PROJECT TITLE: Modified Atmosphere Systems in varying TEmperature Regimes
PROJECT NR.: AIR2-CT-1326
PAPER: FINAL TECHNICAL REPORT

MASTER

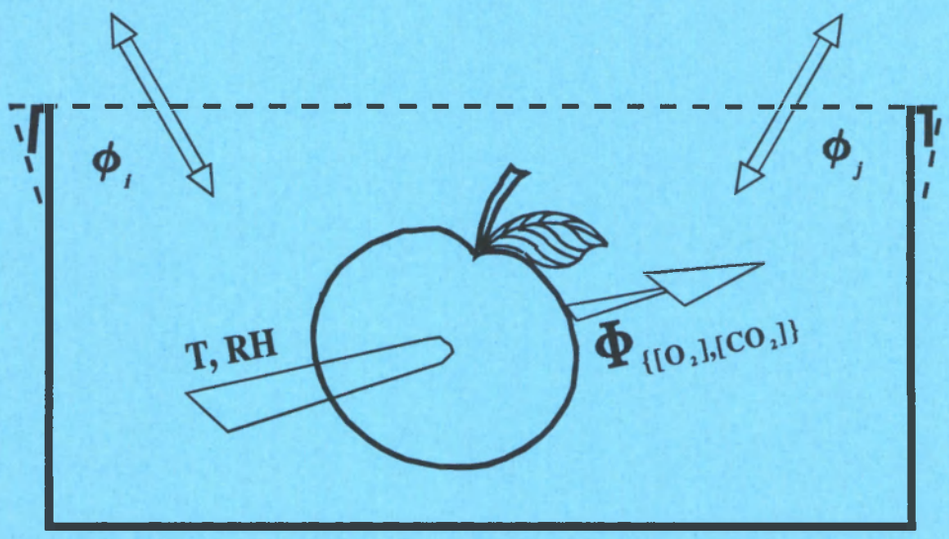

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Table of Contents

1 Introduction

1.1 Structure of the report

Inside the MASTER project, several interlinked tasks had to be performed to achieve the final goal of the project, namely

- a quantitative understanding of the respiratory activity of the packed produce,
- a description of the gas diffusion inside the produce and the skin permeability,
- a description of the permeability of different types of polymer films,
- a methodology to model the combined behaviour of different combinations of packed produce, packaging films and ambient conditions
- and, finally, to create a computer program which was to incorporate these issues.

This interlinked nature does not facilitate a task by task reporting, especially because all tasks had by nature to be formulated before first results were available.

Therefore, to facilitate the reading of this report, we decided to take the following logical sequence as basis for the structure:

- Nature and respiration characteristics of produce, in dependence of all parameters investigated,
- gas diffusion inside the produce,
- permeability properties of selected packaging materials,
- different types of investigated packagings
- and, finally, the combined behaviour of all of the above, together with a description of numerical techniques and the final layout of the computer program.

Table 1.1 helps to identify the sections of this report in correlation to the tasks as laid down in the Technical Annex of this project.

Table 1.1: Tasks and their relation to the sections of this report

Task number and description	Numbers of sections in the report, related to each task
Task 1: Survey and selection of agricultural produce	2.1
Task 2: Gas transport in the product	1.3.2, 2.3, 3.2, 4.2
Task 3: Respiration rate as a function of surrounding gas composition and temperature	1.3.1, 2.2, 3.1, 4.1
Task 4: Modelling of the respiration rate	2.2, 3.1, 4.1
Task 5: Survey and selection of packaging materials	1.3.3, 2.4
Task 6: Temperature dependent gas and water permeability constants	2.4, 3.3, 4.3
Task 7: Modelling of the diffusion process through the packaging material and Task 8: Building databases	2.6, 3.5, 4.5
Task 9: Evaluating the whole system, for selected packaging and product	1.3.6, 2.6, 3.5, 4.5
Task 10: Maturity effects on the respiration rate	2.2, 3.1, 4.1

As the number of single results is very high, exemplary results are shown in the main report to enhance the consistency. That means e.g. that specific phenomena are only shown for one produce even if they are valid for the others. For completeness, the interested expert is referred to the annex which gives a large compilation of the individual results.

Also the description of the software (the MAP program), the operators' manual and the source code is available in the annex.

1.2 General motivation

Overall, the shelf life of fresh agricultural produce is determined by the following biological processes:

- The regular metabolic activity of the produce, which is in direct correlation to its respiratory activity. Oxygen is consumed and carbon dioxide is generated
- Additional irregular metabolic activities, e.g. under anoxic conditions.
- Activities of microorganisms like bacteria or mould.

To extend the shelf life of produce, the concept of **Modified Atmosphere Packaging (MAP)** or **Controlled Atmosphere Packaging (CAP)** is followed. Both strategies are very similar in the way that the decay of the produce is slowed down by the following effects:

- The regular metabolic activity is reduced by higher amounts of CO_2 and lower amounts of O_2 in the surrounding atmosphere.
- Dehydration is reduced by keeping the surrounding atmosphere at near saturation, i.e. 100 % relative humidity.
- Sometimes, additional features are used, such as continuos removal of ethylene which acts as ripening hormone for several types of produce.
- In all cases, however temperatures are applied which also have the effect of lowering all reactions of the produce.

All these effects in total require a modified or controlled atmosphere surrounding the produce.

Technical solutions to achieve a modified or controlled atmosphere are the following:

- The storage of the produce in larger containers under continuous flow of an atmosphere of preset conditions. By this method, bulk storage of produce can be performed under well controlled gas compositions. Its disadvantage is the relatively high effort necessary for set-up and operation and the low flexibility.
- The storage of produce already in a consumer package which - in combination with the respiratory activity of the produce - creates the desired atmosphere. A usual configuration is a tray, wrapped in specific films. Sometimes, additional measures like introduction of sachets filled with chemically active substances or the use of specifically filled film materials may help to reduce the amount of specific gases like ethylene. The latter method is usually called Controlled Atmosphere Packaging or Active Packaging whereas the former method is referred to as Modified Atmosphere Packaging.

The advantages of this method are:

→ Consumer ready packaging at an early stage

→ The absence of the need for relatively expensive gas supply, circulation and control mechanisms

→ Easy transportation, flexibility and independence on specific storage facilities.

For these reasons, Modified Atmosphere Packaging gains more and more interest, especially at suppliers and retail companies, also in view of the rising transport distances of products within the European Union. This was the economic background of the MASTER project, namely to facilitate packaging and distribution of fresh produce.

Modified atmosphere packaging, however, has to face some problems:

- The decrease of O_2 concentration and the increase of CO_2 concentration may be overdone, thus leading to different, sometimes even more problematic deterioration mechanisms:
  - → Anoxia may cause abnormous product metabolism and - even more dangerous - the growth of specific microorganisms
  - → Carbon dioxide in higher concentrations may have a negative influence on the consistency of the plant cells.
- The reduction of water exchange may lead to condensation inside the packagings, which usually increases the tendency for growth of microorganisms.
- The simplicity of the packaging may in turn lead to non-optimal storage conditions in distribution and retail.

Therefore, an optimum has to be kept for every kind of produce for the conditions of the surrounding atmosphere in terms of

- O_2 and CO_2 concentration,
- relative humidity and
- temperature.

Only under these optimum conditions, a maximum shelflife can be expected. The strategy of the MASTER project was to supply a methodology following the sequence

→ to determine the optimum conditions for a given produce in terms of the composition of the surrounding atmosphere

→ to determine the respiratory activity of the produce not only under optimum conditions, but also outside,

→ to determine the permeability of films under conditions relevant for MAP,

→ to select a suitable packaging configuration for a given produce

→ and, finally, to model the combined behaviour of produce and packaging - by help of a dedicated computer program - with respect to

  - ❒ gas composition,
  - ❒ water losses,
  - ❒ exceeding of safe conditions
  - ❒ keeping quality

in view of the temperature / climatic conditions during distribution and storage, to verify the correct selection of a packaging material and packaging geometry for a given produce application.This sequence was to be performed completely for an exemplary selection of different produces and packaging films to verify the applicability of the model.

1.3 Motivation for the project parts, references

1.3.1 Respiration of the produce

The main characteristic of fruits and vegetables, in the retail market, is their physiological activity including respiration, transpiration and ethylene production (Kader, 1986). It has long been demonstrated that the lower the respiration rate, the more prolonged the shelf life (Marcellin, 1975, Church and Parsons, 1995). The easiest way to reduce respiration rate of plant tissues is lowering storage temperature. It is well known that, in the temperature range permitting cell survival, the shelf-life duration is exponentially reduced when increasing temperature. At low positive temperature, depending on each specie, cultivar and even stage of maturity may appear chilling injury (Labuza and Breene, 1989; Brecht 1995).

Respiration control of plant tissues is also attainable through lowering of O_2 partial pressure and elevation of CO_2 concentration (Dilley, 1978, Zagory and Kader, 1988). The individual effects of O_2, CO_2 and temperature may be additive and the total effect can be greater when these factors are combined (Kader et al., 1989, Ulrich, 1975).

Investigations of respiration of plant tissue as a function of temperature and atmosphere composition have been undertaken since the 1960's. Jurin and Karel (1963) assumed that the respiratory quotient of apple was constant and that the respiration rate was independent of the CO_2 partial pressure. More recently Henig and Gilbert (1975) assumed that the respiration rate of tomatoes was linearly dependent on O_2 partial pressure between 4 and 11.5 kPa and constant at higher concentration. Lopez Briones et al. (1992) claimed that a similar model fitted the respiration rate of mushroom. Hayahawa et al. (1975) modified the model proposed by Henig and Gilbert by empirically expressing the respiration rate as a function of both O_2 and CO_2 partial pressure. This model was improved in 1988 by Yang and Chinnan. Cameron et al. 1989 obtained an exponential type equation for expressing the O_2 consumption rate of tomato respiration in a closed system. Lee et al. (1991) after Chevillote (1973) claimed that Michaelis and Menten type equation was suitable for modelling the aerobic respiration of plant tissue. Michaelis and Menten equation which predicts the enzymatic activity as a function of the substrate activity is only valid for mono enzyme-mono substrate systems. However, the respiration chain includes many steps of metabolic reactions which are dependent on the types of respiratory substrates. Moreover, the concentrations of intermediary substrates in glycolysis and Krebs'cycle are unknown. Diffusion rate of gases through fruits and vegetables skin, tissues, cell wall and membrane should also be taken into account. As described by Andrich and Fiorentini in a following chapter of this report the resistence to gas diffusion is mainly located on the skin whereas no limiting gas exchange occur inside apple fruit (Andrich et al, 1990)

The effects of CO_2 on gas exchange combined with O_2 and temperature was reported by Fidler and North (1967). Peppelenbos and Van't Leven (1996) evaluated four types of inhibition for modelling the influence of CO_2 levels on O_2 consumption of fruits and vegetables. Hertog et al. (1997), in this project, limited the inhibitory mechanism of CO_2 on aerobic respiration to competitive and uncompetitive types, whereas Varoquaux et al. (1998) did not find any inhibitory effect of CO_2 on mushroom O_2 uptake from 0 to 20kPa.

Many other phenomena may markedly interfere with O_2 and CO_2 respiration rate of plant tissue such as maturation, micro organism growth, CO_2 dissolution. No predictive model can take into account all possible interferences. This conducts, for example, to the use of an apparent Michaelis constant which takes simultaneously into account the limiting steps of the respiration chain and partially oxygen diffusion from external atmosphere to the respiration sites of cells. The effect of micro organism is not taken into consideration despite it was demonstrated by Varoquaux et al. that microbial respiration rate can account for up to 70% of bean sprout respiration rate at 20 °C. Similarly, bacterial metabolism markedly interferes with endive leaf respiration rate at temperature higher than 15 °C

(Chambroy, 1989). The mathematical analysis of plant tissue respiration rate must be limited to the simplest expression able to give a reasonable prediction of the phenomenon under realistic MAP conditions (including temperature abuse and the onset of anaerobic metabolism).

1.3.2 Internal diffusion in the produce

Although gas exchange between horticultural products and their environment is a basic step of respiration which potentially could play a fundamental role in their MA storage, few papers are available on this topic (Burg and Burg, 1965; Cameron and Reid, 1982; Banks, 1985; Banks and Kays, 1988; Corey and Eydeland, 1989; Knee, 1991; Banks et al., 1993; Dadzie, et al.,1993; Hagenmaier and Baker, 1993; Park, et al.,1993; Renault, et al., 1994).

As according to Burton (Burton, 1950, 1974, 1978; Cameron and Reid, 1982) the resistance to respiratory gases diffusion (G: O_2, CO_2) seems to be mainly located on fruit skin, no resistance to O_2 and CO_2 diffusion seems to occur inside the apple fruit so that an instantaneous equilibrium between the two main phases present inside the fruit (gas phase connected with intercellular space and liquid phase due to cellular sap) was assumed to take place (Andrich et al., 1989a, 1989b, 1990, 1994b, 1997). On this hypothesis every fraction of gas permeated through apple skin is instantaneously splitted into the intercellular space and cellular sap in a ratio equal to the saturation equilibrium constant. So the gas exchange occurring between an horticultural product and its surrounding atmosphere could be regarded as a mass-transfer occurring between two heterogeneous phases: the gas phase and the product phase assumed to be completely homogeneous inside. Resistance to gas diffusion would be so mainly located on product skin and the global mass-transfer rate R_G [mol · kg^{-1}· s^{-1}] calculated as the difference between the two partial rates connected with the gas diffusion between environment and product ($R_{G,i}$) and product and environment ($R_{G,-i}$):

$$R_G = R_{G,i} - R_{G,-i}$$

$$R_{G,i} = k_{i,G} \cdot A \cdot PG$$

$$R_{G,-i} = k_{-i,G} A \cdot [G^*]$$

where:

$k_{i,G}$ = kinetic constant connected with the diffusion occurring between environment and product [mol · m^{-2} · s^{-1} · Pa^{-1}];

$k_{-i,G}$ = kinetic constant connected with the inverse diffusion product-environment [kg · m^{-2} · s^{-1}];

A = the total surface area of the product expressed per unit of weight [m^2 · kg^{-1}];

PG = the partial pressure of the considered gaseous compound in the environment [Pa];

$[G^*]$ = the concentration of G dissolved inside the product [mol · kg^{-1}].

When the equilibrium between product and environment is reached, no mass-transfer occurs and the following relations are obtained:

$$R_G = d[G^*]/dt = R_{G,i} - R_{G,-i} = k_{i,G} \cdot A \cdot PG - k_{-i,G} \cdot A \cdot [G^*] = 0$$

and then:

$$k_{i,G}/k_{-i,G} = [G^*]/PG = H_G \qquad [mol \cdot kg^{-1} \cdot Pa^{-1}]$$

where H_G represents the thermodynamic constant of Henry connected with this saturation equilibrium.

If the system is far from the equilibrium, the G mass-transfer rate would be equal to:

$$R_G = d[G^*]/dt = R_{G,i} - R_{G,-i} = k_{i,G}/H_G \cdot A \cdot ([G^*]_{eq} - [G^*]) \neq 0 \qquad \text{<eq. 1>}$$

In order to calculate the values of the constants involved, the initial rate method can be applied. This approach involves the evaluation of the initial gas-diffusion rate occurring between environment and product previously maintained in an atmosphere lacking of this gas (PG = 0). In these conditions, the inverse diffusion rate (product → environment) is practically negligible and the following simplified equation can be obtained:

$$R_{G,t=0} = R_{G,i,t=0} - R_{G,-i,t=0} \approx R_{G,i,t=0}$$
$$= k_{i,G} \cdot A \cdot PG_{t=0}$$

Figure 1 reports the typical development of gas adsorption curve shown by apples (Andrich et al., 1989a,b). While the tangent to initial part of this curve (run time close to zero) allows to evaluate $k_{i,G}$, the asymptotic part of the curve is connected with an equilibrium condition, so that the H_G constant can be calculated as the ratio between the amount of G permeated inside the fruits and the residual G in the environmental atmosphere.

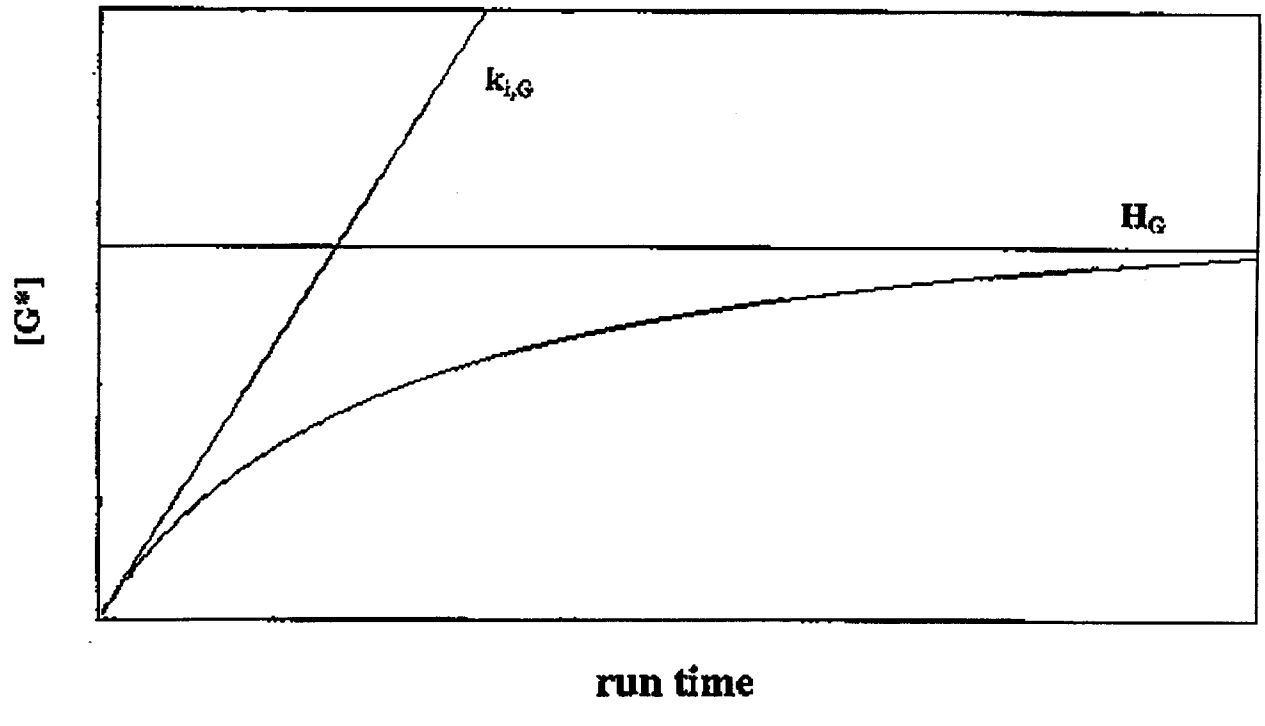


Figure 1 :Gas (G) adsorption curve shown by an horticultural product.*

1.3.3 Packaging materials

To obtain good results in Modified Atmosphere Packaging, a range packaging materials must be available from which candidates can be selected according to the properties and the optimum conditions for the individual produce. This means in more detail:

- The gas permeability should overall be relatively high to allow - although reduced - respiration of produce.
- The ratio of permeabilities for O_2 and CO_2 of the available materials should be variable within a certain range to allow different O_2/CO_2 partial pressures inside a packaging according to the optimum conditions for the individual product.
- A certain range for water vapour permeability should be available, on the one hand to avoid dehydration, but also to avoid condensation within the package. Also here, a selection specific to the produce has to me made.

In our case, O_2 permeabilities ranging from about 500 to 200000 cm^3 / m^2 d bar, CO_2 permeabilities ranging from about 1000 to 200000 cm^3 / m^2 d bar, O_2/CO_2 permeability ratios from about 1:1 to 1:10 and water vapour transmittance values between about 2 g / m^2 d and several hundreds at 85% $\rightarrow$ 0% relative humidity were the initial requirements, all values firstly indicated at standard conditions (23 °C).

These requirements led to the selection of polymeric film materials described in section 2.4.1.These polymers can be separated into three groups:

- Standard polymers (LDPE, EVA/PE, PVC, PS)
- Hydrophilic polymers (PCL, Cellulose, Cellulose acetate, Copolyether-ester)
- and a material in which the permeation mechanism is not dominated by the material properties, but by laser-induced microperforations into PP as a standard polymer (P Plus).

In addition, the behaviour of the permeability of the film materials in terms of temperature, humidity, possibly also under condensation of water is essential for a quantitative understanding of the system packaging / produce / surrounding atmosphere.

Here, values were available in the literature (Yasuda), which are usually taken like material constants. Values obtained in daily practice, however, show that within one type of material or even one type of film, deviations from literature values are large.

These facts required a thorough investigation of

- the dependence of gas permeability on temperature,
- the dependence of gas permeability on relative humidity,
- the dependence of water vapour permeability on temperature and concentration gradient across the films
- and the effects of the contact of liquid water with the film materials selected.

Not many facts over the necessary range of conditions were available. Usually, the temperature dependence of permeabilities for all substances is modelled by an Arrhenius function, thus giving an activation energy for permeation [Yasuda, 1975].

The dependence on the concentration of the permeating species itself is usually neglected which means that the validity of Henry's law is assumed.

For water vapour permeability, it was shown that the temperature-induced effect of the concentration gradient as driving force by far exceeds the temperature effect inside the polymer [Piergiovanni et al., 1995].

In addition, some general trends of the dependence of permeability on the structure of the polymers are known:

- Substances which are dissolved or incorporated into the polymer usually lower the molecular order, increase the amorphous fraction of the material and therefore lead to a higher permeability.
- The main representatives for these substances are

  → Water,

  → and plasticisers.
- Also the processing conditions, which determine the degree of crystallinity, have an influence on permeability.

Related figures are sometimes given by film suppliers for their specific materials, but a generalisation seems to be not possible. Therefore, the a.m. facts have still to be determined for all kinds of films individually.

1.3.4 Permeability of packaging films

In the modified Atmosphere Systems investigated in this project, permeation of substances may occur via two paths: Through the polymer films and through specific microholes (P Plus).

Permeation through polymers

The **permeation** process of substances through polymers, i.e. processes occurring inside the polymers, is usually described by the two-fold mechanism of **solution** and **diffusion.**

The permeation rate, Q', is assumed to be proportional to the product of the solubility S and the diffusion coefficient D, both for simplicity usually assumed to be independent of the concentration of the permeating species under study and of the concentration of the other permeating species. An exception is usually made for water (in terms of relative humidity) which is known to have a marked influence on the gas permeability of many films.

The absolute amount of a species permeating through a polymer film, Q, per unit area and time at a certain temperature is therefore modelled by using the material properties S and D and the concentration difference Δc across the film in the simple equation

$$Q \sim S D \Delta c \qquad (1)$$

in good approximation for most polymers, **for constant temperature and relative humidity conditions if only one permeating species is observed.** This is mostly the case as dedicated equipment is used for the most common gases oxygen and carbon dioxide, but not of combinations of these gases.

Usually, the concentration difference is given in pressure units normalised to standard conditions (STP).

This idealised expression is changed, however, in the presence of **water vapour incorporated in the polymers**, usually leading to higher permeabilities, even more pronounced under condensation conditions.

Permeability through pores

Generally, the amount of a substance diffusing through a hole is given by

$$J = D \Delta c A l^{-1}$$

with J: Diffusion flux, e.g. in mol s^{-1}, D: Diffusion „constant", cm^2 s^{-1}, Δc: concentration difference, e.g. mol cm^{-3}, A: pore area, cm^2, l: length of the pore, i.e. film thickness, cm.

The main problem to use this equation in realistic situations is that D depends not only on temperature, but also on the substances and the composition of the substance mixture, namely with respect to the molecular weight of the permeating species and the gas kinetic collision radii of all species concerned,

and, moreover, shows large variations in values as reported in the literature [CRC, 1982], [Becker, 1979], [Reid et al., 1987].

From

$$D = 1/3 \, \Lambda \, v'$$

Λ: mean free path of permeating species, v': average thermal velocity of permeating species,

and

$$v' = (8 \, k \, T \, \pi^{-1} \, m_0^{-1})^{1/2}$$

a proportionality for D with $T^{3/2}$ at constant total pressure can firstly be derived. From literature values, it seems to be reasonable to assume a common value of 0.165 for the permanent gases O_2 and CO_2 and 0.245 for water vapour in air, all valid at 23 °C, and to neglect the effects of changes in gas compositions.

1.3.5 Packaging procedures

The type of package to be investigated in this project was primarily the consumer type. The usual procedure to pack fresh agricultural produce, thereby achieving both a modified atmosphere as well as some handling protection of the goods are the following:

- Groups of produce are placed on trays of different type of materials. In operation are: → trays from Polystryrene, both sheet material as well as expanded PS (EPS, styrofoam), → pulp trays and → trays from corrugated or solid board.
- The assembly of produce on the tray is placed in a film pouch. This pouch may either be formed by a simple wrap film with self adhering properties or by producing a closed pouch by heat sealing.

Within the tray materials, paper based trays are more expensive, but have the advantage of absorbing water, thus giving some buffer capacity to avoid condensation. This is also related to a higher water vapour permeability of the complete packages as paper practically does not show any water vapour barrier. Besides, paper at present has a better image at the consumer which explains the rising market shares of paper trays.

The plastic film pouches are to be made from the material selected for its specific permeability property. As the permeability is usually relatively high, there is no need to produce tight packagings. Therefore, wrap (cling) films with self adhesive properties are preferred in manual packaging. Films without this property are to be heat sealed. For both cases, however, the permeability properties of the whole package are basically determined by the area of the film.

1.3.6 Modelling of the combined behaviour of packaging and produce

Introduction

The aim of the modelling part within the MASTER project was to develop a generic simulation model able to describe the complete system of Modified Atmosphere Packaging (MAP). The success of MAP strongly depends on the interactions between the packed product and the properties of the package and the environmental Conditions (Kader et al., 1989; Cameron et al., 1995). The most dominant factor affecting all elements of MAP is the environmental temperature. It influences, among other things, the gas exchange rate of the product, and the diffusion characteristics of the foil. Furthermore, the temperature directly or indirectly acts on aspects like the keeping quality of the product, the formation of condensate, partial pressures and, in case of flexible packages, the volume. Over the years, several MAP models with different levels of detail, have been developed (Zagory and Kader, 1988). However, the model developed within the framework of the MASTER project is the first that includes keeping quality of the packed product and that is completely dynamic in time and temperature.

Static-dynamic

Most models describing MAP are static models based on the steady state behaviour of the package, thus neglecting the dynamic phase of reaching steady state. However, for a model which has to be applied for simulating logistic chains dynamic in time and temperature this dynamic phase is of a major importance. In the current model the dynamics of all processes occurring in MAP were therefore maintained and differential equations were used. At constant conditions the dynamic model will eventually converge to the same steady state values as a static model. However, depending on the package defined this can take several hours to days. At dynamic conditions the steady state value will only be reached if the dynamic phase is fast enough as compared to the dynamics of the changing environment.

Gas exchange

The success of MAP depends on reducing the metabolic rate in the product (Burton, 1978; Ulrich, 1975). Several attempts were made to model gas exchange either by empirical models (Cameron et al. 1989; Hayakawa et al., 1975; Jurin and Karel, 1963; Raghavan and Gariépy, 1989; Talasila et al., 1992; Yang and Chinnan, 1988) or strongly simplified models, using for instance a single Arrhenius equation (Mannapperuma et al. 1989, 1994). A more fundamental approach was applied by Chevillotte (1973) who introduced a Michaelis-Menten type approach to respiration. Other workers (Andrich 1991) adopted this approach. Lee et al. (1991) included an uncompetitive type of inhibition because of CO_2. Peppelenbos and Van >t Leven (1996), evaluated four types of inhibition for modelling the influence of CO_2 levels on O_2 consumption of fruits and vegetables as compared to no influence of CO_2. They introduced an equation describing the O_2 consumption rate (V_{O2} in $mmolAkg^{-1}Ah^{-1}$) as inhibited both in a competitive and in an uncompetitive way by CO_2. The gas exchange model implemented in the current MAP model is an extension of the work of Peppelenbos et al..

Keeping Quality

The main objective of MAP is preserving product quality by reducing the rate of the metabolic processes of the packed product. Quality of perishable products is becoming increasingly important to the consumer. Quality, as assigned by the consumer, is affected by fundamental processes in the product, influencing the various quality attributes relevant for the specific product (Sloof et al. 1996). Keeping quality is defined as the time a product remains acceptable (Tijskens and Polderdijk, 1996) and it can be used as a general indication of the overall product quality.

Tijskens (Tijskens, 1995; Tijskens and Polderdijk, 1996) developed a generic model for keeping quality which basically incorporates all aspects of it, including the effects of initial quality, limits of acceptance, dynamic temperature conditions and the different biochemical mechanisms for the reactions underlying quality decay. The static part of the model was validated for more then 60 different

horticultural crops. The dynamic approach was used for implementation in the current MAP model as described by Hertog and Tijskens (1998).

The several sub-models (keeping quality, gas exchange of the product, and temperature dependence of the transmittance of the film for O_2, CO_2, N_2, H_2O) were validated separately, partly within the scope of the MASTER project. The integrated MAP model will be validated by current and future research in the fields of packaging, respiration and keeping quality.

2 Materials and Methods

2.1 Produce

2.1.1 Tomatoes

P5 (VBT)

The tomato cultivar Maëva grown in Belgium was used. The maturity stage of the tomatoes was characterised by means of:

Flesh firmness: Effe-Gi penetrometer [kg/cm^2] or Zwick-penetrometer type 3302

Background colour: colour chart [1 - 12]

Soluble solids: refractometer [% Brix]

Size: diameter [mm]

P2 (INRA)

Tomato of cultivar Daniela grown in Marocco or cultivar Raïsa were sorted on shape and colour bases. Only full red tomatoes without external defects were selected and characterised:

Flesh firmness: expressed as the force needed for a 2% compression

Background colour: colour parameters according to CIE (L*,a*,b*) were determined with Hunterlab Colorimeter

Ethylene production was determined in air at 21 °C, individual fruits were placed in a airtight jar (400ml) and ethylene was monitored by gas chromatography.

P3 (Pisa)

For the gas diffusion measurements, tomatoes available on the local market were used.

2.1.2 Chicory

Chicory endives were grown in the north of France and in the region of Leuwen (Belgium) on commercial farms. Diamant or similar cultivars were used. Endive shoots were sorted at the producer to select "perle du nord" quality. Picked in the morning, the endive shoots were transported under refrigeration (6 °C) to Avignon and were placed in INRA's cold rooms (1-3 °C) within 24 hours after harvest - or less for VBT. Endive shoots were stored under these conditions for more than one day and less than 3 days prior to RR assessment or packing. The 24 hours delay is necessary for the chicory to recover from harvest and transportation stresses (Results : respiration rate of chicory).

All batches of chicory were assessed for initial O_2 and CO_2 respiration rates (RR) plus fermentation rate (FR) under nitrogen at 11 °C and 21°C. All RR and FR were determined using the glass jar technique (See 2.2, respiration INRA).

Just before use, chicories were sorted by size and weight. Appraisal of their apparent stage of maturity was based on visual evaluation of shoot opening and shape. Tentative assays were also carried out to correlate shoot opening with their apparent density. Non conclusive experiments were conducted to characterise chicory shape by image analysis. For apparent density measurements, the shoots were wrapped in a thin strechable PVC foil and dipped into water, apparent (Archimedean) density was expressed as the ratio of shoot weight to the volume of displaced water. Replications of

wrapping on the same shoots showed a significant variability of apparent density (about 10%), however results were well correlated to the visual appraisal of shoots opening.

Image analysis was carried out with a black and white video camera with a resolution of 245x245 pixels and, under our experimental conditions, one pixel corresponded to 0.7mm^2. Various parameters were calculated from digitalised images : length, width, asymmetry, top angle, and shape coefficient (ratio of the surface to the square of the perimeter).

2.1.3 Apples

Golden Delicious apples characterisation was mainly carried out looking to their physiological status evaluated at T = 21 °C measuring their aerobic (O_2 consumption) and anaerobic (CO_2 production - O_2 consumption) respiration rates at $PO_2 \cong 21$ kPa and $PN_2 \cong 79$ kPa for aerobic determination and at $PO_2 \cong 0$ kPa and $PN_2 \cong 100$ kPa for anaerobic.

Moreover, every set of utilised fruits was identified by a personal identification number (PIN) corresponding to a list of specific details as date of purchase, colour number (1-9) evaluated according to VBT chart, flesh firmness obtained as average of many penetrometer measurements carried on three different apple sites (peduncle zone, middle part of the fruit, near the receptacle site).

2.2 Produce respiration and measurement equipment, data processing, evaluation algorithms

P2 (INRA)

Glass jar technique

Plant tissues (250 ± 30g) were poured into 1.5 L glass jars equilibrated at the required temperature and stored in controlled temperature rooms. Jars were left open in the cold rooms. At time intervals, three (or more) jars per temperature were closed and gas samples (50µL) were taken after 1, 2, 3 and 5 hours with an air-tight syringe through a silicone septum set with silicone glue in the jar lid and analysed by gas chromatography. Rubber gaskets and silicone septa on the jars were changed after each experiment to prevent any air leak. Apparent respiration rates (appRR) were calculated by linear regression from O_2 depletion curves and expressed as mmol.hr^{-1}.kg^{-1}. Mean values and standard deviations were measured on the three (or more) replications.

Fermentative rate was assessed the same way except that prior to closing the jars they were flushed with pure N_2

The respirometers

– The former instrument

The former instrument available at INRA Avignon was designed to measure O_2 respiration rate of plant tissues placed into binary atmospheres (O_2, N_2). This instrument consists of two glass jars of equal volume (6.5L) placed in a thermostated (heating - cooling) bath (± 0.05 °C). Plant tissues are poured into the measurement vessel containing a sufficient quantity of soda to trap CO_2. Complete CO_2 trapping results in a decrease in pressure which corresponds to oxygen uptake (multipied by respiratory coefficient if necessary) and which is monitored by a differential manometer connected to the two vessels. When depression in the measurement cell reaches 40 Pa, the microcomputer receiving the information from the manometer orders the injection of pure O_2 through an hydraulic device until the pressure between the two vessels is balanced (about 2mL). The computer stores the exact quantity of injected oxygen and corresponding time. At the end of the run, the computer plots the cumulated O_2 consumption vs time. The linear regression of the straight part of the kinetic allows the calculation of O_2 consumption rate (in m mol. kg^{-1}.hr^{-1}). It is possible to get a rough estimate of $RRCO_2$ by the determination of the total quantity of carbonate in the soda at the end of the run.

In order to fulfil the objectives of the MASTER project, we drastically modified this instrument to permit the determination of RRO_2 and $RRCO_2$ under any ternary (O_2, CO_2, N_2) gas mixtures. We also designed the respirometer for a direct assessment of apparent km of O_2 for the respiration chain.

- The new respirometer (fig. 2.1):
- manifold 1 : Measurement of O_2 and CO_2 respiration rates. Two airtight 6 liter vessels were dipped into a thermostated heating/cooling bath whose temperature was regulated at ± 0.1 °C (Figure 2).

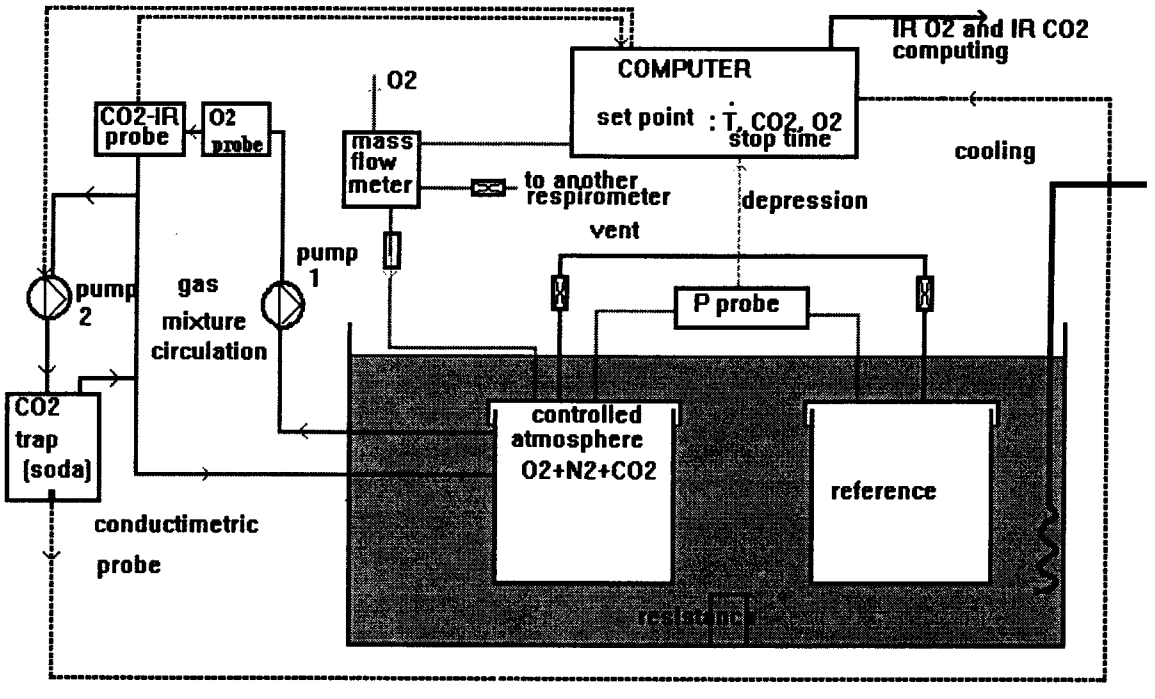


Figure 2.1 : Respirometer used to measure both O_2 and CO_2 respiration rates under constant atmospheric conditions and apparent Michaelis' constant of mushroom respiration by oxygen depletion.

About 500g of plant tissues were placed into the sample vessel, the lid of which was tightly secured. The head space of the whole instrument was flushed with a ternary gas mixture of pre-set composition through 3 calibrated mass flow meters. As soon as the initial atmosphere composition (O_2, CO_2, N_2) was reached and controlled on a gas chromatograph, the vents were shut and the programme was run. Internal gas, at a flow of 40 ml per minute was pumped through an infra-red detector to measure CO_2 concentration. If this concentration were higher than the pre-set value of CO_2 concentration plus a deviation, about 0.1 kPa absolute CO_2 concentration, the computer switched on pump 2 (Fig.2.1) which sent the head space atmosphere, at a 150 ml per min flow rate, through a CO_2 trap filled with 0.1 N soda until the initial CO_2 concentration in the sample vessel was restored. The trapping of the CO_2 in excess resulted in a proportional depression which was detected by a highly sensitive differential pressure probe. The pressures between the two vessels were balanced by the injection of pure oxygen through a mass flow meter. The CO_2 trapped in the soda was continuously measured by amperometry.

The computer logged O_2 injection times and the changes in conductance of the carbonated soda. At the end of the run, it calculated O_2 and CO_2 respiration rates in $mmole.kg^{-1}\ hr^{-1}$.

This accurate instrument permitted the assessment of both aerobic and anaerobic metabolisms, but strict 0% CO_2 was not attainable since the minimum CO_2 concentration at steady state was reached when the rate of CO_2 production by the plant tissue equilibrated the CO_2 trapping rate, i.e. about 0.3 kPa in the normal configuration of the instrument (depending on global respiration of the plant tissue).

- manifold 2 : Direct measurement of apparent Michaelis' constant of endive respiration rate

The effect of O_2 partial pressure on respiration rate of plant tissue has been described as an Michaelis like mechanism. Obviously, Michaelis and Menten's law is not strictly applicable to the respiratory chain of plant tissue since it is a multi enzyme - multi substrate reaction in which the concentrations of intermediary substrates are unknown. Moreover, the apparent Michaelis' constant we calculated also involves gas diffusion from external atmosphere into internal atmosphere and from the latter into each cell. These mass transfers respond to exponential Fick's law and not to an hyperbolic equation. In this respect, it is meaningless to assimilate the apparent km of respiration rate to km_{O_2} of cytochrome c oxidase. The respirometer previously described was slightly modified in order to permit the direct assessment of O_2 consumption rate as a function of the residual oxygen concentration in the head space. Firstly, the CO_2 was continuously trapped and secondly, the injection of O_2 to balance the pressure between the two vessels was replaced with pure nitrogen.

It is noteworthy that, as previously mentioned, at the end of each experiment when the respiration of the plant tissue is very low, there is a 0.3 to 0.5kPa partial pressure (depending on the weight of tissue, temperature and flow rate of the gas circulation pump) in the instrument. This residual CO_2 is continuously removed by soda trap resulting in decrease in pressure and artificial injection of nitrogen. This phenomenon is responsible for an apparent exponentially decreasing O_2 consumption. To avoid this artefact, O_2 monitors (rpe and zirconium O_2 probes) were placed more recently in the gas manifold.

With this instrument it is possible to assess accurately O_2 partial pressure under constant CO_2 concentration as a function of the experiment duration. For example, such a kinetic, obtained with endive shoots at 11°C, is reported in Figure 2.2.

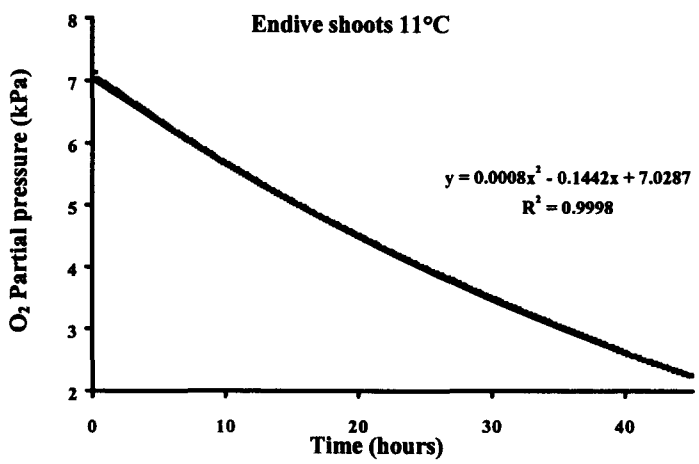


Figure 2.2: Kinetic of O_2 partial pressure (kPa) as a function of time in the vessel of the respirometer containing endive shoots and thermostated at 11 °C.

In order to measure the respiration rate, which is the slope of the curve O_2 *vs* time, we fitted the experimental data with a polynomial equation. An acceptable fitting was obtained with a second order polynome (r^2=0.9998).

The derivate of this second order equation is the O_2 respiration rate at any time of the kinetic. When we draw the Lineweaver and Burk's double reciprocal plotting ($1/RRO_2$ *vs.* $1/O_2$) we find a straight

line that can be extrapolated in Figure 2.3 to measure (for this example) Vm (0.65 mmole/kg.hr) and Km (6.59 kPa).

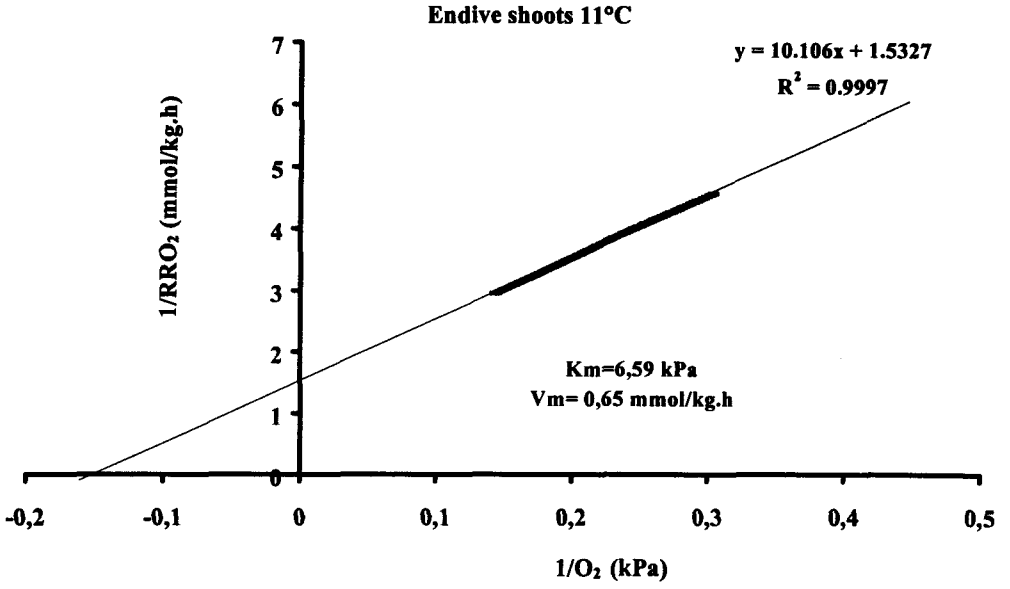


Figure 2.3: Lineweaver and Burk's double reciprocal plotting. The respiration rate values are obtained by derivating the polynomial equation shown in figure 2.

P3 (Pisa)

Experimental apparatus employed -To evaluate simultaneously the rates of CO_2 produced (RCO_2) and O_2 consumed (RO_2) by an horticultural product stored in C.A. conditions, an automatic apparatus was planned and set up. It consists of three main sections: the first devoted to the preparation of desired gas mixture; the second for carrying out and studying aerobic and anaerobic respiration processes; the third devoted to the gas analysis. To operate at wished temperature, the second section is located inside a thermoregulated cell.

Thermoregulation (set temperature ± 1 °C) is ensured by two different heat exchangers led by the same operative control. The first heat exchanger cools the cell atmosphere if its temperature is greater than the set value while the second heats when the set temperature is greater. The sensor of temperature connected to control apparatus is placed inside the glass reactor (second section) filled with tested materials and so it measures directly the temperature of the gas phase surrounding the stored products.

Moreover, the temperature of circulating gas, as well as that present inside the utilized product are continuously monitored during all run time by two sensors placed respectively in contact of the gas phase and internal tissue of used material. The values of temperatures are than collected, memorized and visualized by a suitably programmed computer which is devoted to temperature monitoring and is connected to another computer (F, see Figure 2.4) which ensures the automatic control of this experimental apparatus.

