of reactant B in equation (1.1) is kept very high then the change in concentration of B is negligible. As a consequence, the backward rate constant will be considerably smaller than the forward reaction rate constant. For this case, the rate of reaction can be represented by

$$-\frac{d[A]}{dt} = k'_f[A]^n \tag{1.3}$$

where $k'_f$ is the pseudo forward rate constant, and $n$ is the reaction order. The rate of reaction is described mainly by the concentration of a species. Due to the complex nature of foods, it is difficult to determine the actual mechanisms of the intermediate reactions that lead to a particular change in quality. The following approach is commonly used to analyze general quality changes in foods.

A general rate expression may be written as follows for a quality attribute $Q$

$$\pm\frac{dQ}{dt} = kQ^n \tag{1.4}$$

where $\pm$ refers to either decreasing or increasing value of the attribute $Q$, $k$ is the pseudo forward rate constant, $n$ is the observed order of reaction. It is assumed that the environmental factors such as temperature, humidity and light and concentrations of other components are kept constant.

Equation (1.4) may be rewritten more specifically for a quality attribute that is decreasing with time and following an '$n$th' order of reaction,

$$-\frac{dQ}{dt} = kQ^n \tag{1.5}$$

*1.3.1.1 Zero order reaction.* Consider a quality attribute $Q$, that decreases during the storage period as shown in Figure 1.3. A closer examination of the linear plot implies that the rate of loss of a quality attribute is constant throughout the storage period and it does not depend on the concentration of $Q$. This assumption has been widely used in the food science literature. This linear plot represents a zero order reaction, therefore substituting $n = 0$ in equation (1.5) we get,

$$-\frac{dQ}{dt} = k \tag{1.6}$$

Equation (1.6) may be integrated to obtain

$$Q = Q_o - kt \tag{1.7}$$

where $Q_o$ represents some initial value of a quality attribute and $Q$ is the amount of that attribute left after time $t$.

If the end of shelf life, $t_s$, is noted by the quality attribute reaching a certain level, say $Q_e$, then

$$Q_e = Q_o - kt_s \tag{1.8}$$

Therefore, the shelf life, $t_s$, may be calculated as

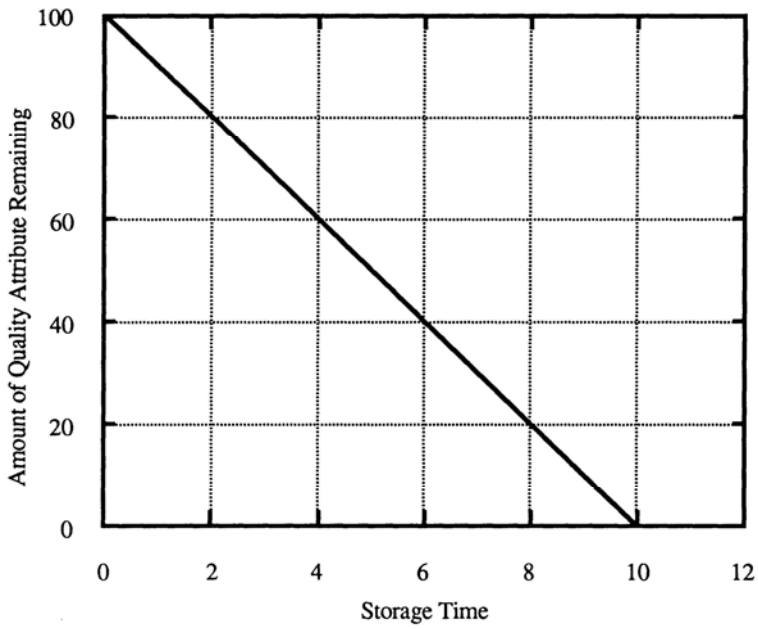



**Figure 1.3** Decrease in a quality attribute of a food during storage (zero order reaction).

$$t_s = \frac{Q_o - Q_e}{k} \tag{1.9}$$

The use of zero order rate equation (1.6) is useful in describing such reactions as enzymic degradation, non-enzymic browning and lipid oxidation that leads to development of rancid flavors.

*1.3.1.2 First order reaction.* Consider Figure 1.4 where a quality attribute, $Q$, decreases in an exponential manner with storage time. The rate of loss of a quality attribute is dependent on the amount of quality attribute remaining; this implies that as time proceeds and the quality attribute decreases so does the rate of reaction. This exponential plot between quality attribute and time represents a first order reaction, $n = 1$, and equation (1.5) is modified as follows,

$$-\frac{dQ}{dt} = kQ \tag{1.10}$$

By integration, we get

$$\ln \frac{Q}{Q_o} = -kt \tag{1.11}$$

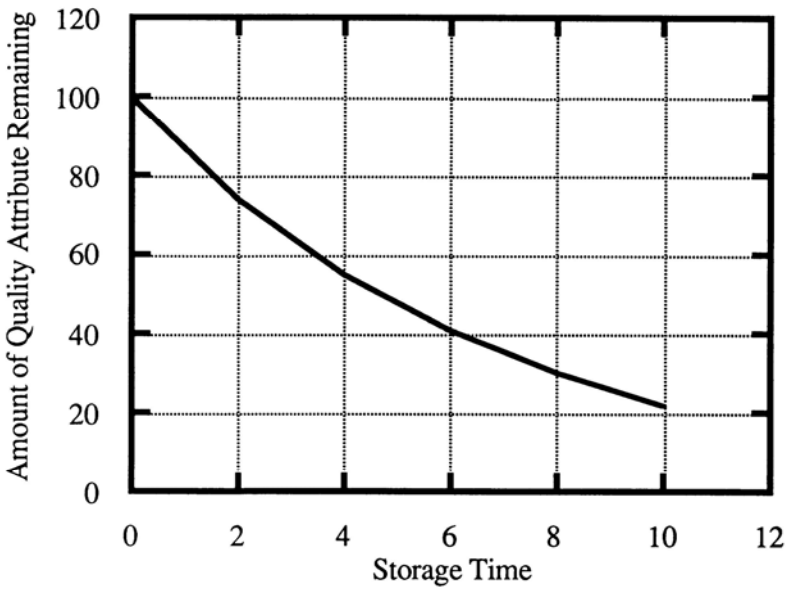



**Figure 1.4** Decrease in a quality attribute of a food during storage (first order reaction).

where $Q$ is the amount of quality attribute left at time $t$.

At the end of shelf life, $t_s$, for a certain final level of quality attribute, $Q_e$, we can also write equation (1.11) as

$$\ln \frac{Q_e}{Q_o} = -kt_s \tag{1.12}$$

or

$$t_s = \frac{\ln \dfrac{Q_o}{Q_e}}{k} \tag{1.13}$$

Sometimes, it is desirable to know the time for half-life of a reaction. To obtain the half-life time, equation (1.13) may be modified by substituting $Q_e = 0.5\ Q_o$,

$$t_{1/2} = \frac{0.693}{k} \tag{1.14}$$

The types of food deterioration reactions that show first order losses include vitamin and protein losses and microbial growth.

In analyzing experimental data on rate of change of a given quality attribute, the following two issues are important. First, the analytical pre-

**Table 1.1** An estimate of percentage error in reaction rate constant, $k$, as a function of analytical precision and change in reactant species monitored

| Analytical precision (%) | 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 |
| ± 5.0 | >100 | >100 | 70 | 35 | 25 | 20 | 15 |
| ±10.0 | >100 | >100 | >100 | 70 | 50 | 40 | 30 |

Source: Benson, 1960.

cision of measuring attribute level affects the value obtained for rate constant. In Table 1.1 an estimate of percentage error in reaction rate constant, $k$, is given for different levels of analytical precision (Benson, 1960). As seen in this table, as analytical precision decreases, when the change in reactant species monitored is small, there is a greater percentage error in the calculated value of the reaction rate constant.

The second important issue in kinetic analysis is the change in reactant species monitored. In Figure 1.5, two plots are shown, one for zero order

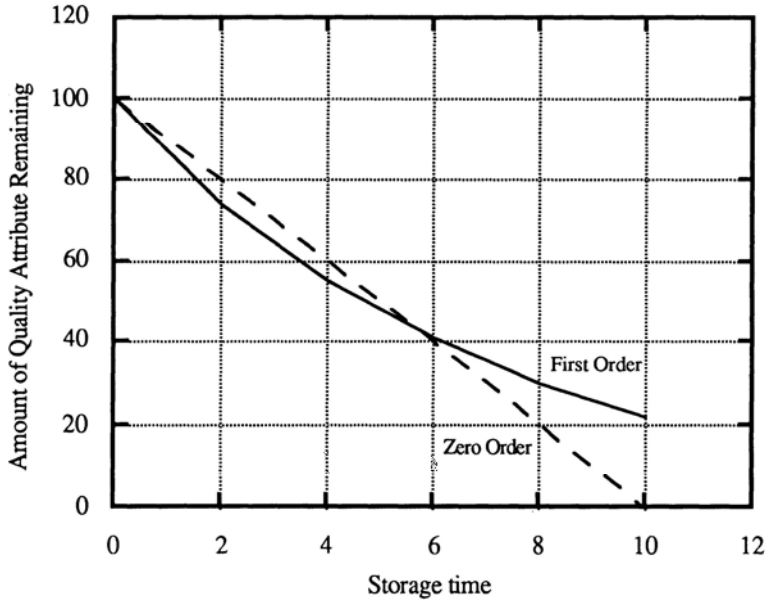



**Figure 1.5** Decrease in a quality attribute of a food following two different orders of reactions.

reaction and the other for a first order reaction. In this case, the overlap between zero order and first order plots, for up to about 55% reduction of the quality attribute, indicates that either zero or first order model can be used to describe the change in the attribute. However, beyond 55% reduction, there is a considerable difference in the level of quality attribute predicted by the zero order and first order models. Therefore, if the experimental data on the rate of change of a quality attribute are available only for less than 55% reduction in the quality of an attribute, then a simple zero order reaction model would be sufficient. However, use of that model to extrapolate more than 55% change can lead to serious errors if the correct reaction order was first order. Thus, caution must be exercised in determining the reaction order. Labuza (1984) has illustrated some of the common pitfalls that should be avoided in using statistical evaluation of rate of loss of quality.

Most reactions showing losses in food quality may be described by zero or first order; there are some studies in the literature that indicate use of other orders. A second order reaction was used by Singh and Heldman (1976) to describe vitamin C degradation in canned infant foods. In studying oxygen uptake in lipid oxidation kinetics, Labuza (1971) found a half order reaction with respect to oxygen for relatively pure lipids. The order of reaction increased to first order when antioxidants were added.

*1.3.1.3 Temperature effects.* The influence of temperature on the reaction rate may be described by using the Arrhenius relationship, as follows

$$k = k_o \exp\left[-\frac{E_A}{RT}\right] \tag{1.15}$$

where $k_o$ is the pre-exponential factor, $E_A$ is the activation energy, $R$ is the ideal gas constant, and $T$ is the temperature (absolute scale).

The temperature dependence of the reaction rate can be shown graphically as in Figure 1.6. On a semilogarithmic axis, a linear plot is obtained between rate constant and the inverse of absolute temperature. The slope of the straight line gives the activation energy. A steeper slope implies that the reaction rate constant is influenced to a larger extent by a change in temperature.

Another parameter that is often used in the literature to describe the relationship between temperature and reaction rate constant is the $Q_{10}$ value. $Q_{10}$ is defined as follows

$$Q_{10} = \frac{\text{reaction rate at temperature } (T + 10)^\circ\text{C}}{\text{reaction rate at temperature } T^\circ\text{C}} \tag{1.16}$$

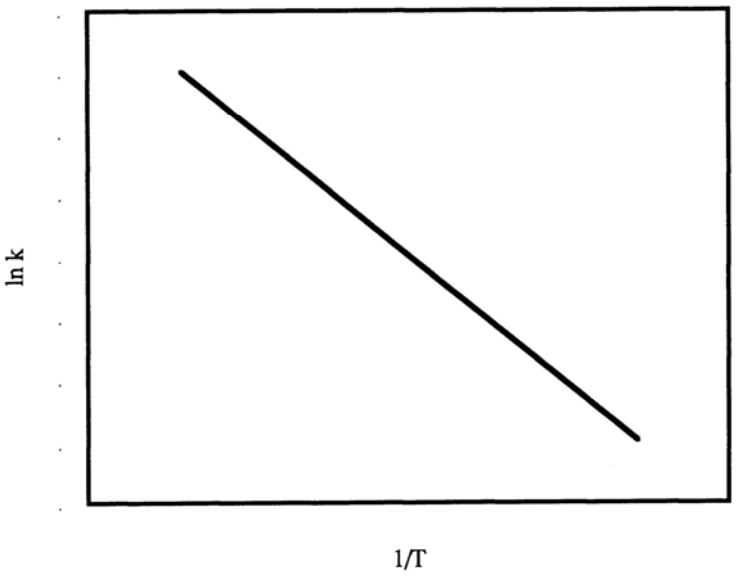



**Figure 1.6** Influence of temperature on the reaction rate constant. Slope = $E_A/R$.

It can be shown that $Q_{10}$ and activation energy $E_A$ are related by the following expression (Singh and Heldman, 1993)

$$\log Q_{10} = \frac{E_A}{2.303R}\left[\frac{10}{T_A(T_A+10)}\right] \tag{1.17}$$

### *1.3.2 Determination of kinetic parameters*

In order to describe the influence of temperature on the reaction rates, such as by use of the Arrhenius expression, it is necessary to know the values of kinetic parameters such as rate constant and activation energy. Two procedures are most commonly employed to determine these kinetic parameters.

(a) The linear regression method involves plotting the log of rate constant against the reciprocal of temperature (absolute). It is necessary to obtain rate constants for at least three different temperatures. Since this plot should be a straight line, linear regression procedures are used to determine the slope and intercept, thus obtaining values for the pre-exponential factor and the activation energy in equation (1.15).

(b) A non-linear regression method suggested by Arabshahi and Lund (1985), Cohen and Saguy (1985) and Haralampu *et al.* (1985) is used to determine the activation energy directly from the concentration or level of

a quality attribute. This method precludes the determination of rate constants. The advantage of this method is the use of original data points related to the variation of quality attribute in calculating the desired kinetic parameters. Standard computer routines such as SAS NONLIN (SAS Institute Inc, 1982) and BMDP 3R (University of California, 1983) are available for non-linear regression.

The expression describing change in quality attribute in a non-linear form for a zero order reaction is as follows:

$$Q_{ij} = Q_o - k_o t_{ij} \exp\left(-\frac{E_A}{RT_j}\right) \tag{1.18}$$

and for a first order reaction, the expression is,

$$Q_{ij} = Q_o \exp\left[-k_o t_{ij} \exp\left(-\frac{E_A}{RT_j}\right)\right] \tag{1.19}$$

where the subscripts $i$ and $j$ indicate the time and temperature of the corresponding quality attribute measurement.