In order to maintain a constant gas composition inside the cell, the amount of CO_2 coming from aerobic and/or anaerobic fruit metabolism is continuously and automatically monitored by a gas chromatograph connected to a personal computer (Figure 2.4). The automatic control of this experimental plant is realised according to the following steps:

1) at desired run times (every 45 min.) the gas-chromatograph (D), prompted by the computer (F), performs an analysis of the gas composition present inside the plant;

2) the automatic sampler (C) collects the amount of gas necessary for the analysis;

3) the electrical signals from the detector of the gas-chromatograph (D) are sent to the integrator/recorder (E);

4) the analytical reports produced by the integrator/recorder (E) are collected, elaborated and then stored by the computer (F);

5) if the CO_2 concentration present inside the plant is greater than the sum of the initial set value plus the tolerance interval, the computer (F) changes the gas course by the electrovalve (G);

6) the gas bubbles through the adsorbing-CO_2 trap (H) for a time calculated by the computer (F) as a function of the amount of the gas to be absorbed and of PCO_2 utilized;

7) the stored product can produce CO_2 according to the following two different pathways of substrate (i.e. hexose) metabolization:

aerobic respiration $C_6H_{12}O_6 + 6\,O_2 \rightarrow \quad 6\,H_2O \quad + 6\,CO_2$

anaerobic respiration $C_6H_{12}O_6 \quad \rightarrow \quad 2\,C_2H_5OH \quad + 2\,CO_2$

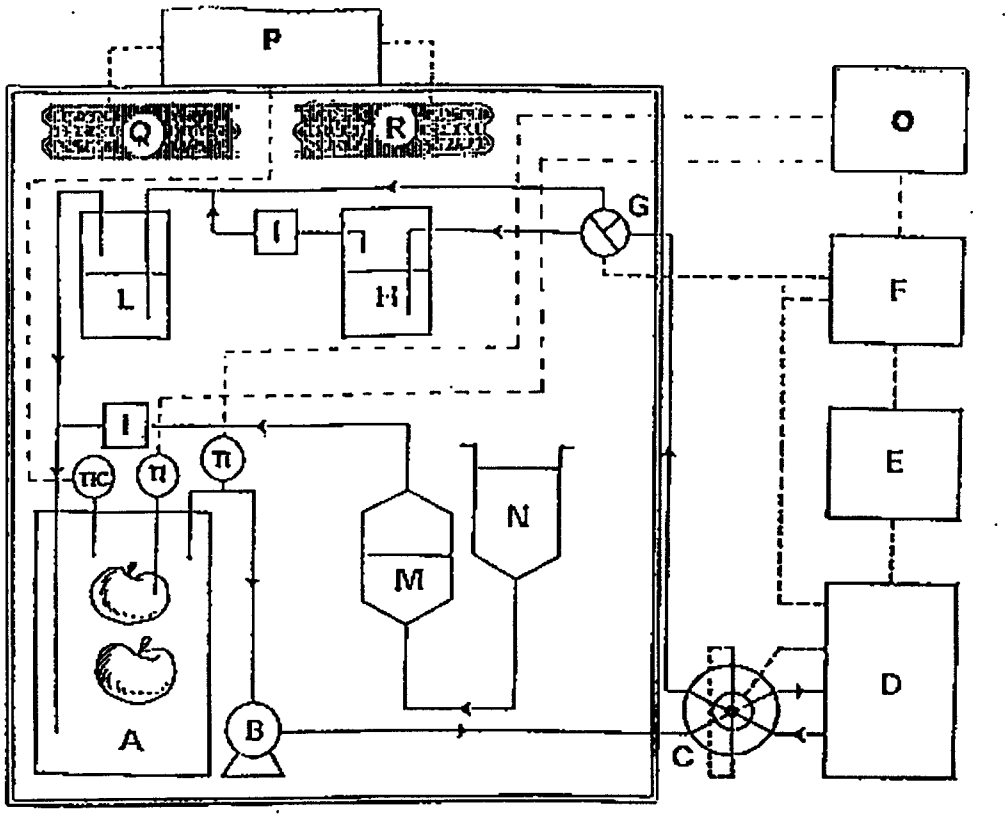


Figure 2.4: Scheme of the experimental apparatus used to evaluate respiratory activity of stored products, double frame indicates the walls of thermoregulated cell.
A = reactor filled with Golden Delicious apples; B = circulating pump; C = automatic gas sampler; D = gas chromatograph; E = integrator/recorder; F = computer; G = automatic electrovalve; H = trap to collect CO_2 produced [aqueous $Ba(OH)_2$]; I = one way valve; L = trap to collect C_2H_4 produced [aqueous $KMnO_4$]; M = graduated O_2 tank; N = tank containing saturated aqueous solution [NaCl]; O = computer connected with temperature sensors; P = temperature controller; Q = heat exchanger to cool; R = heat exchanger to heat.

According to aerobic respiration the volume of O_2 consumed is completely replaced by that of CO_2 produced. The $Ba(OH)_2$ of absorbing trap removes this amount and determines a decrease of pressure of the gas present inside the apparatus which is immediately and automatically compensated for by the addition of a calculated volume of pure O_2 coming from the tank M. In the other case, when an anaerobic fermentation is established, no loss of pressure occurs when CO_2 produced is removed by trap and O_2-tank (M) does not change its level.

While the amount of O_2 replenished (RO_2) gives a measure of the aerobic respiration rate, the difference between the rates of CO_2 produced (RCO_2) and O_2 consumed allows us to calculate the fermentation rate:

Respiration rate = Rae = RO_2

Fermentation rate = Ran = $RCO_2 - RO_2$

P5 (VBT)

Respiration rates were determined as O_2-consumption and CO_2-production. Samples (+-1000g) were placed in a glass container (+- 6 l). The glass containers with the samples were flushed for 24h with the calibrated gas mixtures with a flow 50 ml/min in a temperature regulated room set at the desired temperature. After flushing the containers were closed and the partial pressures of O_2 and CO_2 in the head space were measured. After a specified time interval, depending on the temperature and produce, the partial pressures of O_2 and CO_2 in the head space were measured again. From the changes the respiration rates were calculated.

Partial pressures of O_2 and CO_2 were measured using a micro GC (Chrompack 2002P) with a T.C.-detection system. Separation of the components was achieved on a Molsieve 5A column (70 °C) and a Hayesep A column (90 °C) with Helium as a carrier gas.

2.3 Internal diffusion, data processing, evaluation algorithms

Experimental apparatus employed - To evaluate the skin permeability of an horticultural product to gas diffusion an experimental apparatus has been planned and set up. It consists of three main sections: the first devoted to the preparation of the desired gas mixtures; the second for carrying out and studying the gas-diffusion process; the third devoted to the gas analysis, which consists mainly of a gas-chromatograph connected to a personal computer. To operate at wished temperature, the second section is located inside a thermoregulated cell (Figure 2.5).

Thermoregulation (set temperature ± 1 °C) is ensured by two different heat exchangers led by the same operative control. The first heat exchanger cools the cell atmosphere if its temperature is greater than the set value while the second heats when the set temperature is greater. The sensor of temperature connected to control apparatus is placed inside the glass reactor (second section) filled with tested materials and so it measures directly the temperature of the gas phase surrounding the stored products.

Moreover, the temperature of recirculating gas, as well as that present inside the utilized product are continuously monitored during all run time by two sensors placed respectively in contact of the gas phase and internal tissue of used material. The values of temperatures are then collected, memorized and visualized by a suitably programmed computer which is devoted to temperature monitoring and is connected to another computer which ensures the automatic control of this experimental apparatus.

Each run was carried out in three steps. During the first step, the concentration of the diffusing gas inside the fruits was reduced and maintained very low (PG < 0.4 kPa for ≈ 18 hr). In the second step,

the chamber atmosphere was quickly changed (≈70 s) to a gas mixture rich in G ($20 \leq PG \leq 60$ kPa), the washing gas, previously maintained in a tank placed inside the thermoregulated cell (≈18 hr) to avoid a temperature difference between the diffusing gas-mixture and the horticultural product studied. Finally, the chamber atmosphere was continuously circulated for ≈ 1.5 hr, the gas composition frequently (≈ 90 s) analysed, and the data stored in the computer.

Data processing - As the utilised equipment does not allow any gas exchange with the external atmosphere, the amount of G permeated inside the apples should be always equal to that disappeared from the environmental gas phase, which is continuously monitored by a gas chromatograph connected with the diffusional reactor.

In order to correlate the amount of gas G diffused into the product ($[G]_p$) with the run time, the integrated form of equation <1> must be adopted. At a random time (t=t), the oxygen permeated inside the apple should be equal to the amount of gas which has disappeared from the environment. According to the ideal gas law, the following equation can be written:

$$PG \cdot V/w = R \cdot T \cdot [G]_g$$

where:

PG = partial pressure of gas G in the environment (Pa);
V = free volume inside the experimental apparatus (m^3);
w = weight of utilised product (kg);
R = ideal gas constant ($Pa \cdot m^3 \cdot K^{-1} \cdot mol^{-1}$);
T = temperature (K);
$[G]_g$ = concentration of G in the environment ($mol \cdot kg^{-1}$).

As:

$$[G]_{p(t=t)} = [G]_{g(t=o)} - [G]_{g(t=t)}$$

the following equation is obtained:

$$[G]_{p(t=t)} = (PG_{(t=o)} \cdot V)/(R \cdot T \cdot w) - (PG_{(t=t)} \cdot V)/(R \cdot T \cdot w)$$

and:

$$PG_{(t=t)} = PG_{(t=o)} - [G]_{p(t=t)} \cdot R \cdot T \cdot w/V.$$

According to the definition of Henry's constant:

$$[G^*]_{p(t=t)} = H_G \cdot PG_{(t=t)} = H_G \cdot (PG_{(t=o)} - [G]_{p(t=t)} \cdot R \cdot T \cdot w/V)$$

and so equation [1] becomes:

$$d[G]_{p(t=t)}/dt = k_{i,G}/H_G \cdot A \cdot (H_G \cdot (PG_{(t=o)} - [G]_{p(t=t)} \cdot R \cdot T \cdot w/V) - [G]_{p(t=t)}) =$$
$$= k_{i,G}/H_G \cdot A \cdot [H_G \cdot PG_{(t=o)} - [G]_{p(t=t)} \cdot (H_G \cdot R \cdot T \cdot w/V + 1)]$$

This differential equation can be integrated and the following logarithmic form obtained:

$$\mathbf{\ln(H_G \cdot PG_{(t=o)} - (H_G \cdot R \cdot T \cdot w/V + 1) \cdot [G]_{p(t=t)}) = - k_{i,G}/H_G \cdot A \cdot (H_G \cdot R \cdot T \cdot w/V + 1) \cdot t + \ln (H_G \cdot PG_{(t=o)})}.$$

At the end of diffusion when the mass-transfer of the diffusing specie is no longer detectable, an equilibrium state is reached. Under this condition, the ratio $[G]_p/PO_2$ gives the value of the mass-

transfer equilibrium constant H_G. Furthermore, in order to evaluate the $k_{i,G}$ constant, the least squares regression method can be applied to a modified form of the integrated equation:

$$\ln((H_G \cdot PG_{(t=o)})/(H_G \cdot PG_{(t=o)} - (H_G \cdot R \cdot T \cdot w/V+1) \cdot [G]_{p(t=t)})) = k_{i,G}/H_G \cdot A \cdot (H_G \cdot R \cdot T \cdot w/V+1) \cdot t$$

$$y = m \cdot x$$

In fact, in the plane $t,\ln((H_G \cdot PG_{(t=o)})/(H_G \cdot PG_{(t=o)} - (H_G \cdot R \cdot T \cdot w/V+1) \cdot [G]_{p(t=t)}))$, this last equation represents a straight line, whose slope allows the $k_{i,G}$ to be calculated directly.

Moreover, the first derivative of the integrated equation, evaluated at the initial point (run time = 0), allowed the initial rate, which is directly related to the PG used, to be calculated:

$$[G]_{p(t=t)} = V \cdot H_G \cdot PG_{(t=o)}/(H_G \cdot R \cdot T \cdot w + V) \cdot (1 - e^{-k_{i,G}/H_G \cdot A \cdot (H_G \cdot R \cdot T \cdot w/V + 1) \cdot t})$$

$$[G]_{p(t=t)}' = k_{i,G} \cdot A \cdot PG_{(t=o)} \cdot e^{-k_{i,G} \cdot A \cdot (R \cdot T \cdot w/V + 1/H_G) \cdot t}$$

$$[G]_{p(t=o)}' = k_{i,G} \cdot A \cdot PG_{(t=o)}$$

At the end of diffusion, when the G mass-transfer is no longer detectable, an equilibrium condition is reached where the ratio between the amount of G permeated inside the apples ([G*]) and the residual PG in the surrounding atmosphere allows the constant H_G to be calculated.

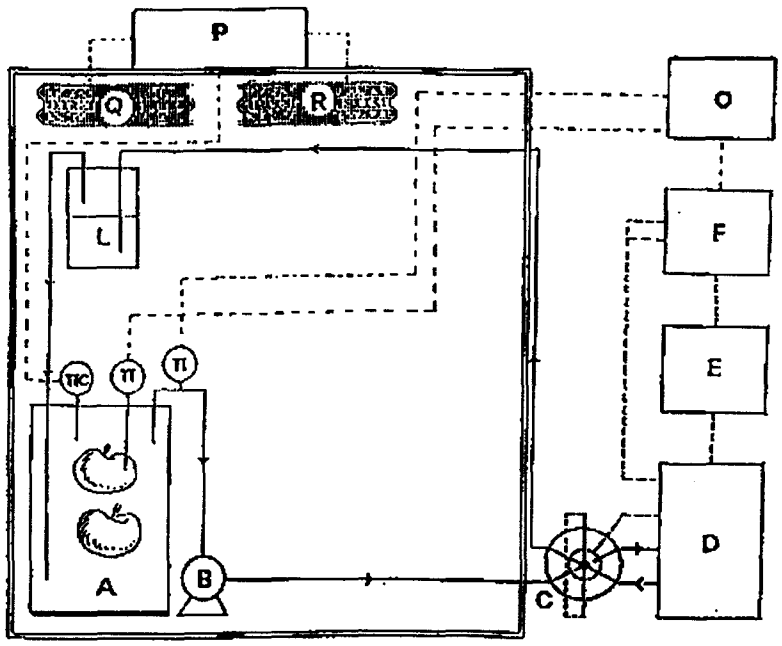


Figure 2.5 : Scheme of the experimental apparatus used to evaluate skin permeability of stored products, double frame indicates the walls of thermoregulated cell.
A = reactor filled with Golden Delicious apples; B = circulating pump; C = automatic gas sampler; D = gas chromatograph; E = integrator/recorder; F = computer; L = trap to humidify the circulating gas; O = computer connected with temperature sensors; P = temperature controller; Q = heat exchanger to cool; R = heat exchanger to heat.

2.4 Packaging materials and their properties

2.4.1 Polymer films

A dedicated selection of packaging materials had been performed in the project period, according to the different criteria important for the application case.

The most important factor was a relatively high permeability for gases, which, except for the Cellulose, was met by all materials.

For water vapour permeability, the materials investigated show a broader range: Relatively hydrophobic materials like Polyethylene and Polypropylene, intermediate types up to very hydrophilic types.

The following specific films were investigated, most of them from industrial sources, one from experimental production at P4, made by different techniques and in different thickness ranges, see thickness indications in micrometers.

- Polyethylene in its most gas permeable form, LDPE, 12 µm, an extruded film.
- Polyvinyl Chloride, PVC, 16 µm, plasticised, extruded.
- Polystyrene, PS, 50 µm, extruded.
- Micro perforated Polypropylene (P Plus), 35 µm, produced by laser-induced micro perforation from cast film extruded and subsequently biaxially oriented Polypropylene. This film was made available in different grades of gas permeability (given in thousands of cm^3 / m^2 d bar) indicated by the indices 10 K, 25 K, 60 K, 100 K and 200 K, respectively, meaning a gas permeability of 10000 cm^3 / m^2 d bar, 25000 cm^3 / m^2 d bar and so on.
- Ethylene vinyl acetate / Polyethylene copolymer, EVA/PE, 14 µm, extruded, a wrapping film intended for replacement of PVC in many applications
- Polyether/polyester copolymer films, 9 µm, extruded a film type with both high gas and water vapour permeability.
- Poly-ε-Caprolactone, PCL, 15 µm, a synthetic, biodegradable polyester with high gas and water vapour transmittance. Films from this material were produced in Lab scale at FhIVV by blow forming.
- Cellulose acetate films with a degree of substitution of 2.7, CA, ds 2.7, 80 µm, cast films from an industrial source, plasticised.
- Cellulose regenerate (Cellophane, German: Zellglas) cast films from pure regenerate cellulose without plasticisers, 25 µm, industrial production, but experimental material.

These films are shown in figure 2.6 in comparison with other polymers, with respect to their permeability for oxygen and water vapour as important parameters.

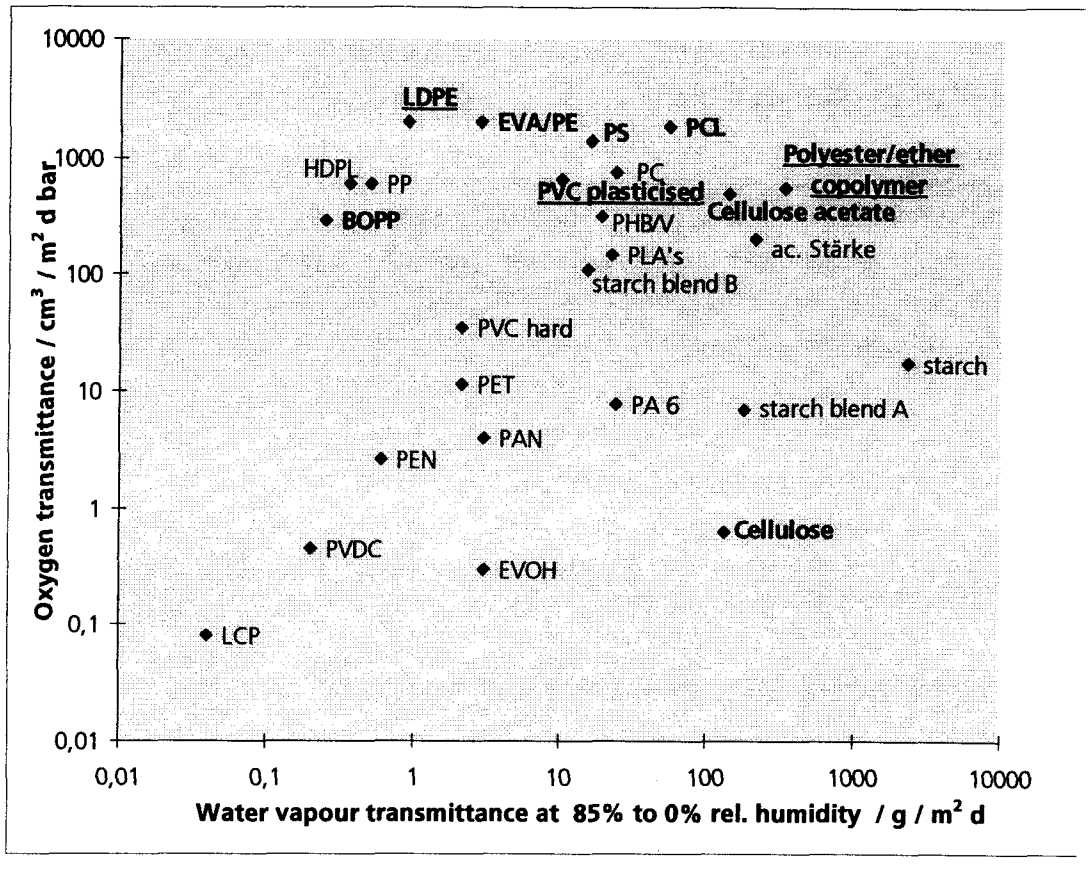


Figure 2.6: A representation of polymers with their permeabilities for oxygen and water vapour at 23 °C as characteristic criteria. The polymers investigated in the project are shown in bold, those which were investigated closer are underlined. The values are normalised to a film thickness of 100 µm.

2.4.2 Measurement of permeability

2.4.2.1 Gas permeability

Gas phase

The basic measurement principles used within this project were: Differential pressure measurements and gas specific carrier gas measurements.

Differential pressure measurements

These operate with different gases and a manometric detection of the permeating gas. Type of equipment used: Brugger (München, D)

Measurement conditions:

* Reliable measurements only at dry conditions (0 % relative humidity)

* Variation of temperature: -20 °C to 80 °C possible, 6 °C to 40 °C applied in this project.

This measurement method has one severe disadvantage and one advantage:

- Due to the differential pressure, the film material may be pressed onto the basis area of the measurement cell, thus reducing the gas flow. For soft films, this can be avoided by placing a porous sheet e.g. of very thin paper (Pergamin) below the film.

- Different gases may subsequently be applied to the film samples under identical conditions.

Gas specific carrier gas measurements

These operate with N_2 as humidified carrier gas, loaded with the test gas (O_2,) in a defined partial pressure, in contact with one side of the sample and the - also humidified - carrier gas alone purging the other side of the sample. Permeated traces of the test gases in the carrier gas are detected by an electrochemical reaction. Types of equipment used: Oxtran® from Mocon, USA, and own - built equipment.

Measurement conditions:

* Application of a defined relative humidity (for O_2) on both sides of the sample (used: 0%, 50%, 75 %, 88% r.h.)
* Variation of temperature: 10 °C to 40 °C

It has to be noted that on both types of measurements the free film area has to be reduced for the higher permeating materials to avoid overrange of the instrumentation. After a systematic investigation (see results section), a final decision for the use of circular masks of 5 cm² area from self adhesive aluminium film was made.

Gas permeation from the water phase (oxygen, carbon dioxide)

Here, a cell with liquid water on both sides of the film, also containing a purging mechanism switchable from nitrogen to the test gas, a test gas concentration detector in the water phase in combination with a gas chromatographic head space analysis had been designed. The layout of the apparatus is shown in Figure 2.7. A film sample masked with self adhesive aluminium film down to a free film area of 5 cm² is placed between the two sections of the cell. Both sections are filled with degassed distilled water, leaving an unavoidable head space volume of less than 50 cm³. After a pre purge with nitrogen to remove the residual oxygen in both sections, the left chamber purge is switched to the test gas to one atmosphere of pressure. The rise of test gas concentration in the sensor chamber, always in combination with the test gas content of the head space, gives lag time and equilibrium permeability of the film sample under conditions of full contact with liquid water.

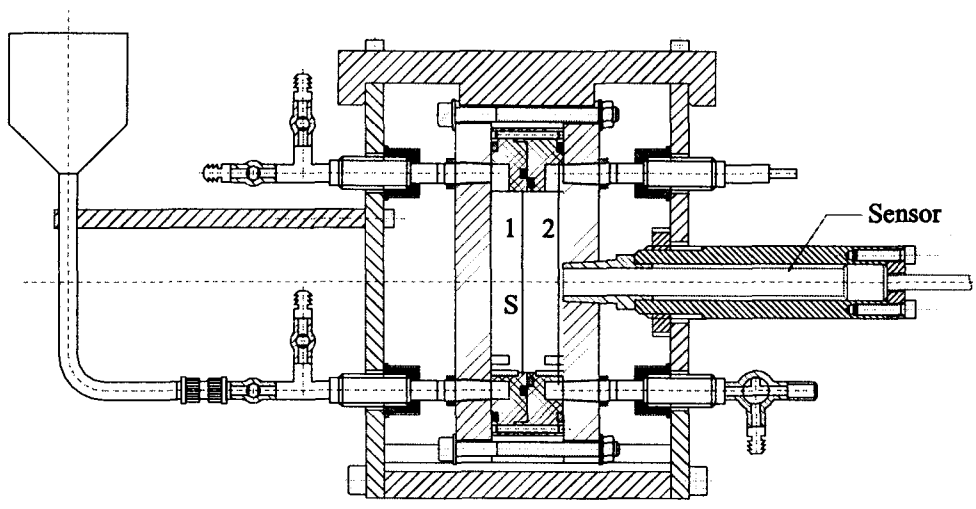


Figure 2.7: Layout of the gas permeation cell operating in liquid water. 1: Chamber purged with test gas; 2: Sensor chamber, S: Film sample

2.4.2.2 Water vapour permeability

Here again, the inherent principle is to establish a partial pressure difference across the samples. Therefore, measurements at constant water concentration conditions inside the samples are - by principle - not possible.

In all cases, a certain gas atmosphere (N_2 or air) with a defined humidity is led to one side of the sample, the water uptake of the atmosphere at the other side of the sample is measured by constantly removing the amount of water vapour.

- **Electrolytic method**: Equipment used: Brugger WDDG (München, D), with dry measurement conditions on one side of the samples, the other sides are loaded with a relative humidity of 85 %.
- **Gravimetric method** (Jar method).

  Here, the following measurement conditions were applied:

  * A climatic chamber of 50 %, 85 % relative humidity, temperatures between 10 °C and 40 °C.
  * Inside the jars 0 %, 5 %, 11 %, 22 %, 45 %, 75 %, and 100 % relative humidity were established, an assessment on the permeability under slight condensation conditions could be derived from the measurements at 100 % relative humidity inside the jars.

Pervaporation

Originally, a cell with liquid water on one side of a film and a water vapour detector on the other had been designed and put into basic operation, but yielded insufficient results. Therefore, a simpler modified jar method was developed which allowed for measurements on 4 different materials.

2.4.2.3 Permeability through pores

The permeability fraction of the pores can be calculated according to section 1.3.4. These formula yield: For water vapour permeability (e.g.for 80 µm diameter pores, 35 µm film thickness, 85% → 0% relative humidity difference):

$Q / g\ d^{-1}$ (at 23 °C) = $5.3 \cdot 10^{-3}$, and $Q / g\ d^{-1}$ (at 10 °C) = $2.4 \cdot 10^{-3}$,

for gas permeabilities (for 80 µm diameter pores, 35 µm film thickness, a diffusion coefficient of $D = 0.165\ cm^2\ s^{-1}$, for 1 bar atmospheric pressure at 23 °C):

$Q/cm^3\ bar^{-1}\ d^{-1} = 205$, normalised to STP.

Dedicated measurements to achieve experimental verifications at single pores failed due to overrange of the measurement equipment. An estimation for packaging measurements at P2, however, allowed a verification (see results section).

2.5 Packaging equipment and procedures

2.5.1 Commercial type

P2 (INRA)

Chicories previously stored at 3 °C for less than 3 days were equilibrated after sorting at the experiment temperature 6, 11, 16 and 21°C.

Four shoots (500-560g) were placed on a cardboard tray into a 0.12m² bag prepared from different films. In the first experiments only microperforated films with calibrated permeabilities to gases were used. The reference foil was polypropylene (OPP) 35µm, kO_2 : 900 and kCO_2 : 4000mL/m².day.atm. Since perforating foil results in the loss of film selectivity (kCO_2/kO_2), only O_2 permeance of microperforated films will be mentioned. For example microperforated films (P Plus) with a permeance of 10 000 mLO_2/m_2.d.atm will be referred as 10k, 15 000 as 15k, 40 000 as 40k and 100 000 as 100k. The other films, polyethylene, Polyester/polyether copolymer, stretchable PVC etc. were previously described in Materials and Methods part materials.

Experiment at constant temperature (6, 11 and 16 °C)

Films used at 6 and 16 °C were : OPP, 10k, 25k, 60k, 100k, osmolux (osm) and at 11°C : OPP, 10k, 15k, 40k, 200k, Polyester/polyether copolymer, polyethylene and stretchable PVC. The packs were placed into a dark temperature controlled room for a total duration depending on the experiment temperature. Gas composition were measured either on a conventional gas chromatograph or a MTI M200 Micro gas chromatograph. With the latter instrument O_2 measurement does not include argon (0.8kPa). Gas composition in packs was assessed on 3 replicated packs and measurement of initial and final RR and FR were made with 4 jars. Results are expressed as kPa.

Weight losses were appreciated using 1/100g precision scales.

Changes in colour were assessed on three points at 120° on the tip of each shoot with a Hunterlab colour quest colorimeter which gives L*, a* and b* parameters in the CIE system.

Experiments at variable temperature

Packs of endive shoots were prepared as previously described but the packaging films were different, they were chosen in order to optimise shelf life and prevent greening : OPP, P Plus 40k, P Plus 200k, 3 Grace Cryovac films PD 900 (PO_2=3000, PCO_2=10000 mL/m_2.d.atm; PH_2O=10 mL/m_2.d.atm), PD961 (PO_2=7000, PCO_2=20000 mL/m_2.d.atm; PH_2O=15.5 mL/m_2.d.atm), PD941 (PO_2=16000, PCO_2=36000 mL/m_2.d.atm; PH_2O=77.5 mL/m_2.d.atm), and a macroperforated film (MP) as air reference. The bags were placed into a controlled temperature room at 11 °C for 3 days and then left in indirect day light at 21 °C for 5 days. In this experiment, changes in colour (from yellowish to green colour) was assessed as previously described.

P5 (VBT): Tomato cv. Maëva

Each package contained 6 tomatoes on a tray which was put in a bag having a surface of 1300 cm² and a void volume of 1160 cm² (Polyester/polyether copolymer or Polypropylene) or was wrapped in the foil with a surface of 590 cm² and a void volume of 435 cm² (PVC). The bags were sealed by heat with a kitchen sealer.

Packaging film used were polyester/polyether copolymer, PVC and micro perforated polypropylene: P^+10 K, P^+25 K, P^+100 K.

Four packaging experiments were carried out with different temperature profiles:

- 2 weeks at 8 °C
- 2 weeks at 13 °C
- 2 weeks at 23 °C with colder period form day 2 to day 5 at 11°C
- 2 weeks: day 1 to 4 at 8 °C, day 5 to 11 at 13 °C and day 12 to 14 at 23 °C

P5 (VBT): Apple, cv Golden Delicious

Each package contained 6 apples on a tray which was put in a bag having a surface of 1300 cm² and a void volume of 1160 cm² (Polyester/polyether copolymer or cellulose-acetate) or was rapped in the foil with a surface of 590 cm² and a void volume of 435 cm² (PVC). The bags were sealed by heat with a kitchen sealer.

Packaging film used were polyester/polyether copolymer (Polyester/polyether copolymer), PVC and cellulose-acetate.
Four packaging experiments were carried out with different temperature profiles:

- 2 weeks at 1 °C
- 2 weeks at 11 °C
- 2 weeks at 21 °C
- 7 days at 1 °C, 3 days at 11 °C and 4 days at 21 °C

2.5.2 Model packagings

P1 (ATO)

A rigid MA packaging system has been developed allowing the researcher to control and measure all the relevant MAP parameters. A modular non flexible packaging system for produce less than 1 kg is made of stainless steel and used in ***the evaluation of the whole system (fig 2.8)***. It can serve as a well defined and controlled model system for all kinds of MAP and gas packages. The packaging material is located between compartment A and B. Its position is fixed by two sintered stainless steel plates which fill both compartments. Connections with the outside of compartments A and B can be made via several Whitey valves (ie for gas-sampling). The product compartment (C) can be mounted at the bottom of the compartment B. The product compartment C and the compartments A, B for fixating the packaging material are available in different sizes. Because of the modular system, packages with all kinds of combination of volumes and packaging surfaces can be obtained. Packaging systems for produces up to 5 kg are made of trespa and the variation of surface area of the film is modified by mounting several compartments (A and B) on each package.

The packaging systems are subsequently placed in a controlled climate room (Weiss $SB11^{500}$). The O_2 and CO_2 concentration inside the packaging systems are measured with a gas chromatograph (Carlo Erba VEGA 6000 or Chrompack Micro GC CP 2002). The gas chromatograph system is equipped with a hot wire detector and a flame ionisation detector. Packed columns filled with Porapak and Molsieve for detection of CO_2, O_2 and N_2 respectively are used. Helium is used as carrier. This gas chromatograph is placed outside the climate control room. A special device including a multiposition valve allows automatic sampling of maximal eight packaging systems without opening the climate controlled room.

P4 (Fh-IVV)

A similar set-up as at P1 was set up at Fh-IVV which was based on glass jars instead of stainless steel ones. It allowed for measurements of O_2 concentrations and CO_2 in "realistic atmospheres", also within and outside simulated packagings including packed goods. 4 measurement containers are used in which the packaging film separates the „model package" with its filled goods (the product space) from the simulated ambient atmosphere (the head space). The gas compositions in both volumes were monitored in regular time intervals for O_2 and CO_2 content. Initially, the detection of O_2 was done by paramagnetic sensors, of CO_2 by infrared sensors. This set-up was developed specifically for the project, but had several times to be modified due to large influences of the gas manifold system on the measured gas composition. Finally, the inside gas composition analysis of the model packages was modified to an off line analysis by a micro gas probe, operating also with a combination of paramagnetic sensors and infrared sensors, additionally checked with a separate control by gas chromatographic methods.

Packaging materials tested in this set-up were PVC, Polyether/polyester copolymer, Cellulose acetate and PE, with and without „Golden Delicious" as filled produce, at 6 °C and 11 °C and 21 °C.

Characteristics:

* The complete behaviour of packaging and product and ambient atmosphere could be simulated and studied, but

* the sensitivity for permeating gases is much lower than for dedicated permeation cells.

Temperature and humidity control of the inside and ambient of simulated packagings were performed by placing the whole equipment inside a well-controlled refrigerator and by moisturising the circulating gas by saturated KCl solution, delivering 88% of relative humidity.

2.6 Modelling of experiments

(ATO)

Introduction

Interpretation of the gathered complex results on gas exchange in function of O_2, CO_2 and temperature can be considerably improved by using a mathematical model. Several attempts were made to model gas exchange either by empirical or strongly simplified models using for instance a single Arrhenius equation. A more fundamental approach was applied by Chevillotte (1973) who introduced a Michaelis-Menten type approach to respiration. Lee et al. (1991) included an uncompetitive type of inhibition because of CO_2.

Peppelenbos and Van't Leven (1996), evaluated four types of inhibition for modelling the influence of CO_2 levels on O_2 consumption of fruits and vegetables as compared to no influence of CO_2. They introduced an equation describing the O_2 consumption rate (V_{O2} in $mmolAkg^{-1}Ah^{-1}$) as inhibited both in a competitive and in an uncompetitive way by CO_2. This combined type of inhibition of O_2 consumption was formulated as:

$$V_{O_2} = \frac{Vm_{O_2} \cdot [O_2]}{Km_{O_2} \cdot \left(1 + \frac{[CO_2]}{Kmc_{CO_2}}\right) + [O_2] \cdot \left(1 + \frac{[CO_2]}{Kmu_{CO_2}}\right)}$$

where $[CO_2]$ and $[O_2]$ are concentrations (%), Vm_{O2} the maximum O_2 consumption rate ($mmolAkg^{-1}Ah^{-1}$), Km_{O2} the Michaelis constant for O_2 consumption (%), Kmc_{CO2} the Michaelis constant for the competitive CO_2 inhibition of O_2 consumption (%) and Kmu_{CO2} the Michaelis constant for the uncompetitive CO_2 inhibition of O_2 consumption (%).

The combined type of inhibition is a comprehensive and flexible formulation that, depending on the values of Kmc_{CO2} and Kmu_{CO2}, can describe all generally distinguished types of inhibitions on the rate of O_2 consumption (competitive, non-competitive and uncompetitive inhibition of O_2 consumption by CO_2; Chang, 1981) including the case of no inhibition. The respiration model without inhibition by CO_2 was successfully applied for several products (apple, Andrich et al., 1991; Blueberry, Cameron et al., 1994; cauliflower, Ratti et al., 1996; red raspberry, Joles et al., 1994). The non-competitive type of inhibition was applied by Peppelenbos et al. (1993) to fresh mushrooms and by Song et al. (1992) to blueberry.

Renault et al. (1994) applied the model of uncompetitive inhibition from Lee et al. (1991), which describes oxidative O_2 consumption, also to describe CO_2 production, assuming a respiration quotient of 1 thereby discarding a possible contribution of fermentative CO_2 production. According to Peppelenbos et al. (1996) CO_2 production (V_{CO2} in $mmolAkg^{-1}Ah^{-1}$) results from both oxidative and fermentative processes simultaneously and can be describe as:

$$V_{CO_2} = RQ_{ox} \cdot V_{O_2} + \frac{Vm_{CO_2(f)}}{1 + \frac{[O_2]}{Km_{O_2(f)}}}$$

where RQ_{ox} represents the respiration quotient (ratio between CO_2 production and O_2 consumption) for oxidative respiration, $Vm_{CO2(f)}$ the maximum fermentative CO_2 production rate ($mmolAkg^{-1}Ah^{-1}$) and $Km_{O2(f)}$ the Michaelis constant for the inhibition of fermentative CO_2 production by O_2 (%).

The two above equations, describing the effect of O_2 and CO_2 on the gas exchange, constitute the basis for the presently used model. The model is however extended with a temperature dependence according to Arrhenius for both $Vm_{CO2(f)}$ and Vm_{O2}. Furthermore, the fermentative CO_2 production is extended with an inhibition term for CO_2.

CO_2 inhibition of fermentation

As stated during the presentation of all the gas exchange measurements in some cases a clear effect of CO_2 on the fermentative CO_2 production was visible. In the current model approach by Peppelenbos this was not included yet. As the available data on this part of the gas exchange is still limited a simple approach was applied. In analogy to the inhibition of fermentation by O_2 a competitive type of inhibition was also introduced for CO_2. So the mechanism can be represented in a simplified way by:

$$\mathrm{Enz} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{AC_1} \xrightarrow{kp_1} \mathrm{Enz} + \mathrm{CO_2}$$

$$\mathrm{Enz} + \mathrm{O_2} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{AC_2}$$

$$\mathrm{Enz} + \mathrm{CO_2} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{AC_3}$$

With O_2 and CO_2 competing with the substrate S for the same enzyme (Enz), thus reallocating the available active enzymes in the inactive complexes AC2 and AC3. Following this mechanism the total CO_2 production can now be described with:

$$V_{CO_2} = RQ_{ox} \cdot V_{O_2} + \frac{Vm_{CO_2(f)}}{1 + \frac{[O_2]}{Kmc_{O_2(f)}} + \frac{[CO_2]}{Kmc_{CO_2(f)}}}$$

To prevent overparameterisation some redundant parameters are already incorporated in the remaining parameters. Any other mechanism could also be possible, but based on the available data it is impossible to discriminate on a more detailed level. Therefore, for sake of usefulness this rough approach was selected and implemented.

Temperature dependence

The Michaelis constants Km_i and Vm_i from Eq. 1 and 2 are all based on individual rate constants belonging to the underlying reactions, like:

$$Vm_{O_2} = kp_1 \bullet [Enz_0]$$

$$Km_{O_2} = \frac{k_{-1} + kp_1}{k_1 \bullet [S_0]}$$

The Km's for inhibition are all based on a ratio like:

$$Kmc_{CO_2} = \frac{k_{-2}}{k_2}$$

$$k_i = k_{i,ref} \cdot e^{\frac{Ea_i}{R_{gas}} \bullet \left(\frac{1}{T_{ref}} - \frac{1}{T}\right)}$$

In general one can state that a Vm is equivalent to a single rate constant while a Km is related to a ratio of rate constants. Each of the mentioned reaction rates depends on temperature presumably according to Arrhenius' law:

where R_{gas} = gas constant (8.314 $JAmol^{-1}AK^{-1}$). The parameter $k_{i,ref}$ stands for the reaction rate constant at the arbitrarily chosen reference temperature T_{ref} (K). The activation energy Ea_i expresses the dependence of the reaction rate k_i on temperature T (K). The appearance of the Arrhenius equation shown (Chang, 1981), has the advantage of replacing the ill defined frequency factor by a meaningful reference reaction rate ($k_{i,ref}$) at a certain reference temperature T_{ref}. As the Michaelis constants Vm_{O2} is directly related to kp_1, Vm_{O2} will also depend on temperature according to Arrhenius= law. Assuming that the rate constants of the equilibrium reactions have activation energies of roughly the same magnitude, each Km*i*, being a ratio of rate constants, will become relatively independent of temperature, as the difference in activation energies is most probably much smaller than the individual activation energies. Preliminary analysis of the current data on gas exchange, allowing a temperature dependence for both the Vm*i* as for Km*i*, did not reveal a significant temperature dependence for Km*i*. Only Vm*i* exhibited a significant temperature dependence. This confirms the assumptions made. From the preceding, it is concluded that the parameters Vm_{O2} and $Vm_{CO2(f)}$ will most strongly depend on temperature according to Arrhenius= law whereas each of the Km*i* will be relatively temperature independent and can be treated as constants.

Statistical analysis

The collected experimental data were analysed statistically with the iterative non-linear regression routine of the statistical package Genstat 5 (release 3.1, Lawes Agricultural Trust, Rothamsted Experimental Station, U.K.). For each of the products, the data of all O_2xCO_2xtemperature combinations were analysed together, using the model formulation of Eq. 1 and 2, together with the temperature dependence according to Arrhenius' law (Eq. 7) applied to Vm_{O2} and $Vm_{CO2(f)}$. The data were analysed using O_2, CO_2 and temperature simultaneously as explaining variables. The experimental data on CO_2 production and O_2 consumption were used simultaneously as variables to be explained. The non-linear equations were applied directly, without transformation to data or equations. The reference temperature for Arrhenius was fixed at 10 °C, in the middle of the applied temperature range.

3 Results

3.1 Respiration of produce

3.1.1 Tomato

Respiration rates were determined at 4 X 5 O_2/CO_2 combinations each at 5 different temperatures (see tables in the Annex). The following 2 graphs show - as an example - the respiration rates for O_2 consumption and CO_2 production at 8°C (figures 3.1 and 3.2). The graphs for the other temperatures are also shown in the annex.

O_2 consumption

At 8 °C the O_2 consumption rate was the lowest. The dependency of the O_2 consumption rate on the CO_2 concentration was limited at this temperature, only a slight dependency on the O_2 concentration at low CO_2 concentration was noticed: The O2 consumption rate is higher at higher O_2 concentrations.

At 13 °C the O_2 consumption rate was somewhat higher than at 8 °C but follows the same pattern.

At 18 °C the O_2 consumption rate was again higher than at 13 °C and besides the same O_2 concentration dependency a dependency on the CO_2 concentration became observable. The higher the CO_2 concentration the lower was the O_2 consumption. This was seen at a O_2 concentration of 21 % but was not so clear at lower O_2 concentrations.

At 23 °C the O_2 consumption rate showed the same overall pattern as at 18 °C only the rates had a somewhat higher value. At 28 °C the rates were the highest and the dependencies of the O_2 consumption rate on the O_2 and CO_2 concentration were the most pronounced.

CO_2 production

At 8 °C the CO_2 production rate was the lowest. The dependency of the CO_2 production rate on O_2 and CO_2 concentrations was limited at this temperature. The CO_2 production rate is higher at higher O_2 concentrations and low CO_2 concentrations.

At 13 °C the CO_2 production rate was somewhat higher than at 8 °C but follows the same pattern.

At 18 °C the CO_2 production rate was again higher than at 13 °C. The dependency on the O_2 concentration was changed. From 21 % to 3 % O_2 a decreasing CO_2 production rate was observed as for the lower temperatures but at 0 % O_2, CO_2 production rates comparable with the rates at 21 % O_2 were seen. The dependency of the CO2 production rate on CO_2 concentration was not obvious.

At 23 °C the CO_2 production rate was somewhat higher than at 18 °C but follows the same pattern. The dependency of the CO_2 production rate on CO_2 concentration was more pronounced than at 18 °C: at lower CO_2 concentrations a higher CO_2 consumption rate was observed.

At 28 °C, the CO_2 consumption rates are much higher especially at the lower CO_2 concentrations.

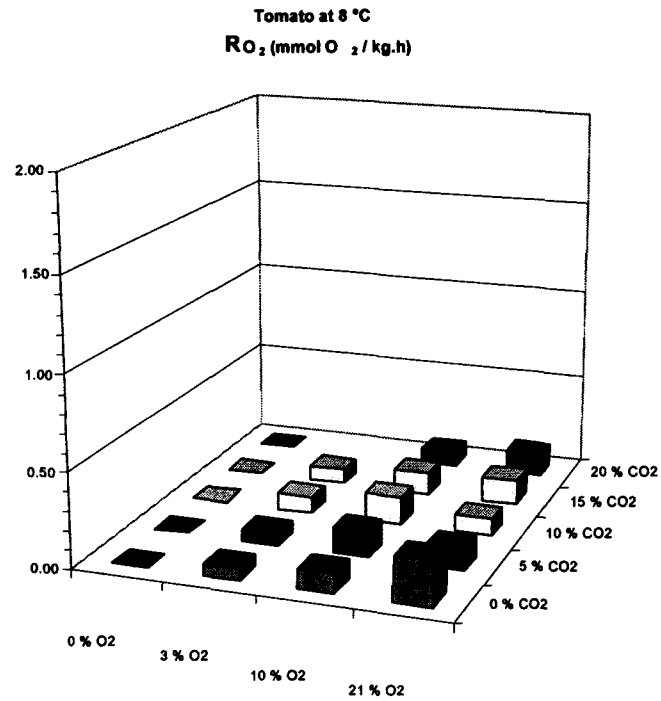


Figure 3.1: Respiration rate of O_2 at 8 °C of tomatoes as a function of O_2 and CO_2 concentration.

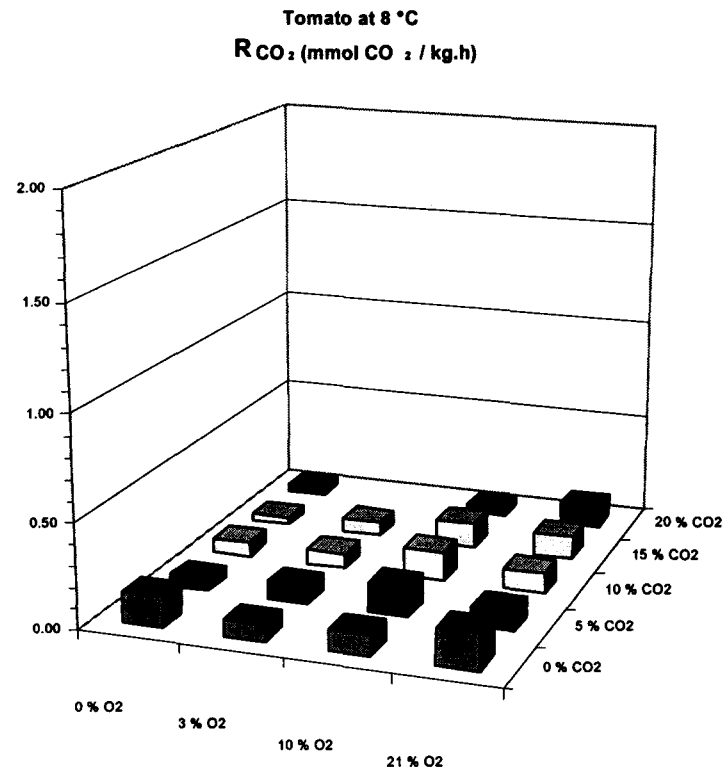


Figure 3.2: Respiration rate of CO_2 at 8 °C of tomatoes as a function of O_2 and CO_2 concentration

Maturity experiments with tomato

Experiment 1: Tomatoes, cv. Maëva, were picked before the start of the red colouring

The respiration activity and the evolution of the red colouring at 13 °C was daily measured during a fortnight.

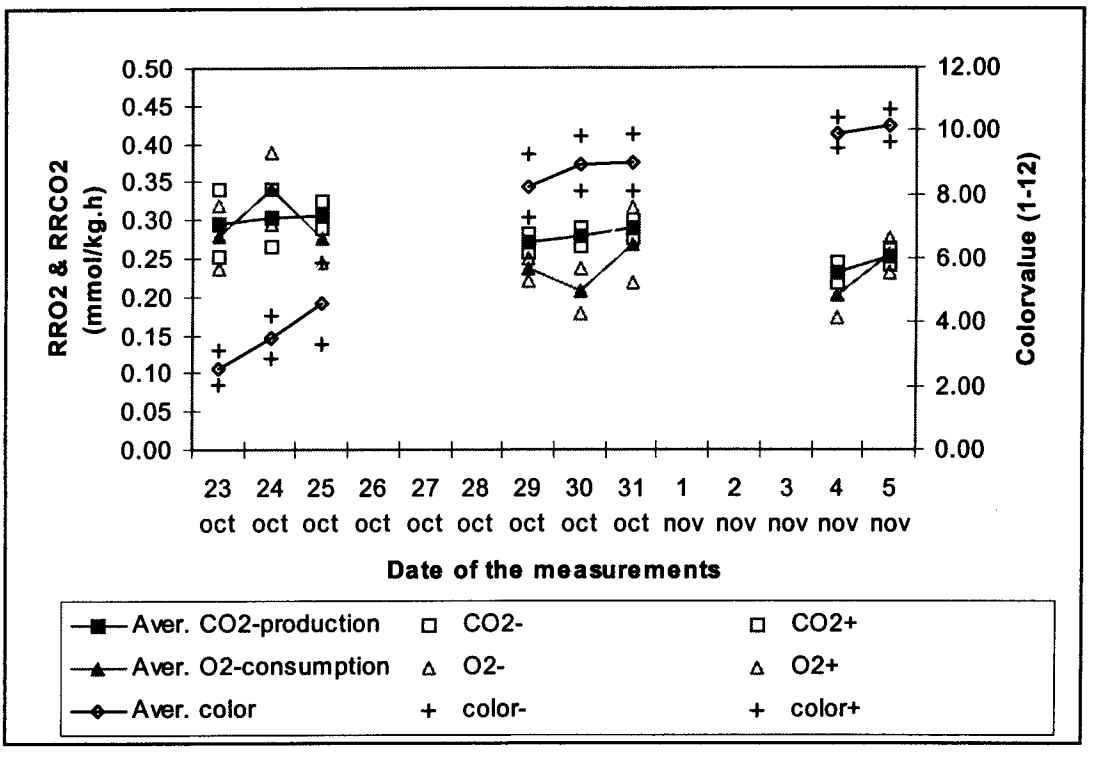


Figure 3.3: Evolution of respiration rate and colour during 14 days after harvest. The tomatoes were harvested at either colour value 2 or 3.