### *1.3.3 Shelf life plots*

Labuza (1982) presented a simple approach to determine the effect of temperature on food quality. His method is particularly suited for situations when the available data are meager, for example in cases where the experimental data are available only as time needed to reach a certain value of a quality attribute. This is true for many published studies on shelf life in the literature. A brief introduction to developing shelf life plots is as follows.

For a given reaction order the following can be written,

$$k = \frac{\text{amount lost at time } t_s}{t_s} \tag{1.20}$$

where the numerator, the amount of quality lost at a time $t_s$, for a first order reaction $= \ln Q_o/Q_e$, and for a zero order reaction $= Q_o - Q_e$

Taking logarithm of both sides of equation (1.20), we get

$$\ln k = \ln(\text{amount lost at time } t_s) - \ln t_s \tag{1.21}$$

The Arrhenius expression, equation (1.15), may be rewritten as

$$\ln k = \ln k_o - E_A/RT \tag{1.22}$$

Equating right hand sides of equations (1.21) and (1.22), and rearranging we obtain

$$-\ln t_s = -\ln(\text{amount lost at time } t_s) + \ln k_o - E_A/RT \tag{1.23}$$

According to the preceding equation, a plot of $t_s$ with respect to $1/T$ on

a semilog paper should give a straight line (Figure 1.7); the activation energy can then be obtained from the slope of the line, $+E_A/2.303R$. For a small temperature range, less than $\pm 20°C$, $t_s$ may be plotted directly against $T$ without significant error (Labuza, 1982) as shown in Figure 1.8. Then the equation for the straight line shown in Figure 1.8 may be written as

$$t_s = t_o e^{-aT} \tag{1.24}$$

where $t_o$ is the shelf life at a reference temperature, $a$ is the slope of the line, and $T$ is the temperature difference between the temperature at which the shelf life, $t_s$, is desired and the reference temperature.

For a zero order reaction, shelf life and rate constant are inversely proportional. Equation (1.16) may be rewritten as

$$Q_{10} = \frac{\text{Shelf life at } T°C}{\text{Shelf life at } (T + 10)°C} \tag{1.25}$$

Then from equations (1.24) and (1.25)

$$Q_{10} = e^{10a} \tag{1.26}$$

or,

$$a = \frac{\ln Q_{10}}{10} \tag{1.27}$$

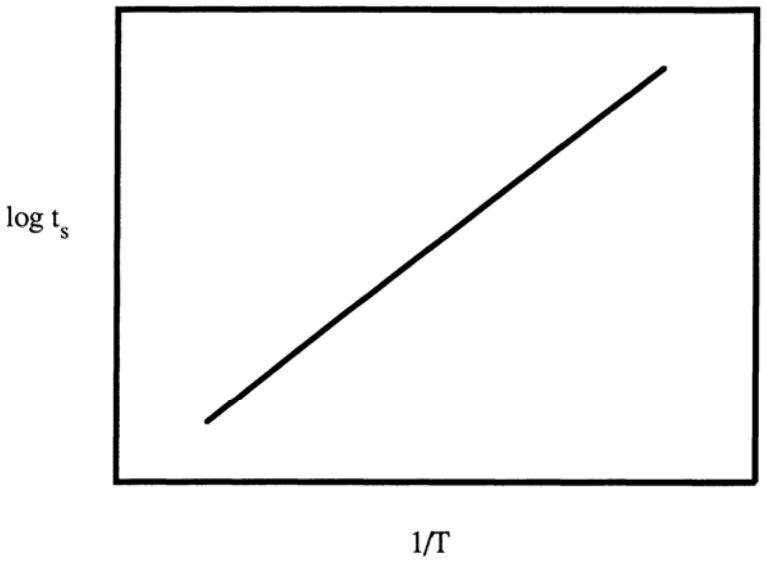



**Figure 1.7** A shelf life plot using inverse of absolute temperature for $x$-axis.

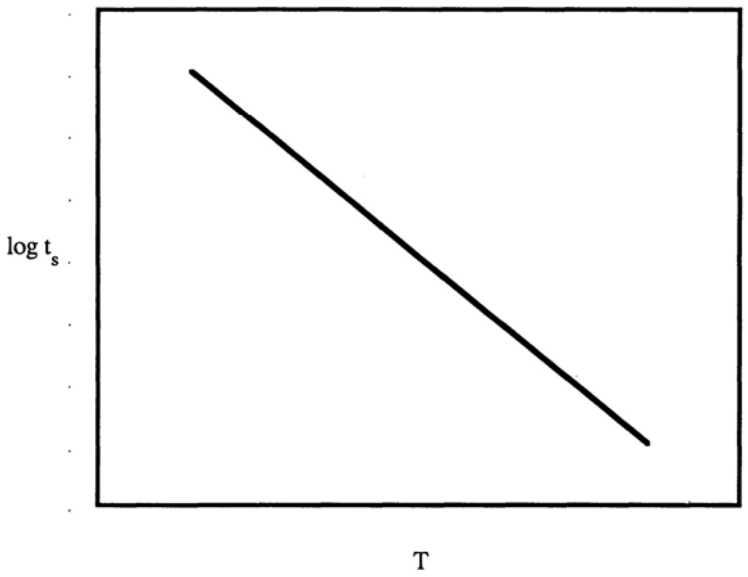



**Figure 1.8** A shelf life plot. Slope = $a$ = ln $Q_{10}/10$.

The preceding equation is useful in designing accelerated shelf life tests. An example is shown in Figure 1.9. If the shelf life at 25°C is 20 months, a series of lines may be drawn through the point representing 25°C and 20 months for different $Q_{10}$ values as shown in Figure 1.9. If the accelerated tests are to be conducted at 40°C, then the accelerated shelf life times for different $Q_{10}$ values may be obtained from this plot. Thus, if $Q_{10} = 4$, the shelf life at 40°C is 2.5 months, if $Q_{10} = 8$, the shelf life at 40°C is 0.88 months. The same procedure can be easily implemented on a computer with a spreadsheet programme. In Figure 1.10, a spreadsheet program and results for the preceding example are shown.

## 1.4 Use of sensors to monitor shelf life of foods

Recently there has been an increased interest in sensors that can be used to monitor quality of stored foods. Many developmental efforts have focused on the time–temperature indicators. As the name suggests, these sensors provide information related to the temperature history. Since temperature is one of the most important environmental factors that influence a number of quality attributes in foods, there is a recognized merit in knowing the temperature exposure of a food consignment during storage

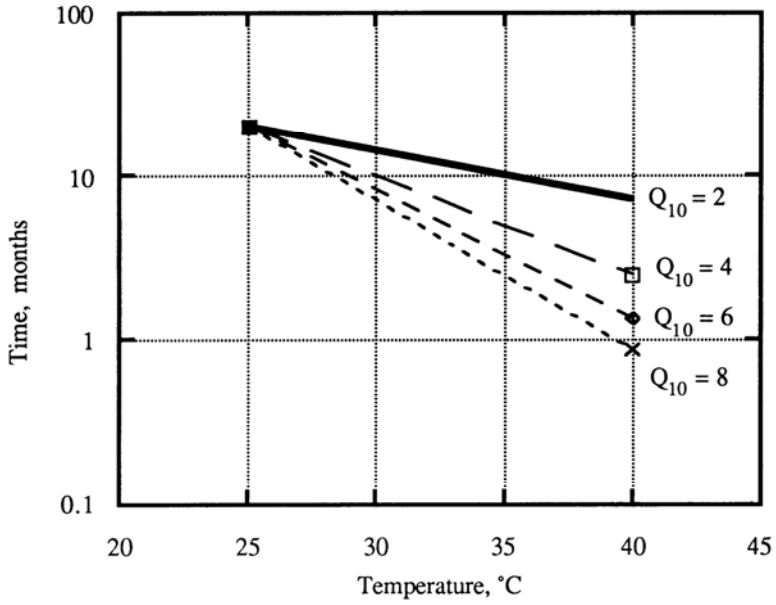



**Figure 1.9** Accelerated shelf life plots for different $Q_{10}$ values.

and distribution. For the indicators to be most useful for this purpose, they must be irreversible. Preferably, they should provide an integrated response of both time and temperature. During the last few decades, a number of patents have been issued related to devices that can indicate the integrated effect of time and temperature (Schoen and Byrne, 1972; Taoukis *et al.*, 1991; Kramer and Farquhar, 1976; Farquhar, 1977; Byrne, 1976; Olley, 1976; and Wells and Singh, 1992). These devices provide an indication of temperature history using a variety of different principles, such as mechanical, enzymic, or chemical change, development of color or movement of color along a scale.

The time–temperature indicators may be classified as either critical temperature indicators, partial history indicators or full history indicators (Taoukis *et al.*, 1991; Singh *et al.*, 1984).

### *1.4.1 Critical temperature indicators*

Critical temperature indicators give a response only when the temperature either goes above or below a certain pre-selected temperature. These indicators do not integrate time with temperature therefore they fail to provide the temperature history effect. These types of indicators are useful to indicate if a certain temperature was reached during the exposure

| | A | B | C | D | E | F |
|---|---|---|---|---|---|---|
| 1 | Ti | 25 | C | | Enter reference temperature Ti in cell B1, temperature T at which shelf life is desired in cell B2, Q10 in cell B3, and shelf life at temperature Ti in cell B5. Enter formulas as shown in cells B4 and B6. The results will be shown in cell B6. | |
| 2 | T | 40 | C | | | |
| 3 | Q10 | 2 | | | | |
| 4 | a | .069 | <=LN(B3)/10 | | | |
| 5 | shelf life at Ti | 20 | | | | |
| 6 | shelf life at T | 7.071 | <=B5*EXP(-B4*(B2-B1)) | | | |
| 7 | | | | | | |
| 8 | | | | | | |
| 9 | | | | | | |
| 10 | | | | | | |
| 11 | | | | | | |
| 12 | | | | | | |
| 13 | | | | | | |

**Figure 1.10** A spreadsheet to calculate accelerated shelf life at a higher temperature.

period, e.g. whether a freeze sensitive product was exposed to freezing temperature. This type of information is useful if quality attributes of the product are sensitive to some critical temperatures. The MonitorMark™ Thaw Indicator and MonitorMark™ Freeze Indicator (manufactured by Packaging Division/3M, St Paul, Minnesota) are examples of critical temperature indicators.

### *1.4.2 Partial history indicators*

The partial history indicators provide a response only when the temperature exceeds (or is below) a certain predetermined value. An example is the MonitorMark™ Extended Response Indicator (manufactured by Packaging Division/3M, St Paul, Minnesota). This type of indicator described in detail by Manske (1976, 1983) contains a pad saturated with a chemical mixture. The chemical diffuses along a porous wick after the pad is brought into contact with the wick and only when the temperature exceeds the melting point of the chemical. Since the diffusion process is temperature dependent, then for temperatures greater than the melting point of the selected chemical, one obtains a time–temperature integrated response from this type of indicator. Different chemicals with their corresponding melting points are used for needed applications. The performance of these indicators and their applications have been reported by Taoukis and Labuza (1989a, 1989b), Taoukis *et al.* (1990), and Fu *et al.* (1992). These types of indicators have been used in the shipment of pharmaceutical products to tropical regions by World Health Organization.

### *1.4.3 Full history indicators*

Full history indicators provide a continuous response based on changes in the temperature; the response of these indicators is at a rapid rate at higher temperature and at slow rate at lower temperature. Examples of full history time–temperature indicators include LifeLines Freshness Monitor (manufactured by LifeLines Technologies, Morristown, New Jersey) and IPOINT Time/Temperature Monitor (manufactured by I-POINT Biotechnologies A.B., Malmo, Sweden). The principle of IPOINT Time/Temperature Monitor is described by Blixt and Tiru (1977), Blixt (1983) and Blixt *et al.* (1977). This indicator involves two pouches, one containing a lipolytic enzyme and the other containing a lipid substrate. The indicator is activated by breaking the seal between the two pouches and mixing their contents. An enzymic hydrolysis of a lipid substrate results in a decrease of pH with a consequent change in color. Different indicator response times can be obtained by changing the concentration of the enzyme-substrates. The activation energies of these indicators can be made to vary from 15 to 35 kcal/mole, which covers a broad range suitable for many quality degradation reactions during storage and distribution. This indicator has been extensively studied by Taoukis and Labuza (1989a) and Wells and Singh (1988c).

The Lifelines™ Fresh-Scan indicator (manufactured by LifeLines Technologies, Morristown, New Jersey) uses a temperature dependent polymerization reaction (Patel and Yang, 1983; Patel *et al.*, 1976; Patel and Yee, 1980; Fields and Prusik, 1986). In this type of indicator di-substituted diacetylene crystals are allowed to polymerize. As the polymer is formed there is a distinct change in color. A specially designed optical reader is used to measure the reflectance of the polymer. The indicator is in active state upon manufacturing therefore it requires special care during shipment prior to its attachment to a food package. The range of activation energy is 20–24 kcal/mole, useful for many food storage applications. The application of this indicator has been explored for a number of foods (Wells and Singh, 1988b, 1988c; Taoukis, 1989; Taoukis and Labuza, 1989a).

The usefulness of these sensors in monitoring quality depends on how well they can mimic changes in quality. Studies conducted to date show that these indicators are suitable to follow changes in selected quality attributes due to temperature. In a comprehensive study conducted with 12 different foods (Wells and Singh, 1988b), selected quality attributes were monitored both sensorily and analytically. It was found that a number of these changes were due to temperature exposure. This study also showed that the indicator response of several models could be used to monitor changes in the selected quality attributes. For example, in the case of frozen strawberries, a decrease in firmness (an attribute measured

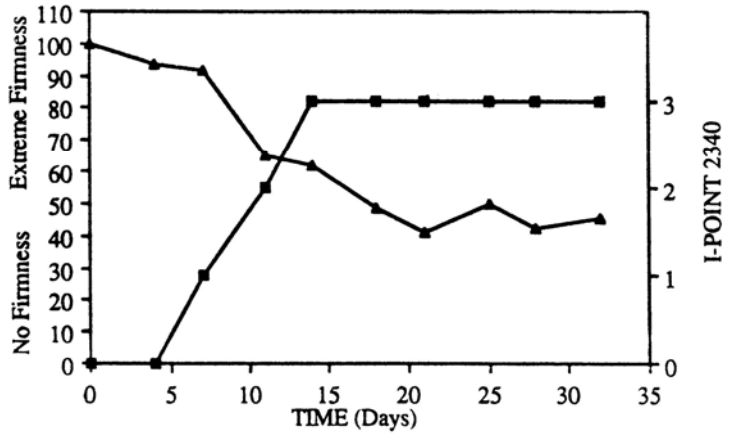



**Figure 1.11** A comparison of mean response of I-POINT model 2340 (■) and mean sensory score of tomato firmness (▲) at 15°C (Wells and Singh, 1988b).

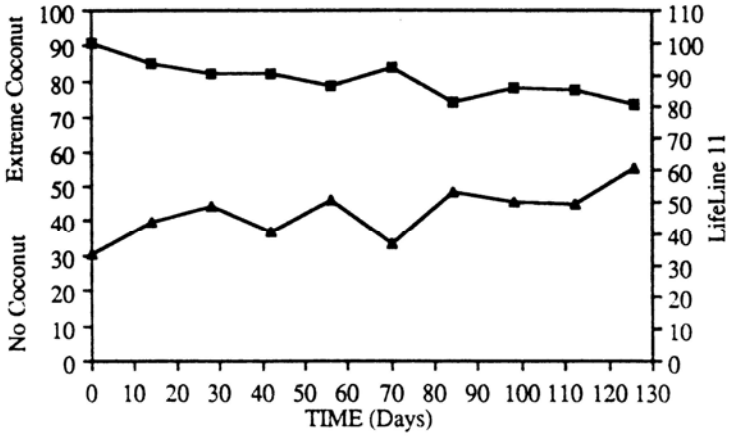



**Figure 1.12** A comparison of mean response of LifeLine model 11 (■) and mean sensory score of coconut flavor (▲) in UHT sterilized milk stored at 5°C (Wells and Singh, 1988b).

using sensory panels) and a decrease in measured amount of ascorbic acid were well correlated with the response of IPOINT model 2340 indicator as shown in Figure 1.11. Similarly the development of coconut flavor in UHT sterilized milk was strongly correlated with the response of LifeLines Freshness indicator as seen in Figure 1.12. Published studies on correlation of time–temperature indicator response with quality attri-

butes in various foods include hamburgers (Singh and Wells, 1985; Chen *et al.*, 1989); frozen strawberries (Singh and Wells, 1987); tomatoes, lettuce, UHT milk, fruitcake (Wells and Singh, 1988b); pasteurized whole milk (Mistry and Kosikowski, 1983; Cherng and Zall, 1989; Grisius *et al.*, 1987); ice cream (Dolan *et al.*, 1985); refrigerated ready-to-eat salads (Campbell, 1986); refrigerated orange juice (Chen and Zall, 1987a); pasteurized cream (Chen and Zall, 1987b) and cottage cheese (Shellhammer and Singh, 1991; Chen and Zall, 1987b).

The mathematical basis of how the full history indicators mimic a given quality attribute is amply presented in the literature (Wells and Singh, 1992, 1988a). Kinetic models are useful to describe changes in food quality along with the response of time–temperature indicators (Wells and Singh, 1992; Fu *et al.*, 1991). Briefly, their approach involved using (a) indicator response at a constant reference temperature and (b) the activation energy of the indicator, to predict a constant temperature equivalent of indicator response change for any interval between successive indicator inspections. The constant temperature equivalent was then used to predict the amount of a food quality attribute expected during the same interval. The mathematical derivations that describe this approach for a first-order reaction model were presented by Wells and Singh (1988a) and for a zero-order reaction by Wells and Singh (1992). The equivalent temperature used by these authors is different from the *effective mean temperature* used by Hicks (1944) and Schwimmer *et al.* (1955). The equivalent temperature is calculated on the basis of time–temperature indicator and the elapsed time between indicator inspections. If the time intervals between the successive inspections is small or the temperature of storage is constant then the equivalent temperature predicted by the time–temperature indicator will be approximately equal to the effective mean temperature calculated from the change in food quality. The advantage of using the equivalent temperature approach is that it does not require the food quality to be observed experimentally or predicted theoretically based on temperature history recorded by a data acquisition system.

The time–temperature indicators have proven to be useful aids in monitoring the quality of foods during storage and distribution. The information provided by the indicators can be implemented in computer-aided quality based inventory management systems (Singh and Wells, 1989; Singh, 1989; Wells and Singh, 1989). It is important to note that a time–temperature indicator provides a history of temperature changes in the immediate vicinity of the indicator. Mathematical models have been proposed to extend this local temperature history to that of the entire unit package used for a food with known thermal properties (Malcata, 1990); these models need to be verified for industrial conditions.

## 1.5 Conclusions

In studying shelf life of foods, it is important to measure the rate of change of a given quality attribute. As shown in this chapter, these rates can be modeled using simple zero-order or first-order kinetics. The shelf life plots are useful in incorporating the effect of temperature on changes in food quality. The principles of shelf life evaluation discussed in this chapter should assist a reader in the development of predictive capabilities. This quantitative treatment is necessary to improve and maintain the storage and distribution segment of the food chain.

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# 2 The methodology of shelf life determination

M.J. ELLIS

## 2.1 Integration of shelf life procedures into a total quality system

Shelf life is an important feature of all foods (Table 2.1). All those involved in the handling of foods should be aware of it. These may include growers, ingredient suppliers, manufacturers, wholesalers, retailers and the consumers. Shelf life of a food product may be defined as the time between the production and packaging of the product and the point at which it becomes unacceptable under defined environmental conditions. Storage and distribution are necessary links in the food chain. Quality (and safety) considerations dictate the conditions and maximum duration of these links in the chain although most food deteriorations take place gradually.

A total quality approach (Figure 2.1) must embrace all aspects of a food from its conception, through development and production to its consumption, and for a manufactured food product this will include:

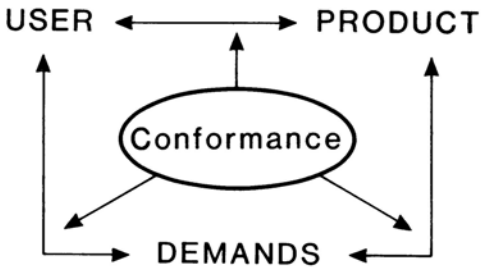
- product design (including hazard analysis and risk assessment to ensure safety)
- specification and testing of ingredients and packaging materials
- manufacturing processes
- transport, storage and retail display
- storage at home and consumption

Since the food must be safe and have an acceptable quality when consumed, the time for which this is maintained – the shelf life – is therefore an essential aspect of product design the control of which is a requirement of Good Manufacturing Practice (GMP) (IFST, 1991) as well as a requirement of the international standard for quality systems, ISO 9001 (ISO, 1987).

Shelf life determination of a new product often requires storage for significant periods, and includes samples from early development stages as well as initial production runs. Through the evaluation of stored samples, potential storage problems can be identified and, either eliminated or controlled before the food goes into production. When in production, an ongoing quality assurance system is equally important, and involves assessment of freshly made products, typically before the production has been released into distribution. Samples stored for up to the assigned shelf life

**Table 2.1** Examples of food products and their typical shelf lives

| Food Product | Typical shelf life | Main limiting factors |
|---|---|---|
| Bread | up to 1 week at ambient | Stale flavour, texture change |
| Sauces, dressings | 1–2 years at ambient | Stale/rancid flavour, colour change |
| Pickles | 2–3 years at ambient | Stale flavour, texture change |
| Chilled foods | up to 4 months at 0–8°C | Microbiological spoilage, flavour change |
| Frozen foods | 1–1½ years in freezer cabinets | Colour/texture change |
| Canned foods (e.g. unlacquered cans) | 1–1½ years at ambient | Tin pick-up |
| Canned foods (e.g. lacquered cans) | 2–4 years at ambient | Texture/flavour change |




**User**

(safety, quality, satisfaction and loyalty)

**Product**

(safety, quality, consistency and perceived value)

**Demands**

(legality, standards, specifications and cost)

**Figure 2.1** A total quality approach – the relationship between user, product and demands.

should also be evaluated, so that any change in the storage performance can be noted, and appropriate actions taken if necessary. Furthermore, an efficient customer complaint management system will provide early warning signals concerning potential shelf life problems. Finally, an up-to-

date, operable and effective product recall system is the last resort should the need to recall an unsafe or defective product arise. Thus an adequate shelf life system will require appreciable resources, and these should be allowed for when planning the overall quality budget.

Since most aspects of shelf life evaluation for new products and monitoring of standard production involve similar sample handling and analysis procedures to the rest of the quality system (perhaps with the added requirement of suitable storage facility), it is logical and normally most convenient to integrate shelf life procedures into the total quality regime. As the manufacturer is likely to be responsible for most if not all product development activities, he will normally be responsible for both the shelf life determination during product development and on-going monitoring once regular production has begun. Even if development work has been sub-contracted out, it is essential for the manufacturer's 'due diligence' system to be able to demonstrate the validity and reliability of any shelf life quoted.

## 2.2 Food legislation and shelf life

Food legislation in many developed countries requires most prepacked foods to carry a date of 'minimum durability'. The inference is that procedures have been established (in the main by the manufacturers) for shelf lives to be evaluated. In the UK, for instance, 'best before' date is the usual date mark required by current legislation to appear on the labelling of prepacked foods. The 'best before' date however must be replaced by the 'use by' date when the food is microbiologically highly perishable and therefore likely after a short period to contribute an immediate danger to human health. It is an offence to sell any food after its 'use by' date.

The 'best before' date is the date up to and including which the food 'can reasonably be expected to retain its specific properties', providing it has been stored properly. Food may still be edible after that date, but its appearance and quality could suffer; for example crisp biscuits might become soggy (MAFF, 1991). Naturally, meaningful storage instructions are required alongside the 'best before' date if the food is to be enjoyed at its best. While the term 'specific properties' may not be well defined for many foods, the regulations, e.g. The Food Labelling Regulations (HMSO, 1984), require that product names and descriptions are correct and it can be expected that these will be considered misleading if the shelf life which is set allows marked changes in the properties of the food between being freshly made and the 'best before' date. Examples of such changes may include the watery or oily separation which occurs during the shelf life of salad cream and mayonnaise. Foods in unlacquered cans may dissolve enough tin to infringe the UK Tin in Food Regulations

**Table 2.2** Examples of some shelf life aspects and their legislative control in the UK[a]

| Shelf life aspects | Examples of relevant legislation |
|---|---|
| Hygiene | *Food Hygiene (General) Regulations* (1970)<br>*Food Hygiene Directive* (93/43/EEC) |
| Temperature control | *Food Hygiene (Amendment) Regulations* (1990)<br>*Food Hygiene (Amendment) Regulations* (1991) |
| Packaging migration | *'Plastics' Directive* (90/128/EEC)<br>*Plastics Materials and Articles in Contact with Food* Regulations (1992) |
| Processing | *Food (Control of Irradiation) Regulations* (1990) |
| Use of preservatives | *Preservatives in Food Regulations* (1989) |
| Strict product liability (design, manufacture, etc.) | *Consumer Protection Act* (1987) Part 1 |

[a]Source: Jukes, 1993.

(HMSO, 1992). Such food may be confiscated as unfit for human consumption. Vitamin claims may become invalid if loss occurs during storage. Cakes may not rise sufficiently during baking as a result of failure of the baking powder in the cake mix to effect the desired chemical aeration. Sensory property of a beverage may be impaired due to either simple flavour loss or deteriorative chemical changes.

The seller is generally legally responsible for compliance when the food is sold to the consumer. However, in the case of manufactured foods a retailer would normally demand goods with sufficient remaining shelf life to sell and for the consumer to store for a reasonable period of time before use. An inappropriate shelf life set by a manufacturer could conceivably lead to prosecution since a retailer would be able to demonstrate due diligence in accepting the manufacturer's data.

It should also be recognised that if foods reach the marketplace in substandard condition the legal sanction imposed by the regulatory authority is likely to be trivial compared with the adverse publicity such action would attract, especially for a large or well known firm. Publicity generated by product recalls, for example, due to yeast contaminated fat free Thousand Island Dressing (*The Daily Telegraph*, 1991) and off-flavour Smarties (*The Globe and Mail*, 1993) respectively is something that every manufacturer would do its best to avoid.

Examples of other shelf life aspects that may need to be considered and are subject to legislative control in the UK are given in Table 2.2.

## 2.3 Forms of quality deterioration during storage

Most foods change progressively during storage, and the changes in most cases render the food less attractive and palatable and eventually unfit for

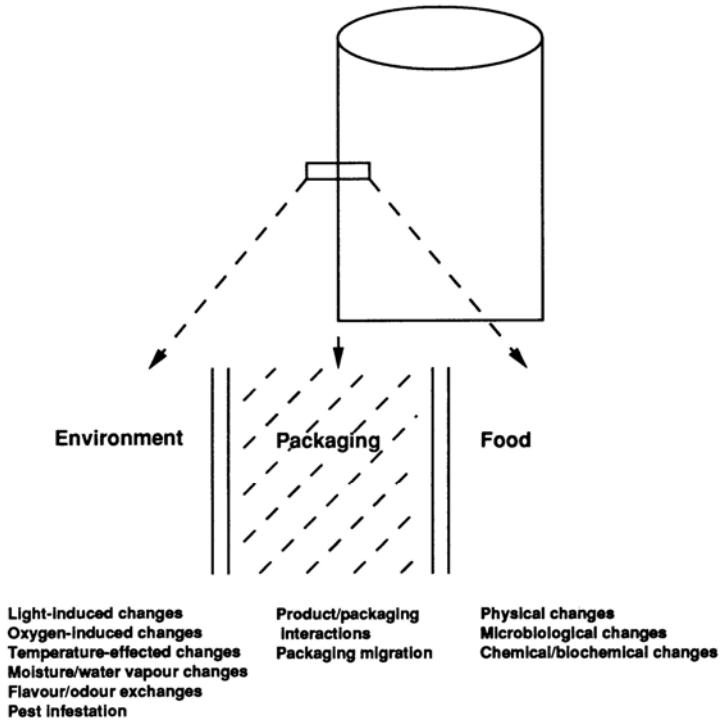



**Figure 2.2** Food spoilage and deterioration – a basic model.

consumption. Figure 2.2. (IFST, 1993) summarises the main deteriorative changes commonly encountered in foods.

Watery separation and 'setting up' can occur in thickened foods in cans and jars while suspended particles tend to settle in thinner products. Oil can separate from emulsion products such as salad cream giving a similarly unattractive appearance. Many food components change in the presence of oxygen. Thus the oil in emulsion products can develop 'rancid' flavours. Many foods acquire a stale, sometimes 'cardboard' like taste as they age. Natural pigments e.g. lycopene, change colour and in the case of tomatoes from red to brown. Filling tomato products in unlacquered tinplate cans mitigates this colour effect as the exposed tin scavenges the headspace oxygen during sterilisation and storage giving the food considerable protection from colour and indeed flavour changes but tin dissolves in the process. This can also give a metallic taste and contravene the UK *Tin in Food Regulations* if the uptake of tin in the food exceeds 200 mg per kg within the assigned shelf life unless the latter is reduced to allow for this. Tin dissolution however can be uneven with

some foods; localised attack can expose the steel base plate which then reacts with the steel to generate hydrogen creating internal pressure (swell) which would normally be interpreted as a sign of microbial growth. Continued attack can eventually perforate the can in extreme cases and allow contamination. Tin dissolution is increased by the presence of dissolved headspace oxygen, nitrate from water or ingredients, or residual sulphur dioxide (FAO, 1986). Tin dissolution can be avoided if the cans are fully lacquered internally, but oxygen-induced changes are then potentially greater.