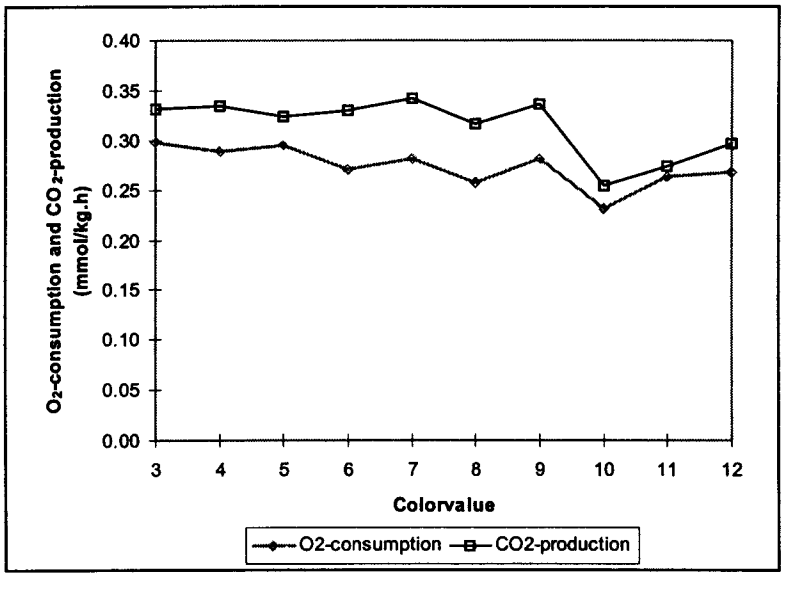


Figure 3.4: Respiration rate right after harvest of tomatoes picked in different colour stages

The tomatoes were picked all green (colour stages 2 or 3). The tomatoes developed their colour in the first 6 days: from stage 2 to stage 9. During the second week the colour changed only from 9 to 10. The respiration rate changes much less and more linearly from 0.3 mmol/kg.h at picking to about 0.23 mmol/kg.h after 14 days (figure 3.3).

Experiment 2: Tomatoes, cv. Maëva, were picked in all stages of the red colouring.

The respiration activity was measured at 13 °C immediately after the harvest and this for all colour values (3 to 12).

CO2 production was 0.34 mmol/kg.h and O2 consumption was 0.28 mmol/kg.h for colour stages 3 to 9. Only colour stages 10 to 12 had a slightly lower respiration rate (figure 3.4).

3.1.2 Chicory

For chicory, the complete evaluation of respiration parameters is shown exemplary in more detail in the following section:

Preliminary experiment: Respiration rate (RR) of endives as a function of storage duration at 1 °C prior to RR assessment at 10 °C.

Endives were assessed for both O_2 and CO_2 RR with the jar technique at 10 °C for 7 hours every day. For each run, respiration rates were calculated over successive incubation periods in jars : T0 (1 to 3 h); T1 (3 to 5h) and T2 (5 to 7hr).

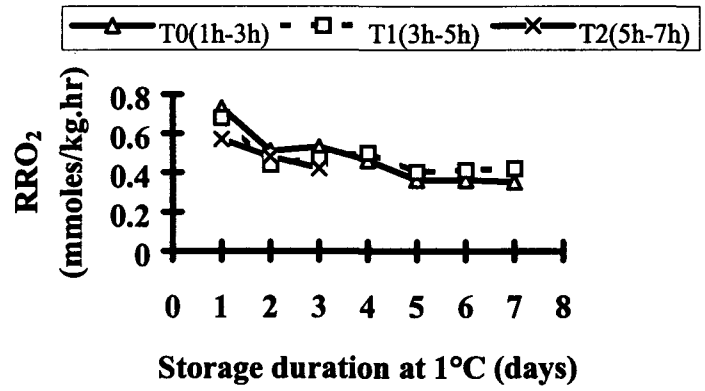


Figure 3.5 : O_2 respiration rate of endive at 10 °C as a function of assessment and storage durations at 1 °C prior to the measurement.

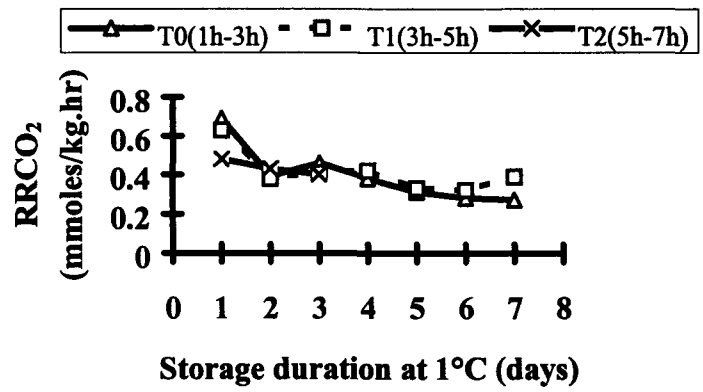


Figure 3.6 : CO_2 respiration rate of endive at 10 °C as a function of assessment and storage durations at 1 °C prior to the measurement.

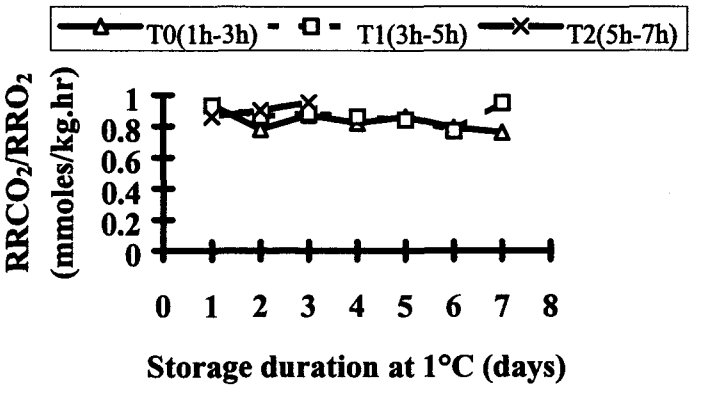


Figure 3.7 : Respiratory quotient of endive at 10 °C as a function of assessment and storage durations at 1 °C prior to the measurement.

As shown in figure 3.5, RRO_2 on "Day1" is very high, about 0.7 mmol/kg.hr, but immediately decreases and tends to stabilise. It seems that the decrease is exponential and 48 hours after arrival (Day2), the endive respiration rate may be considered as stabilised.

Change in $RRCO_2$ mirrors that of O_2 (figure 3.6). After 3 days, $RRCO_2$ averaged 0.35±0.1 mmole/kg.hr, about half that measured upon arrival. A large standard deviation, presumably due to sample variability, was observed. The respiratory quotient (RQ) was rather stable over storage duration and averaged 0.84±0.09 (figure 3.7).

As a consequence, endive shoots were stored at 1 °C for at least 1 day prior to RR assessment or packaging and for less than 4 days. It is noteworthy that frost bite was never observed under our storage conditions. Frost bite is characterised by sunken and sharply limited spots which are located on the external side of leaves. This chilling injury often occurs when the shoots are exposed to a temperature of about 1 °C during forcing or storage after harvesting.

Respiration rate as a function of temperature and atmosphere composition

Products were stored in cold room at 1 °C (endive shoots). Prior to measurement, they were equilibrated overnight at the required temperature (6, 11, 16 and 21 °C for endive shoots). About 1 kg of product (7-8 shoots) was placed into the respirometer (manifold 1) and the vessel containing plant tissues was flushed with a gas mixture at the required composition. This gas mixture was generated from pure O_2 and N_2 cylinders using two calibrated mass flowmeters.

Binary atmospheres (N_2, O_2)

Raw material determination.

From a same tray, size, weight and shape of purchased endive shoots were very variable and no significant relation with the date of purchase was found. Size varied from 10 to 17 cm and weight from 90 to 240g. Bigger shoots displayed a looser structure and had a slightly lower apparent density. Apparent density of shoots weighing 100 to 150g or 180 to 230g were respectively 0.65 +/- 0.05 (23 samples) and 0.59 +/- 0.05 (17 samples). Size and weight of shoots used for respiration rate measurements were in the range 12 - 15 cm and 120 - 160 g except in experiment N°2 where bigger shoots with a looser structure were available.

Measurement of apparent O_2 respiration rates

In experiment N°1, initial O_2 uptake as a function of storage time at 16 °C was not linear (results not shown). The slow O_2 consumption at the beginning of the recording may be due to the gas equilibration time. The shoots were at a good maturity stage with tight structure. In experiment 2 the chart does not

display this lag time. The shoots were at a more advanced maturity stage with loose structure. It was postulated that the loose structure of the shoots facilitated the gas diffusion and, therefore, permitted a faster equilibration of gas transfers.

Variability of results

Ten replications of RR_{O_2} of endive versus O_2 at 16 °C are reported in figure 3.8. As above mentioned we submitted our results to a double reciprocal conversion and reported them in Lineweaver type coordinates (figure 3.9). From these data we calculate a standard deviation of about 11% of RR_{O2} at 20% O_2. The variability of the results increases with decreasing O_2 concentration. The maximum velocity of the respiration rate of endive at 16 °C was 0.75 mmole/h.kg and the apparent km was 1.75 kPa (approximately 1.75% O_2 in the atmosphere). Using individual experiment we found from 0.57 mmole/kg.h to 1 mmole/kg.h for the apparent maximum velocity and from 1.4 to 2.5 kPa for the apparent km (Figure 3.10) at 16 °C.

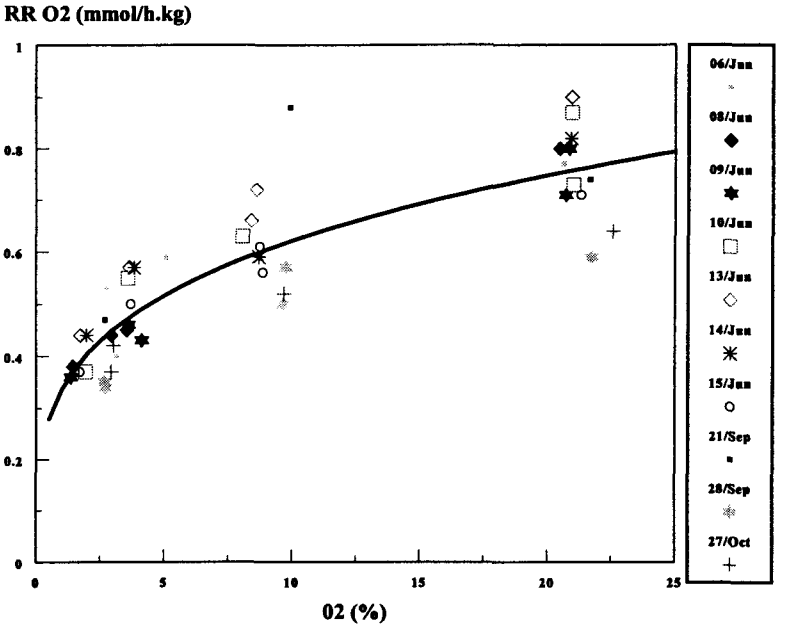


Figure 3.8: Replications of O_2 respiration rate (mmole.kg^{-1}.h^{-1}) of endive shoots as a function of O_2 concentrations (kPa).

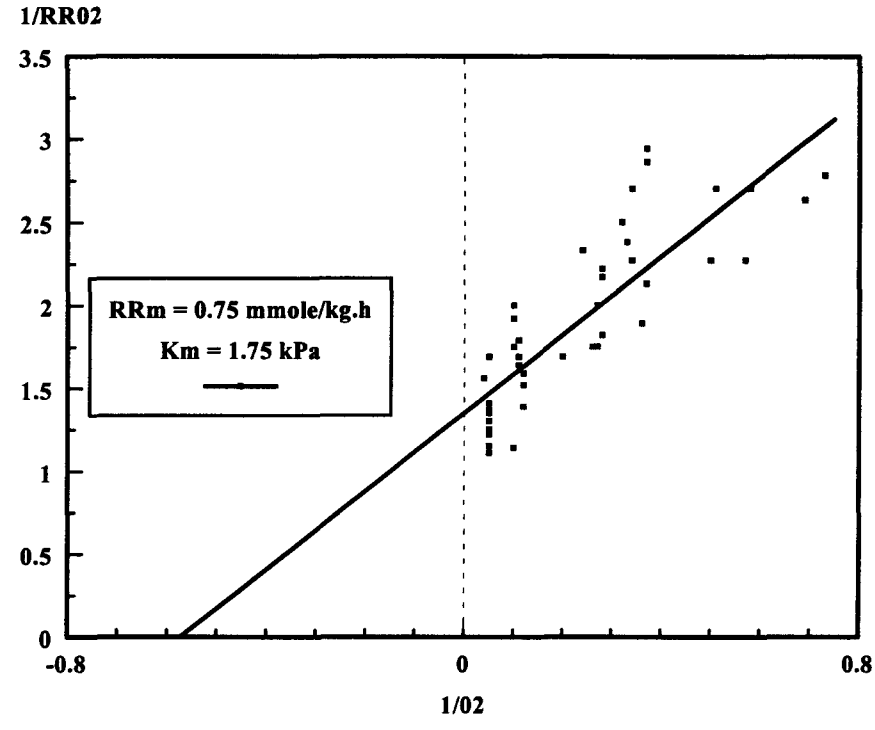


Figure 3.9: Adjustment of data from figure 7 to Michaelis' equation in double reciprocal coordinates.

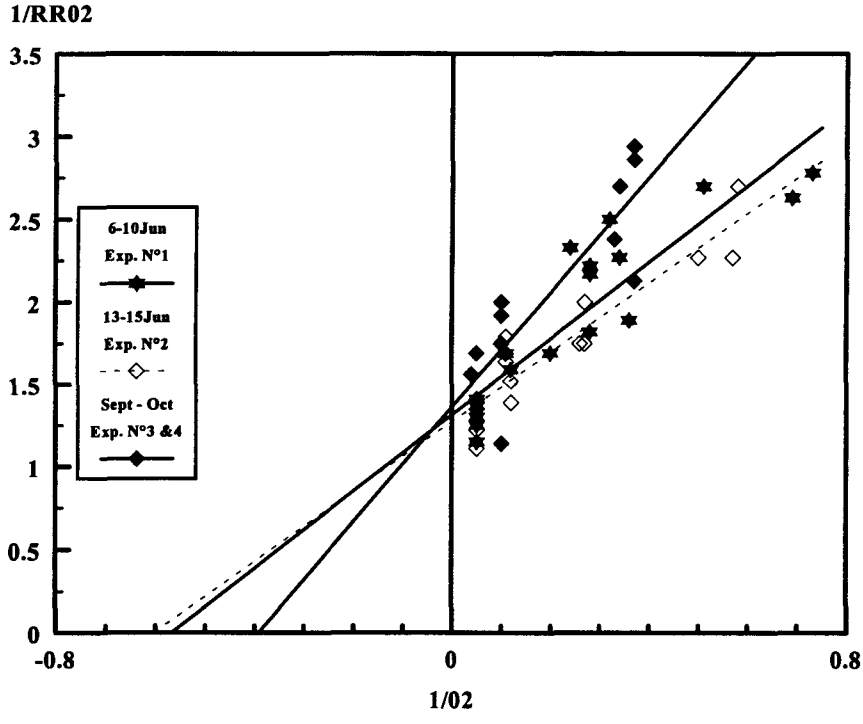


Figure 3.10: Adjustment of 3 replicates (selected from figure 4) to Michaelis' equation in order to calculate the variability of km (kPa) and RRm (mmole.kg^{-1}.h^{-1}) at 16 °C.

Influence of temperature on the respiration rate of endives

The response of RR_{O2} to increasing temperature should follow Arrhenius' law over a narrow range of temperature (from 0 to 25 °C). The respiration rates as a function of oxygen concentration at four tem-

peratures are reported in figure 3.11. Extrapolations below 2% O_2 are based on the fact that RR_{O_2} under anoxia is nil. It must be noted that increasing O_2 concentration from 5 to 21% results in little change in O_2 respiration rate whatever the temperature. In the Lineweaver and Burk's coordinates (figure 3.12), 1/Vm and -1/km decrease with increasing temperature. As expected, Vm increases with increasing temperature and it seems that Km followed the same pattern.

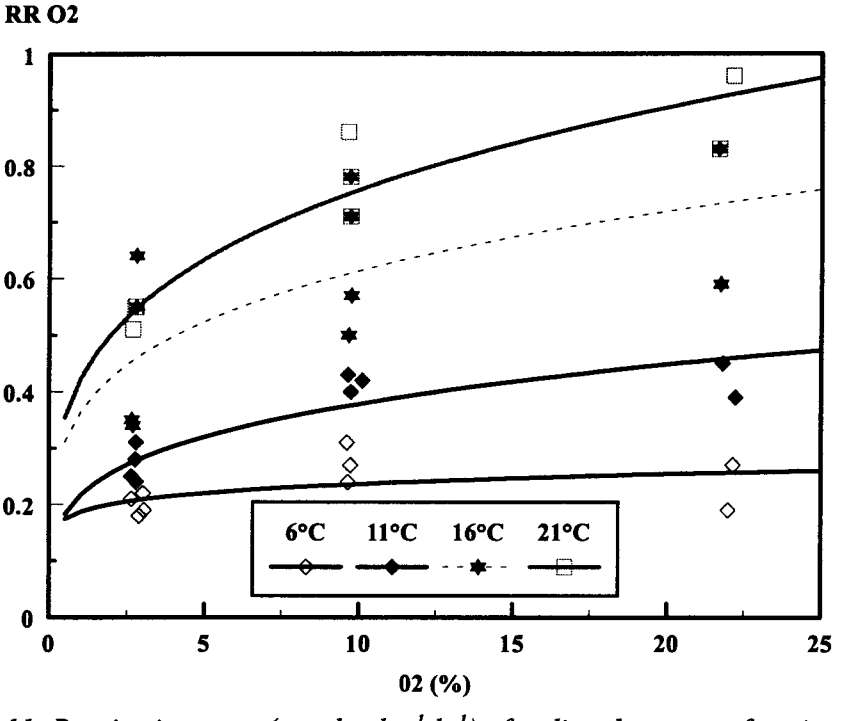


Figure 3.11: Respiration rates (mmole . $kg^{-1}.h^{-1}$) of endive shoots as a function of O_2 concentrations (kPa) at four temperatures (°C).

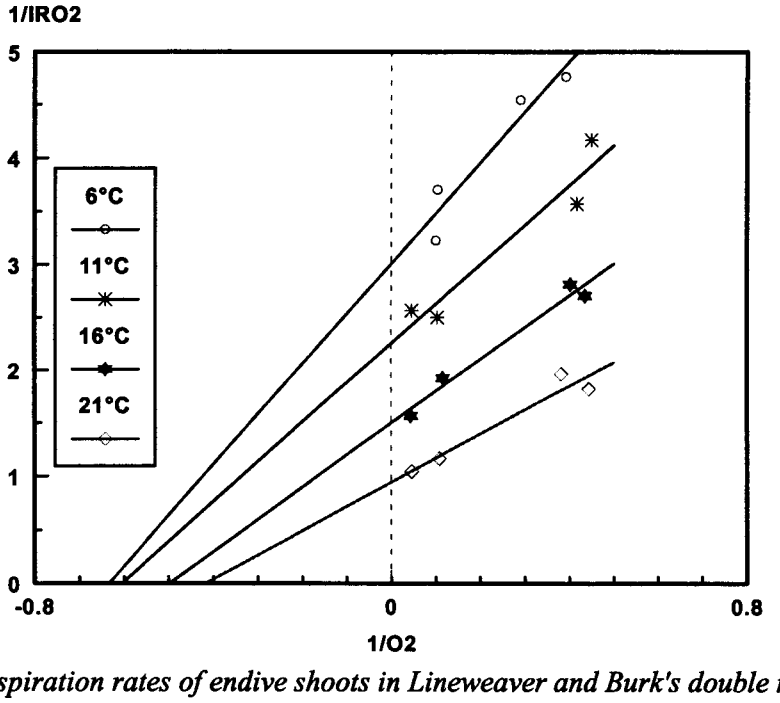


Figure 3.12: Respiration rates of endive shoots in Lineweaver and Burk's double reciprocal coordinates as a function of O_2 concentrations (kPa) at four temperatures (°C).

Effect of temperature on RRm

We submitted the calculated RRm (apparent maximum O_2 respiration rate) to Arrhenius' law (figure 3.13) and, expectedly, we found that the neperian logarithm of RRm was proportional to the reciprocal of absolute temperature (in °K). The square correlation coefficient reached 0.987 and the slope was -6366. The activation energy may be calculated from the slope. We found E=12700 cal/mol or 53086 J/mol. In order to simplify the interpretation of the results we modelled our results according to Gore's approximation that states a proportionality between the decimal logarithm ofRRm and temperature in °C (figure 3.14). The correlation coefficient of the linear regression was 0.997 indicating that the phenomenon closely followed Gore's law over the temperature range from 1 to 20 °C. The thermal coefficient z which is the increase in temperature resulting in a 10 fold increase in appRRm, was 28 °C. Similar values were found in our laboratory for asparagus spears, mushrooms and spinach.

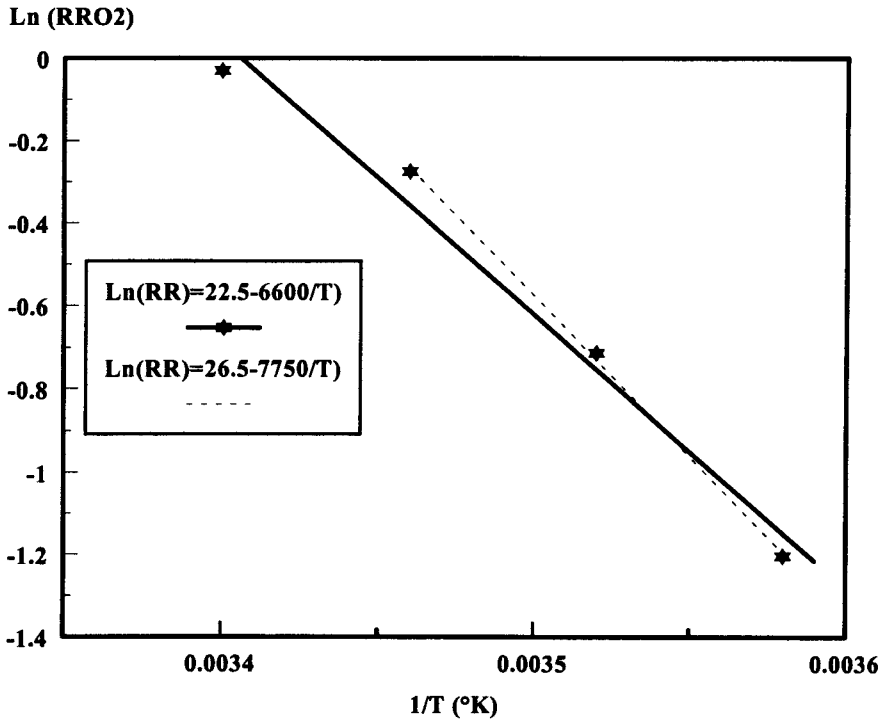


Figure 3.13: Arrhenius' plotting of neperian logarithm of Vm (mmole.kg^{-1}) (RRm) and the reciprocal of absolute temperature (°K).

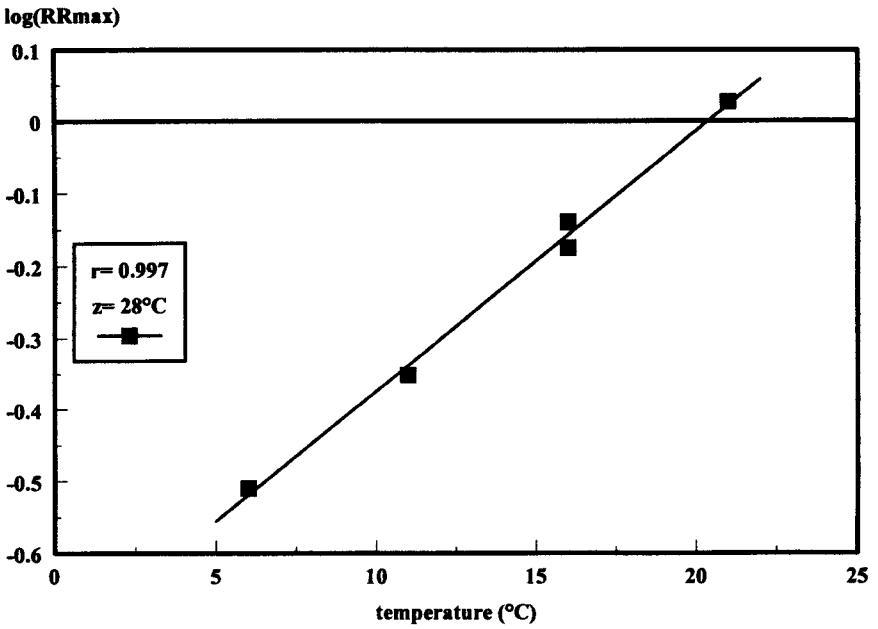


Figure 3.14: Gore's plotting of decimal logarithm of Vm in mmole.kg^{-1}.h^{-1} (RRm) and the temperature (°C).

Effect of temperature on km

The effect of temperature on the km of enzymes depends upon the nature of the binding of the substrate in the active site of the enzyme. In the example reported in figure 3.12, we found that km increased with increasing temperature, indicating a lesser affinity of the enzyme towards O_2. This may be due to a greater instability of the complex substrate-enzyme with increasing temperature. In another experiment, whose results are reported in figure 3.15, the effect of temperature on km is not so clear.

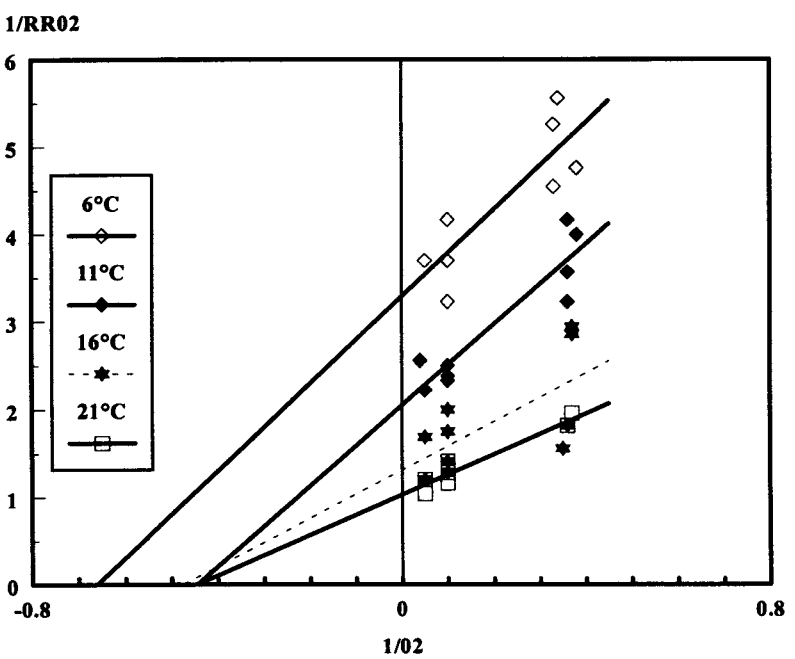


Figure 3.15: Lineweaver and Burk's representation of data showing no clear effect of temperature on km (kPa).

Ternary atmospheres (N_2, O_2, CO_2)

Determinations were performed with three respirometers and reported data are the mean values of several determinations (from 1 to 6) since we had to eliminate some obviously erroneous respiration rates due to identified failures of the respirometers such as power breakdown, water leakage or condensation troubles which were the most important problems we met.

CO_2 and O_2 respiration rates of endive shoots at 6 °C are reported in figures 3.16 and 3.17. Due to high CO_2 dissolution in aqueous solution at low temperature, RR_{CO2} are biased (figure 3.17).

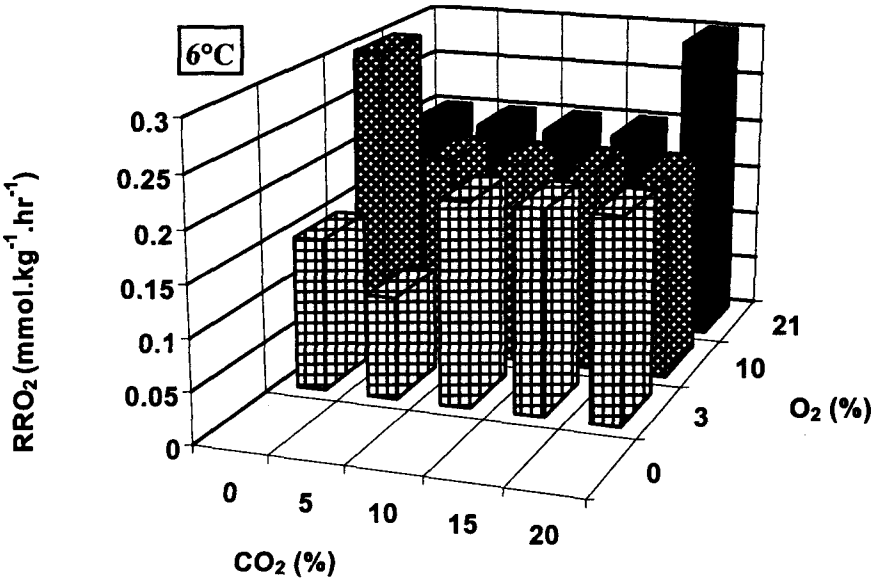


Figure 3.16 : RRO_2 of endive shoots as a function of atmosphere composition at 6 °C.

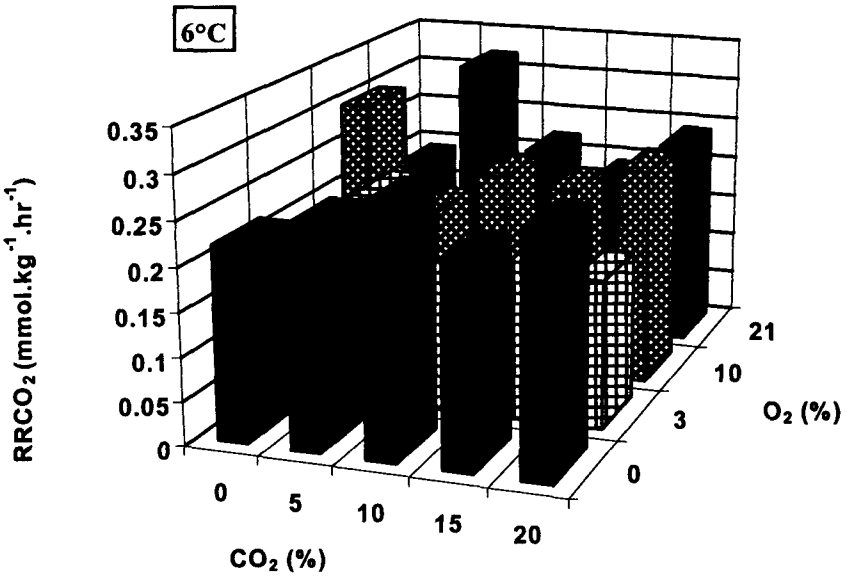


Figure 3.17 : $RRCO_2$ of endive shoots as a function of atmosphere composition at 6 °C.

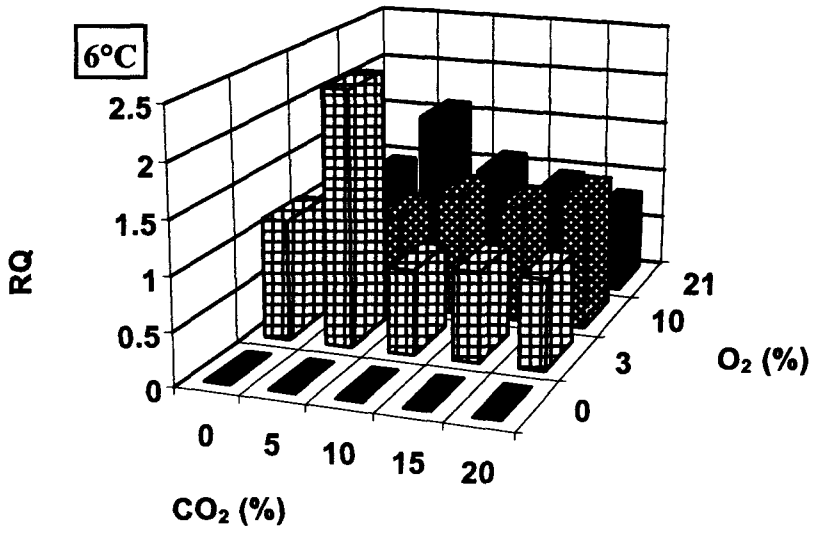


Figure 3.18 : RQ of endive shoots as a function of atmosphere composition at 6 °C.

As expected high O_2 concentration results in increased O_2 respiration rate but, unexpectedly, with no apparent effect on CO_2 respiration rate.

At 11 °C the influence of O_2 and CO_2 on respiration rate is moderate and unclear (figure 3.19) whereas high CO_2 concentrations possibly slow down the fermentative metabolism (figure 3.20).

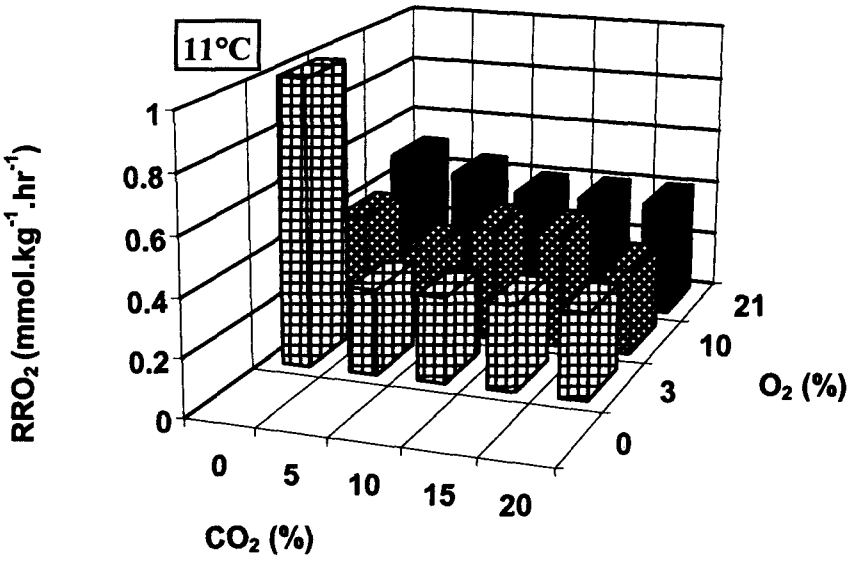


Figure 3.19 : RRO_2 of endive shoots as a function of atmosphere composition at 11 °C.

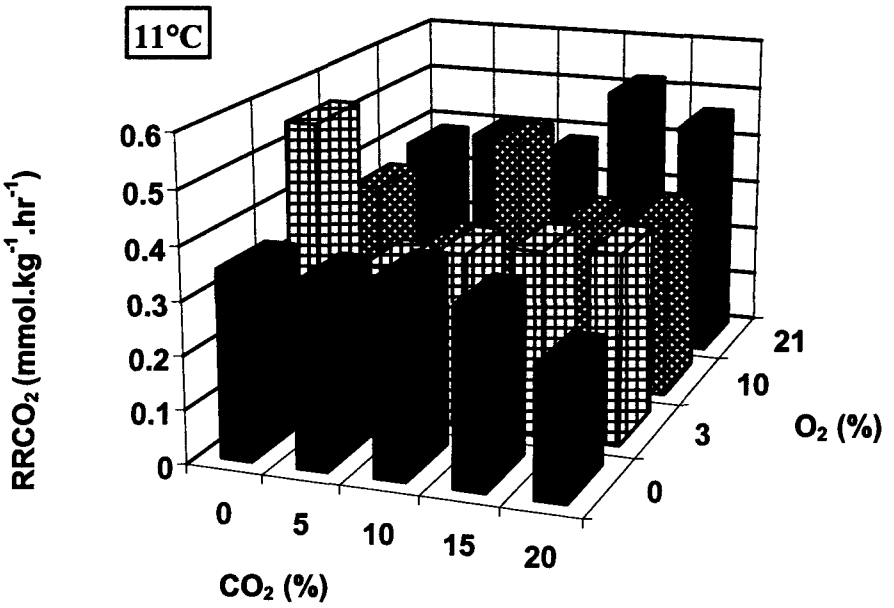


Figure 3.20 : $RRCO_2$ of endive shoots as a function of atmosphere composition at 11 °C.

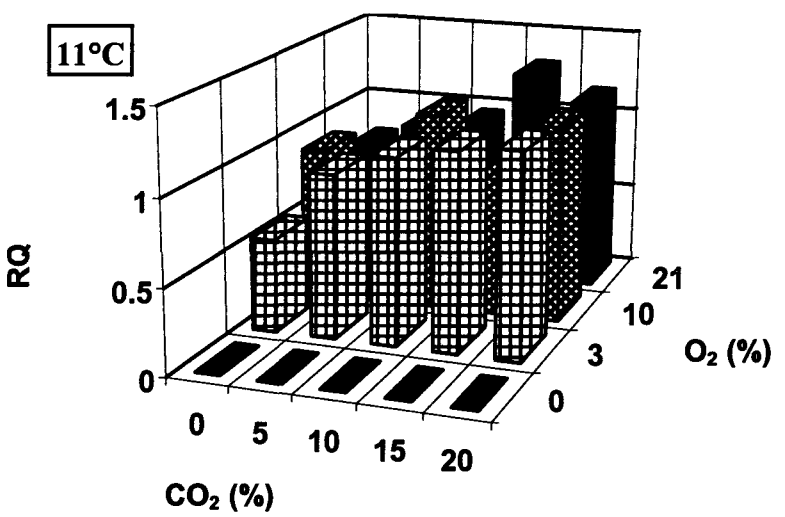


Figure 3.21 : RQ of endive shoots as a function of atmosphere composition at 11 °C.

Surprisingly, CO_2 at high temperature inhibits both aerobic and anaerobic metabolisms. The effect of O_2 partial pressure on RRO_2 is more marked than at lower temperature (figure 3.22). It is therefore likely that km of endive is temperature dependent with much higher km values at 21 °C than at 11 and 6 °C.

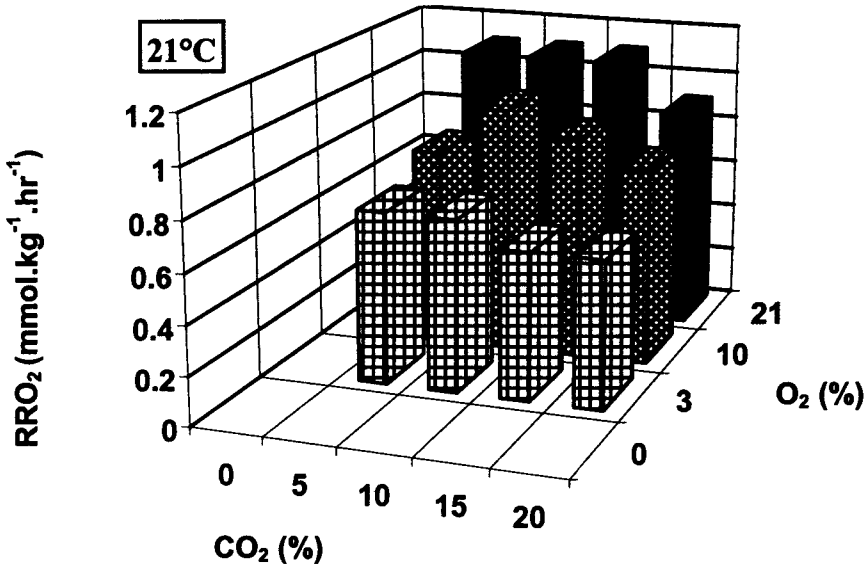


Figure 3.22 : RRO_2 of endive shoots as a function of atmosphere composition at 21 °C.

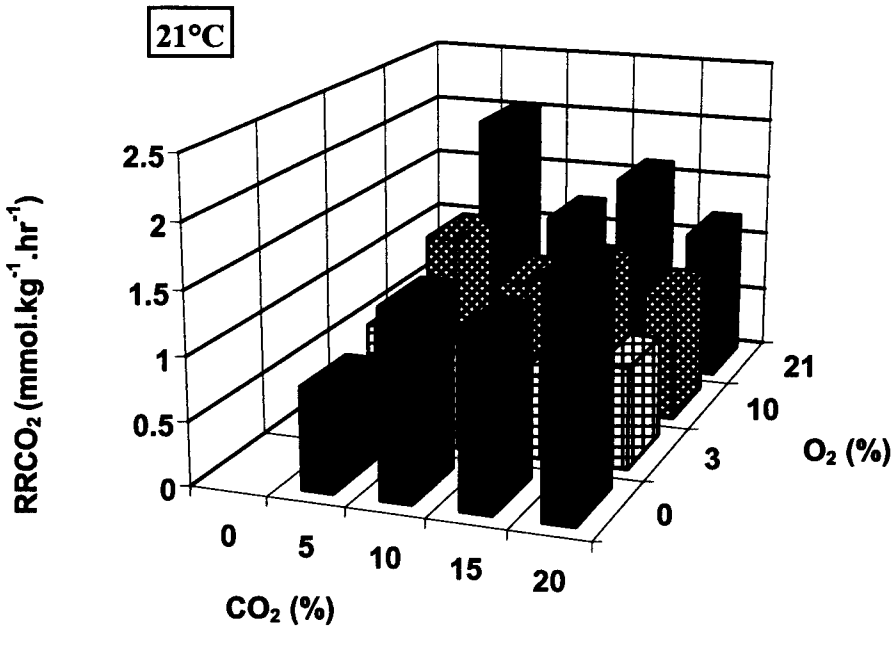


Figure 3.23 : $RRCO_2$ of endive shoots as a function of atmosphere composition at 21 °C.

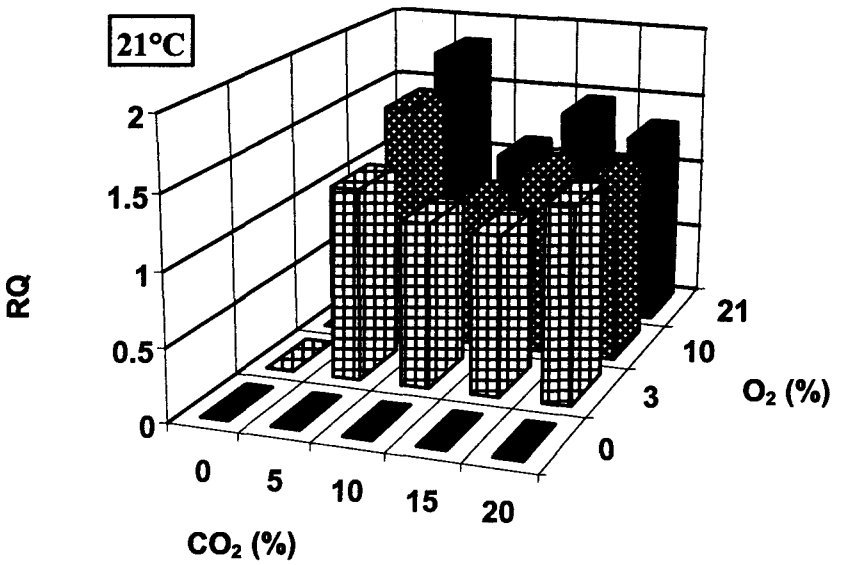


Figure 3.24 : RQ of endive shoots as a function of atmosphere composition at 21 °C.

Direct measurement of apparent Michaelis' constant

Apparent km was measured with the respirometer (manifold 2). The procedure was previously described.

At 6 °C (figure 3.25), 11 °C (figure 3.26) and 21 °C (figure 3.27), app km were 7.2, 6.6 and 23.4 kPa respectively confirming the observation that the limiting enzyme in the respiration chain may display a lower affinity to oxygen at high temperature (20 °C). It must be noted that the variability of app km, whatever the procedure, was very high, for example, app km at 21 °C ranged from 11.5 to over 30kPa O_2. The increase in km value with temperature may be due to bacterial growth which may artificially increase O_2 and CO_2 respiration rate during the experiment.

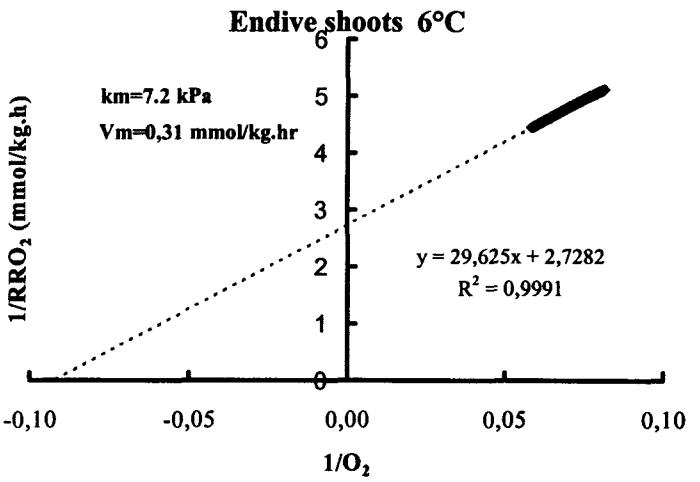


Figure 3.25 : Lineweaver and Burk's double reciprocal plotting : Endive shoots at 6 °C.

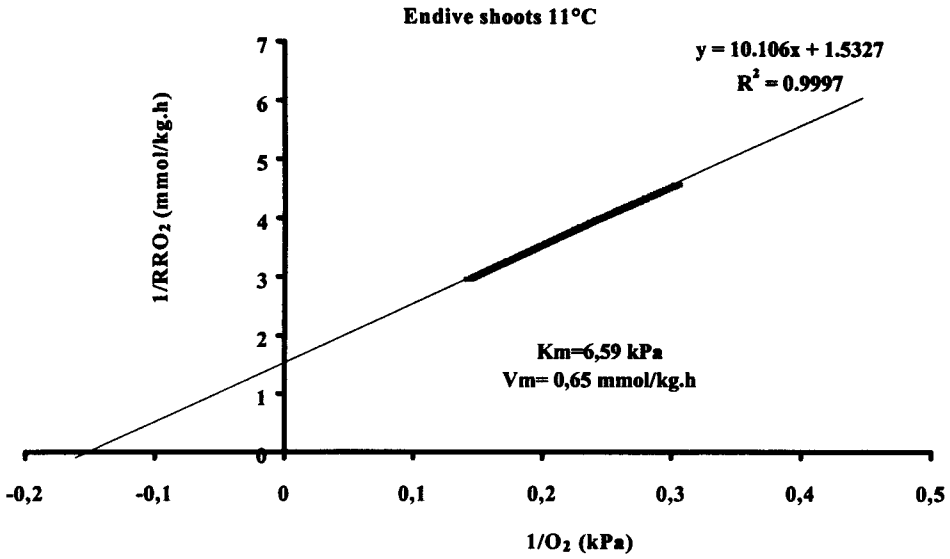


Figure 3.26: Lineweaver and Burk's double reciprocal plotting : Endive shoots at 11 °C.