Glass is inert to all foods so offers no oxygen scavenging effect, and colour and flavour changes can occur in the surface layer of bottled foods due to reaction with oxygen present in the headspace or leaking in the event that the cap seal is not perfect. Sealed plastic packages (bottles and bowls) used for long life foods can give more rapid oxidative changes as all plastics have some oxygen permeability.

During storage of frozen foods, 'freezer burn' may appear as white surface areas caused by sublimation of water vapour from exposed portions. These areas are usually also toughened due to the dehydration. Some components such as vegetables can change colour during frozen storage. Growth of ice crystals and other physical changes in sauces and dessert type frozen foods can give an icy and granular mouthfeel, rather than the desired smooth texture. Ice cream can lose volume during frozen storage due to loss of the air incorporated during manufacture. Since ice cream is normally sold by volume, this loss may cause infringement of the relevant Weights and Measures Regulations.

In dried foods, oxygen sensitive components may be more exposed than in the same foods when fresh, giving rapid development of rancidity in oil containing foods such as formation of 'musty' or 'hay' flavours in dried herbs. Loss of crispness can occur quickly if the food is hygroscopic unless protein is offered by the use of suitable packaging.

Deterioration in many fresh foods is largely due to growth of micro-organisms but wilting of vegetables is a result of water loss while staling of baked goods can be partly explained by changes in the structure of their starch component.

## 2.4 Procedures for direct determination and monitoring of shelf life

Direct shelf life determination requires batches of samples to be taken at significant stages in the development or modification of a product. These samples should be examined during storage, usually under controlled environmental conditions, until their quality becomes unacceptable. The time when this occurs is the maximum product shelf life, and therefore the determination necessarily requires at least this time to complete.

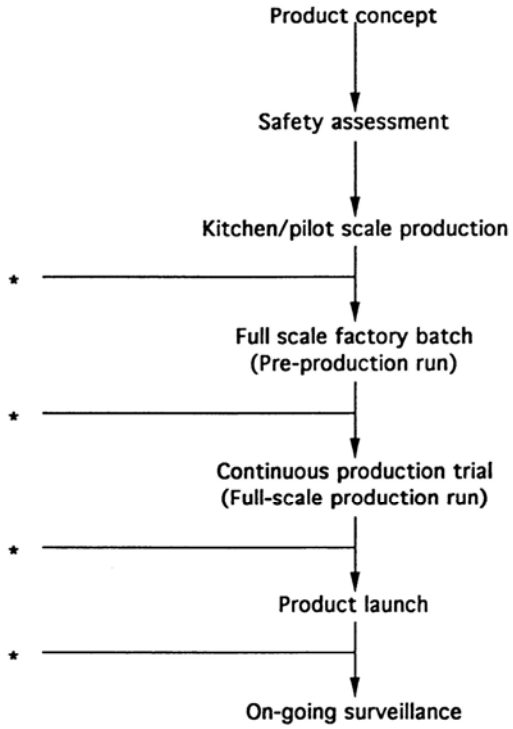



**Figure 2.3** Evaluation of shelf life – significant sampling stages (★).

Section 2.5 outlines methods for shortening the process for long life foods to avoid delays to product launches due to shelf life testing.

Significant sampling stages within the programme of shelf life evaluation include (Figure 2.3):

1. The successful experimental kitchen or pilot plant batch. While scale-up to production will normally highlight some differences, this stage may precede lengthy development activities such as market research or plant construction, allowing longer storage experience to be gained. At this stage it is possible to investigate formulation, process or packaging changes to improve the shelf life without the costs of factory time and material quantities.
2. The successful full scale factory batch. This is the most important sampling stage as the food should be substantially the same as subsequent production and examination of samples of the product will provide data for the setting of shelf life and specification standards.
3. The first continuous production trial. Examination of products should confirm the data from earlier samplings.

4. Early runs of standard production not supervised by development personnel. This constitutes the transition between the development and production stages. Examination of samples from these runs forms a major part of the development review, allowing a first opportunity to adjust the shelf life should the need arise.

As part of an on-going surveillance system, samples should be taken at suitable intervals for storage trial. The sampling interval should typically be 20% of the shelf life which will provide samples of 6 different ages from fresh to the full shelf life, for examination at any time. For long life products more frequent intervals may be useful to detect any changes in storage performance (e.g. every two months for a two year shelf life) while for shorter life products a frequency greater than monthly is usually unnecessary.

Shelf life samples should be subjected to conditions effectively simulating the normal storage and distribution conditions the food is likely to encounter. For ambient stable foods this usually means normal room temperature and relative humidity, but as laboratory and experimental kitchen temperatures are likely to be higher than in the warehouse, a store cooled to and maintained at the mean warehouse temperature may be required.

For foods packed in impermeable packaging, relative humidity of the storage environment is unlikely to be important in influencing shelf life. However if shelf life is limited by moisture gain/loss (for instance biscuits and cakes respectively) or if the food is packed in moisture sensitive oxygen barrier plastics such as ethylene vinyl alcohol copolymer (EVOH), control of the relative humidity becomes a major consideration in the shelf life study.

If performance in tropical or sub-tropical conditions is required, similar storage conditions should be used as many chemical changes will be accelerated under these conditions. Similarly, if temperatures near or below freezing are envisaged, they should be used in testing as the conditions may destabilise thickeners such as modified starches.

Frozen foods are normally stored at between –25°C and –30°C for long periods by manufacturers and –18°C during distribution, retail display and in the home freezer. A realistic storage trial regime incorporating these temperatures should be employed, and, since frozen foods are frequently taken home after purchase in ambient or insulated containers only, a suitable period at an appropriate temperature should also be included. If storage instructions on the pack are to provide permissible periods in 'star' (*) marked freezers or frozen compartments of refrigerators, storage periods at –12°C (**) and –6°C (*) should also be included (UKAFFP, 1978).

Some foods such as jams, pickles, sauces, meat pastes, margarines and

low fat spreads are normally used over a varying period of time (from days to weeks) after the pack has been opened; an 'open' shelf life storage test should be included for these products involving removal of portions for tasting or other examination at pre-determined intervals and re-closing the pack over a suitable time span. Storage of the package between successive openings should be under recommended conditions (or likely conditions if mis-use/abuse is expected). The latter usually means either room temperature or that of a domestic refrigerator.

The basis of shelf life examination of foods is often subjective with appearance, smell, texture and flavour being the main attributes to assess. Such assessments are frequently inexact as there may not be a suitable control sample with which to compare the stored samples, this being particularly so for new products. Freezing can often be a useful means of preserving reference/standard samples but there is no universal method for keeping them. In many cases remaking of reference samples every time a comparison with stored samples is made may be the only option. It follows then that the importance of proper handling, storage and identification of reference samples cannot be overemphasised.

Quantitative measurements, for example of colour, texture, viscosity and amount of water or oil separation should be included if they either closely relate to subjective quality or can be used as reliable indicators of quality deterioration.

Expert or consumer panels producing statistically analysed results may give the best measure of storage changes and acceptability but can be very expensive for regular use. An individual shelf life assessor with proper training and experience of normal storage changes may be employed to carry out most assessments and other resources such as analytical services or expert taste panels used where necessary.

In addition to subjective assessments, other tests may be necessary. These may include tin content of products in unlacquered cans, vitamin content where a claim is made or microbiological examination of fresh or chilled foods.

As previously mentioned, as a general rule, samples of product retained for shelf life determination should be evaluated about 6 times during the assigned shelf life of the product. Thus short life 'fresh' or chilled foods may require daily examination until they become unacceptable, while long life products, for example canned foods, may need to be evaluated once every six months.

As a shelf life scheme generates a substantial body of information, control and documentation of this information is important, especially if a large number of different products are involved and there is a continuing programme of innovation and development. A convenient basis of control is the allocation of a number to each different product and a serial number for each batch of samples tested during development and

the commercial life of the product. For instance, a particular canned soup could be given the number 123 and thus 123/5 might be the fifth batch to be tested. Even if the product name is changed during or after development the same 'shelf life' number can be retained for easy identification. Each batch of experimental or production samples can then be assigned an evaluation record identified by this number and kept as a file indexed by product shelf life number, making the shelf life history of a product readily accessible. Where a substantial number of different products are under development and being monitored on an on-going basis, data control and, in particular, 'cross indexing' to identify similar product or packaging changes over a period of time can still be cumbersome and in this case the use of a computer spreadsheet or database will probably be feasible and worthwhile even if the total record system is not computerised.

## 2.5 Methodology for accelerated estimation of shelf life

The system described in the previous section necessarily requires the full shelf life, possibly several years, to produce results. Development of long life foods will normally require results in a much shorter time to meet product launch schedules. More rapid alternative techniques are available but they should always be supplemented by normal condition testings ('direct determination') for confirmation since it is hardly possible to predict the storage performance of a product under normal conditions with certainty from its behaviour when 'abused'.

A number of accelerated techniques are in use. When using these it is a general rule that the more rapid the degradation induced, and thus the further from normal storage conditions, the less reliable the shelf life estimate is likely to be. The potential problems and possible errors that can arise in the use of accelerated techniques have been described elsewhere (IFST, 1991; Robertson, 1993). There is no advantage in destabilising a product which is perfectly stable during normal storage. The results obtained from accelerated techniques must be interpreted with caution as they are not applicable to all products. Using experience of similar products, the likely shelf life of a new or modified product can often be estimated before any storage tests are done. A conservative shelf life with a generous margin of safety should be given in this case so that the shelf life can be confirmed or modified as soon as accelerated and normal storage data have become available.

Raising the storage temperature will accelerate many ageing processes and this is the basis of many of the accelerated methods. Storage at 30 to 33°C can give a 2 to 3 fold increase for many, in particular, flavour changes. Storage at 35 to 40°C can bring about a 4 fold speed up of oil or

water separation and facilitate tin dissolution in unlacquered cans. Storage at 55°C for a period of 4 to 6 weeks can show up instability in pickle and sauce products. Products that remain stable after this storage will probably be stable for a long time at ambient temperature; however such high temperature has been shown to cause acid hydrolysis of starches in normally stable foods.

Cycling the product between 0°C and room temperature will accelerate watery separation in starch-thickened foods. Absence of any separation after 30 cycles over 2 months normally suggests that the product will be stable for up to 2 years or more at ambient temperature.

Where oxygen causes flavour or colour changes in permeable (e.g. plastics) packaging, high oxygen atmospheres will speed up changes, as will a high relative humidity if EVOH is used as the oxygen barrier layer. Storage of the products in a nitrogen atmosphere should also be considered alongside air or enhanced oxygen conditions so that the effects of oxygen can be isolated from those due to other changes.

Controlled shaking (at 250–300 strokes per minute) to provide moderate product agitation for several hours will cause separation in unstable emulsion products. Shaking rates and package geometry must be closely controlled (or preferably standards should always be shaken alongside experimental samples) as these parameters greatly influence product movement and shearing.

Storage defects in frozen products can be accelerated by storage at higher than normal temperatures. Thus more rapid changes will occur at −18°C compared with the normal long term storage temperature of below −25°C, and still faster changes will occur at −10°C. Certain forms of deterioration, such as ice crystal growth and freezer burn will also be accelerated if the storage temperature is made to fluctuate while the food still remains frozen.

## 2.6 The importance of shelf life to quality and distribution

Production of foods of consistently acceptable quality with shelf lives adequate for their intended uses together with the correct communication to the consumer of their durability are important to the manufacturer, retailer and consumer. The consideration which is most important is that the food must reach the consumer in good condition and retain its quality for the period expected, including a period after the package has been opened if normal use implies this. All other factors are subordinate. Consumers will not continue to buy unsatisfactory products.

Modern manufacturing processes are often more efficient if long production runs are made. This will impose a constraint on shelf life if a number of different products are made on the same plant as inventory

must be accumulated to cover the period between production runs. The quality of the food made before and after the required storage period must be similar, and both must be acceptable.

While consumer demand and rate of production will normally be matched to minimise storage and thus inventory costs, unforeseen fluctuations in demand can necessitate storage of products for longer than intended. For certain food products such as some bakery goods, frozen storage may be used successfully to extend the shelf life as a means of stockpiling prior to an expected period of increased sale. In addition, many foods are distributed nationally or internationally, so time is required for transport, handling and transit storage at various stages. Careful considerations must also be given to the different environmental conditions prevalent in the different export markets in respect of adequate packaging protection to maintain shelf life. Today's larger retailers will normally turn stock over rapidly; small retailers will frequently be slower in selling and may well operate less controlled stock rotation systems.

Finally, the retailer will require time to sell the food to the consumer. Large retailers will usually have rapid stock turnover and thus an actual need for relatively short storage, while smaller shops with lower volumes may need a longer time to sell the food. Also, commercial considerations may dictate that a shorter shelf life will suffice so as to give the product a 'fresher' image. All will require a 'best before' (or 'use by') date sufficiently long after delivery for their needs. With their very large purchasing influence, major retailers may well be in a position to demand in their contracts a long residual shelf life on foods delivered to them.

Frequently there may be a conflict between quality and the logistic requirements of manufacture and delivery, so some compromise may have to be made. Quality (and of course safety) should always be given the greatest weight and statutory quality standards must never be compromised. It may well be better in the long term not to produce and market a food product if quality and an adequate shelf life cannot be simultaneously realised.

## 2.7 Conclusions

For most foods, adequate shelf life can be achieved. Knowledge of the factors affecting shelf life and use of valid and appropriate methodology are vital to the delivery of an acceptable product to the consumer. Sufficient care and adequate resources should be devoted to shelf life evaluation. A safe, high quality product that consistently pleases its customer has its origin in good product design which includes properly conducted and documented shelf life procedures and on-going surveillance, evidence

that can be used to prove that the manufacturer has considered his products and problems and that he does care about what he produces.

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# 3 The principles and practice of shelf life prediction for microorganisms

S.J. WALKER

## 3.1 Introduction

Prior to determining the shelf life of a food, it is essential to determine which factor(s) limit the shelf life. Such factors may cause chemical, physical and biological changes which result in a sensory change in the food. If the limiting factor is not correctly identified, then subsequent studies will be flawed. Unfortunately, in many cases, the factors studied are those most easily measured rather than those which limit the shelf life. For the remainder of this chapter, only microbial changes will be considered. With microbial growth, it is often useful to consider safety and spoilage separately although the controlling factors for both may be identical. Issues relating to safety must take precedence over those relating to spoilage.