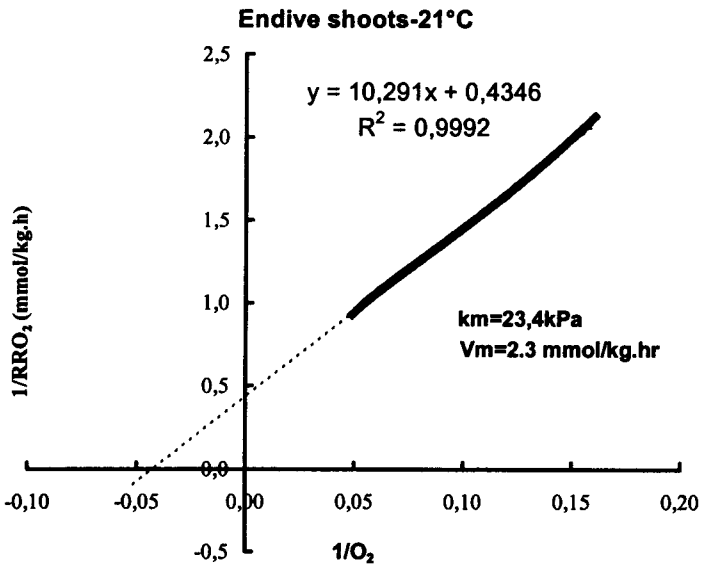


Figure 3.27: Lineweaver and Burk's double reciprocal plotting : Endive shoots at 21 °C.

App km of endive shoot respiration reaches 7.2 and 6.6 kPa O_2 at 6 and 11 °C respectively then increases to 23 kPa O_2 at 21 °C. It seems that high storage temperatures result in a reduction of affinity to O_2 of enzymes involved in aerobic respiration.

3.1.3 Apple fruits

According to Master program, the O_2 consumption and CO_2 production rates of *Golden Delicious* apples were evaluated at five different temperatures:

apple	1 °C	6 °C	11 °C	16 °C	21 °C

using the following 20 different gas compositions (pressures in kPa):

$PCO_2 \rightarrow$ $PO_2 \downarrow$	0	5	10	15	20
0	*0,0*	*0,5*	*0,10*	*0,15*	*0,20*
3	*3,0*	*3,5*	*3,10*	*3,15*	*3,20*
10	*10,0*	*10,5*	*10,10*	*10,15*	*10,20*
21	*21,0*	*21,5*	*21,10*	*21,15*	*21,20*

The experimental data obtained are reported in Table XX (see annex) together with their statistical validation.

These experimental values appear to be strongly different from those found during a former determination (Andrich et al., 1991), although the same apple cultivar (*Golden Delicious*) has been employed. This differences could be ascribed to the different growing place and/or of the different history of the utilized apples. In fact, while the former apples came from an experimental orchard located near Pisa, these last fruits are commercial apples supplied by a production area (Trentino) of north of Italy. This means that a more efficient product identification needs to be individuated to have a more efficient characterization of material employed and to make experimental data obtained exchangeable.

As shown by aerobic respiration and alcoholic fermentation data collected for *Golden Delicious* apples (Table XX of annexes), a significant reduction of aerobic respiration (R_{ar}) as well as of alcoholic fermentation rates (R_{af}) occurs when decreasing values of temperatures are adopted.

When PO_2 increases, also aerobic respiration rate increases and the rate of this increase depends on temperature being more rapid at room temperature to slow when decreasing values of temperature are employed.

On the contrary alcoholic fermentation decreases when increasing values of PO_2 are adopted and the ratio between the alcoholic fermentation and aerobic respiration rates, evaluated at the same PO_2 and PCO_2, seems to increase when decreasing values of temperature are employed.

As well as PCO_2 effect is concerned, its increase induces a clear decrease of both aerobic respiration and alcoholic fermentation rates.

Adopting a $PO_2 \leq 3$ kPa, the RCO_2 greater than RO_2 were obtained, underling the existence of a simultaneous presence of both aerobic respiration ($R_{ar} = RO_2$) and alcoholic fermentation ($R_{af} = RCO_2 - RO_2$).

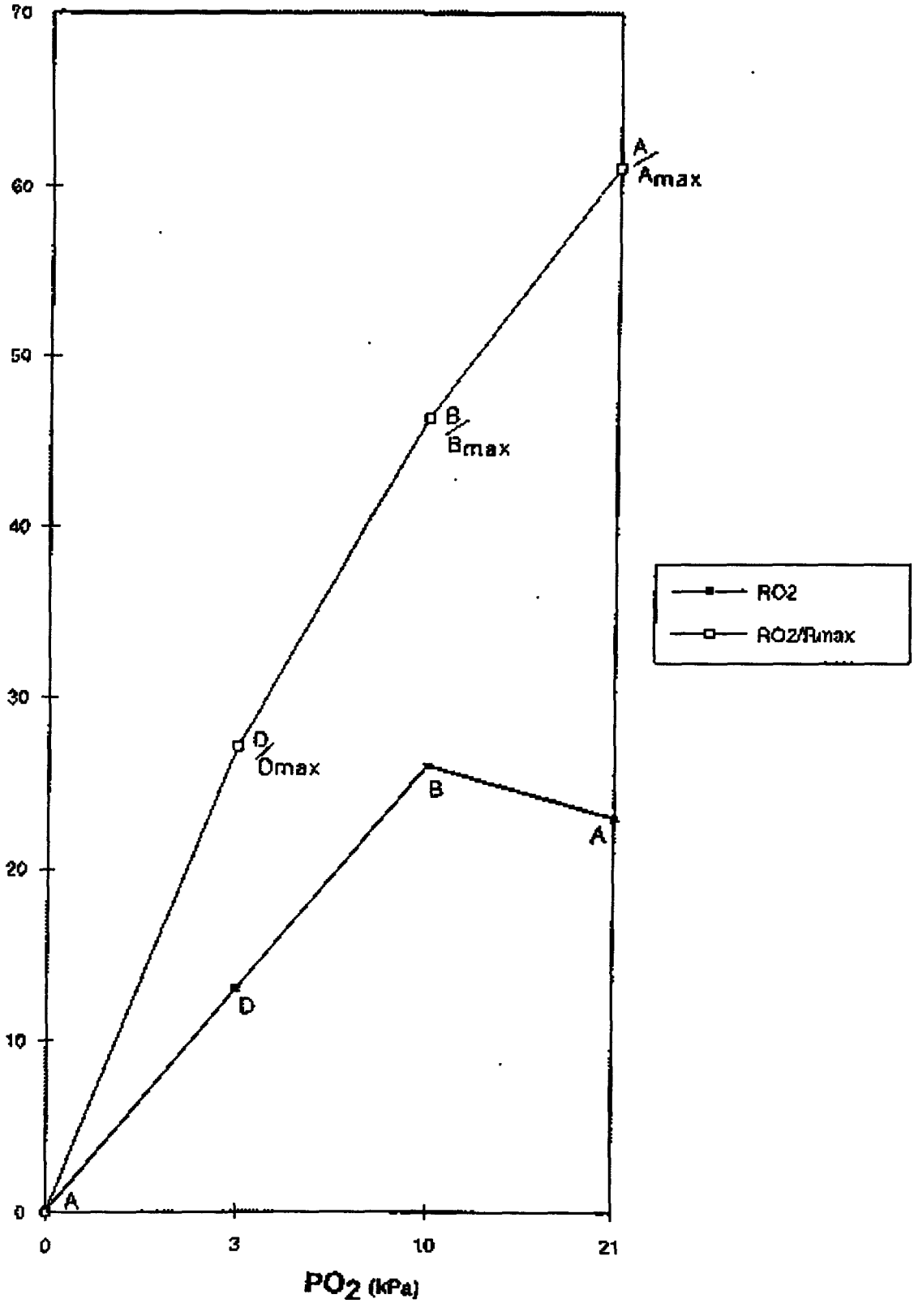


Figure 3.28: Effect of PO_2 on aerobic respiration rates.

3.2 Internal diffusion in produce

Apple fruits

O_2 diffusion.

The resistance to O_2 diffusion of *Golden Delicious* apples has been determined at five different temperatures (21, 16 , 11, 6, 1 °C), to evaluate its potential temperature variation, utilising the following 3 gaseous mixtures:

	I°	II°	III°
PG=PO_2 (%)	20	20	40
PCO_2 (%)	0	20	0
PN_2 (%)	80	60	60

To put in evidence if the diffusion of analysed gas (G = O_2) could vary as a function of the ratio of the other two gaseous components employed (N_2 and CO_2), mixtures having the same content of the diffusing gas but different percentages of other two components were tested. The experimental values connected with the two diffusional constants $k_{i,O2}$ and H_{O2}, evaluated as a function of temperature and gas composition, are reported in Table 1 (see annexes) together with their confidence interval (c.i.; p = 0.05).
The O_2 mass-transfer rate does not seem to be particularly affected by the changes of concentrations of the other two gases (CO_2 and N_2) as shown by the values assumed by $k_{i,O2}$ and H_{O2} constants in the runs carried out at the same temperature and PO_2 but varying the amounts of the other two gaseous components (compare run 7 with 8 and run 10 with 11- Table 1 of annexes).

CO_2 diffusion.

The skin resistance of apple fruits to CO_2 diffusion has been determined at five different temperatures (21, 16 , 11, 6, 1 °C) utilising the following four gaseous mixtures:

	I°	II°	III°	IV°
PG=PCO_2 (%)	20	20	40	40
PO_2 (%)	0	40	0	20
PN_2 (%)	80	40	60	40

Table 2 reports the experimental data connected with $k_{i,CO2}$ and H_{CO2} constants, evaluated as a function of the temperatures and gas compositions employed, together with their confidence intervals (c.i.; p = 0.05). Similar to already reported for O_2 diffusion, the CO_2 mass-transfer rates did not seem to be particularly affected by the changes of concentrations of the other two components as shown by the values assumed by $k_{i,CO2}$ and H_{CO2} constants in the runs carried out at the same temperature and PCO_2 but varying the

amounts and the ratio of the other two gaseous components employed (N_2 and O_2) (compare: table 2 - run 1 with 6, 2 with 7, 3 with 8, 4 with 9).

Chicory

O_2 diffusion:

The possible dependence of the diffusional constants introduced ($k_{i,G}$,$k_{-i,G}$ and H_G) on temperature was then evaluated measuring the ***Witloof*** **(chicory)** resistance to O_2 mass transfer at 5 different temperatures (21, 16 , 11, 6, 1 °C). Moreover, in order to put in evidence if the presence in the diffusing gaseous mixtures of different concentrations of other species can affect the diffusion of analysed gas, 4 diversified gaseous mixtures where employed to study O_2 mass-transfer:

	I°	II°	III°	IV°
PG=PO_2 (%)	**20**	**20**	**40**	**40**
PCO_2 (%)	**0**	**40**	**0**	**40**
PN_2 (%)	**80**	**40**	**60**	**20**

As the adopted mass-transfer equation needs the gas-exchange area (A) to be known the first part of experimental activity was spent to look for a mathematical relation able to calculate this parameter as a function of a more easily measurable variable.

Of all geometrical characteristics analysed, the chicory volume (C.V.) seemed the parameter which better fitted external area (C.S.), by the following mathematical function (Figure 2):

$$C.S. = a \cdot C.V./(b + C.V.)$$

where a and b are two numerical constants (a=509.5; b=289.8).

Moreover, while the specific gravity of whole chicory is equal to about 0.75 $g{\cdot}cm^{-3}$ that of stripped leaves becomes 0.85 $g{\cdot}cm^{-3}$.

To evaluate if the presence of a significant microbial charge on chicory leaves could affect $k_{i,O2}$ and H_{O2} values, a sample of this horticultural product was kept for several hours (≈14) in a storage atmosphere having a PCO_2 close to 40 kPa before to be tested. But no significant differences among the constants measured before (run 22 of Table 3; annexes) and after (run 23 of Table 3) this treatment were found.

The experimental values connected with the two diffusional constants $k_{i,O2}$ and H_{O2} of chicory, evaluated at 21 °C, are of the same order of greatness of those previously found for apples. But, unlikely than apples, these chicory constants seem to vary significantly as a function of temperature (Table 3 of annexes).

As during these permeability determinations a sensible production of CO_2 (0.5 ÷ 1.0 %) occurred, a further data-set of $k_{i,O2}$ and H_{O2} was then collected maintaining a PCO_2 value in the diffusing gaseous mixture of about 40 kPa to avoid that a significant aerobic respiration could take place (Table 4 of annexes). Surprising either the $k_{i,O2}$ than H_{O2} values obtained appeared to be higher than those measured employing a PCO_2 close to 0 kPa.

CO_2 diffusion:

To avoid a too high CO_2 production due to anaerobic fermentation, all experimental runs were carried on in a atmosphere having a O_2 amount close to 3%. The respiration effect on O_2 and CO_2 mass transfer is clearly shown by Figures 3.29 and 3.30. In Figure 3.29 the PCO_2 decrease was evaluated in the environmental atmosphere during two mass transfer runs carried out using analogous values of initial PCO_2 but employing two different temperatures (21 and 1 °C). At 21 °C, the initial decrease of environmental PCO_2 due to its permeation inside chicory is followed by a CO_2 increase connected to respiratory activity. But at 1 °C it was not possible to underline the existence of any significant effect related to respiration. When, at the same temperature (11 °C), two different initial amounts of CO_2 were employed also different PCO_2 evolution were obtained (Figure 3.30). If high PCO_2 were ensured, for all run time no significant deviations were observed (run-a), but operating with more reduced amount of CO_2 a slight but significant increase of PCO_2 at the end of experimental run was put in evidence (run-b). So only diffusing gas mixture having an high CO_2 content could be experimentally tested.

The chicory skin resistance to CO_2 mass-transfer has been then determined at five different temperatures (21, 16 , 11, 6, 1 °C), to evaluate its potential temperature variation, using the following 3 different gaseous mixtures:

	I°	II°	III°
$PG=PCO_2$ (%)	**20**	**40**	**60**
PO_2 (%)	**3**	**3**	**3**
PN_2 (%)	**77**	**57**	**37**

Table 5 reports experimental values connected with the two diffusional constants $k_{i,CO2}$ and H_{CO2}.

Tomato fruits

O_2 diffusion.

The tomato skin resistance to O_2 mass-transfer has been determined at five different temperatures (21, 16 , 11, 6, 1 °C), to evaluate its potential temperature variation, using the following gaseous mixtures:

	I°	II°	III°	IV°
$PG=PO_2$ (%)	**20**	**20**	**40**	**40**
PCO_2 (%)	**10**	**40**	**10**	**40**
PN_2 (%)	**70**	**40**	**50**	**20**

Similar to what already reported for apple fruit, tomato external area was evaluated assuming this fruit as a sphere whose radius could be calculated on the basis of the mean volume of tomato fruits employed.

The total volume of employed fruits (V_{tot}) was evaluated according to the procedure already described for apples (Andrich et al.,1989a), and the volume of the mean tomato calculated as the ratio between the total volume and the number of utilised fruits (n_F):

$$V_M = V_{tot} / n_F$$

and then the radius of mean tomato (r_M) could be calculated together with its surface area (A_M):

$$r_M = (V_M \cdot 3 / (4 \cdot \pi))^{1/3} \; ; A_M = r_M^2 \cdot \pi$$

so that the total exchange area could be evaluated:

$$A = n_F \cdot A_M$$

The mass-transfer constants of a diffusing specie do not seem to be affected by the concentrations of other gaseous components (compare run 11 with 12 of Table 6 of the annexes).

While the experimental values connected with the global mass-transfer constant $k_{1,O2}$ of tomato, evaluated at 21 °C, do not seem to differ greatly from those previously found for apple and chicory the saturation equilibrium constant H_{O2} of tomato appears to be smaller than those found for the other two products tested (Table 13 of annexes).

This may be due to the reduced volume of intercellular space occurring in tomato fruit. In fact its density ($d_{tomato} \approx 1.00$ g/ml), a parameter which is assumed to be inversely proportional to intercellular space, is significantly greater than those found for the other two products ($d_{apple} \approx 0.82$ g/ml and $d_{chicory} \approx 0.85$ g/ml).

As the most of O_2 permeated inside the product is located in the intercellular space a reduction of its volume induce a decrease of saturation equilibrium constant H_{O2}.

Moreover, to avoid that a significant aerobic respiration could affect mass transfer data, these experiments were carried out maintaining tomatoes in an atmosphere rich of CO_2 ($7.0 \leq PCO_2 \leq 41.7$ kPa).

CO_2 diffusion.

To avoid a too high CO_2 production due to anaerobic fermentation could affect mass transfer results, all experimental runs connected with CO_2 diffusion were carried out in a atmosphere rich of O_2:

	I°	II°	III°	IV°
PG=PCO_2 (%)	**20**	**20**	**40**	**40**
PO_2 (%)	**20**	**40**	**20**	**40**
PN_2 (%)	**60**	**40**	**40**	**20**

Also in this case the concentrations of other gaseous components do not seem to affect the diffusion of the analysed gas (compare run 18 with 19 of Table 7 of the annexes).

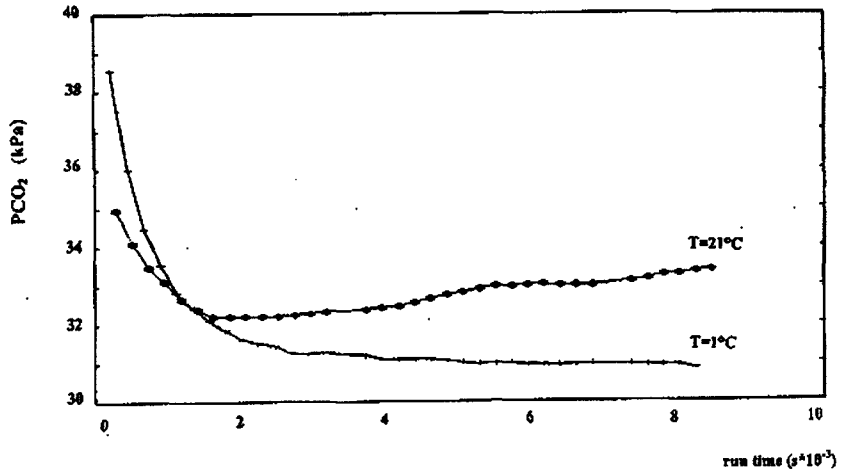


Figure 3.29: CO_2 diffusion in chicory at two different temperatures

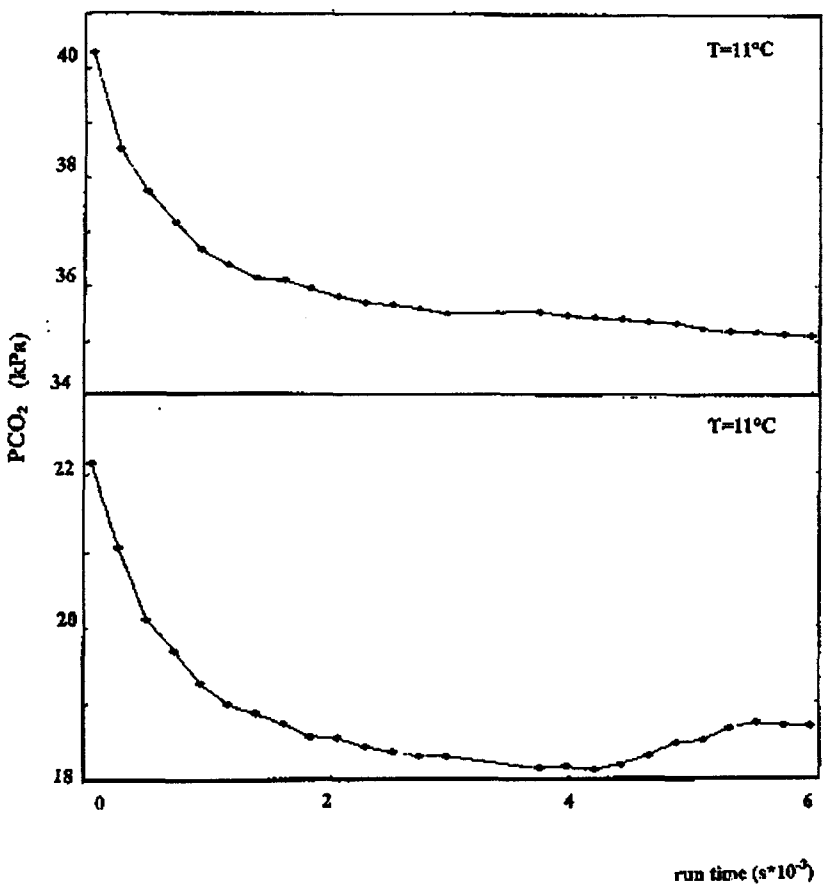


Figure 3.30: CO_2 diffusion in chicory at two different initial PCO_2.

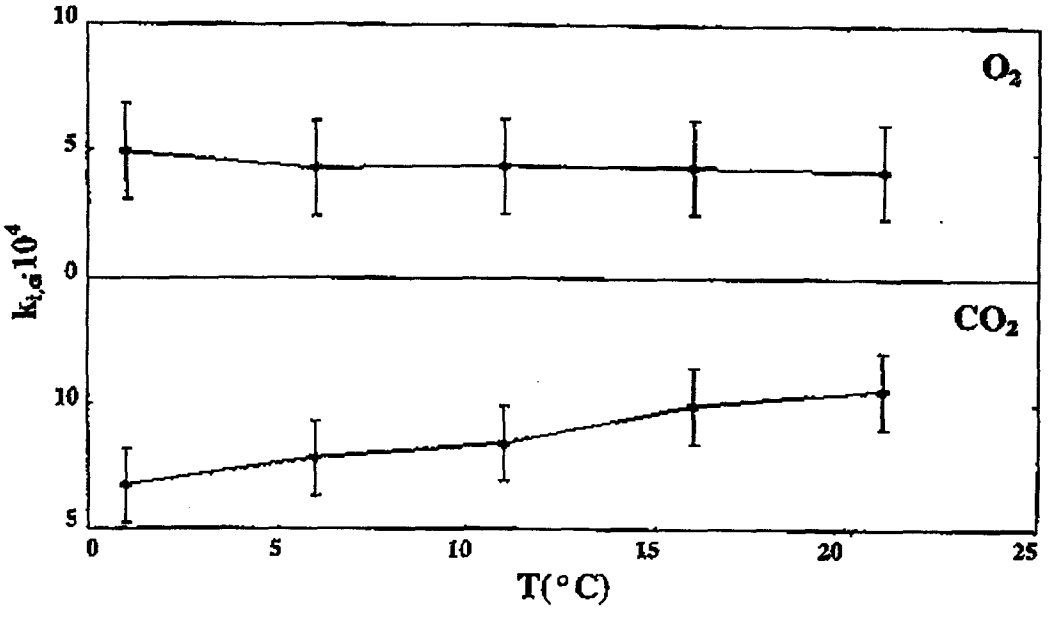


Figure 3.31: Temperature evolution of constant $k_{i,G}$ (O_2 and CO_2) in Golden Delicious apples.

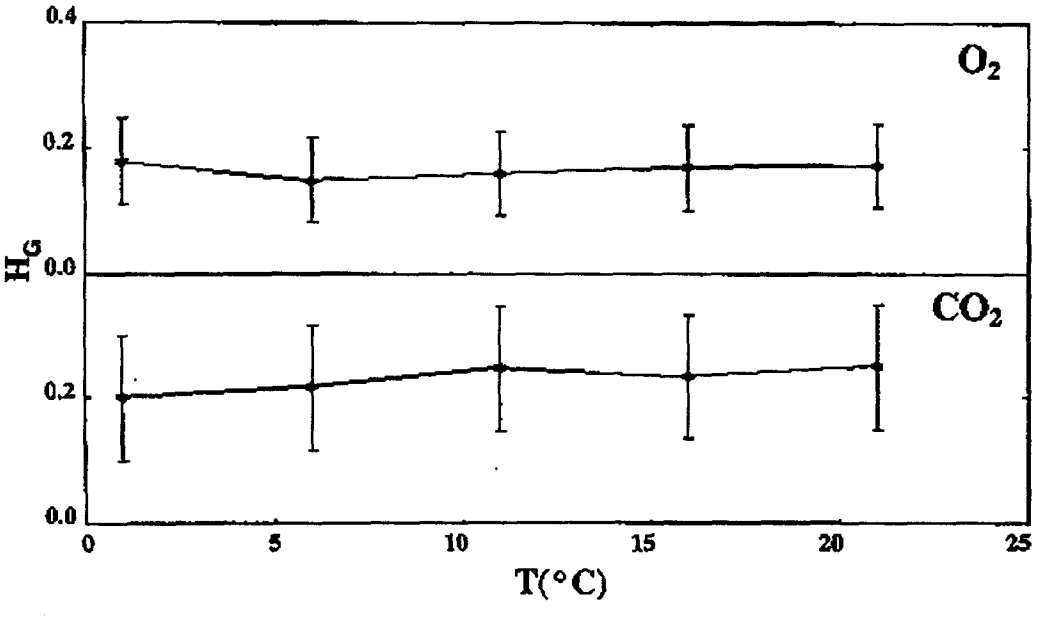


Figure 3.32: Temperature evolution of constant H_G (O_2 and CO_2) in Golden Delicious apples.

3.3 Packaging films

3.3.1 Gas permeability

Survey on different methods and their accuracy
Usually, gas permeability equipment is used for ranges between 1 and some 1000 cm^3/m^2 d bar STP. Here, deviations between different methods performed under dry conditions for identical materials, but different material pieces do not vary over more than 20 %, the main reason being variations in film thickness. This has been monitored over years of practice in our institute and in other places as well, the methods are either already standardised within DIN, ASTM and ISO, or draft standards exist.

To perform similar checks for the less usual types of highly permeable films as used in this project, hundreds of comparative measurements were performed. One special problem was the question whether an influence of the use of masks could be detected. (In case of highly permeable films, masks have to be applied for reduction of film areas in order to avoid overrange of the instrumentation, see section 2). These specific measurements were done for the materials

PVC, Polyether/polyester copolymer, Cellulose acetate, and LDPE,

on biaxially oriented Polypropylene (BOPP) and Polyester (PEP) as reference materials to assess the accuracy of the measurement method

on the manometric, carrier gas and integral types of equipment

and at dry and humid conditions,

for full film areas (where applicable) and for film areas masked down to 0.79, 2.0 and 5.0 cm^2.

The results are shown in Tables 3.1 and 3.2. The following conclusions for the subsequent measurement runs could be derived:

Values do not show a significant dependence on the mask area, if the values for the lowest areas are neglected. Therefore, the masking method is apparently justified.

Single values for higher transmitting materials may vary by a factor of 2 if different samples are measured by different methods.

Within one method, the variability on samples from one roll of film material may be as high as±40% from the average. As the repeatability on single samples is always better than±10% (not shown in this report), it can clearly be stated that the source of the observed variations is a material property. As the macroscopic thickness deviations do not explain this phenomenon, there must be an additional property which so far has not been investigated in enough detail.

Table 3.1: Oxygen permeation, manometric and carrier gas methods, comparison of results from 250 measurements

Material/ thickness/µm	**Measurement area/cm²**	**O_2-Permeability/cm³/m²d bar, at 23 °C and number of measurement**		
		manometric method at 0 % r.h.	**carrier gas methods**	
			0 % r.h.	**50 % r.h.**
PVC,14.9 µm	0.785	8750 ± 1800 / 9		7380 ± 1350 / 4
± 6 %	2.011	10550 ± 3220 / 8	no reliable	9050 ± 2340 / 4
	5.00	8340 ± 3150 / 11	measurements	7580 ± 1960 / 4
	78.50	9580 ± 1350 / 6		overrange
Average		**9200**		**8000**
Polyether/ester-	0.785	6900 ± 2090 / 9	---	6840 ± 630 / 4
copolymer,	2.011	8000 ± 640 / 7	---	7360 ± 410 / 3
9.3 µm ±10 %	5.00	5410 ± 870 / 11	7220 ± 480 / 6	6550 ± 350 / 10
	78.5	6390 ± 65 / 5	---	---
Average		**6550**	**7220**	**6760**
Cellulose ace-	0.785	590 ± 70 / 12	---	740 ± 130 / 3
tate,				
82 µm ± 2.5 %	2.011	600 ± 100 / 11	---	640 ± 100 / 3
	5.00	595 ± 80 / 11	640 ± 10 / 4	550 ± 70 / 8
	78.5	690 ± 145 / 7	---	790 ± 10 / 2
Average		**610**	**640**	**630**
BOPP, 20 µm	0.785	1530 ± 130 / 6	---	---
± 1 %	2.011	1410 ± / 6	---	---
reference	5.00	1510 ± 210 / 8	---	---
	78.5	1450 ± 130 / 10	---	---
Average		**1470**	---	---
PET, 12.2 µm	0.785 *(area too low)*	(160 ± 40 / 12)	---	110 ± 10 / 3
± 0.8 %	2.011 *(area too low)*	(130 ± 30 / 11)	---	105 ± 8 / 4
reference	5.00	110 ± 20 / 10	---	102 ± 10 / 3
	78.5	110 ± 10 / 15	---	---
Average		**110**	**—**	**106**

Table 3.2: Gas permeation, comparative overview over all methods in gas-gas environment (values in bold / italics: latest measurement series end 1997, other values: series 1996/1997)

Material, thickness	**Manometric cell, 6 °C**		**Manometric cell, 23 °C**		**Carrier gas method, 10 °C**				**Carrier gas method, 23 °C**				**Integral cell, 11 °C, 88 %r.h.**		**Integral cell, 21 °C, 88 %r.h.**	
	O_2, dry	**CO_2, dry**	**O_2, dry**	**CO_2, dry**	**dry**	**50 % r.h.**	**75 % r.h.**	**88 % r.h.**	**dry**	**50 % r.h.**	**75 % r.h.**	**88 % r.h.**	**O_2**	**CO_2**	**O_2**	**CO_2**
PVC 15 µm	***2050***	***10300***	***6900*** ... 9200	***30000*** ... 45000	***5450***	***5600***	***5650***	***5630***	***10900***	8000 ... ***11200***	***11500***	***12300***	***8500*** ... 11000	***51400*** ... 67000	***23800***	***76600***
Polyether/ ester-copolymer 9 µm	***1760***	***44400***	***5550*** ... 6550	***92750*** ... 94000	***3500***	***3380***	***3310***	***4050***	7220 ... ***8250***	6760 ... ***8220***	6740 ... ***8210***	8540 ... ***9570***	***3460*** ... 5300	***77000*** ... 108000	***6450***	***90000***
Cellulose acetate 82 µm	***290***	***1750***	***520*** ... 610	1090 ... ***3000***	***440***	***320***	***300***	***330***	640 ... ***740***	630 ... ***630***	500 ... ***630***	525 ... ***630***	770	1560	***3340***	***6440***
PE, 12 µm	***3880***	***17100***	***14300***	***58200***	***8880***	***8740***	***8670***	***8520***	***20550***	***18900***	***19300***	***19400***			***15800***	***64000*** ... ***102000***

Typical values for gas permeability

The values shown in Table 3.3 below had been obtained for all 9 materials and represent the updated values from the averages of all measurements taken in the project. It has to be noted, however, that the latest values obtained in the project for Cellulose acetate show a significant deviation, especially in the CO_2 permeability, from those obtained earlier. As Cellulose acetate contains a high fraction ofplasticiser (up to 40%), it is very likely that ageing effects occurred.

To obtain values for the different gases under realistic packaging conditions, only the relative values obtained on dry conditions for one material should be used, not the absolute ones. Where available, the values should be proportionally corrected by using the reference values for the oxygen permeability under humid conditions, see tables 3.1 and 3.2. The values for microperforated PP cannot simply be normalised to a film thickness of 100 µm as for the other examples. Here, permeability values are to be added from
a) the number of pores per unit area, multiplied by the permeability of a single pore
and b) the transmittance of the bare PP film.

*Table3. 3: Overview on materials (for 100 µm film thickness **(except for P Plus where values are given for 35 µm film thickness and an average pore diameter of 95 µm)**, basis: 23 °C, dry measurement conditions for gases).*

Material	**CO_2/O_2 permeability ratio**	**O_2-permeability (cm^3/m^2 d bar)**	**N_2-permea-bility**	**CO_2-permeability**	**H_2O-permeability (g/m^2 d at 85%→0%r.h)**
PE	4.1	1720	440	7000	1.9
PVC	4.7	1200	285	5600	24.7
EVA/PE-Copolymer	4.0	1700	750	6800	1.7
Copolyether-ester	15.5	550	170	8500	282
Poly-(ε) caprolactone	7.6	2060	580	15640	106
CA ds 2.7	2.0 → 3.6 (ageing?)	460	80	920 → 1680 (ageing?)	139
Cellulose	not known	0.5	below detection limit		131
Polystyrene	4.4	1470	333	6500	11.3
Polypropylene, microperforated (P Plus)	≈1	900 (basic film) + 290 x number of pores/m^2	120 (basic film) + 290 x number of pores/m^2	3900 (basic film) + 290 x number of pores/m^2	1.0 (basic film) +3.75 · 10^{-3} x number of pores/m^2

Dependence on relative humidities

The original suggestion was to describe this by a linear approximation:

$$Q \approx Q_0 (1 + a\, p_{H_2O}). \qquad (4)$$

The complete results, however, show between 0% and 88% relative humidity (see tables 3.1 and 3.2) that the variation of permeability values at the same humidity is much higher for various material samples from the same source than the effects due to different humidities. On the other hand, condensation conditions have the effect of a drastic increase, see below.

Dependence on temperature

The gas permeability in terms of temperature can be described by an activated process, i.e. an Arrhenius behaviour for all polymers except for the microperforated polypropylene:

$$Q = Q_0 \exp(-E_a / RT) \qquad (xx)$$

Table 3.4: Formal activation energies, E_a in kJ mol^{-1}, for the materials studied (first experimental run, manometric method).

Material	O_2	CO_2	N_2
PE	49	46	58
PVC	44	36	50
EVA/PE	48	44	61
Copolyester-ester	50	35	59
PCL	32	19	33
Cellulose Acetate ds 2.7	28	33	31
Cellulose	most values below detection limit		
PS	27	25	35
Polypropylene microperforated	not applicable		

Figure 3.33 shows - as an example - the Arrhenius representation of the gas transmittances for PVC as obtained by the manometric method. Figures for other materials are to be found in the annex.

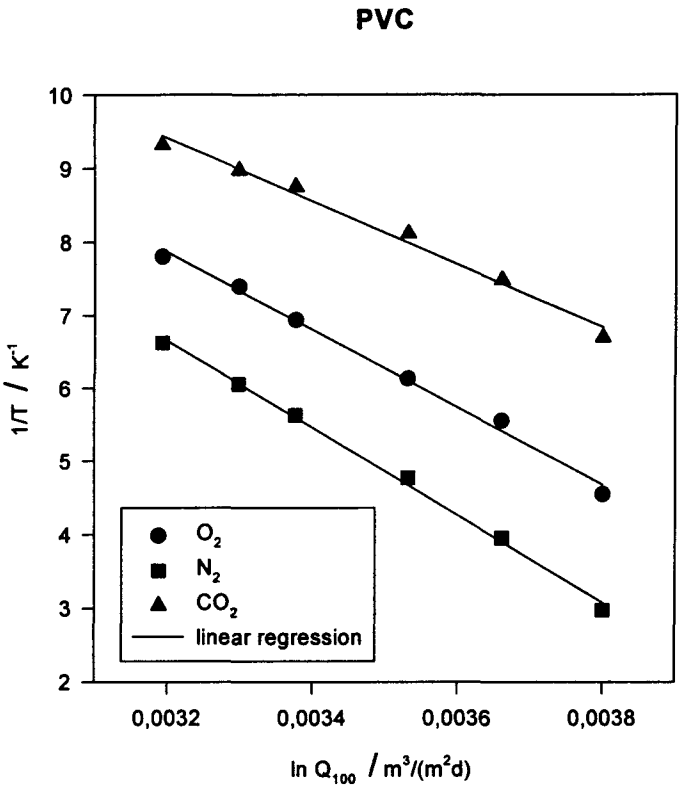


Fig.3.33: Temperature dependence of gas permeability, normalised to 100 µm film thickness (Q_{100}): PVC

A survey of these values together with literature values and values obtained by carrier gas measurements could be made for the materials best studied, namely PVC, Copolyether-ester, CA and LDPE, see table 3.5.

Overall, the span for the activation energies is very high and does not justify to give values of more than two digits.

Table 3.5: Formal activation energies for permeation of O_2, CO_2 and N_2, in kJ/mol.
A: series '95, B: series '97, manometric measurements, C: series '97, carrier gas measurements, L: literature values(Sources: [Polymer Handbook], [Paz]).

Material	O_2				CO_2			N_2		
	A	B	C	L	A	B	L	A	B	L
PVC	44	49	42	55.6	36	43	56.9	50	43	69.1
Copoly-ether-ester	50	46	46	23.7	35	30	25.9 / 41.5	59	50	
Cellulose acetate	28	23	36	20.9	33	22	17.9	31	27	27.1
LDPE	50	58	43	42.6 / 45.1	46	49	38.9	58	60	49.3

Gas permeability in the water phase

Table 3.6 shows the results for oxygen permeation at 23 °C measured in the permeation cell as described in section 2.2.4. The values have been derived from the maximum slopes of the time vs. oxygen concentration curves in the sensor cell. They refer to a pressure difference of 1 bar, given by the initial situation in the cell. Two facts are to be noted: First, the large spread in permeability values, especially for the hydrophilic materials Copolyether-ester and Cellulose acetate, second, the overall large influence of the presence of liquid water, also more pronounced for the hydrophilic materials.

Table 3.6: Oxygen and Carbon dioxide permeation in water at 23 °C, results normalised to O_2 and CO_2 partial pressures and volume equivalent at STP, in cm^3 / m^2 d bar. Also shown: Estimated increase factors for the ratio of permeabilities in the liquid phase vs. permeabilities in dry gas phase.

Material	O_2 permeability under liquid conditions	O_2 permeability: Reference value, dry	CO_2 permeability under liquid conditions	CO_2 permeability: Reference value, dry
PVC, 15 µm	21800 ... 23000	6900 ... 9200	208000 ... 264000	37300
Estimated increase factor for liquid conditions		*2.5 ... 3*		*5.6 ... 7*
Copolyether -ester, 9 µm	15100 ... 72900	7220 ... 8250	706000 ... 1250000	94400
Estimated increase factor for liquid conditions		*2 ... 10*		*7.5 ... 13*
Cellulose acetate, 82 µm	2180 ... 16700	640 ... 730	12400 ... 13600	1120 ... 2050
Estimated increase factor for liquid conditions		*3 ... 26*		*6 ... 12*
LDPE, 12 µm	30000 ... 55900	9750 ... 14300	267000 ... 296000	58300
Estimated increase factor for liquid conditions		*2 ... 5.7*		*4.6 ... 5.1*

Permeation through micropores

In parallel to the measurements at Fraunhofer IVV, INRA estimated the permeability of P Plus films by an integral method. On the average, a gas permeability of 290 cm^3 / m^2 d bar per pore resulted from measurements on 5 different film types. This would mean an average pore diameter of 95 µm, according to equations and values shown in section 2.2.2.

At Fraunhofer IVV, different types of P Plus films were analysed by optical microscopy and image analysis for the size of the laser perforations. The results as shown in Table 3.7 demonstrate two facts: First, the large variation in the average hole size, second, the good overall agreement between measured permeabilities and hole diameters. Therefore, in this case the theoretical approach could be fully verified by the experiment.

Table 3.7: Measurements of pore dimensions, 10 pores per film type

Film type (Manufacturers code)	25 K	60 K	100 K	200 K
Average pore area / $(\mu m)^2$	1750 ± 1040	5600 ± 1750	6370 ± 5530	6780 ± 4190
geometric average of pore diameter / µm	47	85	90	93

3.3.2 Water vapour permeability

Dependence on temperature and water concentration

An overview over the results for all materials is given in Table 3.8.

Here, the general problem occurs that it is not possible to vary concentration difference Δc and maximum and minimum water concentrations on both sides of the films independently. In addition, the concentration difference (Δc, in g / m³) is strongly influenced by temperature (at the same nominal relative humidity difference) and is therefore the main determining factor [Piergiovanni]. Water vapour transmission values are therefore best given in terms of permeance, i.e. normalised to the absolute concentration gradient, as indicated in Table 3.8.

The increase in water vapour transmission due polymer-related temperature effects is of second order in most cases as to be seen from the different temperature related slopes of water vapour transmission rates vs. concentration difference, see figures 3.34 and 3.35 and the other figures in the Annex.

The observed scattering in measured values is mainly due to the limited accuracy of the dish method below water vapour transmissions of about 2 g/m² d (especially for PE, EVA/PE and Polypropylene). For Cellulose, systematic deviations from a linear dependence occur above concentration differences of 8 g m⁻³. Here, a maximum in transmittance is observed with a steep decline to higher humidities at 23 °C, with a similar tendency at 10 °C, see figure in the annex.

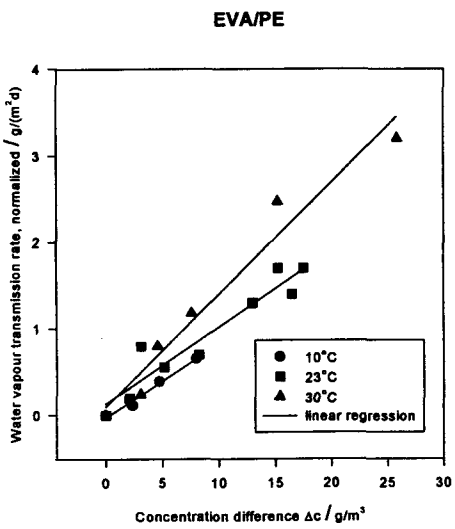


Fig. 3.34: Water vapour transmission rate, normalised to 100 µm film thickness. Dependence on water vapour concentration difference and temperature: EVA/PE

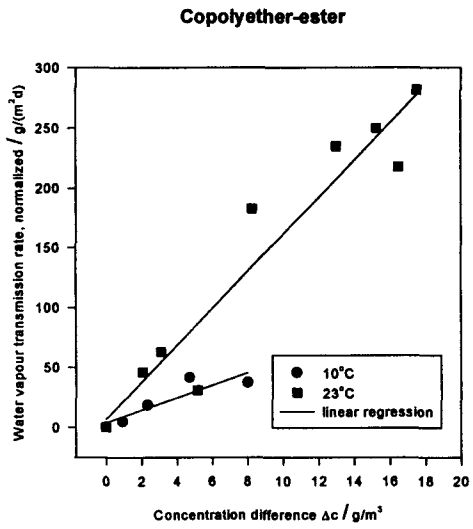


Fig. 3.35: Water vapour transmission rate, normalised to 100 µm film thickness. Dependence on water vapour concentration difference and temperature: Copolyether-ester

Table 3.8: H_2O-transmission:

- *Basic values for 23 °C, 85 % → 0 % r.H.,*
- *increase on slight condensation conditions, as estimated from permeation under saturated water vapour conditions,*
- *permeances (normalised to concentration difference) for 23 °C and for 10 °C, and*
- *the change in permeance for a temperature change of 1°C,*

all values for 100 µm film thickness

Material	**H_2O-transmission / g/m² d**	**Effect of slight condensation conditions, factor:**	**H_2O-permeance, 23 °C, m/d**	**H_2O-permeance, 10 °C, m/d**	**Change in permeance per °C of temp. change**
PE	1.93	1.8	0.11	0.077	0.0027
PVC	24.7	1	1.41	0.98	0.033
EVA/PE	1.7	1	0.09	0.08	0.00077
Copolyether-ester	282	2 ... 3	15.8	5.3	0.81
PCL	106	1	6.2	4.0	0.17
Cellulose acetate, ds 2.7	139	1	8.6	6.8	0.14
Cellulose	130	1	(12.7)	(11.4)	
PS	11.3	1	0.7	0.5	0.015
Polypropylene, without micropores	0.36	1	0.02	below meas. limit	below meas. limit

Resultant calculation formula for permeabilities Q in g/m² d under different conditions:

$$Q = (\text{Permeance at 23 °C}) * (\Delta T / °C) * S * \frac{100}{d/\mu m} * \Delta c / g/m^3$$

Table 3.9: Effect of strong condensation: Pervaporation from the liquid phase

Material	**Film thickness/ µm**	**I) Gas / gas permeation, slight condensation 100%→85% r.h.**	**II) Liquid / gas permeation, liquid →85% r.h.**	**Additional factor of II) vs. I)**
PE	12	6.7	7.65	1.1
PVC	16	28	62	2.2
Cellulose acetate	80	80	196	2.5
Copolyether/ester	9	498	2480	5

Pervaporation of water vapour
Table 3.9 shows the results from pervaporation from the liquid phase through the polymeric materials PE, PVC, Polyether/polyester copolymer and Cellulose acetate into humid air of 85% r.h.. Also shown are the factors of this process relative to transmittance values from saturated humid air (r.h. = 100%) into air of r.h. of 85%. Apparently, there is another increase in water vapour transmission from slight condensation to forced condensation with an area coverage of 100%. The observed factors, however, are less dramatic than expected from the gas permeation measurements in the liquid phase.

3.4 Packaging experiments

3.4.1 Commercial type of packagings

Tomato

Four packaging experiments were carried out with different temperature profiles:

- 2 weeks at 8 °C
- 2 weeks at 13 °C
- 2 weeks at 23 °C with colder period form day 2 to day 5 at 11 °C
- 2 weeks: day 1 to 4 at 8 °C, day 5 to 11 at 13 °C and day 12 to 14 at 23 °C

As an example the CO_2 and O_2 concentration of an experiment at 13 °C and at varying temperature profiles are shown below.

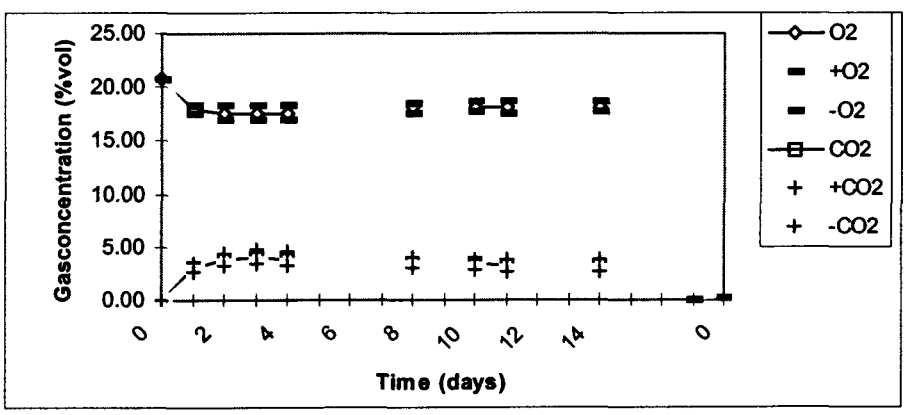


Figure 1.36: O_2 and CO_2 concentrations in a six pack with tomatoes at 13 °C, packaging foil used: P-plus 25K (polypropylene)

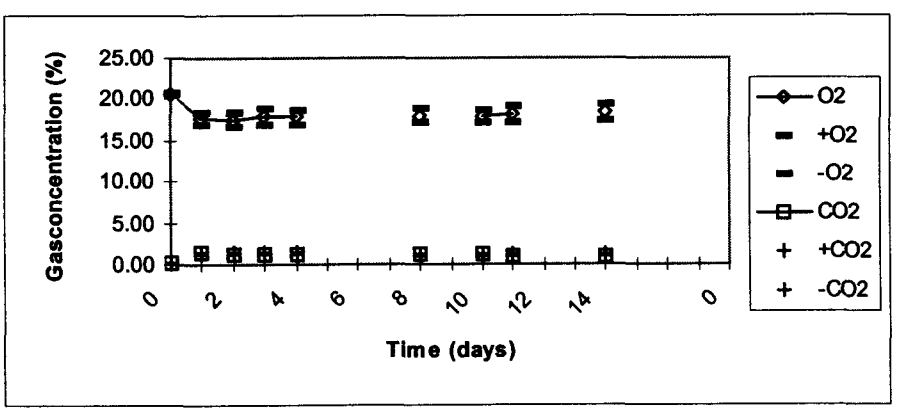


Figure 3.37: O_2 and CO_2 concentrations in a six pack with tomatoes at 13 °C, packaging foil used: PVC

These figures show how O_2 and CO_2 concentrations changed from regular air conditions at the moment of packing to a new equilibrium with higher CO_2 and lower O_2 concentrations in the MAP-package. This equilibrium was reached in about 2 days for all films tested except the P-plus K10 which had the lowest permeability for which it takes about 4 days. Depending on the permeabilities of the packaging films, different equilibrium concentrations were reached. Packages with P-plus K10 film yielded the lowest O_2 (16%) and highest CO_2 concentrations (5%) in the package. The K25 film yields a O_2 concentration of 18% and a CO_2 concentration of 4%. The K100 foil had the highest permeability and yielded CO_2 a concentration of 2% and a O_2 concentration of 20%. The polyether/polyester copolymer and the PVC foil yields lower O_2 concentration (18%) but comparable CO_2 concentrations with the K100 foil.

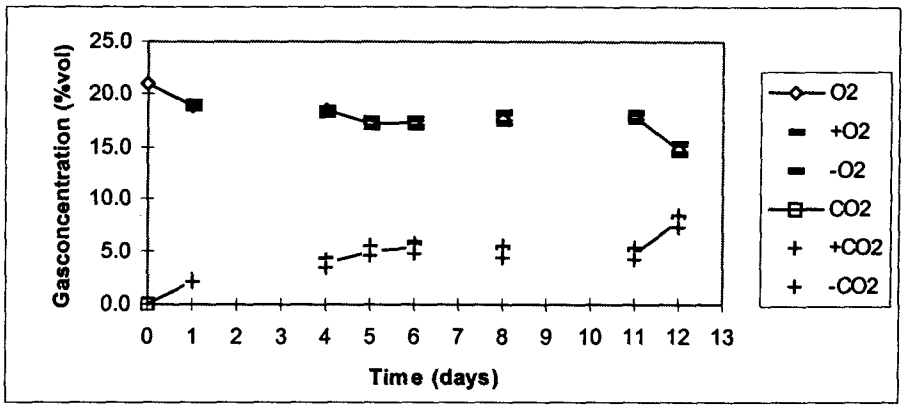


Figure 3.38: O_2 and CO_2 concentrations in a six pack with tomatoes stored for 4 days at 8 °C, 7 days at 13 °C and 3 days at 23 °C, packaging foil used: P-plus 25K (polypropylene)

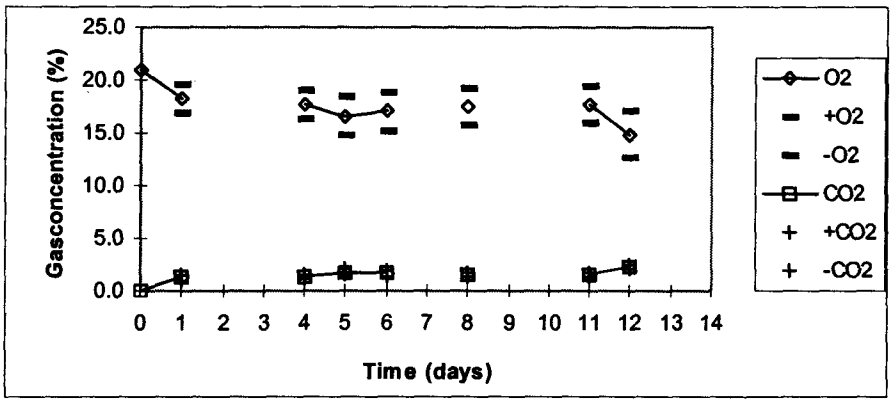


Figure 3.39: O_2 and CO_2 concentrations in a six pack with tomatoes stored for 4 days at 8 °C, 7 days at 13 °C and 3 days at 23 °C, packaging foil used: PVC

These figures show the O_2 and CO_2 concentration changes in the different packages for a varying temperature profile. The O_2 and CO_2 concentrations changed from regular air conditions at the moment of packing to higher CO_2 and lower O_2 concentrations in the MAP-package depending on the temperature. In general, the O_2 concentration evolved to lower values when the temperature is higher. The CO_2 concentration evolved in the opposite direction at higher temperatures.

Apple

Four packaging experiments were carried out with different temperature profiles:

- 2 weeks at 1 °C
- 2 weeks at 11 °C
- 2 weeks at 21 °C
- 7 days at 1 °C, 3 days at 11 °C and 4 days at 21 °C

As an example the CO_2 en O_2 concentration of the experiment at 11°C and the varying temperature profile are shown below.

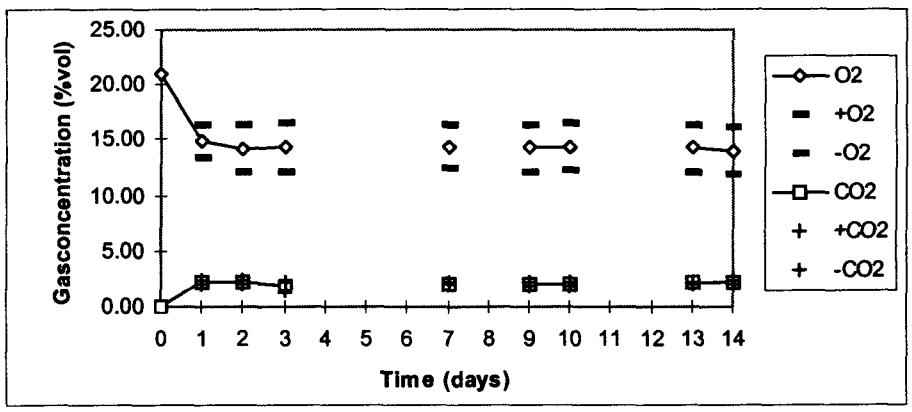


Figure 3.40: O_2 and CO_2 concentrations in a six pack with apples at 11 °C, packaging foil used: PVC

These figures show how O_2 and CO_2 concentrations changed from regular air conditions at the moment of packing to a new equilibrium with higher CO_2 and lower O_2 concentrations in the MAP-package. The biggest changes occur in the first 3 days. Between day 2 and day 4 a minimum in the O_2 concentration and a maximum in the CO_2 concentration was reached depending on the permeabilities of the packaging films. Then the O_2 concentration increased slightly and the CO_2 concentration decreased slightly to a more are less equilibrium state. Packages with cellulose acetate film yielded the lowest O_2 (4%) and highest CO_2 concentrations (7%) in the package. The PVC film yielded a O_2 concentration of 14% and a CO_2 concentration of 2%. The polyether/polyester copolymer yielded comparable O_2 (15%) and CO_2 concentrations (1%).

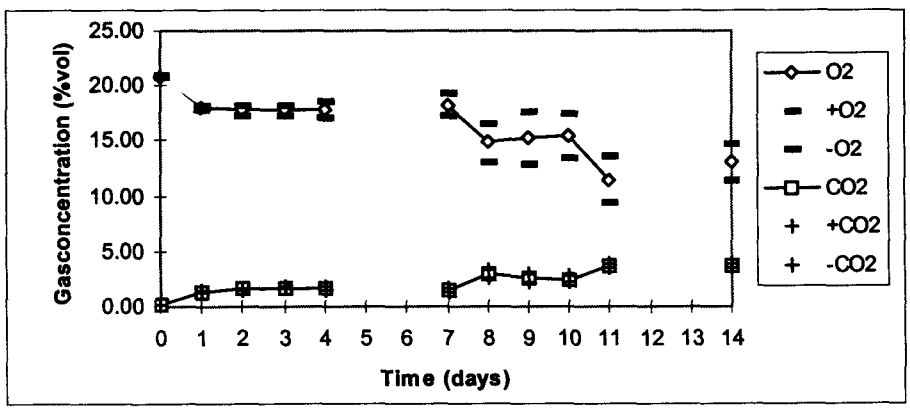


Figure 3.41: O_2 and CO_2 concentrations in a six pack with apples stored for 7 days at 1 °C, 3 days at 11 °C and 4 days at 21 °C, packaging foil used: PVC

These figures show the O_2 and CO_2 concentration changes in the different packages for a varying temperature profile. The O_2 and CO_2 concentrations changed from regular air conditions at the moment of packing to higher CO_2 and lower O_2 concentrations in the MAP-package depending on the temperature. In general, the O_2 concentration evolved to lower values when the temperature is higher. The CO_2 concentration evolved in the opposite direction at higher temperatures.

MAP under constant temperature

Initial and Final Respiration rate at 11 and 21 °C

Mean values of RR and FR (fermentative rate) at day 0 assessed from 4 jars are reported in table 3.10 :

	11 °C		21 °C		
	RRO_2 (mmole/h.kg)	$RRCO_2$ (mmole/h.kg)	RRO_2 (mmole/h.kg)	$RRCO_2$ (mmole/h.kg)	FR (mmole/h.kg)
Mean value	0.38	0.23	0.85	0.60	0.62
St. deviation	0.01	0.01	0.01	0.01	0.02
RQ	0.62		0.70		
(SD)	(0.01)		(0.00)		

Table3.10: Initial respiration and fermentative rates of endive shoots at 11 and 21 °C.

$RRCO_2$ was lower than RRO_2 especially at low temperature, due to high dissolution of CO_2 in the plant tissue. This phenomenon which occurs in MAP plant tissue is not taken into consideration in MAP models. As a consequence, the respiration quotient ($RQ = RRCO_2/RRO_2$) was lower at 11 °C than at 21 °C.

Experiments at 6 °C

Time	PP		10K		25K		60K		100K		OSM	
(days)	CO_2 (kPa)	O_2 (kPa)	CO_2 (kPa)	O_2 (kPa)	CO_2 (kPa)	O_2 (kPa)	CO_2 (kPa)	O_2 (kPa)	CO_2 (kPa)	O_2 (kPa)	CO_2 (kPa)	O_2 (kPa)
0.25	1.7	18.7	1.5	19.2	1.5	19.2	1.2	20.0	1.4	19.8	1.3	19.0
sd	0.1	0.1	0.2	0.3	0.2	0.3	0.1	0.1	0.1	0.3	0.1	0.1
1	4.3	16.5	2.8	18.2	2.9	18.1	1.8	20.0	1.8	20.2	2.0	13.6
sd	0.1	0.5	0.6	1.1	0.1	0.1	0.2	0.2	0.1	0.4	0.1	0.1
2	6.8	9.5	5.4	15.1	4.2	17.4	1.7	20.5	2.0	20.1	1.9	9.3
sd	1.4	3.7	0.6	1.1	0.2	0.4	0.2	0.2	0.3	0.1	0.1	0.1
3	7.2	6.0	4.9	13.3	4.1	16.2	1.6	20.4	1.6	17.8	1.6	10.5
sd	0.3	1.6	0.3	0.9	0.5	1.3	0.1	0.1	0.1	0.1	0.1	0.1
5	10.2	3.1	7.1	13.8	4.0	18.3	1.1	20.9	1.4	20.7	1.2	6.9
sd	0.1	0.1	0.7	1.6	0.4	0.3	0.1	0.1	0.1	0.1	0.1	0.1
8	11.8	1.5	6.6	15.6	5.4	16.9	1.4	20.6	1.8	20.2	1.1	13.0
sd	0.1	0.1	0.6	0.8	0.8	0.8	0.1	0.1	0.6	0.4	0.1	0.4

Table 3.11: Changes in atmosphere composition in packs of endive shoots at 6 °C as a function of time and film characteristic.

At 6 °C, stady state was not reached after 5 days except with highly permeable films (PPlus 60k and 100k) which did not markedly modify the internal atmosphere from ambient. Final atmosphere compositions clearly indicate that permeability to CO_2 of Osmolux and 100k are similar and permeability of Osmolux to O_2 is intermediate between those of OPP and 10k. A significant dehydration was only observed for chicories packed with Osmolux. After 5 days, water loss reached 2% of the initial fresh weight. In this experiment the atmosphere within packages, but OPP, was not sufficiently modified to get a significant effect on endive physiology. The metabolism of endive shoots packed with OPP at 6 °C switched to anaerobic after 8 days. In other packs, whatever the packaging films, the chicories appeared slightly shriveled.

Experiments at 11 °C

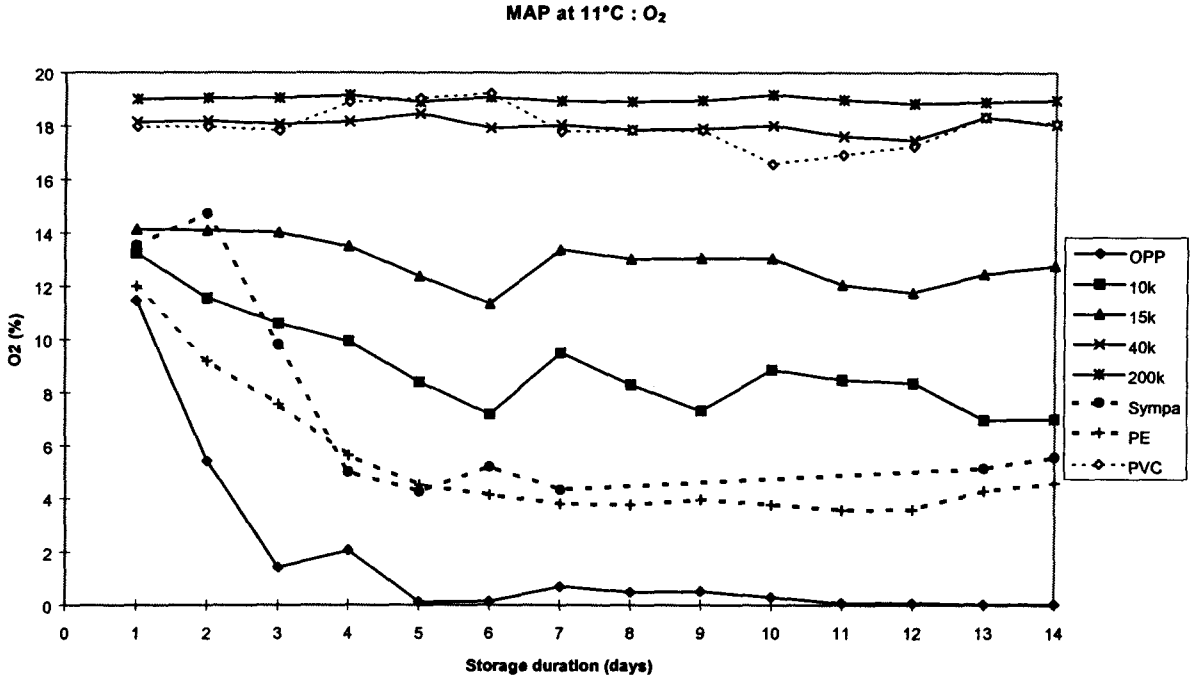


Figure 3.42: Changes in O_2 concentrations as a function of films and storage duration.

O_2 Kinetics

Packing of endive shoots at 11 °C with 200K, stretchable PVC and 40K results in a moderate reduction in O_2. As expected, steady state is established in microperforated films within a few hours. Copolyether-ester permeance to O_2 is similar to that of the polyethylene film (higher than 1000, lower than 10 000 ml of O_2/m^2.d.atm). The atmosphere in the OPP turns anoxic after about 3 days (see figure 3.42).

CO_2 kinetics

Packing in 100K, stretchable PVC, 40K, Copolyether-ester and PE results in a CO_2 concentration at steady state lower than 4kPa CO_2 (figure 3.43). Permeance of Osmolux to CO_2 is higher than that of 200K. After 7 to 8 days at 11 °C, endive shoots packed in OPP start fermentating. CO_2 concentrations in 10K and 15K are too low to trigger anaerobic metabolism but high enough to prevent greening.

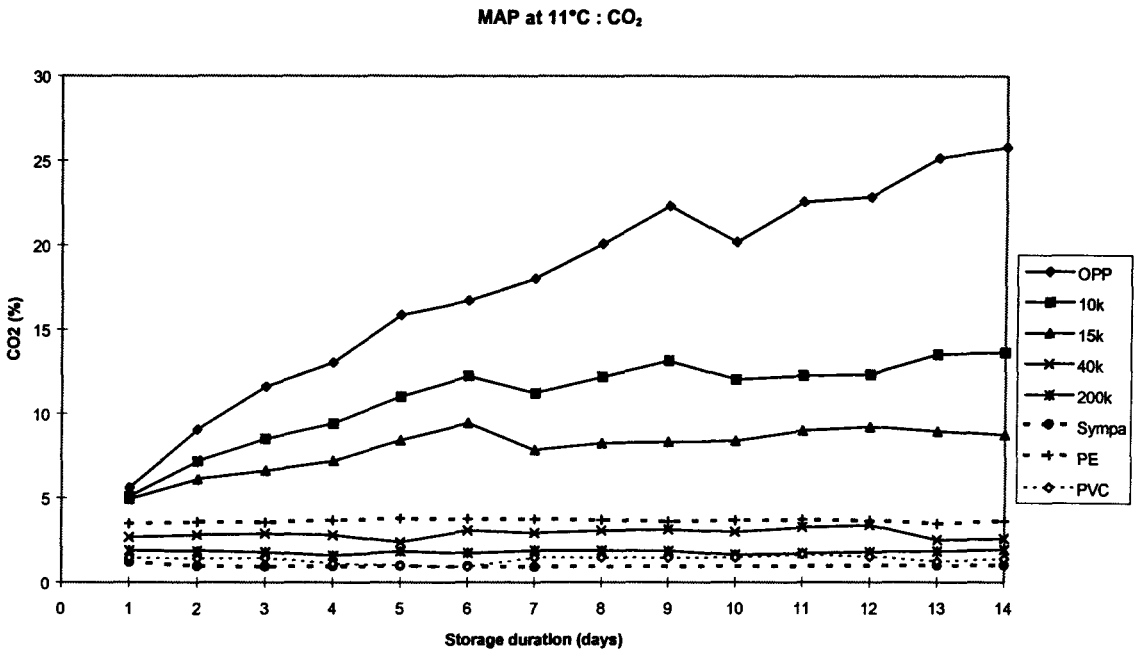


Figure 3.43 : Changes in CO_2 concentrations as a function of films and storage duration.

RR after MAP storage (day 14) at 11 °C

After 14 days storage under the different films at 11 °C, the respiration rate of endive increased in all films but OPP (figure 3.44) . It is likely that the decrease in respiration rate of endives packed in OPP was due to tissue necrosis.

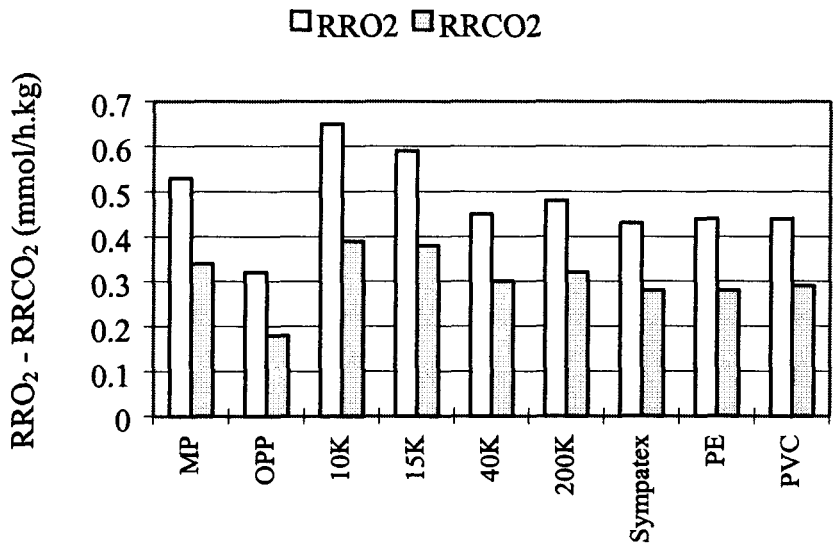


Figure 3.44 : Respiration rates of endives after 14 days storage at 11 °C for the different films.

Weight losses

Weight losses were low (about 1%) in all films but PVC, MP and Copolyether-ester (table 3.12). Weight loss in PE, OPP and P+ films may be due to both water diffusion and metabolite consumption. Weight losses in Copolyether-ester are higher than those in the macroperforated film. Endive shoots packed in Copolyether-ester and, to a lesser extend, in MP were no longer saleable at day 7.

FILM	at Day 6	at Day 11	at Day 14
MP	2,43 +/-0.49	5,53 +/-0.76	7,42 +/-1,09
OPP	0.88 +/-0.05	0,95 +/-0.05	1.00 +/-0.04
10K	0.83 +/-0.02	1.00 +/-0.06	1.13 +/-0.06
15K	0.84 +/-0.02	1.10 +/-0.08	1.20 +/-0.04
40K	0,77 +/-0.03	1.09 +/-0.01	1.16 +/-0.06
200K	0.84 +/-0.03	1.08 +/-0.04	1.20 +/-0.09
Copolyether-ester	5,13 +/-0.36	9,64	12,47 +/-0,97
PE	0.71 +/-0.03	0,94 +/-0.05	1.02 +/-0,03
PVC	1,47 +/-0,06	2,33 +/-0.13	2,71 +/-0.11

Table 3.12 : Weight losses (%) of endives stored at 11 °C packed in different films

Experiment at 16 °C

As shown in table 3.13 gas equilibration was reached in less than 3 days. Final CO_2 concentrations ranged from 2kPa (Osmolux) to 19kPa (OPP) and O_2 from 2kPa (OPP and Osmolux to 19kPa (60k and 100k). Weight loss did not exceed 2% for microperforated films while it peaked at 6% for the "hydrophilic film" Osmolux. At 16 °C respiration rates of packed chicories remained constant or slightly increased during storage but respiration rate of the shoots packed with OPP significantly decreased. This may indicate a faster decay of the plant tissue due to high CO_2 content (up to 19kPa).

Time	PP		10K		25K		60K		100K		OSM	
(days)	CO_2 (kPa)	O_2 (kPa)	CO_2 (kPa)	O_2 (kPa)	CO_2 (kPa)	O_2 (kPa)	CO_2 (kPa)	O_2 (kPa)	CO_2 (kPa)	O_2 (kPa)	CO_2 (kPa)	O_2 (kPa)
0.25	3.5	16.2	3.2	16.9	2.6	17.9	2.3	19.0	2.2	19.2	2.3	17.0
sd	0.4	1.1	0.3	0.8	0.3	0.5	0.3	0.4	0.1	0.3	0.2	0.5
1	8.3	9.5	7.7	10.7	6.2	14.5	3.9	18.2	3.9	18.4	2.6	12.0
sd	0.3	2.0	0.7	1.8	0.5	0.5	0.3	0.4	0.2	0.2	0.1	1.6
2	14.1	2.1	11.5	7.3	7.8	14.0	3.8	18.5	3.7	18.7	2.1	5.5
sd	2.5	1.3	0.7	0.9	1.8	2.3	0.1	0.1	0.5	0.4	0.1	2.3
3	18.7	1.3	11.6	8.8	10.6	11.7	4.0	18.4	3.3	19.1	1.9	3.5
sd	2.2	0.1	1.1	2.4	0.6	0.6	0.1	0.2	0.1	0.1	0.1	0.2
5	18.9	1.6	14.0	6.7	10.9	11.4	3.5	18.9	3.7	18.7	2.0	6.3
sd	0.6	0.1	0.8	2.9	1.4	1.7	0.6	0.6	1.2	1.0	0.1	0.1
8			15.8	3.6	12.0	10.8	3.3	19.1	3.0	19.3	1.8	5.9
sd			1.1	0.9	2.3	2.1	0.4	0.2	0.1	0.1	0.1	0.1

Table 3.13: Atmosphere changes within packed endive shoots stored at 16 °C as a function of duration and films.

MAP under varying temperature regime

Packed endive shoots were stored in the dark at 11 °C for 3 days then placed under intermittent indirect day light at 21 °C for 5 days.

Initial and Final Respiration rates

Table 3.14 shows that, expectedly, values of initial RRO_2 and $RRCO_2$ increase with temperature, however RQ ($RRCO_2/RRO_2$) is systematically low probably due to the dissolution of CO_2 in the plant tissue. This phenomenon is more marked after MAP storage.

	RR O2 (mmole/kg.hr)	RR CO2 (mmole/kg.hr)	RQ
at 11°C (Day 0)	0.38 +/- *0.03*	0.25 +/- *0.01*	0.66
at 21°C (Day 0)	0.86 +/- *0.03*	0.67 +/- *0.02*	0.77
at 21°C (Day 4) under air + day light	1.11 +/- *0.11*	0.84 +/- *0.08*	0.76
at 21°C (Day 9) + day light, under :			
OPP	0.88 +/- *0.03*	0.49 +/- *0.06*	0.56
200K	1.09 +/- *0.05*	0.87 +/- *0.04*	0.8
PD 900	0.89 +/- *0.02*	0.48 +/- *0.01*	0.54
PD 961	0.95 +/- *0.02*	0.60 +/- *0.01*	0.63
PD 941	0.96 +/- *0.05*	0.76 +/- *0.05*	0.79

Table 3.14 : Evolution of RR of endives during a simulation of an actual distribution circuit.

Atmospheres within the pouches

O_2 kinetics

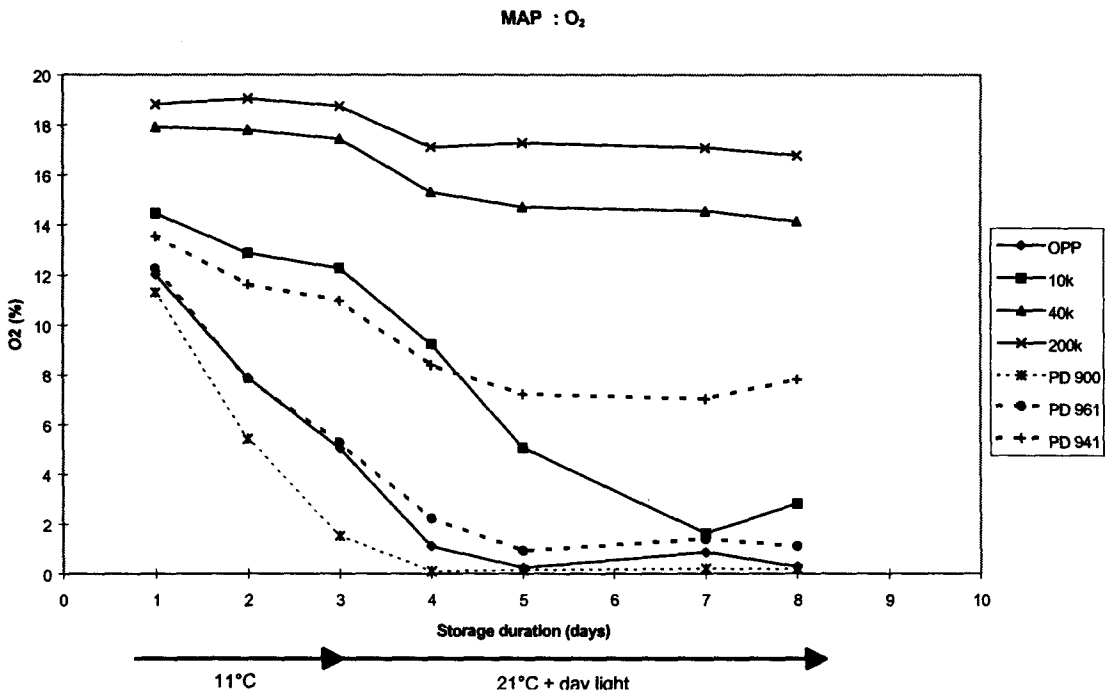


Figure3.44 : Changes in O_2 concentrations as a function of films and storage duration.

At 11 °C, O_2 permeability of PD 900 is lower than that of OPP and at 20 °C, both lead to anoxia. Temperature has no significant effect on O_2 and CO_2 permeabilities (Q10 $\simeq$ 1) of microperforated films whereas permeabilities to gases of polyethylen films increase more markedly with temperature. Exama *et al.* reported a Q10 of polyethylen low density and high density ranging from 1.7 to 2 for O_2 and from 1.6 to 1.7 for CO_2. Polyethylen film (and other polymers) will adjust MAP atmospheres better than microperforated films in case of temperature abuse.

PD 900 and OPP packing lead to severe hypoxia after 1 to 2 days at 21 °C. The most permeable films (200K and 40K) do not sufficiently modify atmosphere composition, even at 21 °C under our experimental conditions, to prevent spoilage (see figure 3.44).

CO_2 kinetics

Packing endive shoots in OPP film results in a strong fermentation process after 4 days at 21 °C; the 10K film behaves the same way as OPP but to a lesser extend (figure 3.45). As previously noticed, polyethylene films buffer the effect of temperature increase while microperforated films display a noticeable increase in CO_2 concentration at 21 °C compared to 11 °C. The selectivity to gases of polyethylene films is, as expected, much higher than that of microperforated films.

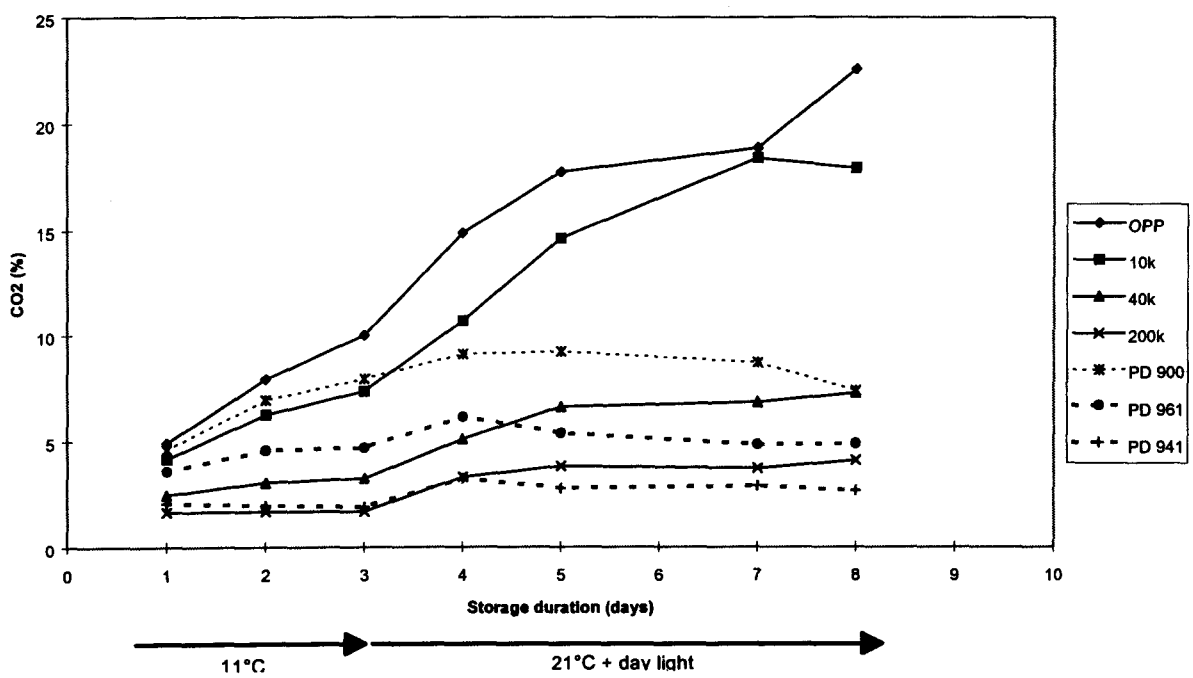


Figure 3.45 : Changes in CO_2 concentrations as a function of films and storage duration.

RR after MAP storage (day 9) at 21 °C + day light

The CO_2 respiration rate after MAP storage should not be taken into consideration since it reflects the previous dissolution of CO_2 more than the $RRCO_2$. The shoots packed in 200K film (with a steady state atmosphere composition not far from normal air) shows a marked increase in RRO_2 which may be due to bacterial growth (figure 3.46).

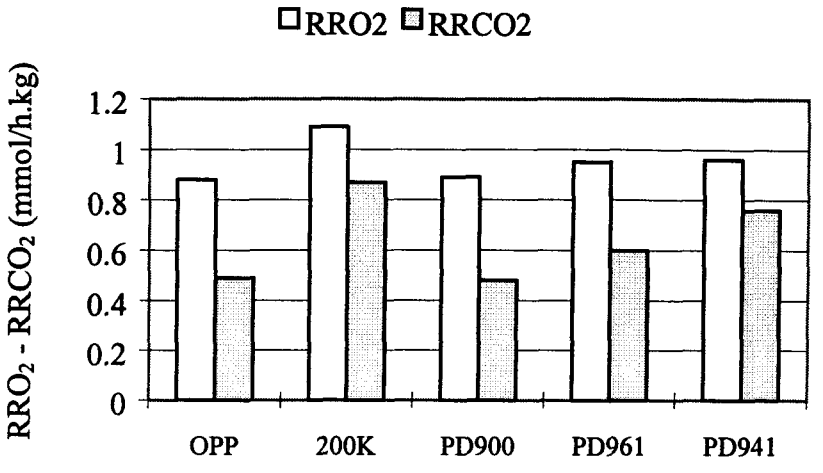


Figure 3.46 : Respiration rates of endives after 14 days storage at 11 °C for the different films.

Changes in colour

L parameter

After threee days at 11 °C in darkness, L parameter of endive did not change. Exposed to day light, colour of the tips of most endive shoots changed rapidly (figure 3.47) . Colour of endive stored in PD 900 and OPP did not change significantly even after 4 days at 21 °C. This phenomenon is due to the influence of atmosphere composition. Prevention of greening seems related more to the hypoxic conditions than to CO_2 concentration since the 10K sample which contained more O_2 and CO_2 is significantly darker (L) and greener (a/b) than both PD 900 and OPP samples.

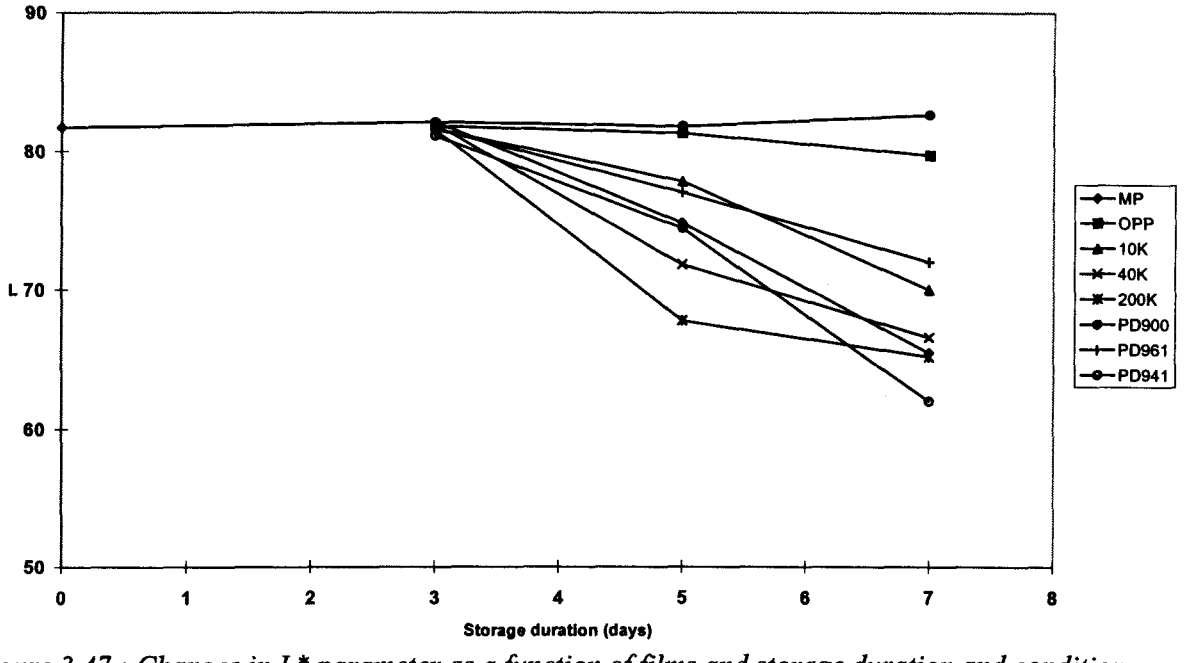


Figure 3.47 : Changes in L parameter as a function of films and storage duration and conditions.*

a/b ratio

Calculation of the ration a/b enhances the greening effect. Endives stored in PD 961 and P+ 10K were subjected to moderate greening (figure 3.48). The tips of the samples stored in the 4 other films turned green and were not saleable any longer when exposed to day light after 2 days at room temperature

(21 °C). Endives that were estimated the poorer by the operators were packed in MP due to the combined effects of greening and dehydration (7.4±1% at day 7).

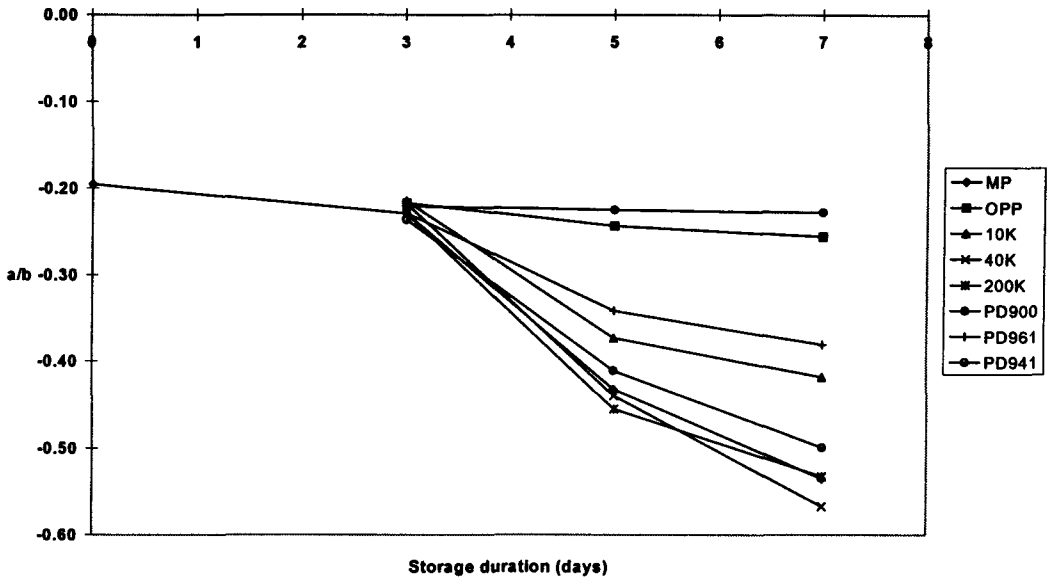


Figure 3.48 : Changes in a/b ratio as a function of films and storage conditions.

Weight losses

Weight losses of endives packed in the polyethylene films were roughly proportional to moisture permeability of the films (table 3.15).

FILM	at Day 3	at Day 5	at Day 7
MP	1.86 +/-0.34	4.02 +/-0.69	7.37 +/-1.01
OPP	0.05 +/-0.02	0.10 +/-0.01	0.14 +/-0.01
10K	0.06 +/-0.01	0.14 +/-0.02	0.21 +/-0.02
40K	0.14 +/-0.09	0.21 +/-0.01	0.30 +/-0.02
200K	0.11 +/-0.01	0.21 +/-0.00	0.33 +/-0.00
PD 900	0.07 +/-0.01	0.16 +/-0.01	0.28 +/-0.00
PD 961	0.08 +/-0.02	0.20 +/-0.01	0.29 +/-0.01
PD 941	0.14 +/-0.01	0.39 +/-0.02	0.70 +/-0.03
	11°C	21°C * at day light	21°C * at day light

Table 3.15 : Weight losses of endives during the simulation of an actual distribution circuit.

3.4.2 Model packagings

In contrast to commercial types of packagings, model packagings allow for an independent variation and determination of produce mass, film area and packaging volume.

For endives packed in model packagings of a volume (V) of 1573 ml and stored at 6 °C, Fig. 3.49 shows the effects of

- different masses (m) of produce packed and
- of different packaging film areas (a) which allow for a higher gas exchange rate.

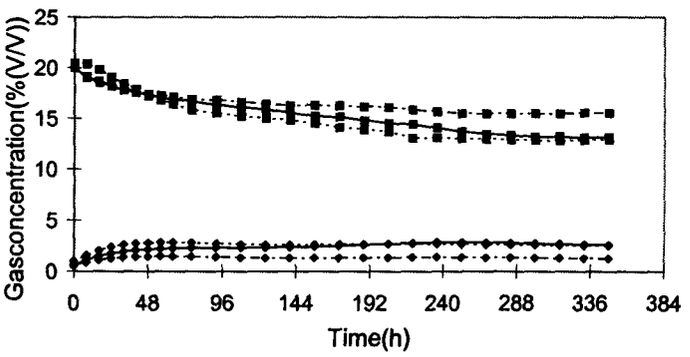


Figure 3.49: Examples of chicory packed in model packagings, packaging film: PE, at 6 °C.
1)solid line: m=231 g, V =1573 ml, A=302 cm²,
2) dashed line: m=508 g, V =1573 ml, A=602 cm²-
3) dashed-dotted line: m=251g, V =1573 ml, A=602 cm².

In addition- for simplicity in tabular form - results on the combined product / packaging behaviour are given in table 3.16 for Golden Delicious apples in model packagings at 21 °C. The initial respiration rates are given together with the initial mass of the products, the equilibrium concentrations of oxygen and carbon dioxide and the equilibration time.

Table 3.16: Apples packed in model packagings, film area:198 cm², volume 3700 cm³ including product

Tempera-ture	Material	Atmospheric conditions Respiration rates in mmol/kg hour		Mass of apple/g	Equilibrium pressures/hPa and equilibration time/days	
		O_2, initial	CO_2, initial		O_2	CO_2
21 °C	PVC	0.59	0.57	150	13.5/6d	2.0/6d
	Copolyether/-ester	0.64	0.64	170	6.5/6d	1.7/6d
	Cellulose acetate	0.54	0.54	130	9.1/9d	7.2/9d
	PE	0.65	0.70	140	12.5/9d	2.4/9d

3.5 Modelling of respiration experiments

Results of the non-linear regression analysis are presented in Table 3.17. During the iterative process of non-linear regression some of the Km*i* tended towards extreme large values, indicating that the concerning type of inhibition was not involved. For these cases, that Km*i* was subsequently fixed at a value of

10000 before completing the non-linear regression analysis. The percentage variance accounted for by the model is expressed for each product by R^2_{adj}. The model is capable of explaining ±88% of the observed variance; this in spite of the distinct source of variation present. Although each of the products exhibits its own apparently different gas exchange pattern in function of O_2, CO_2 and temperature, the same model could explain them all. This proves the generic features of the developed model.

The simulated data for apple, tomato and chicory generated by the model, applying the estimated parameters from Table 1, are shown as solid lines in the respective Figures 3.50, 3.51 and 3.52. O_2 consumption (V_{O2} in $mmolAkg^{-1}Ah^{-1}$; closed symbols) and CO_2 production (V_{CO2} in $mmolAkg^{-1}Ah^{-1}$; open symbols) as measured for apple, tomato and chicory are shown in function of O_2 (x-axes), CO_2 (rows of graphs) and temperature (columns of graphs).

Table 1: Results of the non-linear regression analysis using O_2, CO_2, and temperature simultaneously as explaining variables

	Product		
Parameter	Apple	Chicory	Tomato
parameters describing oxygen consumption: [z]			
$Vm_{O2,ref}$	0.382	0.404	0.439
Ea_{Vmo2}	52886	67275	67337
Km_{O2}	3.75	2.72	23.1
Kmc_{CO2}	7.33	10000 [v]	21.3
Kmu_{CO2}	10000 [v]	10000 [v]	7.85
parameter describing oxidative part of carbon dioxide production: [y]			
RQ_{ox}	0.84	0.89	0.91
parameters describing fermentative part of carbon dioxide production: [x]			
$Vm_{CO2(f),ref}$	0.320	0.248	0.147
$Ea_{Vmco2(f)}$	52363	67738	65159
$Kmc_{O2(f)}$	2.01	1.09	2.74
$Kmc_{CO2(f)}$	19.4	10000	13.0
R^2_{adj} [w]	83.0%	86.5%	87.0%
n	543	489	502

[z] $Vm_{O2,ref}$ = the maximum O_2 consumption rate ($mmol \cdot kg^{-1} \cdot h^{-1}$) at reference temperature T_{ref} (= 10 °C); Ea_{Vmo2} = activation energy ($J \cdot mol^{-1}$) of rate constant Vm_{O2} ; Km_{O2} = Michaelis constant for O_2 consumption (%); Kmi_{CO2} = Michaelis constant for inhibition of O_2 consumption by CO_2 (%); *i*=c: competitive; *i*=u: uncompetitive

[y] RQ_{ox} = respiration quotient

[x] $Vm_{CO2(f),ref}$ = the maximum CO_2 production rate ($mmol \cdot kg^{-1} \cdot h^{-1}$) at reference temperature T_{ref} (= 10 °C); $Ea_{Vmco2(f)}$ = activation energy ($J \cdot mol^{-1}$) of rate constant Vm_{CO2} ; $Km_{O2(f)}$ = Michaelis constant for inhibition of fermentative CO_2 production by O_2 (%)

[w] R^2_{adj} = percentage variance accounted for; *n* = number of data points

[v] fixed value

Interpretation of the model parameters and their values

I. Effect of temperature on respiration. From Table 1 it can be taken that the highest maximum O_2 consumption rate at reference temperature ($Vm_{O2,ref}$) is comparable for the three products. Apple is the least depedent on temperature because of the relative low activation energy (Ea_{Vmo2}; Table 1). For chicory and tomato this parameter is the same.

II. Effect of substrate on respiration. The parameter Km_{O2} is a measure for the saturation of respiration with oxygen. It represents the oxygen concentration at which the level of half the maximum respiration (½ Vm_{O2}) is reached, assuming no inhibition by CO_2. Chicory shows the lowest Km_{O2} (2.72%) and tomato the highest with Km_{O2} of 23.1%. Thus tomato will show the least steep incline of respiration in function of O_2 at 0% CO_2, as can be seen in Figure 2.