Traditionally, food microbiologists have determined the microbial shelf life of foods using 'expert judgement', storage trials or challenge tests. Unfortunately, 'expert judgement' tends to be very subjective and with the greater onus on food manufacturers to demonstrate due diligence, this option has become less desirable. Both shelf life trials and challenge tests, if done correctly, are very powerful weapons in the food microbiologist's armoury and have served the food industry well (Brown, 1992). A challenge test is the laboratory simulation of what may happen to a food during its life and may involve inoculation with specific microorganisms and/or storage at abuse temperatures. Useful guidance on challenge testing is available (Anon, 1987). Whilst the results from these are extremely valuable, challenge tests tend to be costly and time-consuming. Furthermore, the results of a challenge test apply specifically to those conditions tested and any change in a product's formulation or storage temperature may invalidate the results previously obtained. Consequently, there has been a great deal of interest in other ways to determine the shelf life of foods. Perhaps the most promising method is the use of predictive models for microbiology. These models allow the user to predict the fate of microorganisms when a food is stored under specific conditions of temperature, pH, gaseous atmosphere and so on.

The use of predictive models for foods is not new and the safe thermal

processing of many canned goods is based on models for microbial inactivation developed over 70 years ago (Esty and Meyer, 1922). More recently however, there has been much interest in the development of models for microbial growth and non-thermal inactivation. Predictive models for microbial growth can be divided into two main types: those which predict the probability of an event occurring (probability models) and those which predict the change in microbial numbers (kinetic models). In some circumstances, probabilistic models are very powerful and have been used to predict the likelihood of *Clostridium botulinum* growing in cured meat products (Roberts and Jarvis, 1983). Kinetic models are often more useful as they not only indicate the ability to grow but also provide information about the rate and extent of growth that occurs in a given time period. The major advantage of predictive models is that they may be used to predict the fate of microorganisms in conditions not specifically tested during the construction of the model.

## 3.2 Development of predictive models

The development of predictive microbiological models for use in foods is neither simple nor inexpensive. A number of stages must be successfully completed if a model is to be of widespread use and applicable to foods.

### *3.2.1 Experimental design*

As with all scientific research, the experimental design is crucial. An inappropriate design may result in the collection of vast amounts of unnecessary data or in data that cannot be successfully modelled. Furthermore, the factors modelled (e.g. temperature, pH, salt content, atmosphere) and their ranges must be appropriate to the intended use of the model. For example, there is little merit in a model for a psychotrophic pathogen which applies only to high storage temperatures (25–35°C) if the major concern is with its growth at refrigeration temperatures.

### *3.2.2 Data collection*

The accumulation of data on the growth or inactivation of microorganisms is undoubtedly the most costly stage of model development. Most work is done using microbiological media as they are of consistent composition and can be easily and reproducibly adjusted to the conditions required for study. The inherent variability of foods coupled with the microbial response tend to result in few studies directly in foods (Maxcy and Wallen, 1983), although simple models have been developed in largely homogeneous foods such as milk (Griffiths and Phillips, 1988). Most data

have been developed from studies using plate count techniques, although automated techniques such as optical density and conductimetry (Gibson, 1985) have been used. As workers develop models containing four or more factors, the requirement for automated data collection techniques will increase.

Guidelines on data collection and recording have been developed (Walker and Jones, 1993) and a greater standardisation of data collection and recording will certainly aid the future of predictive microbiology throughout the world.

### *3.2.3 Modelling*

To date, a number of techniques have been used to model the data and include Gompertz-polynomial (Gibson *et al.*, 1988; Buchanan and Phillips, 1990) and Bêlehrádek-type (Ratkowsky or square root) models (McMeekin *et al.*, 1993). These models are applicable to growth of the microorganisms. More recently, newer modelling techniques have been developed to predict both the growth, survival, and non-thermal inactivation of microorganisms (Figure 3.1) (Jones and Walker, 1994). Such techniques permit the use of data with greater ranges than models based solely on growth, and so may have greater applicability. At present, it is

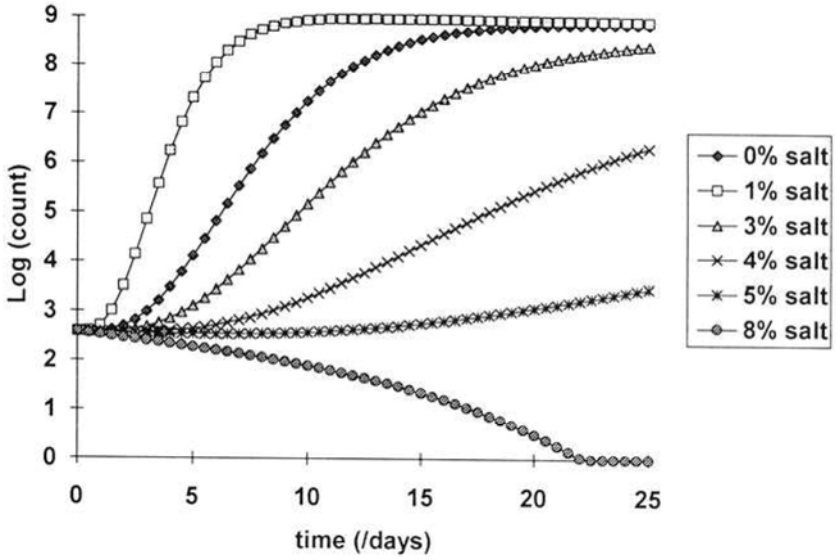



**Figure 3.1** Use of a new modelling technique to predict growth, survival and inactivation of *Yersinia enterocolitica* as affected by salt.

inappropriate to recommend any single modelling technique. Rather, the technique should be suitable for the data used and should be economical. The modelling techniques currently employed are largely descriptive in nature. The development of mechanistic models which are based on an understanding of how a microorganism behaves will be one of the major advances in the future of modelling.

### *3.2.4 Model validation*

Perhaps the most important stage associated with the development of models in microbiological media is their validation. One approach to model validation has been described by McClure *et al.* (1994). The validation should ensure that not only does the model describe accurately the data used to produce it, but it should also demonstrate the applicability of the model to foods. This latter stage is crucial if the users of models are to have confidence in the models' predictions. Food validation may be done using data from the published literature, industry generated data or specific inoculated food studies (Figure 3.2). Any deficiencies in a model to predict well for some, or all, foods should be evident to the model user.

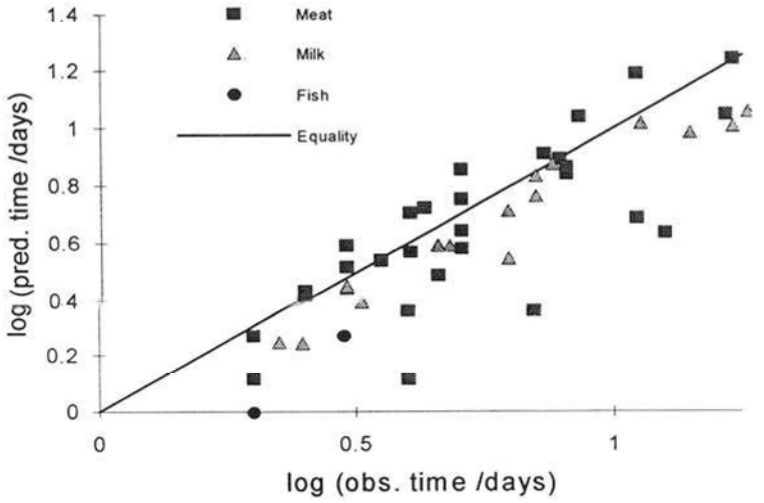



**Figure 3.2** Comparison of model predictions and observed times for 1000-fold increase in microbial numbers from foods inoculated with *Yersinia enterocolitica*.

### *3.2.5 Obtaining predictions*

The final stage of model development is to ensure that the user can obtain predictions. Developments in computer hardware and software have permitted the output of models to be presented in a variety of ways. Some systems available have been described by Buchanan (1991), Zwietering *et al.* (1992) and Jones (1993). The trend is for systems to use personal computers and to offer a lot of flexibility in their use. The vast majority of models available are for pathogenic bacteria, although models have been developed for the spoilage of milk (Griffiths and Phillips, 1988), meat (Zamara and Zaritzky, 1985) and soft drinks (Cole and Keenen, 1987). Part of the reason for this focus on pathogens is the high cost of developing models and major initiatives in the UK and USA are funded by Government with a view to improving food safety. Within the UK, the Ministry of Agriculture, Fisheries and Foods has funded a large research programme (1989–1994) to predict the growth, survival and inactivation of foodborne pathogens and is available as a commercial service, the 'Food Micromodel'. Models have been produced for *Aeromonas hydrophila*, *Bacillus cereus*, *B. subtilis*, *Campylobacter*, psychrotrophic *Clostridium botulinum*, *Clostridium perfringens*, *Escherichia coli* 0157:H7, *Listeria monocytogenes*, *Salmonella*, *Staphylococcus aureus* and *Yersinia enterocolitica*. Further details on this programme have already been described by Gould (1991) and Walker and Jones (1994b).

## 3.3 Uses of models

Once developed, models can be used in a variety of ways to help ensure the safety and quality of foods. Although the majority of applications has been developed for pathogenic bacteria, they may also be used for spoilage microorganisms provided appropriate, validated models are available.

### *3.3.1 Product formulation and reformulation*

The design of a product formulation or reformulation is fundamental to the safety and quality of the food. Relatively small changes in the formulation may have a profound effect on microbial growth and may result in an unsafe product or a product of poor quality. Increasingly, food manufacturers are under pressure to change the formulation of foods (e.g. reduction in salt levels or removal of preservatives), many of which have had a long and safe history. Such changes may potentially permit microbial growth in food previously considered stable. Unfortunately, the microbial safety or quality of a product formulation or reformulation is

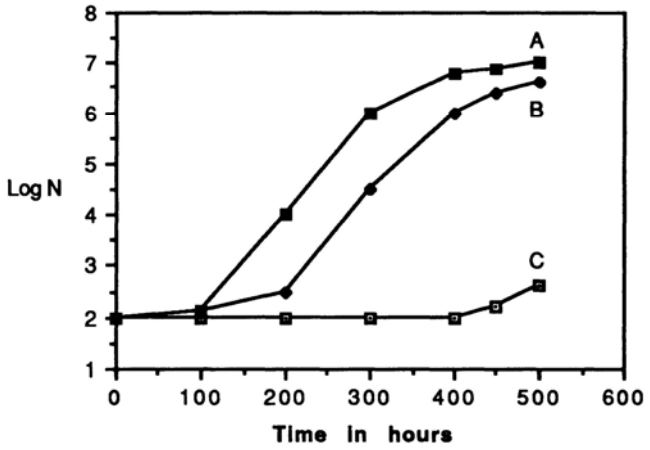



**Figure 3.3** The effect of product formulation on the growth of *Aeromonas hydrophila*. A, *Aeromonas hydrophila*, salt (% w/v) 2.3, pH 6.1, 7.0°C; B, *Aeromonas hydrophila*, salt (% w/v) 4.3, pH 6.1, 7.0°C; C, *Aeromonas hydrophila*, salt (% w/v) 2.3, pH 5.6, 7.0°C.

often one of the last parameters to be considered. If a product is subsequently shown to be microbiologically unstable, then the development costs to this point have been wasted. By using predictive models, the microbial stability of a product formulation can be rapidly assessed. Formulations that are intrinsically unsafe or unstable can be readily eliminated, so that subsequent development work is effectively targeted. Although this could be done using challenge tests, predictive models provide answers rapidly and cost-effectively. The effect of various product formulations on growth of a pathogen is shown in Figure 3.3.

Until predictive models have been widely accepted and have proven their applicability for food products, many food manufacturers may consider it prudent to do a microbiological challenge test on the final product to validate the model predictions. The nature and scope of this challenge test however, will be considerably less than that required if predictive models had not been used.

### *3.3.2 Process design*

The shelf life of many foods is dependent, not only on formulation, but also on processes applied during manufacture (e.g. pasteurisation). Often the product formulation cannot be such to prevent microbial growth and so processing is necessary. With the development of models for inactivation, the process can be designed to ensure that the target microorganism(s) are effectively eliminated.

Although the traditionally used $D$ and $z$ values have been widely used to determine safe processes, as with other types of predictive modelling, alternative approaches to modelling thermal inactivation have been identified (Cole *et al.*, 1994).

### *3.3.3 HACCP*

Hazard Analysis, Critical Control Points (HACCP) is a philosophy that has been applied to the production of food. This concept may be applied to both food safety and food quality. As a technique it has gained wide approval as a proactive way to assure food safety and quality. Seven principles have been identified in the application of a HACCP plan (Anon, 1992):

1. Conduct a hazard analysis. Identify and list the hazards and specify control measures.
2. Identify the critical control points.
3. Establish target level(s) and tolerances which must be met to ensure each CCP is under control.
4. Establish a monitoring system to ensure control of the CCP.
5. Establish the corrective action to be taken when monitoring indicates that a CCP is moving out of control.
6. Establish documentation.
7. Establish verification procedures.

When considering microbial hazards, specific knowledge of factors affecting the growth, survival and inactivation of microorganisms is required. Predictive models can be used to indicate if a hazard exists at a particular process step (principle 1). To determine if a process step is critical (principle 2), use of a decision tree is often recommended (Figure 3.4). Again valuable information to progress through the decision tree can be obtained from models. Once a process step has been identified as a critical control point (CCP), its control is essential. Predictive models can be used to identify the optimal target value for correct operation of this step and the tolerances that may be permitted (principle 3).

The application of models can therefore aid the application of HACCP to food manufacture by ensuring that good quality, systematic and objective information is used in the decision making process.