III. Inhibition of respiration by CO_2. The value for Kmi_{CO2} is measure to what extent respiration can be inhibited by CO_2 (either competitive or uncompetitive). A high value for Kmi_{CO2}, as compared to the imposed levels of CO_2, implies that the backward reaction of the concerned inhibition is much faster than the forward reaction and hence the overall inhibition will not take place. Data from apple showed only the competitive type of inhibition of O_2 consumption by CO_2 (Table 1). Data from chicory showed no inhibition at all as both Kmc_{CO2}, and Kmu_{CO2} are extreme large (Table 1). For tomato a slight level of competitive inhibition was found as Kmc_{CO2} is of the same magnitude as CO_2, but still quite large (21.3%). Tomato shows a clear uncompetitive type of inhibition (Kmu_{CO2}=7.85%).

$$\lim_{[O_2]\to\infty} V_{O_2} = Vm_{O_2}$$

IV. Effect of substrate on the inhibition of respiration by CO_2. The competitive type of inhibition by CO_2, as for apple, can be counteracted by raising the level of O_2, as O_2 and CO_2 are competing for the same active sites. In case of uncompetitive inhibition, as for tomato, the maximum respiration level Vm_{O2} can not be reached by raising O_2, because there will always be a certain amount of intermediate complex (AC_1) available for CO_2 to react with. This can also be deduced from Eq. 1, as in case of competitive inhibition:

but in case of uncompetitive inhibition

$$\lim_{[O_2]\to\infty} V_{O_2} = \frac{Vm_{O_2}}{1+\frac{[CO_2]}{Kmu_{CO_2}}}$$

So, in case of uncompetitive inhibition, the maximum level of respiration possible will always be below the level of Vm_{O2}.

V. Respiration quotient. The estimated respiration quotient for oxidative metabolism (RQ_{ox}) is quite the same for the studied products (Table 1). For each of the products it is below unity: O_2 consumption was always higher than the oxidative CO_2 production.

VI. Effect of temperature on fermentation. The maximum rate of fermentative CO_2 production at T_{ref}, is comparable for apple and chicory (±0.27 $mmol \cdot kg^{-1} \cdot h^{-1}$) but is only half this value for tomato (Table 1). Given a certain temperature, tomato also shows the lowest total metabolic activity per gram fresh weight (Fig. 2 as compared to Fig. 1 and 3)

VII. Inhibition of fermentation by O_2. The parameter $Km_{O2(f)}$ gives the O_2-level at which fermentative CO_2 production is suppressed to half its maximum level (½ $Vm_{CO2(f)}$). As tomato has the highest value for $Kmc_{O2(f)}$ (Table 1), fermentation is still active at relative high O_2-levels as compared to apple and chicory. This can be explained by the low skin permeability of tomato as compared to apple and chicory. As a consequence, tomato will internally generate anaerobic conditions at still aerobic environmental conditions.

VIII. Inhibition of fermentation by CO_2. The parameter $Kmc_{CO2(f)}$ gives the CO_2-level at which fermentative CO_2 production is suppressed to half its maximum level (½ $Vm_{CO2(f)}$). The fermentation of chicory is not suppressed by CO_2 ($Kmc_{CO2(f)}$ = 10000). Apple and tomato both show a substantial inhibition of their fermentation by CO_2.

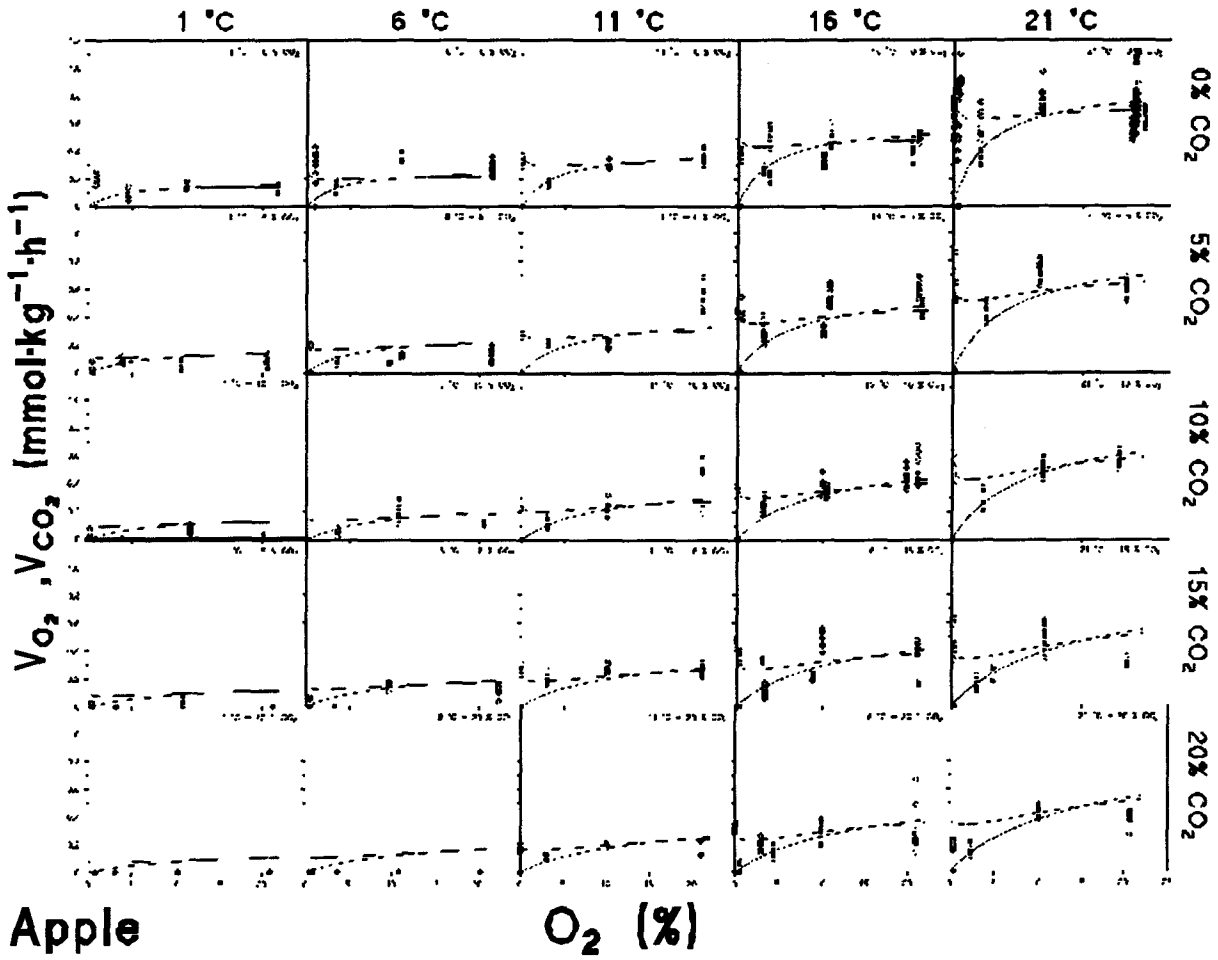


Figure 3.50: O_2 consumption (V_{O2} in mmol•kg^{-1}•h^{-1}; closed symbols) and CO_2 production (V_{CO2} in mmol•kg^{-1}•h^{-1}; open symbols) as measured for Golden Delicious apple in function of O_2 (x-axes), CO_2 (rows of graphs) and temperature (columns of graphs). The solid lines are simulated values according to the model.

Figure 3.51: O_2 consumption (V_{O2} in mmol•kg^{-1}•h^{-1}; closed symbols) and CO_2 production (V_{CO2} in mmol•kg^{-1}•h^{-1}; open symbols) as measured for tomato in function of O_2 (x-axes), CO_2 (rows of graphs) and temperature (columns of graphs). The solid lines are simulated values according to the model.

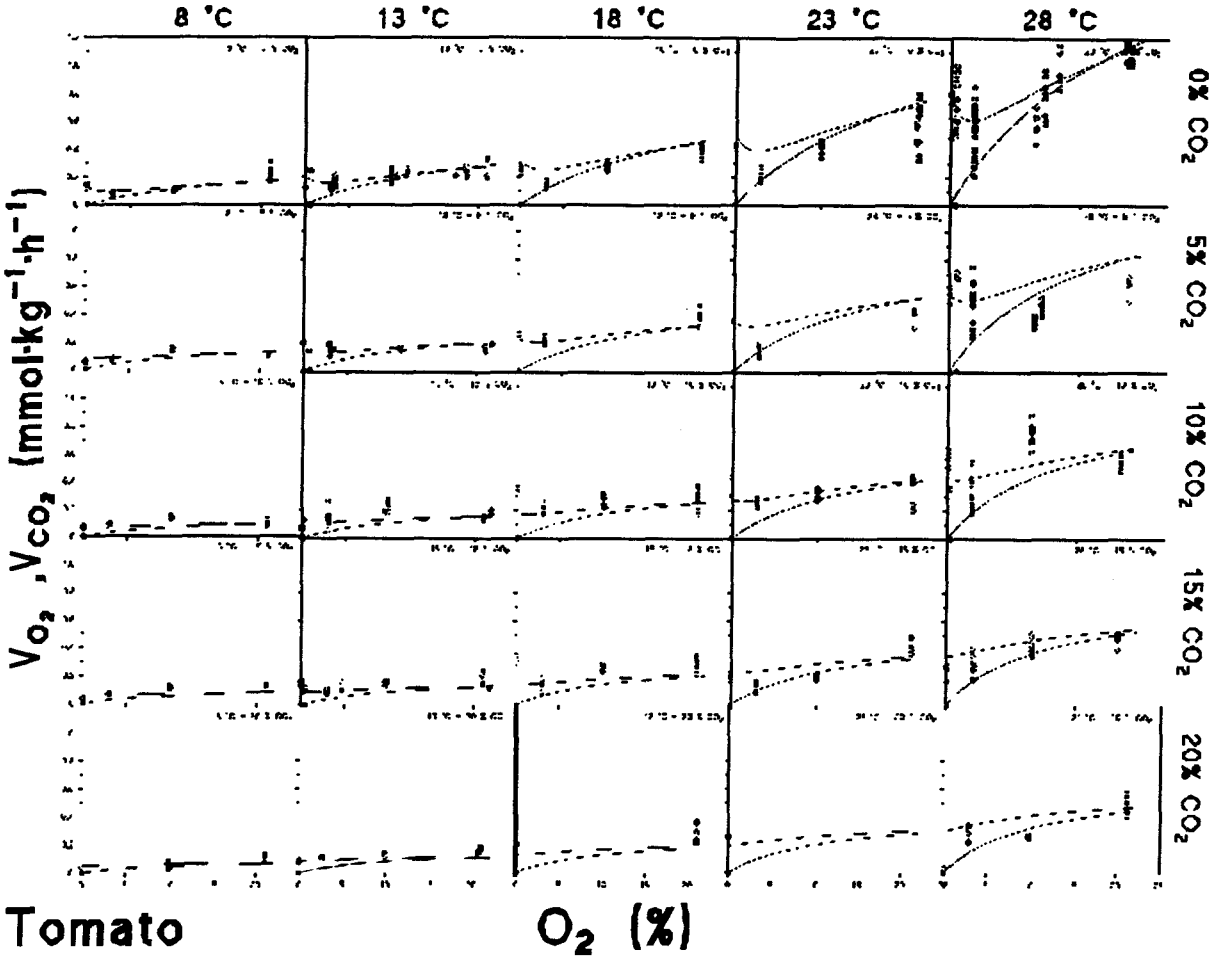
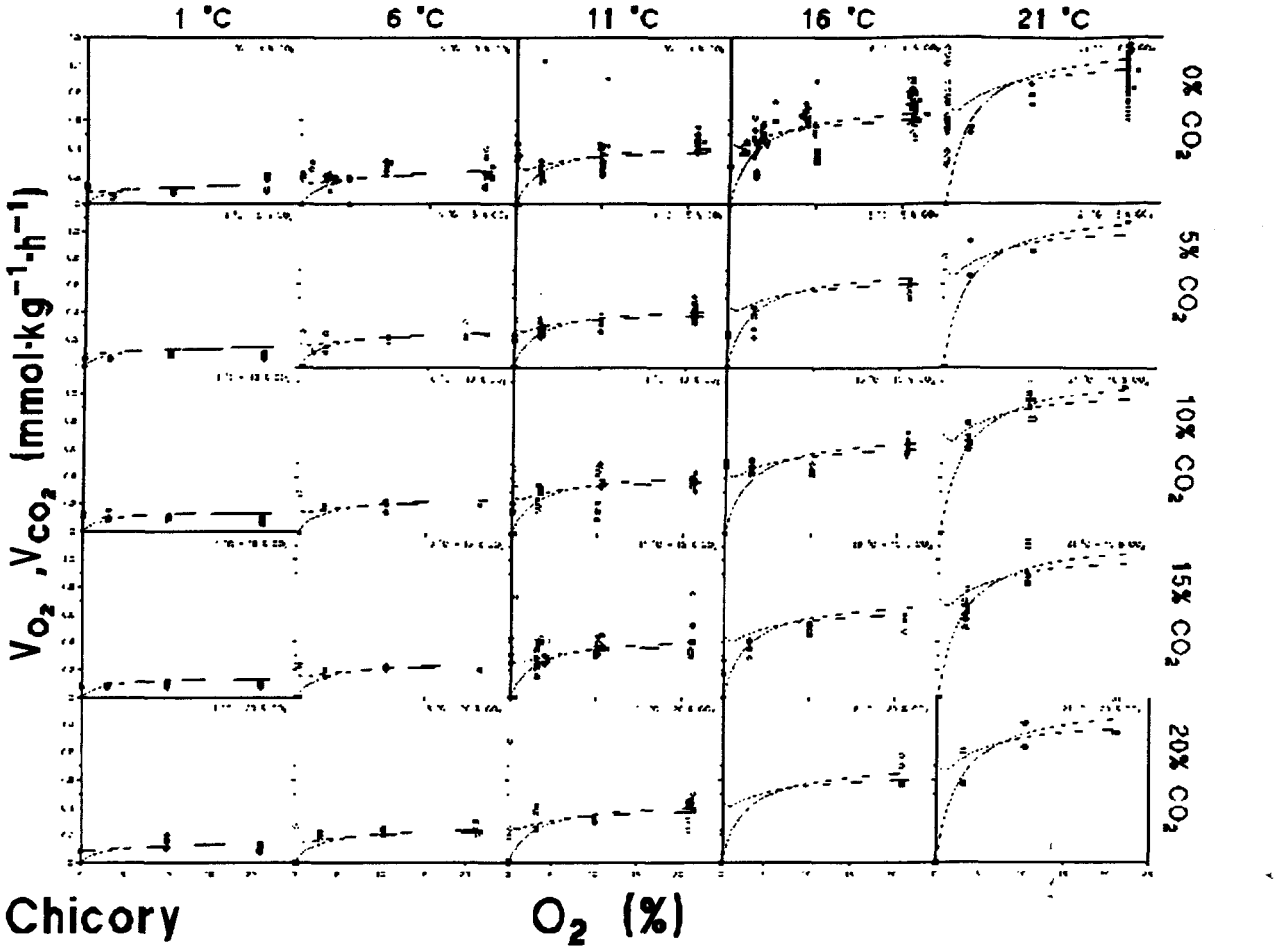


Fig. 3.52: O_2 consumption (V_{O2} in mmol•kg^{-1}•h^{-1}; closed symbols) and CO_2 production (V_{CO2} in mmol•kg^{-1}•h^{-1}; open symbols) as measured for chicory in function of O_2 (x-axes), CO_2 (rows of graphs) and temperature (columns of graphs). The solid lines are simulated values according to the model.



4 Discussion

4.1 Respiration of produce

4.1.1 Tomato

From the result it was seen that both the O_2 consumption rate and the CO_2 production rate were dependent on O_2 and CO_2 concentration in the atmosphere as well as on temperature. The higher the temperature the higher were the respiration rates. However, this increase with temperature is not a linear one and an Arrhenius-like dependency will be appropriate to model this. The dependency of the respiration rates on CO_2 concentration was limited. In general, higher CO_2 concentration had a small inhibitory effect on the respiration. High O_2concentrations resulted in high respiration rates. However at very low O_2 concentrations (0 %) the CO_2 production rate increases again. This means that the aerobic metabolism which occurs at high O_2 concentrations was altered in a fermentative metabolism which produces CO_2 without needing O_2. This switch over was especially seen at the higher temperatures.

Maturity experiments with tomato

The effect of maturity of the tomatoes on the respiration rates was limited. Only when the tomatoes reach the colour stage 9 or higher the respiration rates are somewhat lower. This was seen in the first experiment, in which tomatoes were picked before the start of the red colouring and followed in time, as well as in the second experiment in which tomatoes were picked in all stages of the red colouring and immedately measured.

(VBT)

4.1.2 Chicory

The aerobic respiration of plant tissue is the result of enzymatic reaction involved inKrebs' cycle, we will consider the slowest oxidative step of the chain and assimilate the respiration rate to this enzymatic reaction. Therefore, the change in respiration rate versus O_2 concentration should follow Michaelis' law according to which the reciprocal of the respiration rate is proportional to the reciprocal of the O_2 concentration. Using Lineweaver and Burk's double reciprocal coordinates, we determined the maximum apparent velocity and the apparent Michaelis' constant in kPa. It must be taken into account that the rate of the oxidative reaction also depends upon the concentration of the other substrates of the enzyme i.e. the carbon source which should not be a limiting factor. We don't know the actual nature and concentration of the substrates of the enzyme and several enzymes may be involved in the limiting step, therefore the results are relative and called apparent. The reported data are valid only under specific experimental conditions.

4.1.3 Apple

As the greatest source of variability which affects O_2 consumption and CO_2 production data is mainly due to the different histories of utilised samples (harvesting time, storage conditions adopted, possible treatments and so on), the raw data were usefully transformed to make them comparable apart from their harvesting time and production site. A physiological characterisation of material used could be carried out looking to O_2 consumption and CO_2 production rates (RO_2 and RCO_2) using two different surrounding atmospheres: aerobic condition (gas composition close to that of air), when the O_2 consumption rate reaches its maximum value (aerobic metabolism); atmosphere of pure nitrogen, where RCO_2 reaches its

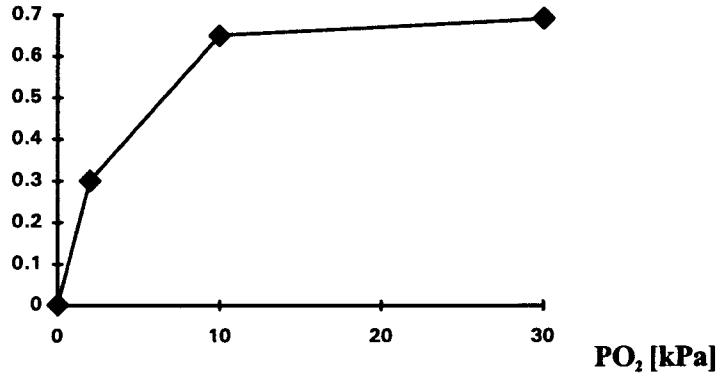
maximum value (alcoholic fermentation). All other respiratory data could be related to these and expressed as their percentages.

In fact, the aerobic respiration process can be regarded as the cellular oxidation of a metabolic substrate which, at least for apple, is mainly constituted by sugars which react with O_2 to give H_2O and CO_2 and to produce energy stored as APT:

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ + Energy (36 ATP)

The aerobic respiration rate (R_{ar}) changes as a function of PO_2 of the surrounding atmosphere and increases when increasing values of PO_2 are employed to reach a maximum asymptotic value according to Michaelis-Menten kinetics:

$R_{ar}=R_{O2}$ [mmol·kg^{-1}·h^{-1}]



$$R_{ar} = \frac{k_c \cdot E^\circ \cdot [O_2]}{K_M + [O_2]} \qquad \text{<eq. 8>}$$

While k_c and K_M represent respectively the kinetic and the Michaelis constant connected with the enzymatic unit involved in the rate determining step, E° is the

sum of the concentrations (moles/kg of apples) of all possible chemical forms (free or bound) shown by this active protein.

If the total enzymatic concentration (E°) could be strongly affected by the history of employed apples, the specific activity of this molecular unit (k_c and K_M) would remain quite unchanged.

The aerobic respiration rate data can be expressed as a function of the maximum asymptotic rate ($R_{ar,max}$) which is equal to the product between k_c and E°:

$$\lim_{[O_2]\rightarrow\infty} \frac{k_c \cdot E^\circ \cdot [O_2]}{K_M + [O_2]} = \frac{k_c \cdot E^\circ \cdot [O_2]}{[O_2]} = k_c \cdot E^\circ = R_{ar,max}$$

so that the following equation could be obtained:

$$\frac{R_{ar}}{R_{ar,max}} = \frac{[O_2]}{K_M + [O_2]}$$

According to this equation apples characterised by different histories, would have the same behaviour if their aerobic respiratory activity are connected to their maximum aerobic respiration rate to make comparable the experimental data obtained using fruits characterised by different histories.

In fact, the ratio between the aerobic respiration rate, evaluated at a certain value of PO_2, and the corresponding $R_{ar,max}$ would be independent from the sample of apple employed.

While the raw R_{ar} experimental data, evaluated using three different apples supplies, do not show any logical evolution as a function of PO_2 employed, the R'_{ar} transformed data increase regularly when PO_2 increases (Figure 8 of the annexes).

According to results previously obtained (Andrich et al, 1994a) and data reported in literature (Kerbel et al., 1990), when a PO_2 value greater than 5÷7 kPa is employed, a CO_2 production rate (RCO_2) similar to that of O_2 consumption (RO_2) is obtained, even when high values of PCO_2 are adopted (0÷20 kPa). The lack in these conditions of significant differences between RO_2 and RCO_2 underlines the absence of any alcoholic fermentation (Table 15 of annexes).

Moreover utilizing a kinetic approach, the role of PCO_2 on aerobic respiration rate was also investigated. The CO_2 inhibition on respiratory activity is essentially due to its ability to bind one or more enzymes involved in the respiratory pathway. As a function of the location of the binding site of CO_2, it was possible to hypothesise two different kinetic mechanisms which generated two different mathematical equations (Andrich et al., 1994a). According to Kerbel et al. (1990), the experimental data elaboration seemed to support the hypothesis of a binding site of CO_2 located in the glicolitic pathway. It could explain the lack of any fermenting activity working at room temperature (2±1 °C) and at a $PO_2 > 7$ kPa, even if increasing values of PCO_2 were adopted. In fact, increasing values of PCO_2 would induce a decrease of glicolitic rate, without changing that of following oxidative step. So the rate of O_2 uptake would be equal to that of CO_2 production, as no fermentation occurs.

The data collected maintaining PO_2 close to zero and increasing PCO_2 are really close to those reported in a previous paper (Andrich et al., 1994c).

The amounts of CO_2 produced (RCO_2) as well as those of O_2 consumed (RO_2), were measured using fruits stored at PO_2 close to zero (PO_2 = 1 kPa) and at increasing values of PCO_2 ($0 < PCO_2 < 40$ kPa).

In order to verify the biological status of utilised apples, their respiratory activity was also evaluated, before and after every cycle of anaerobic determinations, using gas mixtures similar to air.

The RO_2 values, calculated during these aerobic runs, were enough close to those of RCO_2 and did not seem to be significantly affected by the previous anaerobic conditioning.

If, in anaerobic conditions ($PO_2 = 0$), PCO_2 is increased, a sensible decrease of fermentation rate is observed. Moreover the decrease of anaerobic respiration rate is linearly well correlated to PCO_2, as shown by the value of the correlation coefficient obtained (r = - 0.95).

The experimental data related to CO_2 production and O_2 consumption rates shown by *Golden Delicious* apples, maintained at a PCO_2 value close to zero and at different values of both PO_2 (0, 3, 5, 10 and 21 kPa) and temperature (21, 16, 6 and 1 °C), were utilised to evaluate the temperature evolution of aerobic respiration rate (Table XX of annexes).

The rate of aerobic respiration (R_{ar}) was assumed to be directly related to the amount of O_2 dissolved in the cellular solution ($[O_2]_{cs}$), valuable as a function of temperature utilised by the equations already reported in the modelling of internal diffusion (Table 14).

So the Michaelis Menten equation introduced to describe the evolution of aerobic respiration could be expressed as a function of the concentration of O_2 dissolved in the cellular soap:

$$R_{ar} = k_{ar} \cdot [O_2]_{cs} / (K_M + [O_2]_{cs}) \qquad \text{<eq. 8>}$$

where: k_{ar} is equal to the product between the kinetic constant and the total enzyme concentration involved in the rate determining step, and represents the maximum rate of this oxidative step then also of aerobic respiration. K_M is the Michaelis constant connected with the same enzyme.

The mean values of the rates connected to CO_2 production and O_2 consumption by *Golden Delicious* apples maintained at a PCO_2 value close to zero and with different values of both PO_2 (0, 3, 5, 10 and 21 kPa) and temperature (21, 16, 6 and 1 °C) were determined (Table 16 of annexes). At all the temperatures tested RCO_2 was similar to RO_2 when $PO_2 \geq 10$ kPa. However RCO_2 exceeded RO_2 when the amount of O_2 in the surrounding atmosphere decreased (5, 3 and 0 kPa). When PO_2 decreased, both R_{res} and R_{af} took place simultaneously, and with a PO_2 close to 0 the aerobic respiration was not detectable while the alcoholic fermentation reached its maximum value. Aerobic and anaerobic respiration decreased as storage temperature decreased.

To evaluate the temperature dependence of the two kinetic constants k_{ar} and K_M involved in eq. 8, the concentration of O_2 dissolved in the cellular solution ($[O_2]_{cs}$) must be known. The $[O_2]_{cs}$ value can be calculated as a function of temperature and PO_2 by equation 7:

$$K_{1,2,O2\,(T=T)} = [O_2]_{cs} / [O_2]_{is} \qquad \text{<eq. 3>}$$

$$= R \times T \times d_{ap} \times K_{p,O2\,(T=21°C)} \times e^{-\Delta H°O2/R \times [1/(T) - 1/(294.15)]} / I.S. \qquad \text{<eq. 7>}$$

where:

R	= ideal gas constant	= 8.31	$[m^3 \times Pa \times mol^{-1} \times K^{-1}]$;
d_{ap}	= apple density	= 820	$[kg \times m^{-3}]$;
$K_{p,O2}$	= equilibrium constant (T = 21°C)	= 5.1×10^{-10}	$[mol \times kg^{-1} \times Pa^{-1}]$;
DH°O2/R	= reaction enthalpy / ideal gas constant	= -3.70×10^3	[K];
I.S.	= volume fraction due to intercellular space	= 0.21;	

At steady state, the rate of O_2 diffusion through the apple skin becomes equal to that of RO_2 and the concentration of O_2 dissolved in the cellular solution ($[O_2]_{cs}$) of the apples could be evaluated on the basis of respiratory activity experimentally measured:

$$RO_2 = k_{1,-1,O2} \times A \times (H_{O2} \times PO_2 - [O_2*]) \qquad \text{<eq. 1>}$$

Combining equations 1, 7 and 8 and then solving for $[O_2]_{cs}$ the following expression could be obtained :

$$[O_2]_{cs} = K_{1,2,O2(T=T)} \times (k_{1,-1,O2} \times A \times H_{O2} \times PO_2 - RO_2) / (k_{1,-1,O2} \times A \times (1 + K_{1,2,O2(T=T)})) \qquad \text{<eq. 9>}$$

So on the basis of PO_2 employed and of related experimental values of RO_2 obtained it was possible to calculate the corresponding $[O_2]_{cs}$.

In the plane ($1/RO_2$; $1/([O_2]_{cs})$ the inverse of equation 8 represents a straight line whose slope is equal to the K_M/k_{ar} ratio while its intercept with the y-axis allows $1/k_{ar}$ to be calculated:

$$1/RO2 = K_M/k_{ar} \times 1/[O_2]_{cs} + 1/k_{ar}$$

The values of k_{ar} and K_M constants involved in the Michaelis-Menten-like equation (eq. 8) were then determined at 4 temperatures, applying the least squares method to the inverse form of equation 8 (Table 17 of annexes).

The values of the squares of the correlation coefficients (r^2) calculated for the four straight lines obtained give a measure of the reliability of the hypothesis adopted as well as of the mathematical equations obtained (Table 17 of annexes).

The experimental data so obtained clearly shown that the kinetic constant k_{ar} increased with temperature adopted while the Michaelis constant K_M decreased when temperature increased.

The temperature dependence of both constants could be satisfactorily described by Arrhenius' equation:

$$k_{ar(T=T)} = k_{ar}^{\circ} \times e^{-\Delta E^{\circ}ar/(R \times T)} \qquad \text{<eq. 10>}$$

$$K_{M(T=T)} = K_M^{\circ} \times e^{-\Delta E^{\circ}M/(R \times T)} \qquad \text{<eq. 11>}$$

where ΔE°_{ar} and ΔE°_{M} represent the two activation energies.

To evaluate the two parameters involved in each equation (k_{ar}°, ΔE°_{2} and K_M°, ΔE°_{M}) the least squares method was applied to $k_{ar(T=T)}$ and $K_{M(T=T)}$ data (Table 16) utilising the linearized form of equations 10 and 11. In fact, in the plane (ln (k_{ar} , K_M) ; 1/T) eq. 12 and eq. 13 represent two straight lines whose slopes are equal to the ratio between the activation energies ($\Delta E^{\circ}_{ar,M}$) and the ideal gas constant (R), while the intercepts with the y-axis allow the values of k_{ar}° and of K_M° to be determined (table 18 of annexes):

$$\ln(k_{ar}) = \ln(k_{ar}^{\circ}) - \Delta E^{\circ}_{ar}/R \times 1/T \qquad \text{<eq. 12>}$$

$$\ln(K_M) = \ln(K_M^{\circ}) - \Delta E^{\circ}_{M}/R \times 1/T \qquad \text{<eq. 13>}$$

Moreover the ratio between the activation energy ($\Delta E^{\circ}_{ar} = 8.31 \times (5097 \pm 3727) = 42.4 \pm 31.0$ kJ×mol^{-1}) to the ideal gas constant (R) calculated for k_{ar} was 5097 ± 3727 °K very close to that (5447 ± 4864 °K) reported in a previous paper where a different theoretical approach was employed (Andrich et al., 1995).

4.2 Internal diffusion in produce

Apple fruits

O_2 diffusion. The means of $k_{i,O2}$ and H_{O2} evaluated at room temperature [T = 21±1°C, $k_{i,O2} = (4.3 \pm 1.2) \cdot 10^{-4}$ mmol · s^{-1} · m^{-2} · kPa^{-1}; H_{O2}, = 0.17±0.07 mmol · kg^{-1} · kPa^{-1}; p=0.05] seem to be very close to those obtained during previous research [T = 21±1°C, $k_{i,O2} = (4.4 \pm 0.9) \cdot 10^{-4}$ mmol · s^{-1} · m^{-2} · kPa^{-1}; H_{O2} = 0.17±0.04 mmol · kg^{-1} · kPa^{-1}; p=0.05] where *Golden Delicious* apples supplied from a different production site were employed (Andrich et al., 1989b).

To demonstrate the possible existence of a statistically significant evolution of the values calculated for $k_{i,O2}$ and H_{O2}, as a function of the temperature used, analysis of variance was carried out. As the values of F calculated for both constants ($F_{ki/O2} = 0.23$ and $F_{H/O2}=0.48$) were lower than the tabulated one (Ftab = 4.53; p=0.05), a statistically significant change with temperature could not be proved. In Figures 6 and 7 (see annexes) the averages of $k_{i,O2}$ and H_{O2} values are plotted as a function of the corresponding temperatures together with their confidence intervals evaluated on the basis of the value assumed by the least significant difference (LSD). According to analysis of variance (F test), the experimental points, which

differ between themselves less than the LSD, are randomly placed around the mean value [$k_{i,O2} = (4.4 \pm 0.9) \cdot 10^{-4}$ mmol $\cdot$ s^{-1} $\cdot$ m^{-2} $\cdot$ kPa^{-1}, $H_{O2} = 0.17 \pm 0.04$ mmol $\cdot$ kg^{-1} $\cdot$ kPa^{-1}; p=0.05).

While it is not so easy to explain the lack of any significant change of the global O_2 mass-transfer constant ($k_{i,O2}$) with temperature, an explanation for the same behaviour shown by the equilibrium constant (H_{O2}) can be tentatively proposed. This parameter is related to the amount of gas permeated into the fruit when the equilibrium condition between apples and the gaseous surrounding atmosphere is reached. In these conditions, the large fraction of permeated gas fills the intercellular space (21-23% of total apple volume - Bauman and Henze, 1983) and its amount cannot vary significantly within the range of temperatures tested. In fact, if the ideal gas equation is applied, an equivalent gas accumulation inside the intercellular space is obtained:

$$n_{T1=1°C}/n_{T2=21°C} = [(P \cdot V_{i.s.})/(R \cdot T_1)]/[(P \cdot V_{i.s.})/(R \cdot T_2)] = T_2/T_1 = 1.07$$

where:

n	= moles of gas in the intercellular space	[moles];
$V_{i.s.}$	= volume of intercellular space in 1 kg of apples	[l];
R	= ideal gas constant	[atm·l·mol^{-1}·°K^{-1}];
T	= temperature	[°C].

CO_2 diffusion. As reported for O_2 diffusion, the mean values of the data connected with the two mass-transfer constants evaluated at room temperature [T = 21 °C, $k_{i,CO2} = (10.5 \pm 2.4) \cdot 10^{-4}$ mmol $\cdot$ s^{-1} $\cdot$ m^{-2} $\cdot$ kPa^{-1}; $H_{CO2} = 0.25 \pm 0.02$ mmol $\cdot$ kg^{-1} $\cdot$ kPa^{-1}; p=0.05] do not appear to be significantly different from those obtained during previous research [T = 21 °C, $k_{i,CO2} = (6.5 \pm 3.2) \cdot 10^{-4}$ mmol $\cdot$ s^{-1} $\cdot$ m^{-2} $\cdot$ kPa^{-1}; $H_{CO2} = 0.13 \pm 0.12$ mmol $\cdot$ kg^{-1} $\cdot$ kPa^{-1}; p=0.05] where *Golden Delicious* apples supplied from a different production site were employed (Andrich et al., 1989a).

While, as found for O_2 mass-transfer, the F value calculated for the equilibrium constant H_{CO2} is not statistically significant ($F_{H/CO2}$,calc. = 0.23 versus Ftab.= 3.63; p=0.05), the $F_{ki/CO2}$ (18.16) is greater than this tabulated value (3.63), thus emphasising the existence of significant change of this parameter with temperature.

As reported for H_{O2}, the experimental points connected with H_{CO2}, which are randomly placed around the mean value [$H_{CO2} = 0.23 \pm 0.07$ mmol $\cdot$ kg^{-1} $\cdot$ kPa^{-1}; p=0.05), do not differ more than LSD (Figure 7), while, as temperature decreases, a slight but statistically significant decrease in $k_{i,CO2}$ values can be seen (Figure 6).

According to the Arrhenius' equation, the dependence on temperature of the constant $k_{i,CO2}$ can be expressed by the following equation:

$$k_{i,CO2,T} = A \cdot e^{-\Delta E^*_{CO2}/(R \cdot T)}$$

whose logarithmic form allows the related activation energy to be calculated:

$$\ln k_{i,CO2,T} = \ln A - \Delta E^*_{CO2}/R \cdot 1/T$$

In fact, in the plane [1/T ; ln $k_{i,CO2;T}$] this equation represents a straight line ($r^2 = 0.88$), whose angular coefficient is equal to $\Delta E^*_{CO2}/R$ ratio (1785±397°K; p=0.05) while the intercept with the y-axis (- 0.78± 1.40; p=0.05) gives the value of ln A:

$\Delta E^*_{CO2} = \Delta E^*_{CO2}/R \cdot R = (1785.3 \pm 397.2) \cdot 1.987$ $= 3547 \pm 789$ $[cal \cdot mol^{-1}] \cdot$

$= 3.55 \pm 0.79$ $[kcal \cdot mol^{-1}]$

While the temperature behaviour of H_{CO2} can be explained similarly to that proposed for H_{O2}, it is more difficult to explain the difference shown by the global mass-transfer constant k_i as a function of the respiratory gas analysed. The greater water solubility of CO_2 could play a role in determining both its higher mass transfer rate and the sensitivity to temperature found in this experiment.

***Witloof* Endive (chicory)**

O_2 diffusion. As the effect of temperature on gas permeation is concerned, Table 8 and 9 (see annexes) report the evolution of the means of constants $k_{i,O2}$ and H_{O2} as a function of temperature and PCO_2 adopted.

While a significant temperature evolution could be put in evidence for values collected using a PCO_2 close to 0 kPa, this did not happen when a $PCO_2 \approx 40$ kPa was employed as shown by analysis of variance carried on both data sets obtained (F test).

Experimental data connected to O_2 mass transfer trough chicory skin seemed to be largely affected by respiratory metabolism which changes significantly the gas composition inside the product and could invalidate mass transfer data collected. Only adopting suitable working conditions (high PCO_2 values) it is possible to reduce respiratory incidence and to obtain a valid experimental measure of skin permeability.

CO_2 diffusion. As shown by data reported in Table 10 (see annexes), the experimental values obtained are affected by increasing variability as temperature increases. In fact the confidence intervals (c.i. p=0.05) related to the mean values of these two constants and particularly of $k_{i,CO2}$ are higher for data collected at 21 than 1°C.

H_{CO2} mean values do not seem to vary significantly with temperature while $k_{i,CO2}$ data increase when temperature increases but, as shown by the related c.i. values, no significant evolution could be put in evidence.

Tomato fruits

O_2 diffusion. As previously found for chicory and partially also for apple fruit, no significant temperature evolution could be put in evidence both for $k_{i,O2}$ and H_{O2}. In fact, as shown by analysis of variance reported in Table 11 (see annexes), F_{calc} is in any case minor than the tabulated value F_{tab} (p=0.05).

CO_2 diffusion. Analogously to what already reported for O_2 mass transfer constants also for $k_{i,CO2}$ and H_{CO2} none significant temperature evolution could be underlined as shown by statistical analysis reported in Table 12 (see annexes).

In fact F_{calc} values are marked smaller than the tabulated F_{tab} (p=0.05).

Conclusion

As shown by data reported in Table 13 (see annexes), the saturation equilibrium constant H_G does not seem to vary as a function of gas analysed for apple and chicory ($H_{O2} \approx H_{CO2}$) while H_{O2} of tomato is significantly different from all the other two H_{O2} values. The saturation equilibrium constant H_G is related to the total amount of gas permeated inside the product and in particular to the intercellular space where the great part of permeated gas is located. As the densities of apple (0.83 $g \cdot cm^{-3}$) and chicory (0.85 $g \cdot cm^{-3}$) do not seem to differ significantly, also the volumes of intercellular spaces would be comparable, this is not the case of tomato which shows a more high density (1.00 $g \cdot cm^{-3}$) and then also a more reduced

intercellular space which would justify tomato H_{O2} value. The H_{CO2} of tomato does not seem to differ from those related to the other two products, this may be due to the different solubility showed by the two respiratory gases in aqueous solutions. In fact while CO_2 is largely soluble O_2 shows a more reduced water affinity. Tomato is richer of water than apple and chicory and this may justify the values assumed by H_G constant as a function of the respiratory gas analysed.

As global mass transfer coefficient $k_{i,G}$ is concerned, no particular differences were found as a function of product used, when O_2 was employed as diffusing specie; on the contrary, when CO_2 was utilised, significant differences could be underlined. A significant temperature evolution was found for $k_{i,CO2}$ when apples were employed, while for chicory high values were obtained for this constant although these data are affected by a consistent variability. Tomato shows a $k_{i,CO2}$ value of the same order of greatness of that of apple but unlikely than this not temperature dependent.

It is not easy to explain these different behaviours, which could be length to the different role of the two gases in the respiration process. In fact, while O_2 represents an essential substrate of aerobic respiration, CO_2 is a catabolic product which has to be quickly removed from cellular sap acting on stomatic regulation. The stomatic regulation, whose efficiency could change with horticultural product analysed, would act as a function of CO_2 amount to be removed and temperature adopted to make easier its permeation trough product skin so to determine deeply varying values of $k_{i,CO2}$.

Modelling

As according to Burton (Burton, 1974, 1978; Cameron and Reid, 1982) the resistance to respiratory gases diffusion (G = O_2 and CO_2) is mainly located on product skin, no resistance to G diffusion was assumed to occur inside the horticultural product so that an instantaneous equilibrium between the two main phases present inside the product (gas phase connected with intercellular space and liquid phase due to cellular sap) was assumed to take place (Andrich et al., 1989a, 1989b, 1990). On this hypothesis every fraction of gas permeated through product skin is instantaneously splitted into the phases (intercellular space and cellular sap) in a ratio equal to the saturation equilibrium constant $K_{i,2,G}$. The driving force (gradient), connected with the mass transfer expression, will be given by the difference between the G concentration in the storage atmosphere (PG), evaluated by the corresponding equilibrium value of saturation ($H_G \cdot PG$; H_G = Henry's constant relating to saturation equilibrium), and the sum ($[G^*] = [G]_s + [G]_{cs}$) of concentrations connected with the two phases:

$$R_G = d[G]/dt = k_{1,-i,G} \cdot A \cdot (H_G \cdot PG - [G^*]) \quad \text{<eq. 1>}$$

where:

$R_G = d[G]/dt$ = mass-transfer rate, moles of G which diffuse in an hour into a kg of the product apples [$mol \cdot kg^{-1} \cdot h^{-1}$];

$k_{1,-i,G}$ = global mass-transfer constant [$kg \cdot h^{-1} \cdot m^{-2}$];

A = the surface area of product per unit of weight [$m^2 \cdot kg^{-1}$];

H_G = Henry's constant relating to saturation equilibrium, which is equal to the ratio between the G permeated inside a kg of product ($[G^*] = [G]_s + [G]_{cs}$) and the corresponding PG in the surrounding atmosphere when the equilibrium between these two phases would have been reached = $[G^*]_{eq} / PG_{eq}$ [$mol \cdot kg^{-1} \cdot Pa^{-1}$];

PG = partial pressure of G in the storage atmosphere [Pa];

$[G^*]$ = G concentration inside the product ($[G^*] = [G]_s + [G]_{cs}$) [$mol \cdot kg^{-1}$].

The G permeated into a kg of fruits ($[G^*]$) will be quickly splitted into the two main phases (cellular saps and intercellular spaces) which can be individuated inside an horticultural product (Andrich et al., 1991):

$$[G^*] = [G]_{is} + [G]_{cs} \qquad \text{<eq. 2>}$$

where:

$[G]_{cs}$ = concentration of G dissolved in the cellular solution of a kg of product [mol·kg^{-1}];

$[G]_{is}$ = concentration of G present in the intercellular space [mol · kg^{-1}]

In fact, according to Burton's hypothesis (1974; 1978), inside apple fruit an instantaneous equilibrium between the intercellular space and the cellular sap takes place such that:

$$K_{1,2,G} = [G]_{cs} / [G]_{is} \qquad \text{<eq. 3>}$$

where $K_{1,2}$ is the related not dimensional equilibrium constant.

Combining equation 2 with 3 the following relation can be obtained:

$$[G^*] = [G]_{is} + [G]_{cs} = [G]_{cs} / K_{1,2,G} + [G]_{cs}$$
$$= [G]_{cs} \cdot (K_{1,2,G} + 1) / K_{1,2,G} \qquad \text{<eq. 4>}$$

$K_{1,2,G}$ can be calculated on the basis of the assumptions and data reported in literature as a function of another parameter ($K_{p,G}$), which describes the equilibrium occurring between the concentration of G dissolved inside product cells ($[G]_{cs}$) and the partial pressure ($PG_{i.s.}$) of this gas in the intercellular space. The $K_{1,2,G}$ value can be calculated by the following equation (Andrich et al., 1991):

$$K_{1,2,G\,(T=T)} = R \cdot T \cdot d_p \cdot K_{p,G\,(T=T)} / I.S. \qquad \text{<eq. 5>}$$

where:

R = ideal gas constant [m^3·Pa·mol^{-1}·K^{-1}];

T = temperature [K];

d_p = product density [kg · m^{-3}];

$K_{p,G}$ = equilibrium constant [mol · kg^{-1}· Pa^{-1}];

I.S. = fraction of product volume occupied by the intercellular space.

While the diffusional ($k_{1,-i,G}$) and the equilibrium (H_G) constants connected with the G mass-transfer through product skin were assumed to be temperature independent, at least in the range tested, the $K_{1,2,G}$ is affected by temperature (eq. 3). So that of the parameters involved in equation 5 only $K_{p,G\,(T=T)}$ was assumed to vary with temperature. In fact both d_p (product density) and I.S. (fraction of product volume connected with intercellular space) should not change significantly.

The temperature dependence of $K_{p,G}$ has been described according to Vant'Hoff's equation:

$$K_{p,G\,(T=T)} = K_{p,G\,(T=21°C)} \cdot e^{-\Delta H°_G / R \cdot [1/(T) - 1/(294.15)]} \qquad \text{<eq.6>}$$

In the plane (1/T - 1/294.15 ; ln $K_{p,G\,(T=T)} / K_{p,G\,(T=21°C)}$) equation 6 represents a straight line passing through the origin of the axes whose slope is equal to $-\Delta H°_G/R$ ratio:

$$\ln (K_{p,G\,(T=T)} / K_{p,G\,(T=21°C)}) = -\Delta H°_G/R \cdot [1/(T) - 1/(294.15)]$$

Applying the least squares method to this linearized form of Vant'Hoff's equation and using data reported by Burton (1974), who assumed the respiratory gases solubility in the cellular sap to be equivalent to that occurring in a 0.4 M sucrose aqueous solution, it was possible to calculate the slope $\Delta H°_G/R$.

Combining equations 5 and 6, the following relation was obtained, which allows the calculation of $K_{1,2,G}$ constant as a function of temperature employed:

$$K_{1,2,G\,(T=T)} = [G]_{cs} / [G]_{is}$$

$$= R \cdot T \cdot d_p \cdot K_{p,G\,(T=21°C)} \cdot e^{-\Delta H°_G/R \cdot [1/(T) - 1/(294.15)]} / I.S. \qquad \text{<eq. 7>}$$

Table 14 reports (see annexes) the equations and variables involved in the modelling of internal diffusion.

4.3 Packaging films, gas and water vapour permeability

The results obtained for the materials investigated show for gas permeability, that this may be modelled by an

→ Arrhenius behaviour

in terms of temperature. Nevertheless, the individual influences of different sections of identical films are relatively large and of the same order of magnitude as the temperature effect in the range investigated:

Observed deviations obtained in measurements by using different types of equipment and different samples from the same sample roll may be as high as ± 25 %. In addition, a systematic deviation of themanometric equipment vs. the carrier gas equipment is observed, the latter giving values overall higher by 20 %

For the dependence of gas permeability on relative humidity, the situation is even more complex:

Under measurement conditions, it is difficult to maintain reproducibly relative humidity values above 90 %, due to unavoidable slight differences in local temperature. That means that it is practically impossible to achieve conditions which are close to realistic situations in a defined way. Under realistic conditions, the humidity inside packagings will always be close to 100 %; otherwise the selected film does not represent an optimum with respect to preservation of humidity of the packed produce. In this case, we will always have some condensation, which may be kept relatively low by a proper choice of the film material, but will in principle be generally present.

As to be seen from section 3.3, we have to calculate with an increase in gas permeability of about factor 2 ... 10 under liquid conditions which has also to be taken into account under condensation conditions, according to the surface coverage of the films with water condensate. Therefore, it appears to be reasonable to avoid an analytical expression of the dependence of gas permeability on humidity by allowing a schematic increase of the permeability by a factor of 2 relative to dry conditions due to the humidity released by the produce. This is in concert with the observation on measurements on model packagings which overall show that the gas permeabilities as obtained under conditions without condensation are too low by a factor of about 2.

The same argument is valid for the water vapour permeability which also may rise substantially under condensation conditions. Also here, the assumption of an enhanced water vapour permeability by a factor of 2 appears to be reasonable, see section 3.3.

4.4 Packaging experiments

4.4.1 Commercial type of packagings

Tomato

The gas composition in the package of tomatoes hardly changed for the co-polyester-ether package and the PVC-package while for the P plus-packages the O_2- and CO_2-concentration changed increasingly as the amount of micro perforations falls off. Changes are more pronounced at higher temperatures. Important temperature dependencies were only observed for the P plus 10 K foil.

The weight loss of the tomatoes during the packaging experiment was minimal for the 10 K film and reached a maximum value for the co-polyester-ether-film.

Chicory

Films with low oxygen permeability such as PD 900 and OPP for packaging chicories result in a perfect prevention of greening when the shoots are exposed to indirect daylight but severe hypoxia generated by the films is responsible for fermentation with, as a consequence, an unpleasant smell at the opening of the packs.

Films with intermediary oxygen permeability (PD 961 and 10K) do not trigger anaerobic metabolism but do not completely prevent greening. However, the colour of endive shoots is still acceptable after two days at 21 °C and under daylight.

More permeable films (40K, 200K, PD941) result in a marked reduction in wiltering compared to control samples packed in a macroperforated film but all these films do not prevent greening.

Hydrophilic films (Copolyether-ester and Osmolux) are not suitable for endive shoots packing since dehydration of outer leaves makes commodity not saleable after 3 days at 11 °C.

Apple

Overall, the polyester/polyether copolymer gave the highest O_2 and lowest CO_2 concentrations at all temperatures. PVC yielded slightly higher CO_2 and slightly lower O_2 concentrations in comparison with the polyester/polyether copolymer. Cellulose acetate film was much less permeable and gave much higher CO_2 and lower O_2 values. However the temperature dependency of the gas concentrations was much higher than the PVC and the polyester/polyether copolymer foils, especially for CO_2.

For the trials with a varying temperature the gas composition will change more and more as the temperature increases and this for both PVC and polyester/polyether copolymer. The cellulose-acetate film has a very low permeability for O_2 and CO_2 and at 1 and 11 °C the O_2-concentration gets below 5 kPa, right up to ±1 kPa; at the higher temperature of 21 °C there's an important change in permeability of the film. The permeability for O_2 and CO_2 increases so that the O_2- and CO_2-pressure in the package changes to more safe values. The weight loss during these experiment were not significantly different for the three types of film.

4.4.2 Model packagings

These experiments mainly served as verification for the MASTER model. The overall finding - see also above - was that the gas and water vapour permeability measurements yielded too low values compared with realistic conditions. This can be explained by the additional effect of condensation.

4.5 Modelling of experiments

Discussion of the MAP model

The basic elements of a MAP model are the processes for the respiration of the product and the diffusion through the film. They are discussed elsewhere in detail. In addition the development from a general MA model towards the MASTER model is caused by the incorporation of specific (flexible) packaging characteristics, a dynamic temperature, the waterhoushold from the product and finally the keeping quality is included in order to have some grip on the feasibility of the package from quality point of view.

The respiration and diffusion are combined at the level of the fluctuation in particles of the individual gases(dn/dt). It is assumed that all gases behave as ideal gases. From the general gas law P.V=n.R.T follows that the change of partial pressures in the microclimate:

$$\frac{dP}{dt} = \frac{R_{gas} \bullet T_{macro}}{V_{micro}} \bullet \frac{dn}{dt}$$

The volume inside the package is calculated as difference between package volume and product volume. In case of a flexible package (bag) the pressure inside the package will be constant and the volume will adapt itself to the amount of particles present. Depending on the situation the volume can decrease (shrink to fit the product) or increase up to a maximum allowable volume. From this moment the internal pressure will change again.

The temperature outside the package ($temp_{macro}$) is in the model defined by the user. The temperature inside the package ($temp_{micro}$) is assumed to follow the macroclimate instantly. The change of the temperature of the product can be described as:

$$\frac{d\ temp_{prod}}{dt} = \frac{\lambda \bullet A_{prod} \bullet (temp_{micro} - temp_{prod})}{c_{heat} \bullet mass_{prod} \bullet R_{prod}}$$

with l as the heat conductivity , c_{heat} the specific and R_{prod} and A_{prod} the radius and area of the product assuming a spherical body.

The water housekeeping is build up by the diffusing through the foil and the product transpiration. Depending on temperature, air can contain more ore less water until a certain saturation level. Beyond this level condensate is formed. The temperature effect is included as a result of the fact that the saturation of the relative humidity (RH) depends on the temperature.

The transpiration of the product $(dH_2O/dt)_{prod}$ is calculated using the given specific transpiration:

$$\left(\frac{dH_2O}{dt}\right)_{prod} = spec_{mois} \bullet mass_{prod} \bullet (ph2o_{sat}(temp_{prod}) - ph2o_{micro})$$

The mass loss of the product is restricted only as water loss because of transpiration. The internal vapour pressure of the product is fixed at saturated vapour pressure at the product temperature. This indicates that in the situation of saturated air inside the package there is no driving force left for transpiration, unless the product temperature differs from the surrounding temperature.

As MAP is aiming at prolonging shelf life, also a general model on keeping quality is incorporated to give an indication of the success of the MA package in terms of keeping quality. The change of keeping quality (Polderdijk et al. 1995; Sloof et al. 1996; Tijskens, 1995; Tijskens en Polderdijk, 1996) is calculated based on the relative respiration in terms of CO_2 production which is de actual respiration as compared to the respiration under standard atmospheric conditions:

$$rel_{resp} = vco\frac{2}{vco\,2(\text{atmospheric conditions}, T_{standard})}$$

The initial keeping quality at standard conditions is given by:

$$KQ_{stand,0} = \frac{KQ_{ref}}{k_{st}}$$

The actual decay of quality in MAP is described by the (compound) rate k_{kq}. The rate of decay at given standard conditions is described by the (compound) rate k_{st}. Both of the rates are temperature dependent according to Arrhenius. This results in:

$$\frac{dKQ_{stand}}{dt} = rel_{resp} \bullet \frac{k_{kq}}{k_{st}}$$

Within the project the models of respiration of the product and the diffusion principles of the packing materials were verified The models were combined with specific (flexible) packaging characteristics, a dynamic temperature, the water household from the product and the keeping quality. This finally leads toward a simulation model with the complete behaviour of a MA package in a varying temperature regime. Analysing the results of the MASTER model together with the MA packing experiments the model seems appropriate to support the packaging technologist. The MASTER model is able to simulate the MAP experiments. within a few absolute % in the gas concentration. Never the less the user should be aware of the fact that working with natural products inherently means dealing with sources of biological variation. Furthermore, plastic films are also not perfectly homogeneous. So, the question emerges what the effect is of these sources of variation on the performance of the package. To enable the user to evaluate the effect of variation the system is equipped with a Monte Carlo type simulation generator.

Possible sources are:
- mass of the packed product
- gas exchange rates of the product
- thickness of the film
- initial quality

- size of the package in case of a flexible bag

Several sources of variation can be combined. Multiple simulation are generated using random input values for the parameters mentioned above using normal distributions with the specified deviations. As a result the mean behaviour will be calculated together with the limits covering 95% of the simulated values. In this way the user can evaluate the effect of variation.

Summarising the MASTER model is a valuable tool to support the packaging technologist. The model is flexible. It has a wide range of functionality's by setting the correct values of the input parameters. The most important are: MA-packaging in varying temperature regimes, gas-packaging in varying temperature regimes, quality effects of unpacked product and in CA-storage, and analysing compound foils during diffusion measurements.

Despite the fact that the MASTER model is very powerful simulation tool for a broad range of applications it should be noted that the validity can be limited because of the boundaries of this project.

· The individual models incorporated are all of them physically or physiologically founded. Still, when using models outside the range where they were validated one runs a certain risk. So the MAP-model should be applied within or around the area validated (0-21% O_2, 0-20% CO_0, 0-21°C).

· The MAP-model was developed for simulating small size consumer packages assuming a homogeneous temperature inside the package corresponding to the temperature of the environment. When simulating larger packages, or pallets with packages, one should take into account the changed dynamics of heating and cooling and the inhomogeneous heat distribution. To overcome this partly, the possibility is created to feed the model with measured temperatures, for example for the package in the centre of a pile.

· The model also assumes a homogeneous distribution of O_2, CO_2, N_2, H_2O in the gas phase inside the package. So no diffusion within the package is described. For the small sized consumer packages this is a realistic approach.

5 Conclusion

The aim of the MASTER project was to supply a measurement methodology which allows

- to assess the parameters for packed produce and for the packaging materials relevant for Modified Atmosphere Packaging
- and to model different combinations of produce, packaging materials and packaging layouts.

The experimental assessment of the parameters for produce and packaging should follow the sequence

→ to determine the optimum conditions for a given produce in terms of the composition of the surrounding atmosphere (oxygen, carbon dioxide, temperature, relative humidity),

→ to determine the respiratory activity of the produce not only under optimum conditions, but also outside over a certain span of partial pressures of the relevant gases and of temperatures,

→ to determine the permeability of the skin of the produce and the internal diffusion, with respect to the relevant gases,

→ to determine the permeability of films in dependence of temperature, relative humidity and to give an assessment of the effect of condensation.

After having gathered the necessary data, a proper selection of a packaging system should be possible in the following way:

→ To do a first tentative selection of a packaging configuration (material, material thickness, geometry)

→ to model the combined behaviour of produce and packaging - by help of the MAP simulation program - by taking into account the external conditions, namely temperature and climatic conditions during distribution and storage. The results of this modelling procedure are the following parameters:

- ❒ Gas composition inside the packaging over storage time
- ❒ Water losses of the produce
- ❒ Possible situations where safe storage conditions are exceeded
- ❒ An assessment of keeping quality

The comparison of these parameters with the optimum conditions for the produce should help either to verify or to approach the correct selection of a packaging material and packaging geometry for a given produce application.

The experimental verification of this approach by using three different produces in combination with 9 selected packaging materials showed the following:

⇒ The respiration properties of the produces tested can be well described by a scientifically based approach: Michaelis Menten kinetics in dependence of the partial pressure of oxygen, accompanied by an Arrhenius behaviour of the rates in terms of temperature.

⇒ The skin permeability/internal diffusion of the produce can also be described by an Arrhenius term. The effective permeability values, however, are very high in comparison to the permeability of the packaging films investigated. In first order, this effect may therefore be neglected.

⇒ The gas permeability of the packaging film materials also follows the Arrhenius type of temperature dependence.

⇒ The dependence of gas permeability on relative humidity and condensation conditions is not consi s-tently accessible by analytical expressions. The reason is that the effects of humidity are large in the humidity region around 100 %, where the conditions inside a closed packaging are not well defined.

⇒ For water vapour permeability, the temperature-induced variation at constant relative humidity grad i-ent is mainly caused by the temperature effect on the absolute humidity. Temperature effects on the materials are of second order in most cases. Also here, the effect of condensation is relatively large.

⇒ Overall, the description of the parts of the whole system produce / packaging cannot be made in a deterministic way as individual differences are relatively large both for the produce as well as for the polymeric film materials. This induces a statistical character of all values which has to be taken into account in the modelling procedure.

Therefore, a Monte Carlo simulation routine was added to the program which allows for a preset statisti-cal variation of the relevant parameters. With this feature, the modelling of the different experimental data obtained gave overall good agreement.

As a final conclusion, it can be stated that the approach of the MASTER project has been justified. A valuable tool is now available which may be extended to other produces, packaging materials and pac k-aging systems with relatively low effort.

6 Annexes

6.1 Respiration of produce

Table 15 - Rates of O_2 consumption (RO_2; mmol·kg^{-1}·h^{-1}) and CO_2 production (RCO_2; mmol·kg^{-1}·h^{-1}) as a function of PO_2 and PCO_2 adopted (Temp.= 21± 1 °C) [Andrich et al., 1994a]

Run	PO_2 (kPa)	PCO_2 (kPa)	PN_2 (kPa)	RO_2 (mmol·kg^{-1}·h^{-1})	RCO_2 (mmol·kg^{-1}·h^{-1})
1	23.3	1.5	0.06	0.70	0.72
2	19.9	2.5	0.12	0.73	0.69
3	33.2	3.6	0.11	0.89	0.91
4	29.2	4.5	0.15	0.94	0.87
5	10.3	14.3	1.39	0.62	0.63
6	25.9	14.9	0.57	0.65	0.65
7	20.8	15.8	0.76	0.79	0.71
8	19.0	16.4	0.86	0.66	0.62
9	7.3	18.3	2.51	0.50	0.52
10	15.8	18.7	1.18	0.67	0.63
11	16.6	20.8	1.25	0.71	0.75
12	10.2	30.3	2.97	0.47	0.53
13	9.0	30.5	3.39	0.58	0.59
14	16.3	36.4	2.23	0.51	0.56
15	17.0	46.0	2.70	0.60	0.57
16	14.0	52.3	3.73	0.47	0.45
17	12.8	59.1	4.62	0.45	0.56
18	9.8	72.9	7.44	0.59	0.48
19	8.8	74.5	8.47	0.30	0.41

Table 16 - Mean values of O_2 consumption (RO_2 [$mmol \cdot kg^{-1} \cdot h^{-1}$]) and CO_2 production rates (RCO_2) by *Golden Delicious* apples stored at a PCO_2 close to 0 and at 4 different temperatures (21, 16, 6 and 1°C)

PO_2 (kPa)	Temperature (°C)							
	21°		16°		6°		1°	
	RO_2	RCO_2	RO_2	RCO_2	RO_2	RCO_2	RO_2	RCO_2
0	0.00	0.85	0.00	0.63	0.00	0.31	0.00	0.26
3	0.40	0.76	0.27	0.35	0.14	0.21	0.08	0.16
5	0.61	0.78	0.35	0.38	0.19	0.24	0.11	0.15
10	0.94	0.96	0.59	0.56	0.39	0.38	0.15	0.14
21	0.83	0.86	0.60	0.63	0.31	0.27	0.21	0.25

Table 17 - Temperature variation of k_{ar} and K_M constants involved in the Michaelis-Menten like equation together with their related confidence intervals (c.i.; p=0.05) and the squares of the correlation coefficients obtained for the linearized form

Temp. (°C)	$k_{ar} \pm$ c.i. [$mmol \cdot kg^{-1} \cdot h^{-1}$]	$(K_M \pm$ c.i.$) \cdot 10^2$ [$mmol \cdot kg^{-1}$]	r^2
21	1.01 ± 0.54	2.1 ± 1.3	0.96
16	0.70 ± 0.47	5.6 ± 4.0	0.94
6	0.48 ± 0.72	18.2 ± 18.8	0.90
1	0.25 ± 0.07	99.9 ± 24.0	0.97

Table 18 - Logarithms of pre-exponential factor and activation energies connected with k_{ar} and K_M temperature evolution

	$\ln(k_{ar}°; K_M°) \pm$ c.i.	$\Delta E°_{ar;\,m}/R \pm$ c.i. [°K]	r^2
k_{ar} [$mmol \cdot kg^{-1} \cdot h^{-1}$]	17.3 ± 13.0	5097 ± 3727	0.94
K_M [$mmol \cdot kg^{-1}$]	- 52.9 ± 31.1	- 14445 ± 8830	0.96

Apple

R_{O_2}

T	O_2	CO_2 0	5	10	15	20
1	0	0.00	0.00	0.00	0.00	0.00
	3	0.06	0.09	0.00	0.00	0.00
	10	0.16	0.06	0.07	0.05	0.00
	21	0.11	0.06	0.03	0.00	0.00
6	0	0.00	0.00	0.00	0.00	0.00
	3	0.12	0.07	0.05	0.00	0.00
	10	0.36	0.11	0.24	0.16	0.00
	21	0.29	0.11	0.12	0.13	0.00
11	0	0.00	0.00	0.00	0.00	0.00
	3	0.18	0.19	0.11	0.17	0.11
	10	0.31	0.21	0.20	0.25	0.20
	21	0.38	0.49	0.53	0.23	0.12
16	0	0.00	0.00	0.00	0.00	0.00
	3	0.24	0.28	0.23	0.20	0.17
	10	0.37	0.41	0.37	0.33	0.27
	21	0.45	0.55	0.46	0.35	0.23
21	0	0.00	0.00	0.00	0.00	0.00
	3	0.37	0.45	0.28	0.16	0.17
	10	0.75	0.73	0.52	0.53	0.43
	21	0.74	0.59	0.59	0.29	0.40

R_{CO_2}

T	O_2	CO_2 0	5	10	15	20
1	0	0.20	0.06	0.05	0.03	0.00
	3	0.14	0.08	0.00	0.00	0.00
	10	0.13	0.07	0.06	0.03	0.00
	21	0.14	0.10	0.02	0.00	0.00
6	0	0.31	0.19	0.03	0.06	0.00
	3	0.17	0.07	0.05	0.00	0.00
	10	0.36	0.08	0.17	0.13	0.00
	21	0.25	0.13	0.10	0.09	0.00
11	0	0.34	0.27	0.23	0.26	0.18
	3	0.17	0.21	0.18	0.22	0.13
	10	0.28	0.19	0.27	0.27	0.18
	21	0.31	0.59	0.22	0.28	0.23
16	0	0.44	0.43	0.38	0.40	0.21
	3	0.43	0.29	0.27	0.20	0.15
	10	0.40	0.46	0.38	0.37	0.31
	21	0.44	0.49	0.50	0.34	0.36
21	0	0.71	0.64	0.52	0.45	0.19
	3	0.60	0.43	0.31	0.20	0.14
	10	0.77	0.74	0.49	0.49	0.41
	21	0.68	0.63	0.59	0.32	0.36

Chicory

R_{O_2}

T	O_2 \ CO_2	0	5	10	15	20
1	0	0.00	0.00	0.00	0.00	0.00
	3	0.07	0.06	0.12	0.08	*
	10	0.09	0.11	0.11	0.12	0.18
	21	0.20	0.09	0.10	0.10	0.14
6	0	0.05	0.00	0.00	0.00	0.00
	3	0.16	0.12	0.19	0.18	0.22
	10	0.28	0.21	0.17	0.22	0.22
	21	0.25	0.21	0.20	0.20	0.30
11	0	0.00	0.00	0.00	0.00	0.00
	3	0.33	0.28	0.29	0.28	0.31
	10	0.40	0.29	0.33	0.36	0.31
	21	0.46	0.42	0.38	0.37	0.43
16	0	0.15	0.00	0.00	0.00	0.00
	3	0.42	0.30	0.51	0.39	*
	10	0.55	*	0.44	0.51	*
	21	0.72	0.58	0.65	0.58	0.57
21	0	0.00	0.00	0.00	0.00	0.00
	3	0.54	0.66	0.65	0.58	0.57
	10	0.78	0.84	0.95	0.87	0.83
	21	1.05	1.06	1.06	1.11	0.94

R_{CO_2}

T	O_2 \ CO_2	0	5	10	15	20
1	0	0.13	0.06	0.12	0.08	0.09
	3	0.05	0.06	0.08	0.08	*
	10	0.08	0.08	0.08	0.09	0.12
	21	0.10	0.07	0.05	0.09	0.09
6	0	0.21	0.25	0.28	0.23	0.27
	3	0.17	0.21	0.16	0.17	0.17
	10	0.30	0.18	0.23	0.22	0.25
	21	0.20	0.32	0.22	0.19	0.23
11	0	0.37	0.26	0.26	0.41	0.28
	3	0.25	0.28	0.26	0.31	0.34
	10	0.28	0.29	0.35	0.33	0.35
	21	0.39	0.38	0.38	0.46	0.39
16	0	0.32	0.23	0.51	0.22	0.21
	3	0.43	0.39	0.46	0.35	*
	10	0.50	*	0.46	0.48	*
	21	0.61	0.52	0.56	0.48	0.69
21	0	0.69	0.80	1.47	1.37	1.84
	3	*	0.92	0.74	0.63	0.80
	10	*	1.31	0.97	1.03	1.01
	21	0.95	2.02	1.23	1.61	1.19

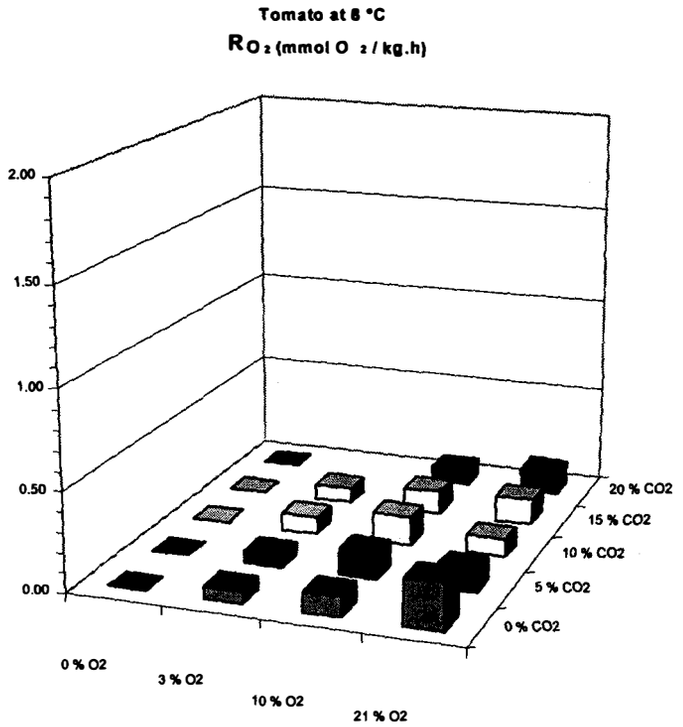
Tomato

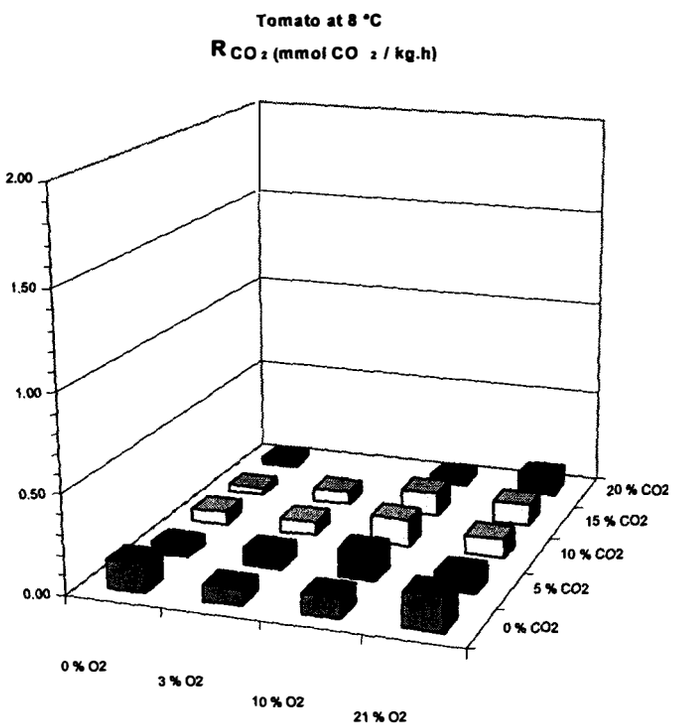
R_{O_2}

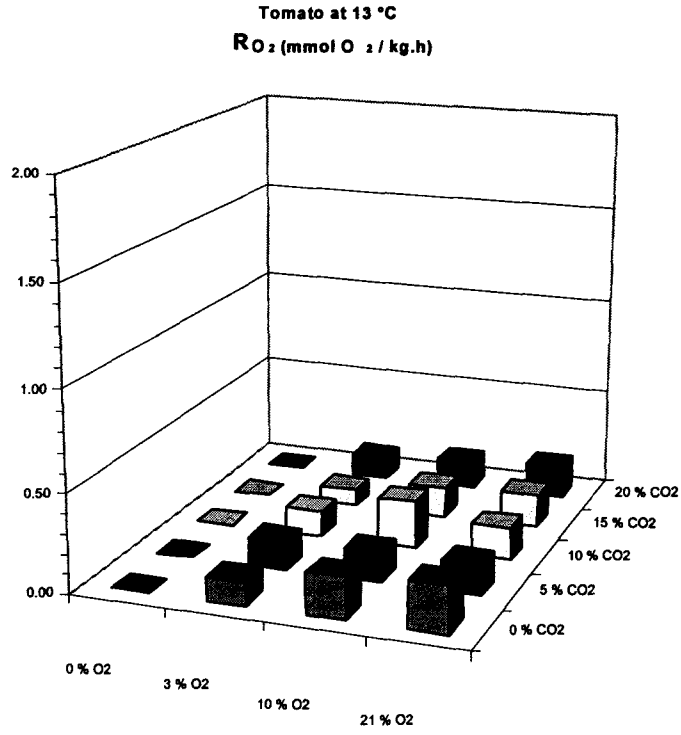
T	O_2 \ CO_2	0	5	10	15	20
8	0	0.00	0.00	0.00	0.00	0.00
	3	0.06	0.06	0.09	0.08	*
	10	0.10	0.13	0.15	0.12	0.08
	21	0.24	0.11	0.09	0.13	0.12
13	0	0.00	0.00	0.00	0.00	0.00
	3	0.12	0.14	0.13	0.09	0.11
	10	0.21	0.15	0.24	0.16	0.14
	21	0.23	0.16	0.16	0.17	0.17
18	0	0.00	0.00	0.00	0.00	0.00
	3	0.13	0.21	0.19	0.15	*
	10	0.27	*	0.30	0.24	*
	21	0.41	0.42	0.33	0.32	0.22
23	0	0.00	0.00	0.00	0.00	0.00
	3	0.18	0.11	0.25	0.09	*
	10	0.40	*	0.30	0.19	*
	21	0.46	0.43	0.42	0.47	*
28	0	0.00	0.00	0.00	0.00	0.00
	3	0.34	0.30	0.23	0.21	0.22
	10	0.68	0.38	0.77	0.37	0.25
	21	1.17	0.65	0.58	0.49	0.48

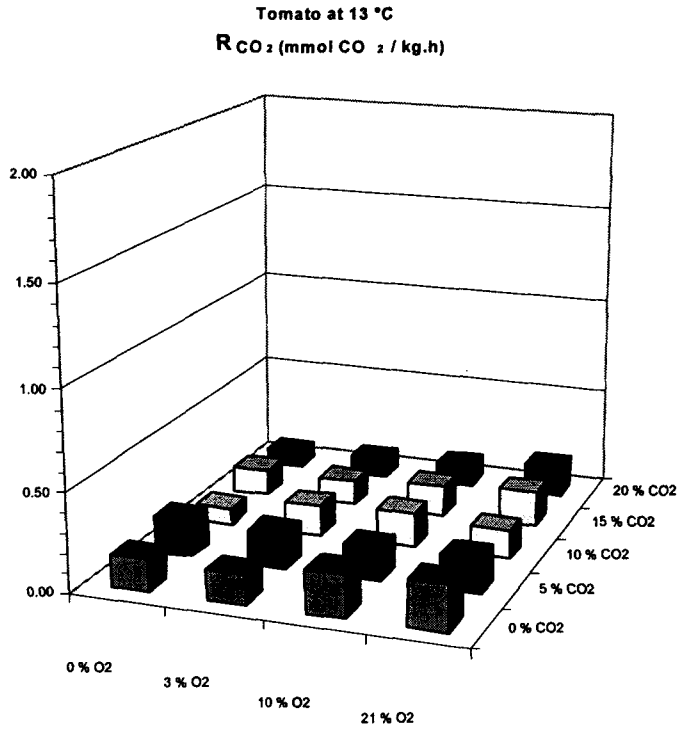
R_{CO_2}

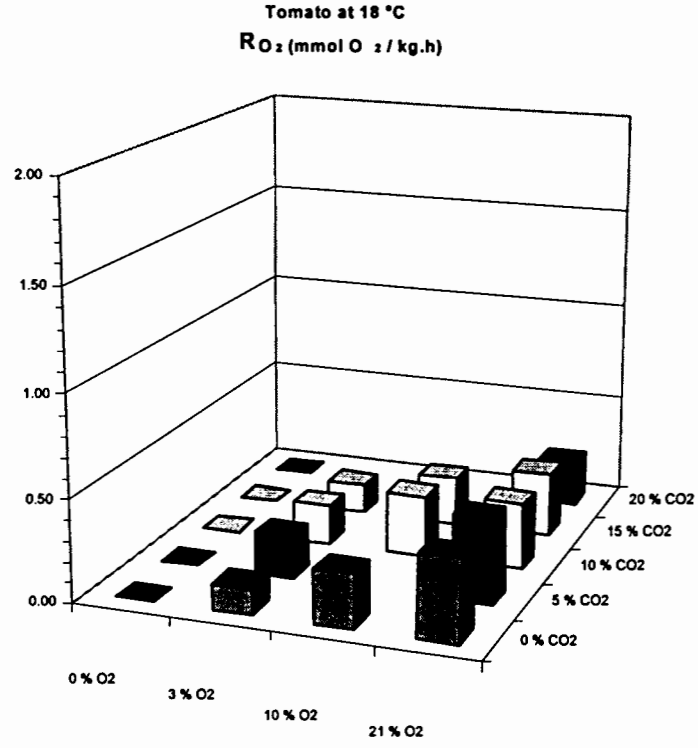
T	O_2 \ CO_2	0	5	10	15	20
8	0	0.14	0.06	0.07	0.04	0.04
	3	0.08	0.08	0.07	0.07	*
	10	0.10	0.14	0.14	0.12	0.04
	21	0.18	0.09	0.10	0.11	0.11
13	0	0.16	0.19	0.08	0.13	0.08
	3	0.15	0.18	0.16	0.12	0.10
	10	0.22	0.17	0.17	0.16	0.11
	21	0.23	0.18	0.14	0.18	0.16
18	0	0.25	0.27	0.35	0.33	0.20
	3	0.17	0.23	0.23	0.14	*
	10	0.28	*	0.23	0.28	*
	21	0.35	0.33	0.23	0.28	0.34
23	0	0.42	0.36	0.36	0.20	0.25
	3	0.23	0.18	0.27	0.15	*
	10	0.45	*	0.31	0.21	*
	21	0.58	0.31	0.22	0.39	*
28	0	0.72	0.62	0.50	0.24	0.04
	3	0.66	0.58	0.45	0.33	0.31
	10	0.83	0.43	0.76	0.45	0.27
	21	1.13	0.61	0.54	0.48	0.50

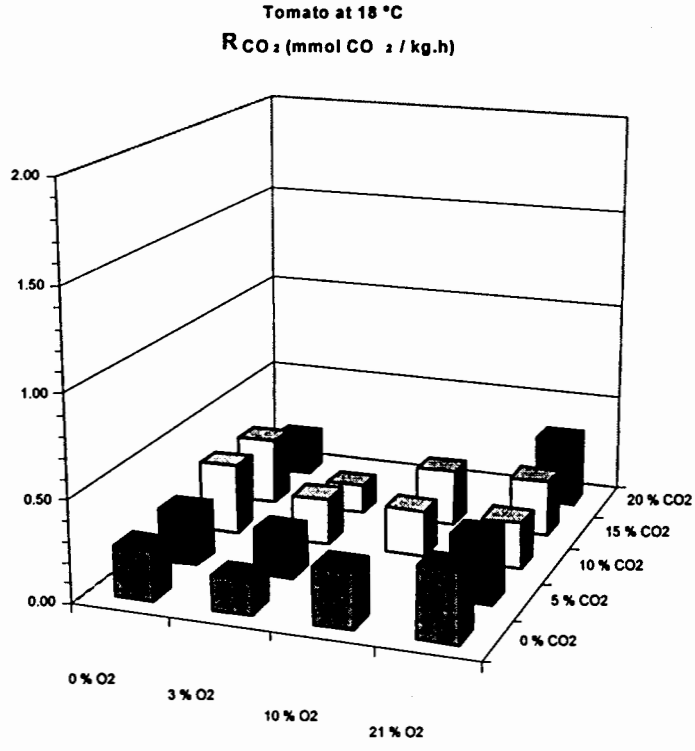

Tomato at 8 °C
R_{O_2} (mmol O_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

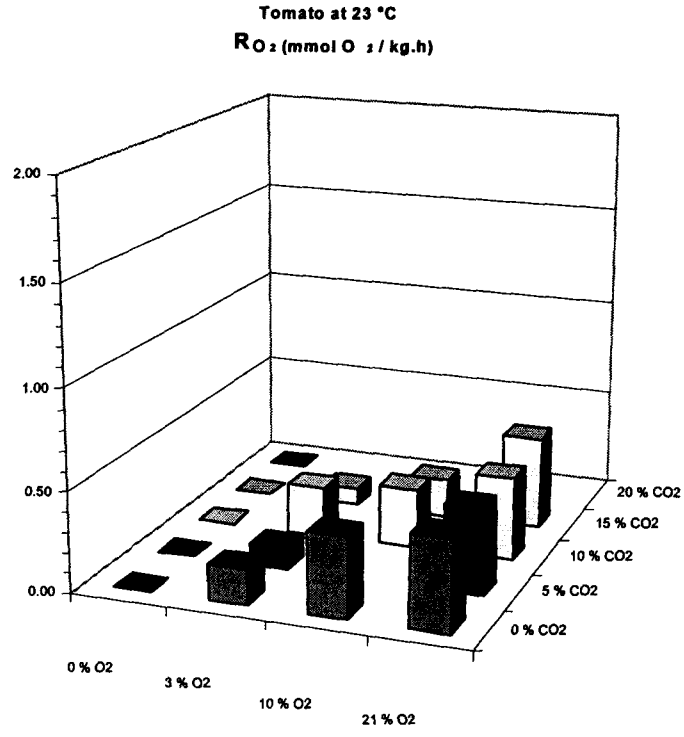

Tomato at 8 °C
R_{CO_2} (mmol CO_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

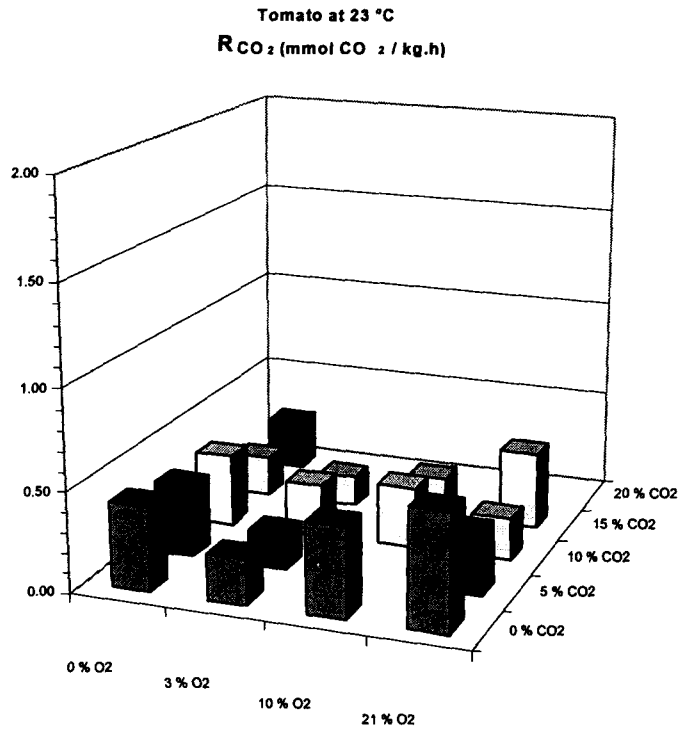

Tomato at 13 °C
R_{O_2} (mmol O_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

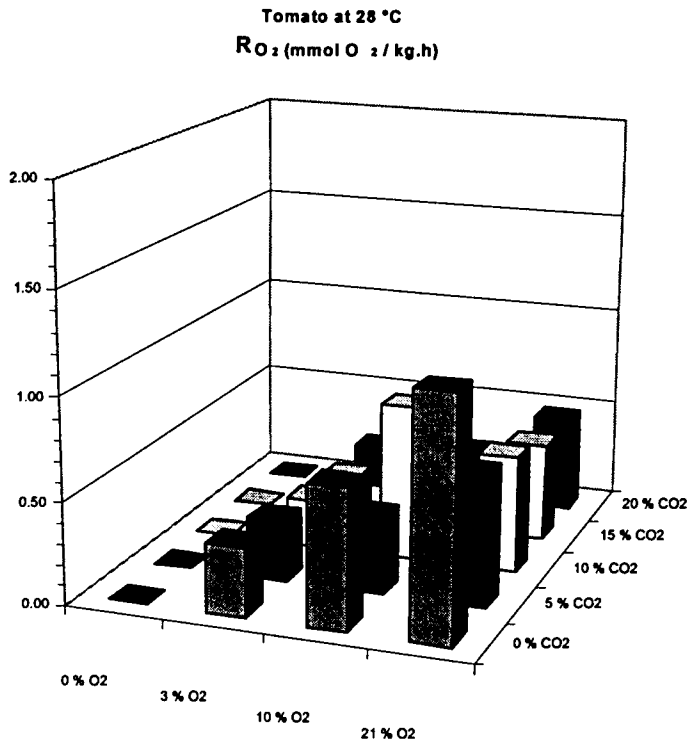

Tomato at 13 °C
R_{CO_2} (mmol CO_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

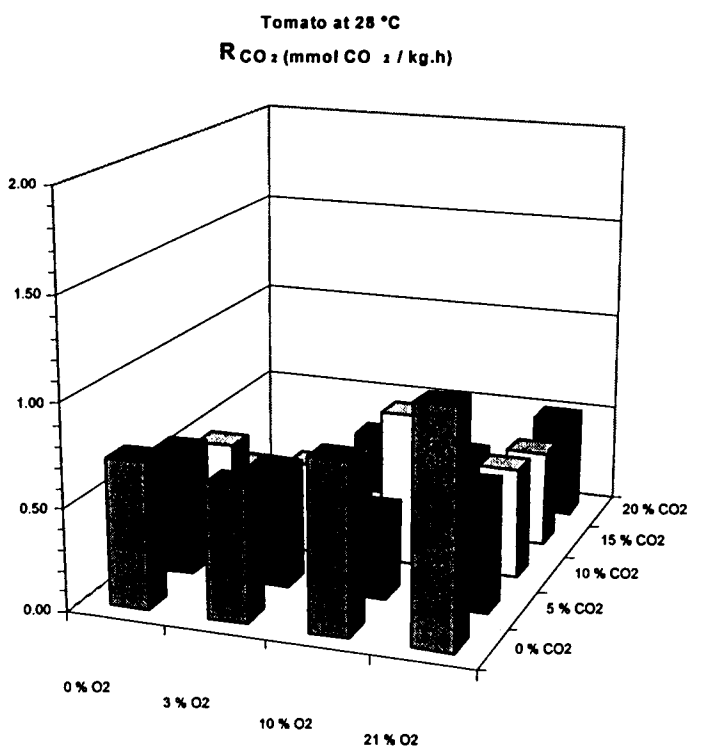

Tomato at 18 °C
R_{O_2} (mmol O_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

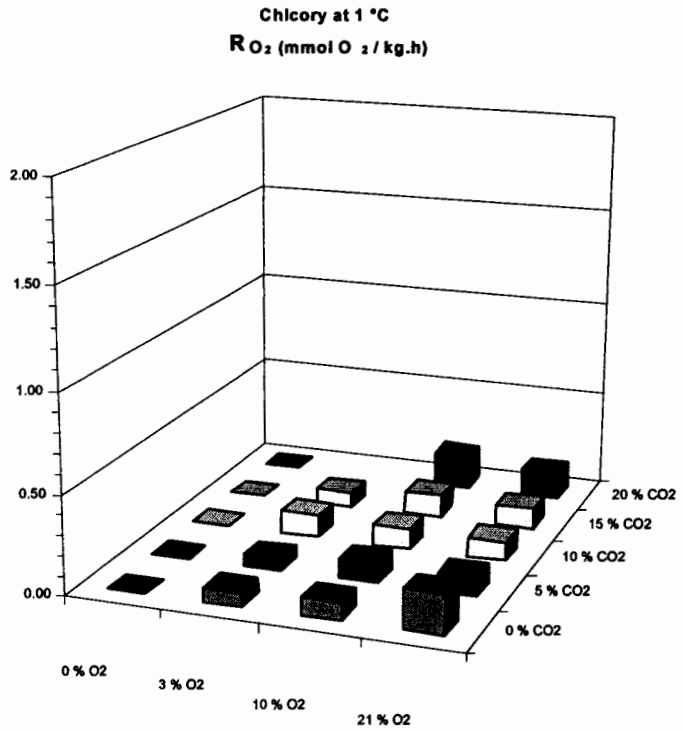

Tomato at 18 °C
R_{CO_2} (mmol CO_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

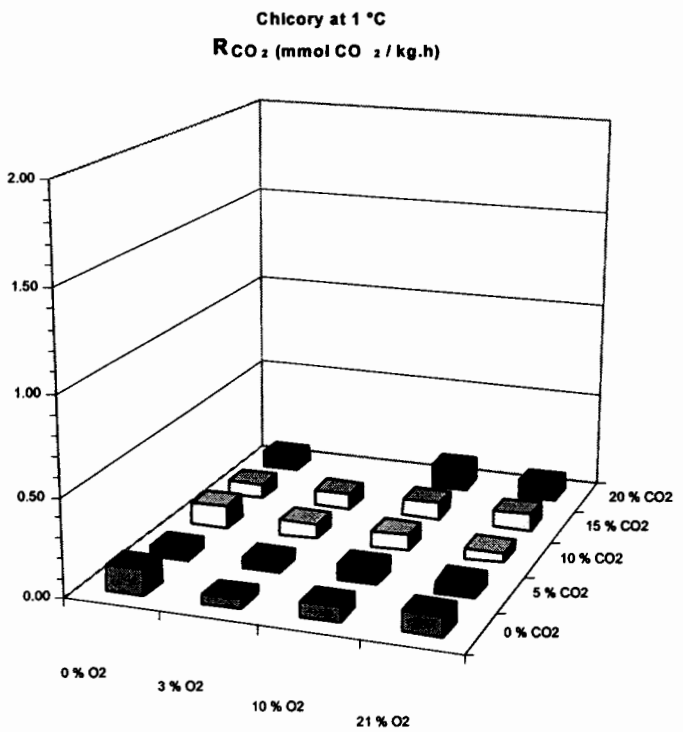

Tomato at 23 °C
R O2 (mmol O 2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

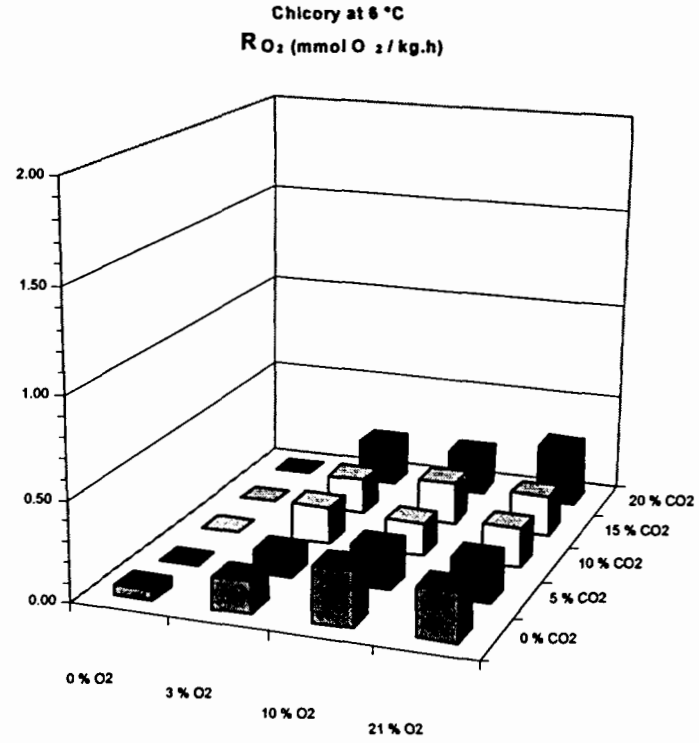

Tomato at 23 °C
R CO2 (mmol CO 2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

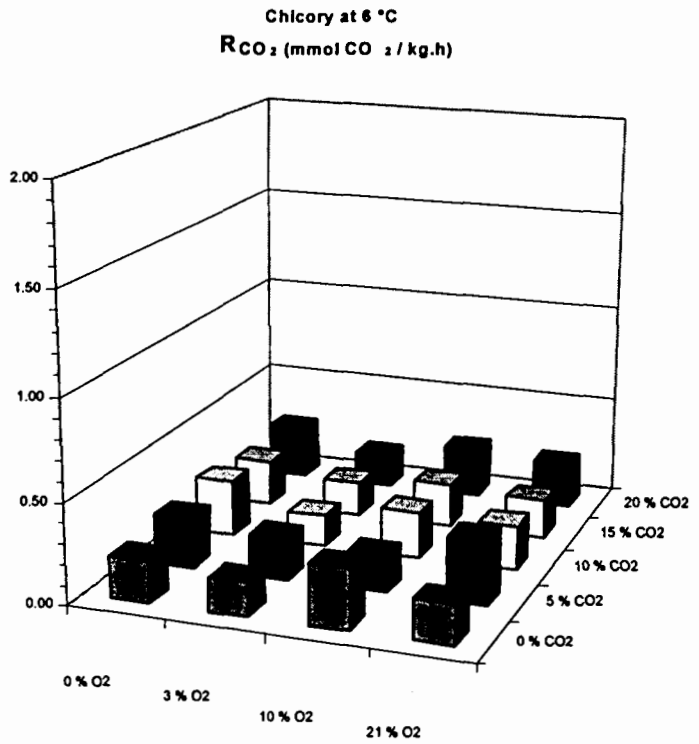

Tomato at 28 °C
R_{O_2} (mmol O_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

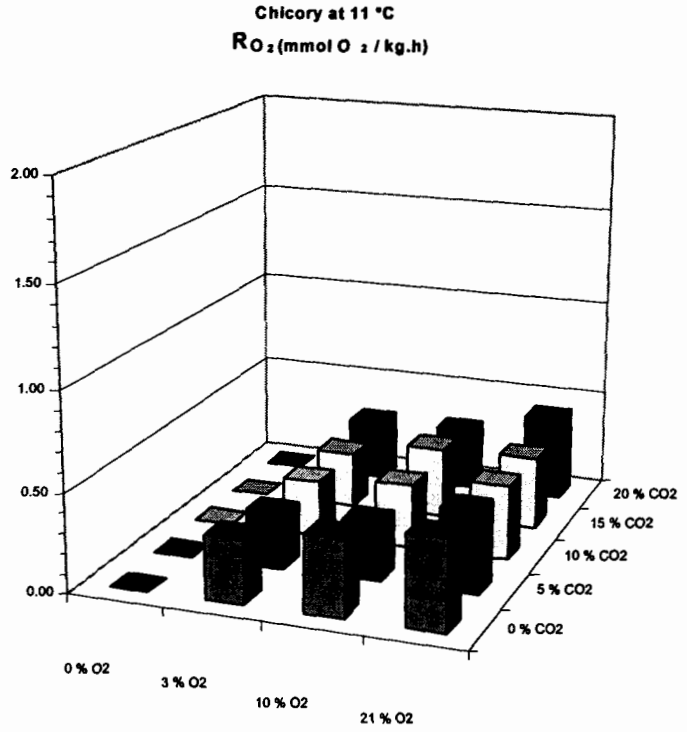

Tomato at 28 °C
R_{CO_2} (mmol CO_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