### *3.3.4 Time–temperature profiles*

With many foods, particularly those stored chilled, the control of temperature during storage of a food is important in ensuring the safety and quality. During storage, the food will be subject to a fluctuating temperature profile. If this profile is known, predictive models can be used to

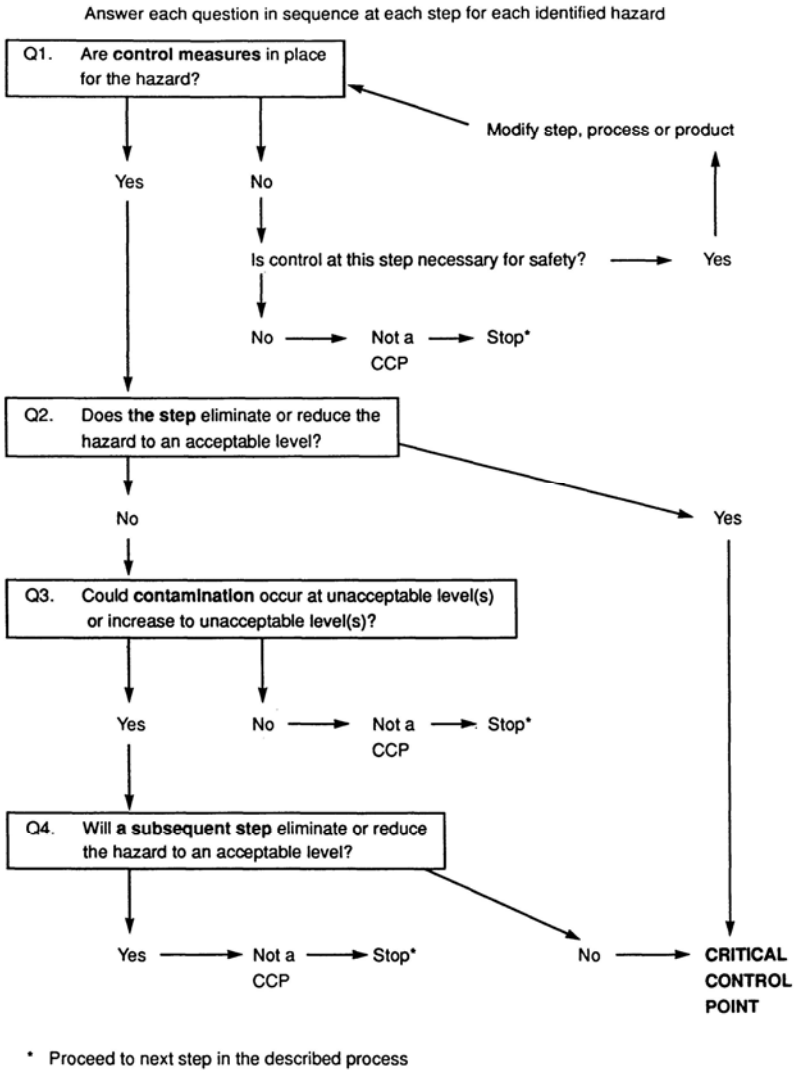



**Figure 3.4** CCP Decision Tree for HACCP Analysis (Anon, 1992).

determine the cumulative effects of this storage (Gould, 1991). Obviously the quality of the prediction is dependent on the quality of the time–temperature profile collected. For example, if only the air temperature is monitored, the prediction of microbial growth in the food, which may not mimic the air temperature profile, may be erroneous.

### *3.3.5 Training and education*

The development of predictive models in a user-friendly PC format can provide a useful training and educational tool. It provides a rapid and cost-effective mechanism whereby the benefits of doing a job correctly, or conversely the consequences of failing to do a job correctly, can be readily demonstrated. For example, the results of inadequate cooking, failure to use the correct product formulation or improper storage of a food can be demonstrated and quantified.

As an educational tool, the use of predictive models in the basic training of food scientists and food technologists will allow them to appreciate more fully how factors (e.g. temperature, pH) act independently and together to affect the growth, survival and inactivation of microorganisms.

## 3.4 Limitations of models

Whilst predictive models for microbiology are very powerful, care is needed to ensure their correct use. Misuse of models may give the user a false sense of security about the microbial safety or quality of a food.

Firstly, it is important that the user understands which microorganism(s) is of concern. If this is incorrect then all subsequent predictions may be inappropriate. Whilst most systems currently available are based on foodborne pathogens, the growth of food spoilage microorganisms often limits the product shelf life. Therefore, both must be considered when determining the shelf life.

Secondly, the factors (temperature, pH etc.) used for the predictions must be carefully identified and measured. If there is a natural variation in these factors (e.g. batch-to-batch variation) this must be considered. Normally, the levels of the factors that are least inhibitory to microorganisms would be selected otherwise the use of the prediction may result in some batches which may be of poor quality or even hazardous.

The majority of models available are based on foodborne pathogens. As discussed previously, the microbiological shelf life of many foods is based on both the microbial safety and quality of those foods. In the absence of generally accepted and validated models for microbial quality, the estimation of a product life will require storage trials and/or challenge tests. Some work in predicting spoilage has started (McClure *et al.*, 1993).

There has been concern with the errors associated with predictions from microbial models. With validated models based on good quality data, experience has shown that the errors obtained are generally less than those associated with repeating microbiological challenge tests.

Finally, most models available indicate the likelihood or the extent of

microbial growth or inactivation that will occur. They do not indicate that a food will be safe or do not indicate the microbial shelf life of a food. Both these activities require judgement from an experienced microbiologist. In the absence of definitive data about the minimum infectious doses to cause disease for many pathogens and a poor understanding about the relationship between microbial numbers and food spoilage, the ability of predictive models to indicate the shelf life of a food will be limited.

### 3.5 The future

The shelf life of a food is dependent on the raw material quality, the formulation of that food, the processes applied, the hygiene of production and storage and the temperature of storage, distribution and sale. This will be aided by the use of quality systems which incorporate well trained staff. It is obvious that predictive models can be applied to many of the stages involved in the manufacture and sale of foods which minimises the risks posed by microorganisms. Models therefore, do not replace the food microbiologist, but should result in the food microbiologist having better information, on which to base judgements.

In addition to a very active and co-ordinated programme of research in the UK, much research in predictive microbiology has also been carried out in the USA, continental Europe and Australia. One of the next major hurdles to be overcome is that of international collaboration. The collection and storage of data in a common format will allow data sets from around the world to be combined. The resultant models will have greater useful ranges of applicability and may be more robust. With collaboration, unnecessary duplication of data collection, which tends to be extremely costly, can be managed and perhaps additional factors may be studied. Furthermore the development and acceptance of an agreed system internationally, will enable models to be used to facilitate international trade and perhaps legislation.

The development of validated predictive models for the microbial spoilage of foods, will be very important from a commercial perspective. Essential to this, however, is an understanding not only of microbial growth but also an understanding of microbial activity and how this relates to sensory changes in foods. When such understandings are available it will then be possible to develop expert systems for the application of predictive models. Some developments in this area have started (Zweitering *et al.*, 1992).

Predictive food microbiology has emerged from within food microbiology to become a discipline in its own right with an undoubted future. To date, the development of models has been progressed largely by food

microbiologists. In the future, inclusion of other scientific disciplines, particularly microbial physiology, mathematics, statistics, computer programming and knowledge engineering, will aid the next stages in the development of predictive models (some of which may become truly mechanistic), application software and expert systems. Consequently, the power, flexibility and application of predictive models will ensure their greater use by the food industry to provide good quality information in a rapid and cost-effective manner. This will in turn permit better decisions on microbial safety and quality to be reached.

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# 4 Packaging and food quality

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## 4.1 Introduction

In the developed world, the purchase of fresh farm produce is not a viable option. The time available for family shopping is too limited to allow the frequent visits to numerous retail outlets that such a system would require. The supply of exotic foodstuffs that consumers have learned to take for granted would also be impossible to maintain without some means of preservation and packaging. However, different products have different demands. Some products are sensitive to oxygen or moisture, others to microbial growth or light. Thus there is no general packaging solution and the type of packaging to be used must be determined individually for each product.

Packaging systems should not only ensure that the food is microbiologically sound, make it easy to handle and convey pack information to the consumer, but also retain the desired sensory characteristics of the food. Such retention of sensory characteristics requires the package to act as an oxygen barrier, moisture barrier, aroma barrier or light barrier depending on the sensitivity of the particular food and the prevailing environment. Thus packaging plays a vital role in the maintenance of the shelf life of foods and it is this aspect of packaging and that of plastics packaging in particular, which will be dealt with in this chapter.

Primary packaging may be flexible, made from plastics film, paper or thin laminate; semi-rigid, like thermoformed plastics, aluminium foil, laminate and paperboard; or rigid, such as thick plastics, metal and glass (Miltz, 1992). In many of today's food products, plastics are used in the primary packaging. These plastics may be used together with aluminium or paper in laminates. The main advantages of plastics are their great diversity and range of properties. Most plastics polymers have a density of around 1000 kg/m$^3$, making them lightweight materials. They are also relatively cheap, easily processed and shaped. The major technical drawback is that they do not provide an absolute barrier to gases and vapours and that they may interact with the packed food.

Environmental awareness has caused a great deal of attention to be focused on what is regarded as overpackaging. A long maximum storage time is not always perceived as a positive attribute. Nevertheless, an abundant supply of high quality food is demanded by the consuming

public. To ensure this high quality in an environmentally friendly way is one of today's most challenging tasks for the packaging and food manufacturers.

In the following sections, the most commonly used plastics as well as some packaging systems including some recent developments will be reviewed. Finally, two examples (sections 4.4 and 4.5) are given to illustrate that packaging can have major influence on the storage quality and shelf life of foods.

## 4.2 Plastics packaging materials for food

### *4.2.1 Polyolefins*

The most widely used polymers for food packaging applications are the polyolefins. Because of their characteristic heat sealing properties, polyolefins are often used as internal linings in flexible pouches or box-type containers for beverages (Shorten, 1982). The main properties of two polyethylenes (PEs), polypropylene (PP) and ionomers are outlined below.

*4.2.1.1 Polyethylene (PE).* The molecular formula of PE is $(CH_2)n$ and the presence of branches prevents close packing of the polymer chains so that the density of the finished product is low. The presence of many branched chains also lowers the overall degree of crystallinity which has a major effect on some of the properties of the polymer (Brydson, 1982). There are four main types of polyethylene available, which differ in structure and properties as well as with respect to the manufacturing processes that produce them. They are:

- high density polyethylene (HDPE)
- low density polyethylene (LDPE)
- medium density polyethylene (MDPE)
- linear low density polyethylene (LLDPE).

*(a) LDPE.* This variety accounts for the largest proportion of plastics for packaging. It is relatively inert chemically, moderately permeable to water vapour but highly permeable to oxygen. In general, the permeabilities to gases are high, with poor odour barrier characteristics. LDPE can be laminated, extrusion-coated, or in some cases, coextruded. The main attractive features of PE, in addition to its low price, are good processability, toughness, flexibility, containing relatively few additives and, in thin films of certain grades, transparency. LDPE has good heat sealability and is easily coated onto other materials such as paper and aluminium.

*(b) HDPE.* Compared with LDPE, HDPE is stiffer, harder, less transparent, and has a less waxy feel. It is more resistant to oils and greases, and has a higher softening point but lower impact strength and permeability to water vapour.

*4.2.1.2 Polypropylene (PP).* PP is the next member in the series of polyolefins. It is possible to prepare PP in which the methyl ($CH_3$) groups are largely arranged on the same side of the polymer chain. The regular arrangement of the $CH_3$ groups produces a polymer with a higher crystallinity. This polymer is harder, has a higher softening point than HDPE and greater resilience. Its permeability to water vapour and gases lies between those of LDPE and HDPE. Further uses of this polymer are in biaxially oriented films and bottles. The material is stretched in two directions at right angles, under suitable temperature conditions. The resulting material has improved clarity, impact strength and barrier properties to water vapour and oxygen. Commercially available PPs have a density of 900–910 kg/m$^3$, one of the lowest among polymers.

*4.2.1.3 Ionomers.* Ionomers are defined as polyolefins copolymerised with a minor portion of an acid such as methacrylic acid, with some of the acid groups present in the form of a metal or quaternary ammonium salt. Ionomers are flexible, tough, transparent, and have excellent heat sealability. One of the trade names for ionomers is 'Surlyn'.

### *4.2.2 Polyvinyl chloride (PVC)*

A number of plastics are available in which a hydrogen atom of ethylene has been substituted by a halogen or other group. These constitute the vinyl plastics. PVC is hard, stiff and clear, with excellent resistance to moisture, low gas permeability and high impact strength. Incorporation of plasticisers makes the resulting film softer and more flexible but lowers its tensile strength. PVC offers good resistance to oils and fats.

### *4.2.3 Polyvinylidene chloride (PVdC)*

The monomer contains an additional chloride atom substituted into the ethylene molecule. The polymer is hard with a high degree of crystallinity. It produces a clear film with good strength properties and very low permeability to gases and water vapour. 'Saran' is a common trade name for PVdC.

### *4.2.4 Ethylene vinyl alcohol (EVOH)*

Ethylene vinyl alcohol (EVOH) is commonly used in packaging because of its good gas barrier properties. EVOH, trade name 'EVAL', is an

excellent gas barrier and commercially available in several grades with different ratios of ethylene/vinyl alcohol in the chain. The major limitation of EVOH is that its effectiveness as an oxygen barrier is severely reduced at high levels of humidity, due to disruption of the polymer–polymer hydrogen bonds. Also, because of the hydroxyl groups in the polymer backbone, EVOH tends to be extremely soluble in water.

### *4.2.5 Polystyrene (PS)*

Styrene consists of an ethylene molecule in which one of the hydrogens has been replaced by a phenyl group. The bulky nature of the phenyl group prevents close packing of the macromolecular chains. Hence, PS is amorphous. The polymer is transparent and a good barrier to gases, except water vapour. It is brittle, but this may be overcome by copolymerisation with butadiene and/or acrylonitrile (ABS and SAN respectively). Another way of modifying PS is by making a blend of polystyrene and rubbery materials, i.e. a polystyrene SBR blend. This high impact polystyrene (HIPS) has greater impact strength than ordinary polystyrene but lower tensile strength as well as hardness, and a lower softening point.

### *4.2.6 Polyamides (nylons)*

These comprise a series of polymers prepared by condensation of di-acids with di-amines or through self-condensation of certain amino acids. The amide group (CO–NH) is strongly polar and promotes strong hydrogen bonding between the CO and NH groups on adjacent polymer chains. Hence, nylons are strong, highly crystalline materials with high melting and softening points and low gas permeability. They absorb moisture depending on the relative proportions of hydrocarbons and amide groups in the polymer chain and may lose up to 50% of their strength when wet.

### *4.2.7 Polyesters*

Polyester resins exist in many forms. The most widely used polyester is polyethylene terephthalate (PET). PET has good mechanical properties, excellent transparency and relatively low permeability to gases. Biaxially oriented PET is often used in the production of bottles for carbonated beverages. Laminates with PET as one of the components are also very common in sterilisable pouches and 'boil-in-bag' applications.

### *4.2.8 Polycarbonates (PC)*

Polycarbonates are linear polyesters of carbonic acid with aromatic or aliphatic dihydroxy compounds. Most commercial polycarbonates are tough, stiff, hard and transparent. Their disadvantages are high cost and the fact

that they absorb moisture, with resulting deterioration of their mechanical properties and processability. An additional disadvantage, for packaging, is their poor gas barrier properties.

### *4.2.9 Lamination and coextrusion*

Many new packaging materials or combinations of materials have been used in food packaging in recent years. The main driving force has been to increase the barrier properties of the package and thereby the protection of food products with more complex material structures. A single polymer is often unable to provide all the properties necessary to create suitable barrier characteristics. This has generated a need for multilayer structures and techniques such as lamination and coextrusion. Coextrusion is not simply a competitive alternative to lamination. There are laminate properties that coextrusion is unable to meet, and non-thermoplastic materials such as paper and aluminium foil, which are often used in the lamination process, obviously cannot be coextruded. In addition, printing ink which can be protected if enclosed in a laminate, can only be applied on the surface of a coextruded film. There are also applications where the two technologies are combined, i.e. when a coextruded film is used in a laminate. For example, ionomers have excellent sealing characteristics, but are relatively expensive. PE/ionomer coextrusion can give the sealing properties needed in a more cost-effective way than an ionomer monofilm (Meadows, 1991). Such a structure may be produced by adhesive lamination of the materials or by coextrusion coating of the other material. The principal advantage of coextrusion over lamination is that the materials are extruded simultaneously, without a separate lamination process (Meadows, 1991).

In flexible packaging, laminates and metallised films have replaced single material structures. This has greatly improved the light and oxygen barrier properties of the materials, and extended the product shelf life. A drawback of the metallised laminates is the environmental load, even though only tiny amounts of metal are used. The long established trend towards using more laminates may be hit by recycling legislation when the industry will be controlled by requirements to make packaging products recyclable. Even though laminates exhibit many advantages such as flexibility in terms of stiffness, strength, barrier and sealing properties, many structures may have to be simplified, and there may have to be an increased use of compatible base films so that the whole structure can be recycled via the same path (Meadows, 1991). However, the need for high-performance barrier packaging to give shelf stability under a wide range of storage conditions continues to grow. Table 4.1 lists typical oxygen (OTR) and moisture vapour transmission rates (WVTR) for various plastics films for food uses (Turtle, 1987).

**Table 4.1** Oxygen and moisture vapour transmission rates for various plastics films

| Film (25 μ) | OTR ($cm^3/m^2/24h/atm$ at 25°C and 50% RH) | WVTR ($g/m^2/24h$ at 25°C and 75% RH) |
|---|---|---|
| PVdC | 2 | 1 |
| EVOH | 0.5–10* | 40 |
| Nylon 6 | 50–150* | 40 |
| Polyester | 80 | 8 |
| PVC (unplasticised) | 200 | 20 |
| HDPE | 1400 | 2 |
| OPP | 1600 | 1.5 |
| LDPE | 8000 | 5 |

*Humidity dependent.
*Source:* Turtle, 1987.

## 4.3 Some packaging systems and recent developments

### *4.3.1 Trends in food packaging*

The rate of development of new packaging materials and packaging techniques in recent years has been remarkable. Many of the new packaging materials have been developed to complement developments in new preservation techniques such as modified atmosphere packaging (MAP), or to meet increased demands for recyclability or other environmental considerations (Yokoyama, 1992).

### *4.3.2 Silica-coated films*

To achieve extra barrier properties, films have been coated with silica ($SiO_2$). Silica-coated plastics, also referred to as glass-coated, have several benefits: being clear barrier materials, they are microwaveable, retortable and recyclable without any step to separate components being required. So far, the $SiO_2$ coating has been deposited on PET containers, polyester, LDPE, and PP films. The film requires no pretreatment in order to obtain good adhesion of the $SIO_2$ coating to the film (Rice, 1992b). A 30 nm (300 Å) $SiO_2$-coated LDPE film has a 10 $cm^3/m^2/day/atm$. oxygen transmission rate. The oxygen transmission rates for coated OPP (biaxially oriented polypropylene) are said to be comparable to those of metallised OPP. Silica-coated PET films have a 1 $cm^3/m^2/day/atm$. oxygen transmission rate. Consequently, these coated films could offer barrier properties approaching those provided by multilayer plastics structures, foil laminates or metallised films. Silica-coated plastics enable the use of a monolayer plastics film with an extremely thin $SiO_2$ layer.

Early problems reported in the development of these products were yellowing and fragility of the glass coatings. However, these problems seem to have been overcome (Rice, 1992a). There have also been reports of micro-cracks in the $SiO_2$ coatings. These cracks make tunnels through which oxygen may diffuse into the container (Yoshii, 1992). At this point, there seem to be three factors slowing down the commercial application of glass-coated packaging materials (Rice, 1992a):

- economy;
- technical difficulties in ensuring good silica adhesion to certain substrates;
- lack of converter and packer's experience of these new packaging materials.

In 1988 a multilayer microwaveable pouch with a glass-coated polyester barrier layer was introduced in Japan. Today, several other applications are available. These are discussed by Rice (1992a).

### *4.3.3 Active packaging technologies*

Active packaging systems involve an interaction between the packaging material itself, the internal atmosphere and the food. The intention is to extend the shelf life of foods. New technologies which combine active packaging with modified atmosphere packaging (MAP) are being developed (Sneller, 1986; Wolpert, 1987).

*4.3.3.1 Packaging materials with preferential permeability.* Selected permeable packaging materials can be regarded as highly functional barrier packaging materials. In general, the gas transmission rates of gas barrier resins such as PVdC and EVOH increase in the order of nitrogen, oxygen and carbon dioxide, and their transmission ratios (e.g. $CO_2/O_2$) are constant for each barrier resin. Some foods require not only permeation of unfavourable gas generated from the inside but also maintenance of the oxygen barrier. Demands for packaging materials to meet these contradictory requirements have risen recently. An example of this is a packaging material which allows compounds from the smoking process to penetrate into the surface of, for instance, sausages under high temperature. After processing this material affords high barrier characteristics below ambient temperature, thus maintaining the quality of the product (Yoshii, 1990). Another example, this time from the dairy industry, is a packaging material with preferential permeability during the ageing of cheese. This material allows permeation of the carbon dioxide formed during the ageing process of Cheddar and Gouda cheese, yet prevents oxygen ingress from the outside.

*4.3.3.2 Oxygen scavenging.* Another new trend in barrier packaging materials concerns chemical barriers or oxygen-absorbing materials. These materials can be effectively used together with modified atmosphere packaging techniques. These chemical barriers are used together with the so-called physical barriers, such as PVdC or EVOH. One example is the 'OXBAR' system, with PET as the main component (96%), poly-metaxylylene adipamide (MXD-6) as the oxidisable component (4%) and an organic cobalt salt added as the oxidising catalyst at a 50–200 ppm level. This composition can be extruded to make blown bottles, which are said to be able to maintain the oxygen level inside the container at as low as 0% for two years (Yoshii, 1992). Barrier life time is a function of two main variables: scavenging capacity and rate of consumption. The former depends on the composition of the blend (MXD-6 and cobalt salt content) and the latter, the wall thickness of the container and the environmental conditions. Another example is an oxygen-absorbing plastic called 'Long Life', which can extend the shelf life of oxygen-sensitive drinks. This material is said to be insoluble in water and of a structure similar to that of haemoglobin (Yoshii, 1992). The hydroxyl groups of the base polymer react with silica, which also combines with a metal to form a complex.

Another method for actively controlling the oxygen level in a food package is to use an enzyme reactor surface, which will react with certain substrates to scavenge incoming oxygen. A new active packaging system developed by PharmaCal Co. (USA) utilises glucose oxidase and catalase enzymes for the removal of oxygen from liquid products (Yoshii, 1992).

There is one commercial application that uses a mixed iron powder–calcium hydroxide sachet in which both oxygen and carbon dioxide are scavenged (Labuza and Breene, 1989). It is being used to pack fresh ground coffee in flexible bags. This packaging system is said to more than triple the shelf life of the product. Other chemical scavenger systems include reactive dyes, ascorbic acid and cathecol-based reducers.

*4.3.3.3 Temperature-compensating films.* A newly developed film called 'Intelimer' has a temperature 'switch' point at which the permeation of the film changes abruptly. The switching mechanism is accomplished by the long-chain fatty alcohol-based polymeric side chains patented by the Landec Corporation (Figure 4.1). Below a preset temperature, these side chains are crystalline and provide a relatively effective gas barrier. However, above this preset temperature, these side chains convert reversibly to an amorphous structure, which is up to 1000 times more permeable to gas and may be tailored to the very large increase in respiration rates of fresh produce at temperatures above 5°C (Day, 1993). Because the change is physical and not chemical, this process is continuously

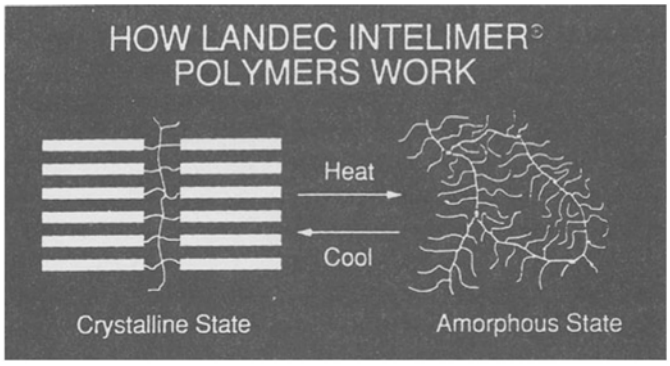



**Figure 4.1** At a specified temperature the side chains of the Intelimer® film melt and convert to an amorphous structure that renders the film gas permeable (Anon, 1992).

reversible. The transition point can be moved by increasing or reducing the average number of carbon atoms in a chain. The switch point may be set anywhere between 0 and 45.5°C, and controlled within 2°C. The switch also changes the adhesiveness and stiffness of the film. Intelimer films are intended to be used for packaging highly respiring produce, but commercialisation is still several years away (Anon, 1992).

Another temperature-compensating film for produce has recently been patented and relies on the same principle as a bimetallic strip, but uses two different plastics films instead of two metals. Temperature sensitive apertures are cut into laminated plastics film in the form of small strips or 'petals'. At a selected temperature, the laminated film is flat and has minimum opening area. However, at higher temperatures the free area for gas exchange increases as the petals curl, and the permeability of the film can be engineered to increase proportionally to the rise in the respiration rate of the produce. The rate of curl is a function of the coefficient of expansion of the two separate films, and the extent of opening is controlled by the length and shape of the petals surrounding the aperture.

*4.3.3.4 Moisture absorbers.* Humidity will build up in the headspace of a food package either due to respiring produce or due to water vapour from moist foods. This in time will allow the growth and development of microorganisms. A desiccant film or sachet can be used to overcome this problem (Geeson *et al.*, 1985). A Japanese company has developed a film which is made into a pillow with entrapped propylene glycol (Labuza and Breene, 1989). When placed in contact with the surface of meat or fish, it absorbs water and slows the growth of spoilage bacteria.

### *4.3.4 Modified atmosphere packaging (MAP)*

MAP is defined as the enclosing of food products in an atmosphere inside gas-barrier materials, in which the gaseous environment has been modified to slow down respiration rate, microbial growth and reduce enzymic degradation, all with the intention of extending the shelf life (Parry, 1993). Such modifications usually result in a reduced oxygen content in the headspace atmosphere, but increased carbon dioxide and nitrogen levels.

Carbon dioxide is the most important constituent in the gas mixture. Several factors influence the antimicrobial effect of carbon dioxide, specifically the microbial load, gas concentration, temperature and packaging film permeability. To be effective against aerobic spoilage microorganisms, a concentration of 20–60% carbon dioxide is required in the package headspace (Greengrass, 1993). One of the most important factors influencing the antimicrobial effect of carbon dioxide is the permeability of the packaging film (Gill, 1990). The success or failure of MAP for foods depends on the impermeability of the packaging materials to both oxygen and carbon dioxide, in order that the correct gas mixture in the package headspace can be maintained. In addition, films used in MAP packaging should have low water vapour transmission rates (WVTRs), so as to minimise changes in moisture content inside the pack.

Plastics commonly used for gas packaging of foods include polyester, PP, PVdC, EVOH, and PE. Since all of the desired characteristics of a packaging film, i.e. strength, impermeability, and heat sealability, are seldom found in one single material, separate materials are laminated to one another to produce films with the desired characteristics for gas packaging of foods. Examples of such laminated structures include nylon/PE, nylon/PVdC/PE and nylon/EVOH/PE. Such composite structures have the desired characteristics for the gas packaging of food products: strength is provided by the outermost layer of nylon; gas and moisture vapour barrier is provided by EVOH and PVdC; and heat sealability by PE (Brody, 1989).

Development of optimum gas packaging materials is even more challenging for fruits and vegetables as these products respire. The ideal packaging material for gas packaging of these products must be able to keep low oxygen concentrations within the package headspace while preventing the build-up of high carbon dioxide concentrations. Packaging films commonly used to achieve such a balance include LDPE and PVC (Zagory and Kader, 1988). Packaging films with the correct permeability must be chosen to avoid depletion of oxygen and accumulation of carbon dioxide caused by respiring products. Recently developed highly permeable microperforated films such as P-Plus and Crop appear to be most suitable at present (Gill, 1990; Geeson *et al.*, 1988). These films allow the product to breathe as it ripens inside the package.

A key feature of the MAP described below is the controlled permeation of $O_2$ and $CO_2$, as well as the scavenging of ethylene or controlled release of other compounds which could have a preservative effect on the food (Labuza and Breene, 1989). One way of controlling the oxygen level directly in a package is to use an oxygen scavenger system (Takahashi *et al.*, 1984). The simplest scavenger is reduced iron. The amount of iron needed depends on the initial oxygen level in the headspace, the amount dissolved in the food and the oxygen transmission rate of the film (Labuza and Breene, 1989). One gram of iron will react with 300 $cm^3$ of oxygen. The iron is separated from the food by being kept in a small highly oxygen-permeable pouch.

### *4.3.5 Aseptic/ultra-high temperature (UHT) packaging*

Packaging materials for aseptic processing/packaging must be sterilisable, suitable for aseptic filling and permit the maintenance of sterility of the product during storage and handling (Smith *et al.*, 1990a). Glass containers offer similar advantages as metal containers, but have the additional disadvantages of fragility and high density. Plastics materials offer versatility, but cannot be used alone as they do not possess all of the required properties. Consequently, they must be laminated to other materials to give packages with the appropriate requirements.

At present, the Tetra Pak concept, using a paperboard-foil-plastics laminate, is widely used for aseptic packaging. This laminated structure consists of as many as six layers of materials: PP, Surlyn, foil, PE, paperboard, and PE as the inner food contact layer. Other combinations that can be used include laminations of EVOH, PE and PS; or a metallised polyester. Aluminium foil is the most commonly used barrier material. PP or PE, i.e. polyolefins, are the most common heat sealing and food contact materials used. Foils need to be protected from mechanical damage, and protection is usually provided by paperboard which also gives rigidity. All of the composite materials described act as barriers to moisture, oxygen, light and microbes, and have the strength and heat sealability needed for aseptic packaging.

A review of aseptic processing has been made by Lopez (1987). Historical perspectives on aseptic packaging technology and the use of plastics packaging materials are further described in other recent publications (Downes, 1989; Eidman, 1989; Fox, 1989; Kern, 1989).

### *4.3.6 Sous vide (vacuum cooking/packaging) technology*

There has been a tremendous increase in recent years in the use of 'sous vide' processing technology to extend shelf life and maintain the quality

of fresh food (Smith *et al.*, 1990b). This technology has been developed in response to consumer demands for ready-to-eat, microwaveable, convenience foods with extended shelf life, that retain 'closer-to-fresh' characteristics. The term sous vide means 'under vacuum'. In sous vide processing, foods are cooked in sealed, evacuated, heat-stable pouches or thermoformed trays in such a way that much of the natural flavour, aroma and nutritional quality is retained by the product. This technique requires highly controlled packaging/cooking conditions. Packaging materials used in sous vide processing must withstand pasteurisation and chill temperatures as well as protecting and maintaining product quality.

### *4.3.7 Edible films*

Recently, an edible film of polysaccharides has been used in certain packaging applications (LaBell, 1991). The polysaccharide film looks like a plastics film. The edible polysaccharide beads are seamless spheres of polysaccharide measuring 1–8 mm in diameter, which are dissolved by heat and moisture. Dry ingredients, such as spices and seasoning mixes, can be portion-packed in edible film pouches. The entire pouch can be added, for instance, to a soup, and it will dissolve quickly. However, the polysaccharide films are more permeable to gases than plastics films. In addition, their tensile strength is not as high as that of plastics films. This will create problems in automatic form/fill/seal machines.

In Japan, edible polysaccharide films are already widely used in the meat industry for packing of processed meats, such as ham and poultry products (Labell, 1991). Processors can wrap the meat in edible film before smoking and steaming. The smoke flavour permeates the film during the smoking process and the film dissolves during steaming. The surface structure and texture of the finished ham are improved. Also, yields are better, as less moisture is lost during processing.

The shelf life of fresh fruit and vegetables can be extended by using an edible film. Plastics films can be used to provide a gas barrier to protect the products, but moisture from the packed material will collect inside the film. An edible packaging film will gradually absorb the moisture given off from the product, preventing it from accumulating inside the package. This would lead to reduced risk of mould growth. Eventually, the moisture absorbed may cause the film to dissolve.

## 4.4 The influence of 'scalping' on food

As plastics packaging is becoming more widely used for direct contact with foods, compatibility with the food must be considered. The sorption of flavour compounds, or scalping, is one of the most important compat-

ibility problems. The problem of aroma absorption by plastics packages has been recognised for many years. The tendency towards absorption varies with the type of plastics. For example, polyolefins can absorb certain flavour constituents selectively from products (Foster, 1987).

The quality of juices packed in aseptic cartons has been the subject of intensive research in recent years. Early work focused on volatile absorption from sources external to the package (Gilbert and Pegaz, 1969). Haydanek *et al.* (1970) and Gilbert *et al.* (1982) examined the volatile uptake by various packaging materials. PE and PP have been used widely in contact with food in packages due to their low costs, heat sealability and relative lack of additives, but they are particular susceptible to pervasion by organic vapours. The use of PE and PP in plastics packages has raised questions concerning sorption of intrinsic food flavours (Durr *et al.*, 1981).

### *4.4.1 The limonene controversy*

Most juices that are filled aseptically are packed into laminated carton packages such as the Tetra Pak or Combibloc, in which the food contact material is PE (Mannheim *et al.*, 1987). Mannheim found that the product shelf life of orange and grapefruit juices was significantly shorter in laminated cartons than in glass jars. Moshonas and Shaw (1989), Mannheim *et al.* (1988) and Sizer *et al.* (1988) have investigated how aseptic packaging can affect the quality of citrus products, with the emphasis on flavour loss. Hirose *et al.* (1988), Shimoda *et al.* (1984) and Durr and Schobinger (1981) have studied the sorption of citrus flavour components by packaging materials. Baner *et al.* (1991) found that the food contact layer, usually polyethylene, largely controlled the sorption behaviour. This means that any improvements of flexible materials regarding aroma sorption must come from new food contact layers and not from new barrier layers.

Citrus flavour has often been used in model systems for flavour absorption studies (Durr and Schobinger, 1981; Marshall *et al.*, 1985; Hirose *et al.*, 1988; Kwapong and Hotchkiss, 1987). (+)-Limonene, the predominant volatile in citrus oils and essences, is often used as a probe compound in such studies. Compositionally, limonene is a non-polar, unsaturated terpene hydrocarbon. Many flavour compounds contain an ester, alcohol, and other polar functional groups. Essential oils from citrus fruit consist of terpenes, sesquiterpenes, oxygenated terpenoids, and non-volatile components. The oxygenated compounds are important contributors to the citrus flavour (Moshonas and Lund, 1969). Many research groups have reported that polar compounds are absorbed to a much lower extent in PE than limonene and other hydrocarbon volatiles. An understanding of the differences between various plastics materials as

regards the sorption of essential oil constituents could help the processor reduce the flavour absorption problems.

### *4.4.2 The influence of pulp content on scalping*

Shimoda *et al.* (1984) showed that in juice from satsuma mandarins, the limonene sorption by plastics is lower in the presence of juice pulp. Maeda *et al.* (1984) and Osajima (1983) reported that a low pulp content in orange juice resulted in higher absorption of aroma compounds. This is in agreement with the results of Gherardi (1982) and Granzer (1982). Fruit juice volatiles remain stable in the juice while they are absorbed by or suspended in the pulp (Yamada *et al.*, 1992). However, the amount of pulp, such as cellulose powder, which must be added if it is to be used to control the sorption of volatiles by LDPE is large.

### *4.4.3 Comparison of instrumental and sensory analysis*

Mannheim *et al.* (1985) documented changes in aseptically packed citrus juices by sensory as well as chemical analysis. They related loss of orange juice flavour to the absorption of (+)-limonene into the polyolefin packaging material. However, in a comparison of the sensory quality of orange juice stored in polyethylene-lined paperboard cartons at different temperatures, Durr *et al.* (1981) reported the temperature to be the main variable affecting the flavour, even though orange oil expressed in terms of limonene was absorbed by the polyolefin food contact layer. They suggested that limonene absorption was an advantage, since limonene was known to be a precursor of off-flavour compounds. They also reported that desirable aroma volatiles were practically unabsorbed.

Although it is well documented that certain constituents of orange juice are absorbed by polymeric materials and that the absorption of flavour compounds changes the aroma profile (Mannheim *et al.*, 1985), it has not been established unequivocally that these changes are caused by absorption of odour-active constituents of orange juice (Marin *et al.*, 1992).

Most reported studies on flavour scalping in orange juice were performed with model solutions, not actual orange juice, or with orange juice which had not been commercially produced and packaged (Pieper *et al.*, 1992). Many of the investigations too, were performed without sensory evaluation. Pieper *et al.* (1992) showed that a sensory panel could not distinguish between orange juice stored in glass bottles and juice stored in laminated paperboard packages with LDPE as the food contact plastic, even though absorption of up to 50% of the (+)-limonene and small amounts of aldehydes and alcohols by the packaging materials was observed.

Marin *et al.* (1992) exposed plastics packaging materials, i.e. PE and Surlyn, to orange juice and measured the changes in the limonene content of the juice using a gas chromatograph equipped with a flame ionisation detector (GC–FID). They determined the components which were most important to the aroma using gas chromatography–olfactometry (GCO). More than 70% of the limonene content was absorbed by the plastics in 24 hours at 25°C. However, results from the GCO analysis indicated that the limonene had only trace odour activity. Furthermore, the plastics did not substantially alter the odour-active components detected in orange juice. These reports emphasise the importance of using real food systems whenever possible, and supplementing the instrumental analysis with organoleptic evaluation.

### *4.4.4 Influence of scalping on barrier and mechanical properties*

As has been shown in the reports outlined above, the scalping process may not alter the sensory quality of packed juices. However, absorption of flavour components by the package may alter the mechanical properties of the plastics, causing delamination, or modifying the barrier properties of the packaging materials. Miltz *et al.* (1990) showed that the absorption of (+)-limonene increased the oxygen permeability of the three plastics films used. If the efficiency by which a packaging material reduces the entry of oxygen into the package is impaired, foods sensitive to oxygen will deteriorate quickly. The result will be a shortened shelf life of the product.

### *4.4.5 Methods of suppressing scalping*

Yamada *et al.* (1992) suggested methods of suppressing the sorption of volatiles by the food contact layer.

1. Sorption of volatiles could be reduced considerably by reducing the thickness of the heat seal layer. This could, however, cause the sorbed compounds to permeate the polyolefin layer and change the structure and properties of the barrier layer, or result in delamination of the laminate.
2. Sorption of volatiles could also be reduced by using a food contact layer that has already absorbed some fruit juice essence (i.e. presorption).

Treatments of the plastics surface and judicious selection of materials, such as use of plastics with crystalline polymers (Shimoda *et al.*, 1988), use of polymer blends (Subramanian, 1990), fluorination of plastics surfaces (Hobbs *et al.*, 1990), and inert coatings, e.g. silica, on the plastics

surfaces (Charara, 1987) have also been proposed in the literature to circumvent the scalping of flavour compounds from food products.

### 4.5 Flavour transfer problems in refillable PET bottles

The debate about the environmental impact of packages and the demands for reuse and recycling of packages have led to the development of the refillable PET bottle system for soft drinks. All refillable systems involve certain problems with regard to product safety. Legislation and hygiene are essential aspects in this context. The washing procedure is a particularly critical step in the refilling of PET bottles, due to the limited heat resistance of the packaging material. To avoid shrinkage of the bottle the temperature must not exceed 58–59°C. It is crucial to the sensory quality of the packed product that aroma compounds from one product are not absorbed by the material and then transferred to the next product filled in the bottle. Numerous chemical substances can be absorbed in the PET material (Figure 4.2), and some of these compounds may impart off-flavours to subsequent fillings.

In order to assess the risk of flavour transfer between products when a returnable PET bottle is refilled with a different soft drink, sensory

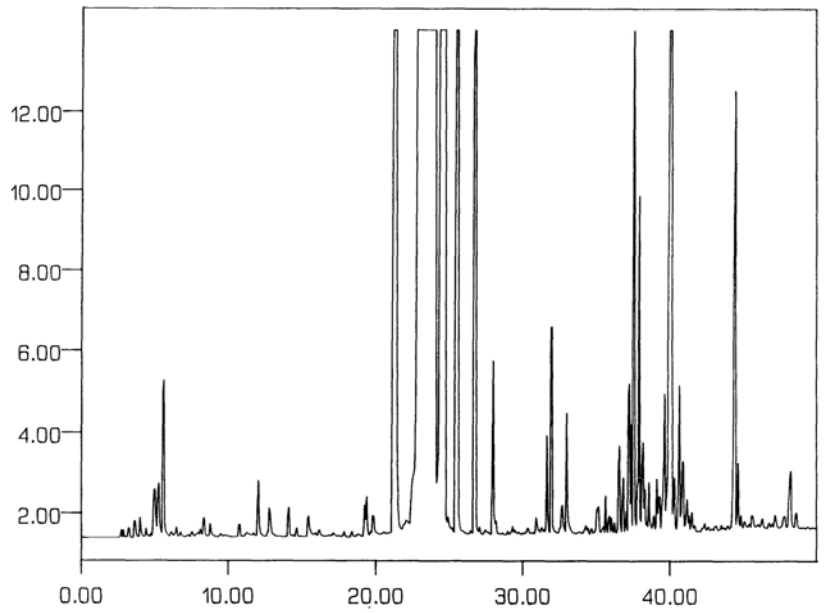



**Figure 4.2** Gas chromatogram of a headspace sample of a PET bottle that has been filled with a citrus drink.

analyses are performed. First the bottle is filled with the test product. After storage the bottle is emptied, washed and refilled with the second product on which the assessment of possible flavour transfer will be made. Different kinds of soft drinks such as citrus drink, cola and mineral water have been used as the second fillings. For each of these products the intensity of any flavour transfer is evaluated separately. The test product will be approved for filling in returnable PET bottles only if it is approved in all the tests using the different soft drinks. Results so far showed that some products are unsuitable for the refilling system, especially those which have a very intense and strong flavour. For this reason some ciders and citrus fruit drinks have been rejected because some of their flavour has been detected in the second product filled in the bottle. Highly delicate products such as mineral water are to date only filled in new bottles.

To supplement the sensory evaluation of the soft drinks, chemical analyses are needed to determine which flavour/aroma compounds are absorbed by the PET material and eventually migrate into the product filled subsequently. If this could be done, the next step would be to investigate their role as flavour components in the soft drinks and, if possible, replace or reduce them. In a production situation, it will be important to have equipment set up to identify foreign odours prior to refilling in order to avoid customer-introduced contamination.

## 4.6 Conclusions

The sensory quality of a packaged food is the result of a complex interaction between the food, the pack and the environment. Substances from both the food and the environment can be absorbed/adsorbed in the packaging material. Such sorption from the food and the environment may not only change the taste of the food *per se* but also change the barrier and other physical characteristics of the packaging material. Changed barrier characteristics may result in a higher diffusion of oxygen into the package, resulting in the development of off-flavour due to oxidation of the food. The oxidation products may also, for better or worse, be absorbed into the packaging material. These interactions between aroma compounds, oxygen and the pack can result in a dynamic and time-dependent change of the food quality.

A number of sophisticated technical solutions to preserve food for a long time are available today. Whether or not these solutions are economically and environmentally acceptable or even marketable have to be considered for each specific application. It is pointless to make a completely impermeable package if the consumer refuses to buy the product because it is considered to be artificial (it will 'keep too long') or over-

packaged (environmentally unsound) compared with other similar products on the market. In the future, it will be of increasing importance to a food manufacturer to use environmentally friendly packaging materials if he plans to stay in business. On the other hand, packaging in an environmentally friendly way cannot be allowed to comprise the fundamental requirement of having always to ensure the safety and quality of the food.

In addition to such obvious considerations as keeping the food microbiologically safe, a food manufacturer has to decide what his product should taste like, and the length of time it should remain acceptable. Once these decisions have been made, an economically and environmentally suitable packaging solution can be sought. To stay in business, food manufacturers and packaging suppliers must co-operate in order to face up to the demands of the product, the demands of the environment and the expectation of the consumer.

Finally, it should always be remembered that the ultimate decision is made by the consumer in terms of whether to buy or not to buy.

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