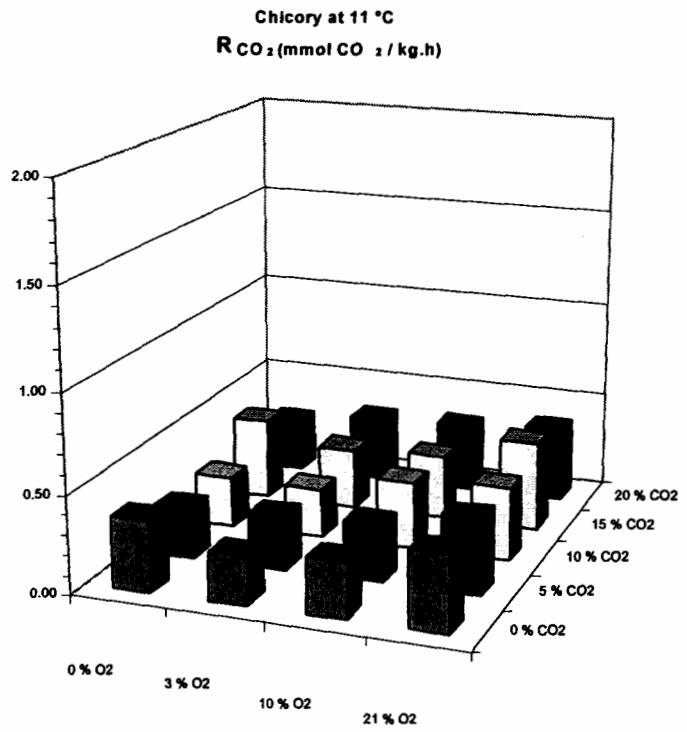

Chicory at 1 °C
R O2 (mmol O 2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

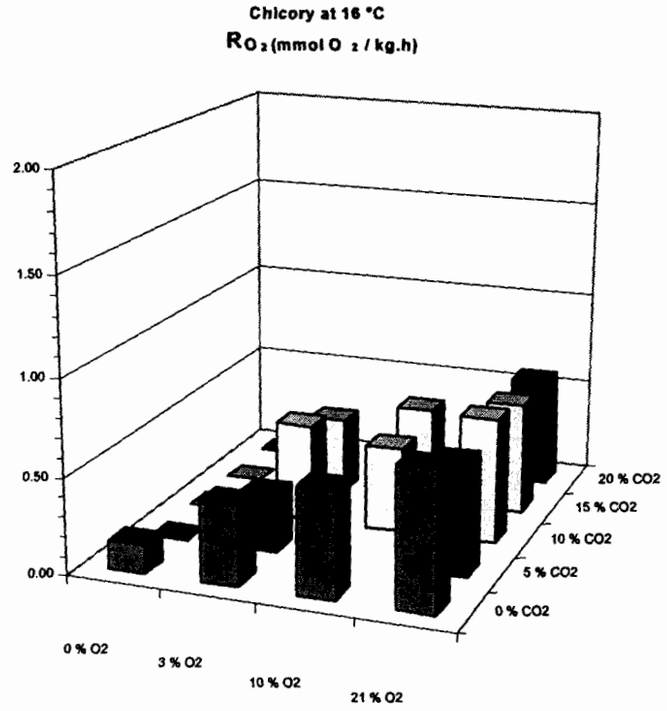

Chicory at 1 °C
R CO2 (mmol CO 2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

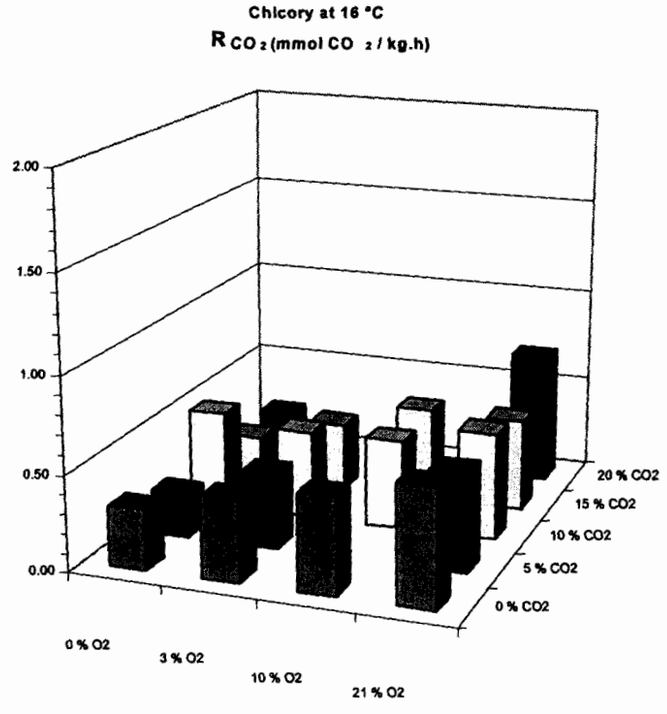

Chicory at 6 °C
R O2 (mmol O 2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

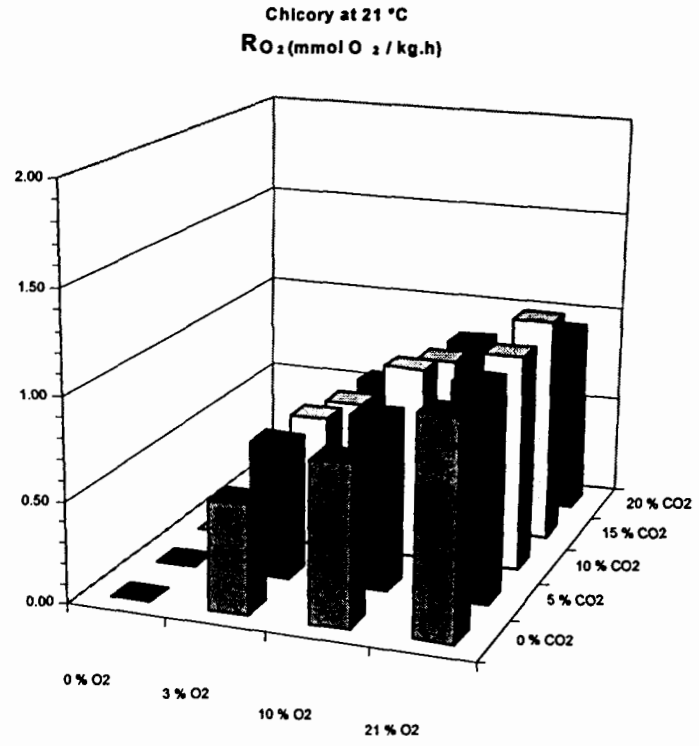

Chicory at 6 °C
R CO2 (mmol CO 2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

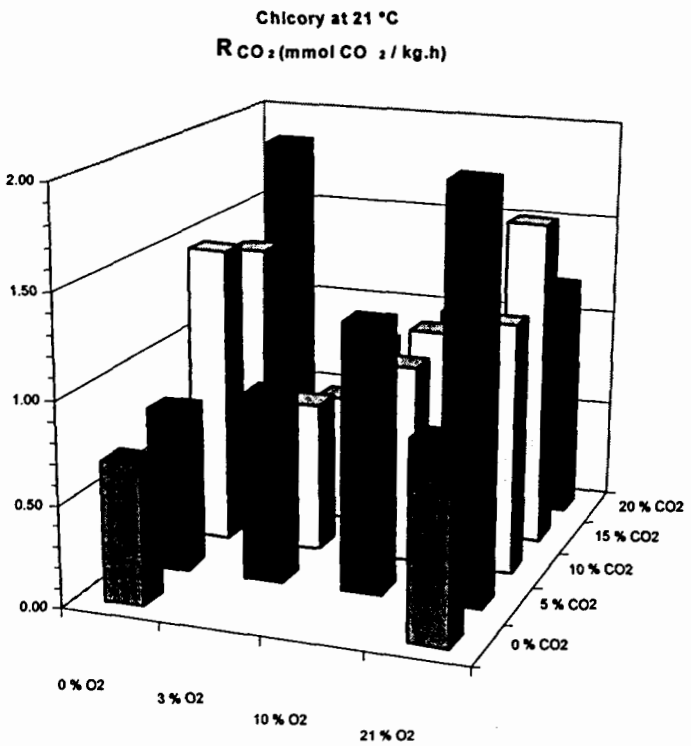

Chicory at 11 °C
R_{O_2} (mmol O_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

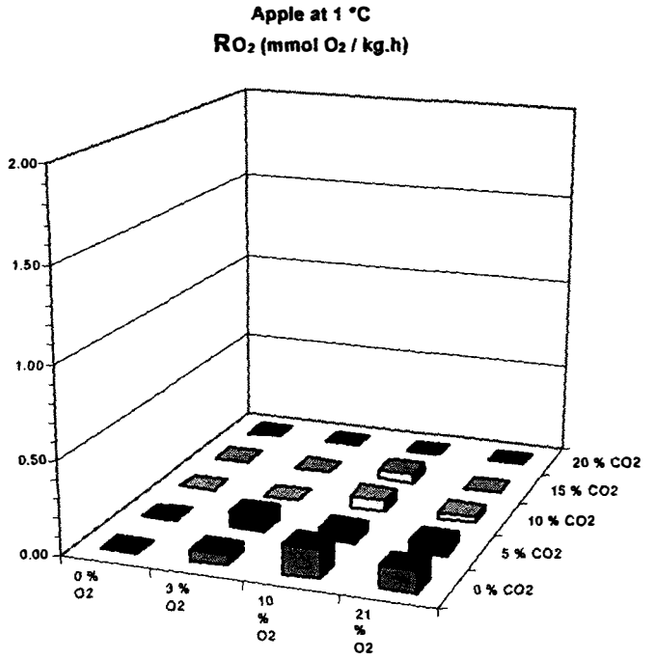

Chicory at 11 °C
R_{CO_2} (mmol CO_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

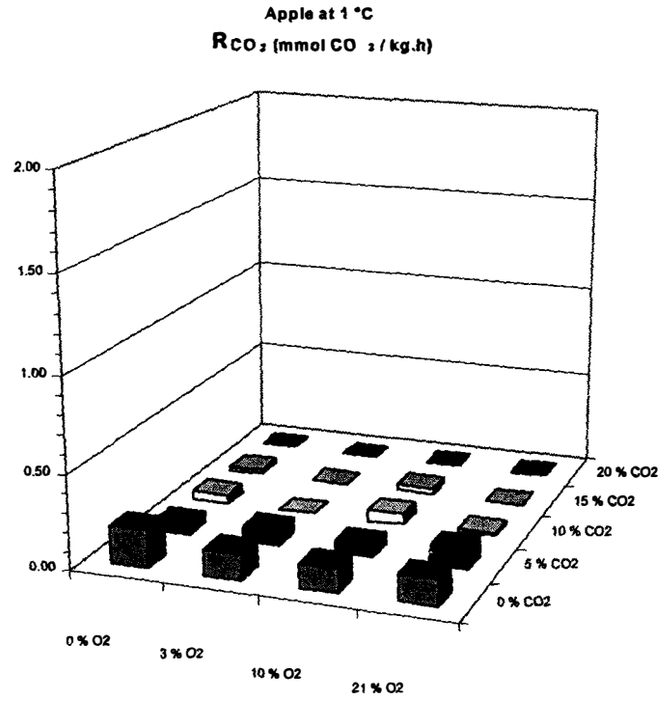

Chicory at 16 °C
R_{O_2} (mmol O_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

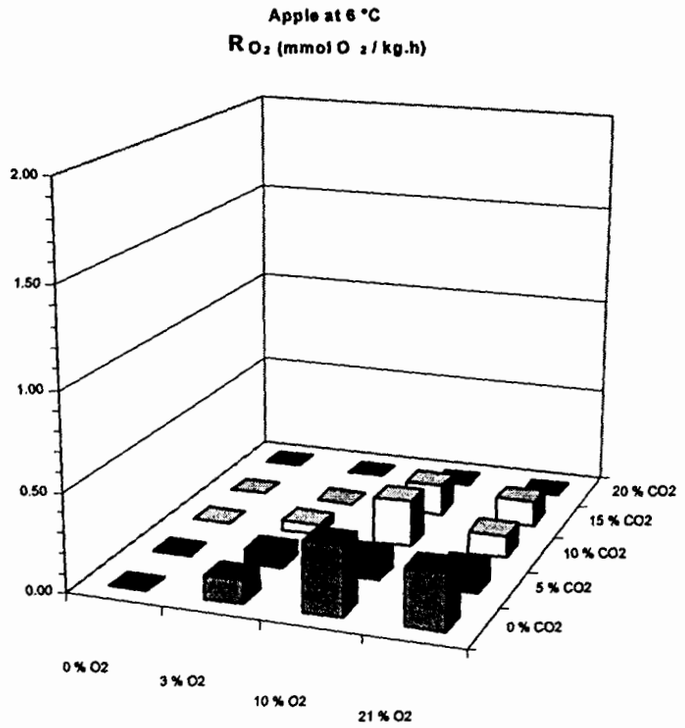

Chicory at 16 °C
R_{CO_2} (mmol CO_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

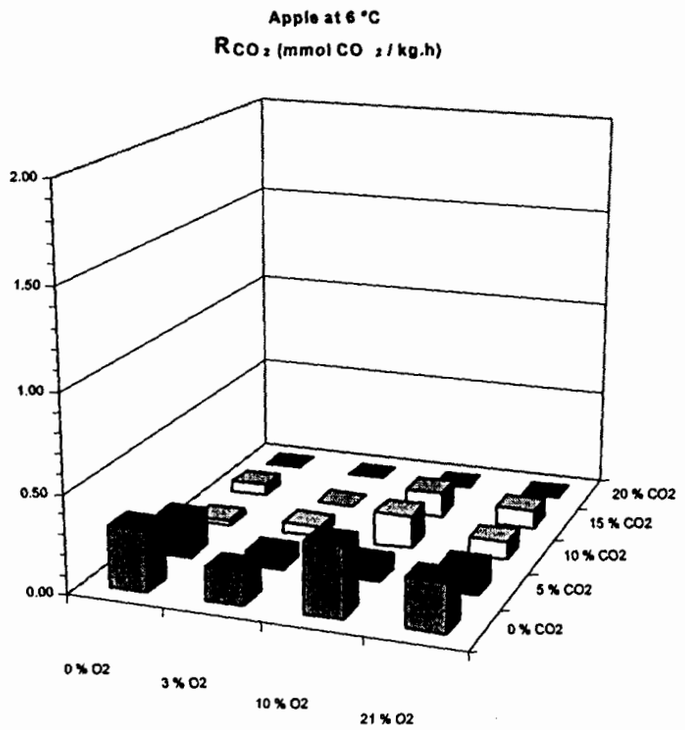

Chicory at 21 °C
R_{O_2} (mmol O_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
0 % CO2
5 % CO2
10 % CO2
15 % CO2
20 % CO2

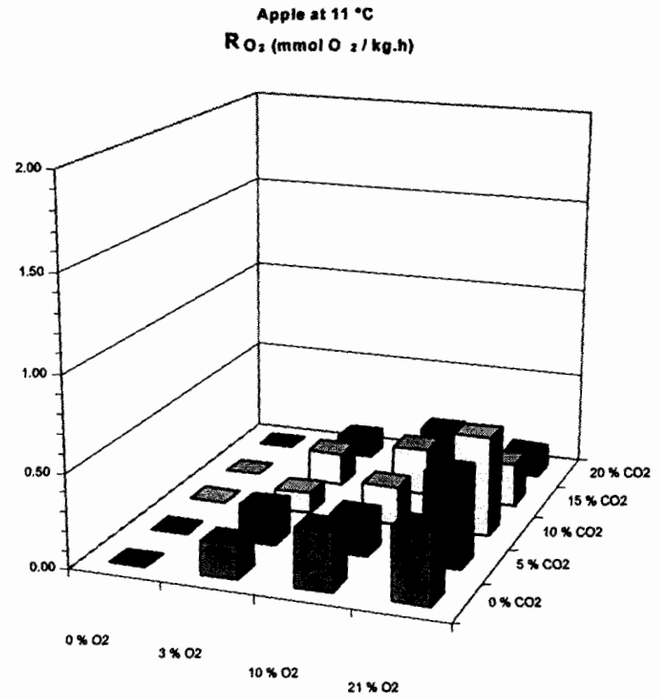

Chicory at 21 °C
R_{CO_2} (mmol CO_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
0 % CO2
5 % CO2
10 % CO2
15 % CO2
20 % CO2

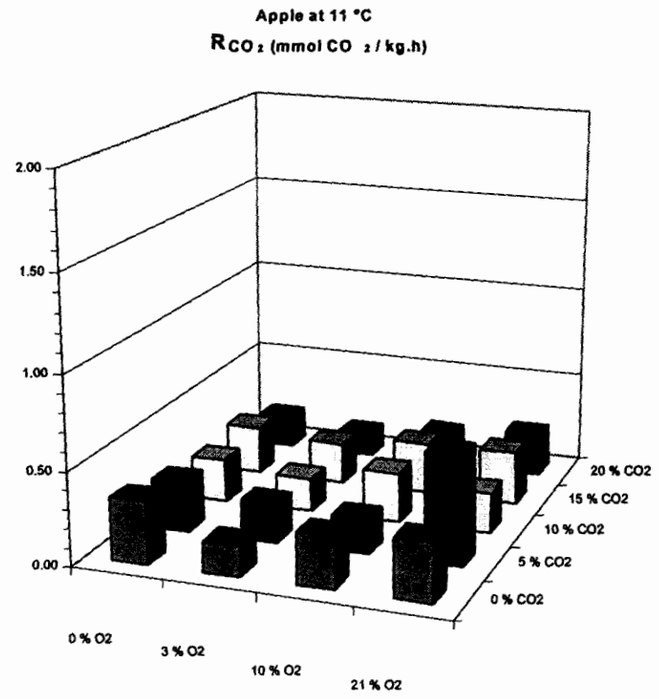

Apple at 1 °C
RO2 (mmol O2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

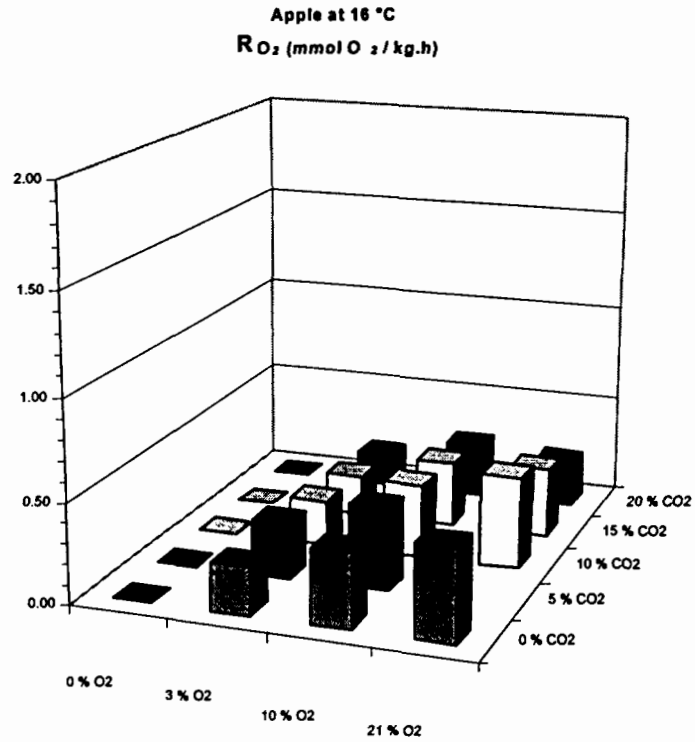

Apple at 1 °C
RCO2 (mmol CO 2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

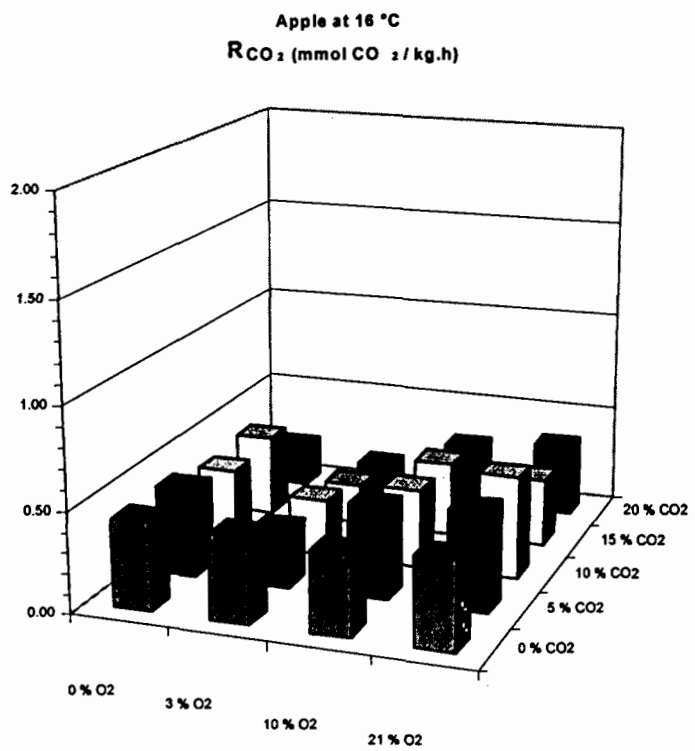

Apple at 6 °C
R_{O_2} (mmol O_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

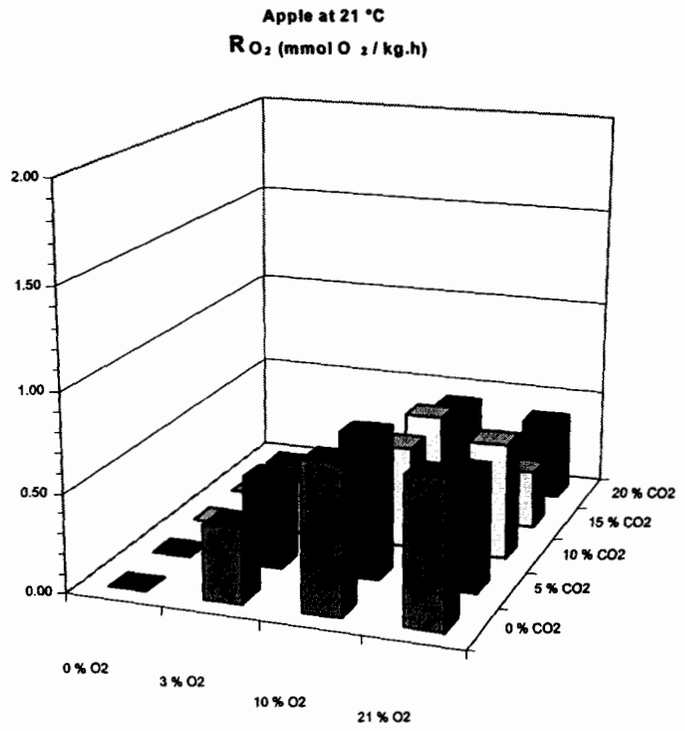

Apple at 6 °C
R_{CO_2} (mmol CO_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

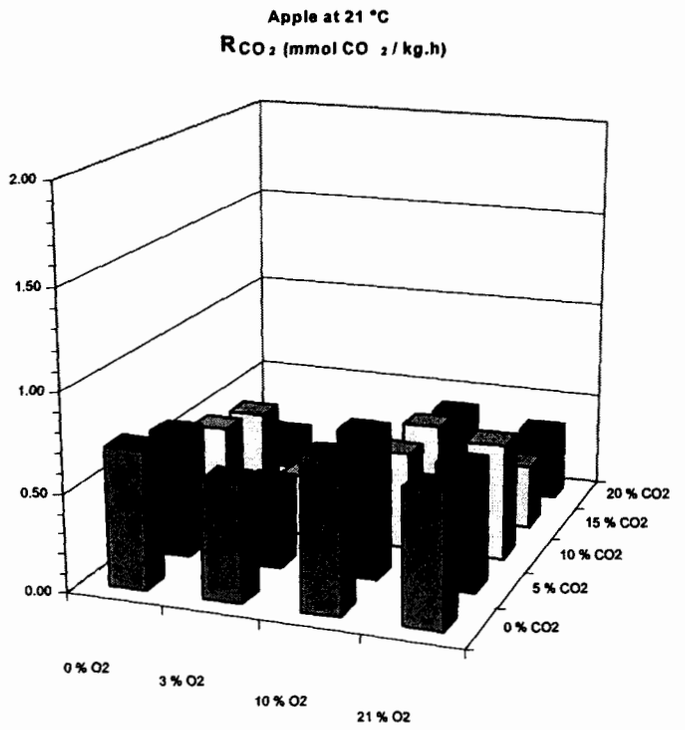

Apple at 11 °C
R_{O_2} (mmol O_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2


Apple at 11 °C
R_{CO_2} (mmol CO_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2


Apple at 16 °C
R_{O_2} (mmol O_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2


Apple at 16 °C
R_{CO_2} (mmol CO_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2


Apple at 21 °C
R_{O_2} (mmol O_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2


Apple at 21 °C
R_{CO_2} (mmol CO_2 / kg.h)
2.00
1.50
1.00
0.50
0.00
0 % O2
3 % O2
10 % O2
21 % O2
20 % CO2
15 % CO2
10 % CO2
5 % CO2
0 % CO2

6.2 Internal diffusion in produce

(Pisa, Viterbo)

Table 1 - Apple fruits - O_2 diffusion. Experimental values of diffusional constants $k_{i,O2}$ and H_{O2} (c.i. = confidence interval, p = 0.05) as a function of temperature and gas composition

N°	PG=PO_2 (kPa)	Temp. (°C)	PCO_2 (kPa)	PN_2 (kPa)	$(k_{i,G} \pm c.i.) \cdot 10^4$ [mmol/(s · m^2 · kPa)]	H±c.i. [mmol/(kg · kPa)]
1	18.7	1±1	17.7	63.6	5.05±0.23	0.16±0.02
2	38.2	1±1	0.8	61.0	4.95±0.25	0.18±0.01
3	18.3	6±1	17.3	64.4	3.54±0.15	0.13±0.01
4	38.6	6±1	0.7	60.7	5.17±0.17	0.17±0.01
5	19.1	11±1	0.9	79.7	3.99±0.27	0.14±0.03
6	38.3	11±1	0.6	61.1	4.88±0.46	0.18±0.02
7	18.7	16±1	0.7	80.6	4.01±0.39	0.16±0.01
8	17.5	16±1	19.2	63.3	4.38±0.21	0.17±0.01
9	37.7	16±1	0.7	61.6	4.80±0.37	0.18±0.02
10	18.5	21±1	1.5	80.0	4.14±0.16	0.17±0.01
11	17.0	21±1	19.6	63.4	4.72±0.53	0.20±0.01
12	36.2	21±1	0.8	63.0	3.94±0.27	0.15±0.01

Table 2 - Apple fruits - CO_2 diffusion. Experimental values of diffusional constants $k_{i,CO2}$ and H_{CO2} (c.i. = confidence interval, p = 0.05) as a function of temperature and gas composition

N°	PG=PCO_2 (kPa)	Temp. (°C)	PO_2 (kPa)	PN_2 (kPa)	(k_i±c.i.) · 10^4 [mmol/(s · m^2 · kPa)]	H±c.i. [mmol/(kg · kPa)]
3	40.0	1±1	0.3	59.7	6.92±0.38	0.18±0.01
8	40.6	1±1	19.4	40.0	6.60±0.37	0.19±0.01
13	20.9	1±1	5.0	74.1	6.68±0.63	0.24±0.02
2	40.0	6±1	0.7	59.3	7.48±0.44	0.20±0.01
7	39.5	6±1	20.6	39.9	7.58±0.73	0.18±0.03
12	19.2	6±1	4.0	76.8	8.39±0.93	0.27±0.05
1	40.4	11±1	0.5	59.1	7.78±0.80	0.20±0.02
6	40.9	11±1	20.2	38.9	8.32±0.48	0.23±0.03
11	20.8	11±1	0.6	78.6	9.23±1.34	0.31±0.09
5	39.1	16±1	20.9	40.0	9.56±0.86	0.23±0.01
10	20.4	16±1	0.6	79.0	10.22±0.78	0.24±0.03
4	39.2	21±1	19.1	41.7	10.37±0.77	0.25±0.04
9	20.3	21±1	0.2	79.5	11.37±3.57	0.27±0.08
14	20.6	21±1	39.3	40.1	9.70±0.90	0.23±0.05

Table 3 - *Witloof* Endive - O_2 diffusion. Experimental values of diffusional constants $k_{i,O2}$ and H_{O2} (c.i. = confidence interval, p = 0.05) as a function of temperature and gas composition ($PCO_2 \cong 0\%$)

N°	PG=PO_2 (kPa)	Temp. (°C)	PCO_2 (kPa)	PN_2 (kPa)	(k_i±c.i.) · 10^4 [mmol/(s · m^2 · kPa)]	H±c.i. [mmol/(kg · kPa)]
1	17.1	1 ± 1	0.1	82.8	0.37 ± 0.11	0.03 ± 0.01
2	17.3	1 ± 1	0.2	82.5	0.25 ± 0.04	0.02 ± 0.01
3	30.0	1 ± 1	0.2	69.8	0.17 ± 0.04	0.02 ± 0.04
4	31.0	1 ± 1	0.6	68.3	0.15 ± 0.05	0.01 ± 0.08
5	31.1	1 ± 1	0.6	68.3	0.22 ± 0.11	0.01 ± 0.01
6	42.7	1 ± 1	0.6	56.7	0.48 ± 0.03	0.01 ± 0.01
7	42.3	1 ± 1	0.6	57.1	0.34 ± 0.13	0.02 ± 0.02
8	16.8	6 ± 1	0.1	83.1	0.18 ± 0.10	0.08 ± 0.01
9	17.8	6 ± 1	0.2	82.0	0.38 ± 0.07	0.04 ± 0.01
10	18.5	6 ± 1	0.3	81.2	0.48 ± 0.13	0.04 ± 0.01
11	17.8	11 ± 1	0.3	81.9	0.71 ± 0.11	0.07 ± 0.01
12	18.0	11 ± 1	0.2	81.8	0.82 ± 0.34	0.07 ± 0.02
13	41.4	11 ± 1	0.4	58.2	0.33 ± 0.05	0.03 ± 0.01
14	42.0	11 ± 1	0.4	57.6	0.32 ± 0.09	0.03 ± 0.01
15	42.6	11 ± 1	0.3	57.1	0.28 ± 0.18	0.02 ± 0.02
16	17.2	16 ± 1	0.2	82.6	2.27 ± 0.24	0.20 ± 0.03
17	17.8	16 ± 1	0.2	82.0	1.32 ± 0.10	0.16 ± 0.01
18	18.0	16 ± 1	0.2	81.8	1.52 ± 0.16	0.14 ± 0.02
19	19.0	16 ± 1	0.3	80.7	1.82 ± 0.26	0.18 ± 0.03
20	17.2	21 ± 1	0.2	82.6	2.22 ± 0.29	0.17 ± 0.03
21	17.9	21 ± 1	0.2	81.9	2.22 ± 0.20	0.23 ± 0.03
22	18.5	21 ± 1	0.3	81.2	1.91 ± 0.15	0.24 ± 0.02
23*	18.6	21 ± 1	0.3	81.1	1.66 ± 0.15	0.19 ± 0.02
24	19.0	21 ± 1	0.3	80.7	1.48 ± 0.19	0.16 ± 0.03
25	20.1	21 ± 1	0.1	79.8	1.79 ± 0.19	0.20 ± 0.03
26	20.2	21 ± 1	0.2	79.6	1.84 ± 0.16	0.24 ± 0.02
27	21.0	21 ± 1	0.3	78.7	3.33 ± 0.12	0.36 ± 0.02
28	21.5	21 ± 1	0.3	78.2	3.81 ± 0.59	0.27 ± 0.11

Table 4 - *Witloof* Endive - O_2 diffusion. Experimental values of diffusional constants $k_{i,O2}$ and H_{O2} (c.i. = confidence interval, p = 0.05) as a function of temperature and gas composition ($PCO_2 \cong 40\%$)

N°	PG=PO_2 (kPa)	Temp. (°C)	PCO_2 (kPa)	PN_2 (kPa)	(k_i±c.i.) $\cdot 10^3$ [mmol/(s · m^2 · kPa)]	H±c.i. [mmol/(kg · kPa)]
1	20.6	1 ± 1	38.0	41.4	2.27 ± 0.62	0.24 ± 0.11
2	39.2	1 ± 1	41.1	19.7	1.10 ± 0.13	0.11 ± 0.02
3	39.5	1 ± 1	43.4	17.1	1.28 ± 0.20	0.11 ± 0.05
4	21.0	6 ± 1	38.0	41.0	1.32 ± 0.27	0.18 ± 0.04
5	33.0	6 ± 1	42.4	24.6	1.39 ± 0.16	0.13 ± 0.05
6	39.6	6 ± 1	44.0	16.4	1.67 ± 0.27	0.11 ± 0.02
7	20.3	11 ± 1	39.4	40.3	3.75 ± 0.58	0.41 ± 0.12
8	40.0	11 ± 1	42.0	18.0	2.55 ± 1.04	0.20 ± 0.11
9	43.0	11 ± 1	38.2	18.8	3.18 ± 0.43	0.22 ± 0.06
10	17.2	16 ± 1	39.4	43.4	2.94 ± 0.67	0.36 ± 0.11
11	33.6	16 ± 1	35.6	30.8	1.57 ± 0.26	0.18 ± 0.04
12	37.0	16 ± 1	44.0	19.0	0.91 ± 0.12	0.13 ± 0.01
13	19.9	21 ± 1	42.9	37.2	1.50 ± 0.25	0.48 ± 0.04
14	40.6	21 ± 1	41.8	17.6	2.16 ± 0.27	0.16 ± 0.04
15	43.5	21 ± 1	42.5	14.0	3.16 ± 1.12	0.40 ± 0.20

Table 5 - *Witloof* Endive - CO_2 diffusion. Experimental values of diffusional constants $k_{i,CO2}$ and H_{CO2} (c.i. = confidence interval, p = 0.05) as a function of temperature and gas composition ($PO_2 \cong 3\%$)

N°	$PG=PCO_2$ (kPa)	Temp. (°C)	PO_2 (kPa)	PN_2 (kPa)	$(k_i \pm c.i.) \cdot 10^3$ [mmol/(s · m² · kPa)]	H±c.i. [mmol/(kg · kPa)]
1	42.0	1 ± 1	4.0	54.0	2.42 ± 0.39	0.28 ± 0.09
2	43.2	1 ± 1	4.9	51.9	2.47 ± 0.10	0.26 ± 0.10
3	31.6	1 ± 1	3.4	65.0	1.50 ± 0.39	0.45 ± 0.13
4	37.5	1 ± 1	4.3	58.2	1.44 ± 0.26	0.44 ± 0.21
5	55.0	1 ± 1	4.4	40.6	2.91 ± 0.47	0.27 ± 0.10
6	56.0	1 ± 1	2.9	41.1	4.71 ± 1.04	0.33 ± 0.62
7	35.4	1 ± 1	3.4	61.2	0.89 ± 0.10	0.29 ± 0.09
8	33.3	1 ± 1	4.7	62.0	1.76 ± 0.32	0.28 ± 0.10
9	24.3	1 ± 1	3.8	71.9	0.76 ± 0.36	0.37 ± 0.48
10	22.5	1 ± 1	3.9	73.6	1.10 ± 0.89	0.32 ± 0.74
11	35.2	6 ± 1	5.6	59.2	1.65 ± 0.10	0.29 ± 0.06
12	46.0	6 ± 1	4.4	49.6	9.70 ± 0.80	0.47 ± 0.14
13	62.6	6 ± 1	2.9	34.5	9.37 ± 0.93	0.61 ± 0.09
14	37.3	6 ± 1	2.8	59.9	5.60 ± 1.13	0.45 ± 0.77
15	30.7	6 ± 1	3.5	65.8	2.32 ± 2.07	0.30 ± 1.79
16	36.4	6 ± 1	2.9	60.7	2.01 ± 0.26	0.29 ± 0.19
17	38.5	6 ± 1	3.3	58.2	3.06±1.59	0.38 ± 3.49
18	20.6	6 ± 1	4.1	75.3	0.84 ± 1.26	0.22 ± 0.26
19	21.8	6 ± 1	3.9	74.3	1.63 ± 1.27	0.42 ± 0.30
20	30.6	11 ± 1	4.5	64.9	0.80 ± 0.08	0.39 ± 0.07
21	39.6	11 ± 1	3.4	57.0	2.58 ± 0.44	0.32 ± 0.06
22	39.6	11 ± 1	4.2	56.2	2.47 ± 0.39	0.38 ± 0.11
23	41.2	11 ± 1	4.6	54.2	4.14 ± 1.03	0.45 ± 0.84
24	41.4	11 ± 1	2.9	55.7	2.64 ± 1.58	0.40 ± 0.46
25	20.7	11 ± 1	4.6	74.7	0.57 ± 0.21	0.27 ± 0.36
26	20.2	11 ± 1	4.1	75.7	1.62 ± 1.38	0.24 ± 0.27
27	30.4	16 ± 1	4.6	65.0	0.56 ± 0.12	0.25 ± 0.06
28	66.5	16 ± 1	5.1	28.4	11.39 ± 0.67	0.48 ± 0.03
29	40.0	16 ± 1	4.7	55.3	8.84 ± 0.49	0.47 ± 0.06
30	44.7	16 ± 1	3.6	51.7	10.46 ± 1.54	0.75 ± 0.34
31	24.0	16 ± 1	4.3	71.7	10.43 ± 1.54	0.66 ± 0.32
32	21.1	16 ± 1	3.6	75.3	0.47 ± 1.59	0.20 ± 0.39
33	33.5	21 ± 1	3.9	62.6	1.08 ± 0.06	0.58 ± 0.22
34	38.9	21 ± 1	4.1	57.0	7.95 ± 0.13	0.31 ± 0.23
35	31.0	21 ± 1	4.6	64.4	15.14 ± 0.79	0.58 ± 0.32
36	77.4	21 ± 1	3.7	18.9	21.34 ± 0.37	0.58 ± 0.41
37	46.2	21 ± 1	4.3	49.5	10.00 ± 0.87	0.61 ± 0.29
38	41.2	21 ± 1	3.7	55.1	4.33 ± 1.63	0.29 ± 0.37
39	40.5	21 ± 1	4.2	55.3	2.25 ± 0.63	0.29 ± 0.11
40	27.5	21 ± 1	3.2	69.3	8.85 ± 1.27	0.68 ± 0.65

Table 6 - Tomato fruits - O_2 diffusion. Experimental values of diffusional constants $k_{i,O2}$ and H_{O2} (c.i. = confidence interval, p = 0.05) as a function of temperature and gas composition

N°	PG=PO_2 (kPa)	Temp. (°C)	PCO_2 (kPa)	PN_2 (kPa)	($k_i \pm$ c.i.) · 10^4 [mmol/(s · m^2 · kPa)]	H ± c.i. [mmol/(kg · kPa)]
1	20.1	1±1	23.2	56.7	2.75±0.18	0.053±0.007
2	21.1	1±1	10.7	68.2	5.06±2.86	0.054±0.021
3	21.3	1±1	9.6	69.1	3.43±0.25	0.050±0.007
4	39.5	1±1	17.4	56.7	2.75±0.18	0.053±0.007
5	41.0	1±1	19.5	39.5	5.15±2.44	0.073±0.011
6	41.1	1±1	38.2	20.7	3.49±0.90	0.062±0.009
7	20.2	6±1	7.0	72.8	3.36±0.50	0.056±0.009
8	20.4	6±1	21.5	58.1	2.24±0.35	0.050±0.003
9	21.0	6±1	8.2	70.8	2.32±0.37	0.051±0.005
10	36.8	6±1	18.1	45.1	6.55±2.73	0.080±0.035
11	41.5	6±1	20.9	37.6	3.22±0.47	0.047±0.008
12	41.5	6±1	36.3	22.2	3.27±0.53	0.052±0.003
13	20.8	11±1	8.7	70.5	2.07±0.56	0.068±0.017
14	21.6	11±1	19.5	58.9	2.48±0.83	0.075±0.009
15	38.9	11±1	19.4	41.7	3.74±1.55	0.059±0.016
16	40.8	11±1	41.7	17.5	3.12±1.09	0.076±0.018
17	21.3	16±1	8.3	70.4	2.19±0.49	0.076±0.009
18	24.1	16±1	20.9	55.0	2.56±0.90	0.063±0.009
19	38.7	16±1	18.5	42.8	3.39±0.52	0.045±0.013
20	41.1	16±1	38.8	20.1	3.08±1.03	0.071±0.015
21	23.0	21±1	22.1	54.9	2.11±0.20	0.077±0.007
22	40.9	21±1	39.9	19.2	3.55±0.80	0.066±0.011
23	41.1	21±1	20.8	38.1	1.84±0.26	0.065±0.005
24	41.8	21±1	41.0	18.2	2.46±0.09	0.087±0.003

Table 7 - Tomato fruits - CO_2 diffusion. Experimental values of diffusional constants $k_{i,CO2}$ and H_{CO2} (c.i. = confidence interval, p = 0.05) as a function of temperature and gas composition

N°	PG=PCO_2 (kPa)	Temp. (°C)	PO_2 (kPa)	PN_2 (kPa)	($k_{i,CO2}$ ± c.i.) · 10^4 [mmol/(s · m^2 · kPa)]	H_{CO2} ± c.i. [mmol/(kg · kPa)]
1	20.1	1±1	39.6	40.3	5.11±0.68	0.292±0.036
2	20.7	1±1	39.4	39.9	4.73±0.33	0.203±0.018
3	23.2	1±1	19.8	57.0	2.96±0.17	0.144±0.006
4	20.5	6±1	20.1	59.4	3.47±0.31	0.259±0.014
5	21.9	6±1	20.1	58.0	2.98±0.19	0.105±0.007
6	22.1	6±1	38.6	39.3	4.47±0.38	0.217±0.030
7	36.0	6±1	21.3	42.7	4.02±0.69	0.197±0.024
8	38.6	6±1	20.3	41.1	5.66±1.24	0.221±0.052
9	20.5	11±1	39.8	39.7	5.00±0.63	0.232±0.059
10	21.4	11±1	40.0	38.6	5.93±.33	0.246±0.081
11	21.7	11±1	22.3	56.0	1.91±0.38	0.075±0.007
12	21.9	11±1	20.4	57.7	2.93±0.37	0.089±0.006
13	27.7	11±1	20.6	51.7	5.84±0.84	0.265±0.049
14	38.4	11±1	20.4	41.2	5.52±0.95	0.265±0.093
15	19.5	16±1	41.5	39.0	3.64±0.68	0.131±0.076
16	24.6	16±1	19.8	55.6	4.20±0.48	0.153±0.018
17	38.5	16±1	20.9	40.6	2.57±0.51	0.258±0.034
18	20.3	21±1	22.2	57.5	2.99±0.62	0.161±0.033
19	20.5	21±1	39.7	39.8	4.88±0.63	0.133±0.025
20	37.8	21±1	20.4	41.8	4.16±0.37	0.276±0.017

Table 8 - *Witloof* Endive - $k_{i,O2}$ temperature evolution as a function of PCO_2 employed

Temperature (°C)	$k_{i,O2}$,(PCO2 ≅ 0) $\cdot 10^4$ [mmol·s^{-1}· m^{-2}· KPa^{-1}]	$k_{i,O2}$,(PCO2 ≅40) $\cdot 10^4$ [mmol·s^{-1}· m^{-2}· kPa^{-1}]
1 ± 1	0.28±0.23	1.55±1.84
6 ± 1	0.55±0.61	1.46±0.54
11 ± 1	0.49±0.54	3.16±1.75
16 ± 1	1.73±0.97	1.81±3.02
21 ± 1	2.25±1.50	2.27±2.43
F calc.	19.96	2.84
F tab. (p = 0.05)	2.82	3.48

Table 9 - *Witloof* Endive - H_{O2} temperature evolution as a function of PCO_2 employed

Temperature (°C)	H_{O2},(PCO2 ≅ 0) [mmol · kg^{-1} · kPa^{-1}]	H_{O2},(PCO2 ≅40) [mmol · kg^{-1} · kPa^{-1}]
1 ± 1	0.019±0.015	0.152±0.219
6 ± 1	0.052±0.067	0.143±0.105
11 ± 1	0.043±0.051	0.275±0.338
16 ± 1	0.169±0.061	0.223±0.353
21 ± 1	0.223±0.113	0.347±0.486
F calc.	26.84	1.75
F tab. (p = 0.05)	2.82	3.48

Table 10 - *Witloof* Endive - $k_{i,CO2}$ and H_{CO2} values as a function of temperature adopted

Temperature (°C)	($k_{i,CO2}$ ± c.i.) · 10^3 [mmol·s^{-1}· m^{-2}· kPa^{-1}]	H_{O2}, ± c.i. [mmol · kg^{-1} · kPa^{-1}]
1 ± 1	2.00 ± 2.18	0.33 ± 0.13
6 ± 1	4.02 ± 6.33	0.38 ± 0.22
11 ± 1	2.12 ± 2.39	0.35 ± 0.15
16 ± 1	7.02 ± 10.32	0.47 ± 0.44
21 ± 1	8.87 ± 12.89	0.49 ± 0.31

Table 11 - Tomato fruits - $k_{i,O2}$ and H_{O2} values as a function of temperature adopted

Temperature (°C)	$(k_{i,CO2} \pm$ c.i.) $\cdot 10^3$ [mmol·s^{-1}· m^{-2}· kPa^{-1}]	$H_{O2,} \pm$ c.i. [mmol · kg^{-1} · kPa^{-1}]
1 ± 1	3.96 ± 1.94	0.059 ± 0.008
6 ± 1	3.49 ± 3.19	0.056 ± 0.025
11 ± 1	2.85 ± 1.72	0.070 ± 0.018
16 ± 1	2.80 ± 1.26	0.064 ± 0.032
21 ± 1	2.49 ± 1.76	0.074 ± 0.024
F_{calc}	1.59	2.32
F_{tab} (p=0.05)	2.90	2.90

Table 12 - Tomato fruits - $k_{i,CO2}$ and H_{CO2} values as a function of temperature adopted

Temperature (°C)	$(k_{i,CO2} \pm$ c.i.) $\cdot 10^3$ [mmol·s^{-1}· m^{-2}· kPa^{-1}]	$H_{O2,} \pm$ c.i. [mmol · kg^{-1} · kPa^{-1}]
1 ± 1	4.27 ± 3.35	0.21 ± 0.22
6 ± 1	4.12 ± 2.19	0.20 ± 0.12
11 ± 1	4.52 ± 3.42	0.19 ± 0.18
16 ± 1	3.47 ± 2.42	0.18 ± 0.20
21 ± 1	4.01 ± 2.78	0.19 ± 0.22
F_{calc}	0.36	0.08
F_{tab} (p=0.05)	3.06	3.06

Table 13 - Mass-transfer constants of apple, chicory and tomato

	APPLE	CHICORY	TOMATO
$(k_{i,O2} \pm c.i.) \cdot 10^4$ $[mmol \cdot s^{-1} \cdot m^{-2} \cdot kPa^{-1}]$	4.3 ± 1.2	2.1 ± 1.6	3.2 ± 1.9
$H_{,O2}$ $[mmol \cdot kg^{-1} \cdot kPa^{-1}]$	0.17 ± 0.07	0.23 ± 0.22	0.063 ± 0.020
$(k_{i,CO2} \pm c.i.) \cdot 10^4$ $[mmol \cdot s^{-1} \cdot m^{-2} \cdot kPa^{-1}]$	10.5*	46.0 ± 79.9	4.1 ± 2.0
$H_{,CO2}$ $[mmol \cdot kg^{-1} \cdot kPa^{-1}]$	0.25 ± 0.02	0.37 ± 0.22	0.20 ± 0.12
d $[g \cdot cm^{-3}]$	0.82	0.85	1.00

* Significative temperature evolution

Table 14: Basic equations, variables and constants involved in the modelling of internal diffusion

Basic equations

1) $R_G = k_{1,-i,G} \cdot A \cdot (H_G \cdot PG - [G^*])$

2) $[G^*] = [G]_{c.s.} + [G]_{i.s.}$

3) $K_{1,2,G} = [G]_{c.s.}/[G]_{i.s.}$

7) $= R \cdot T \cdot d_p \cdot K_{p,G\,(T=21°C)} \cdot e^{-\Delta H°G/R \cdot \{1/(T) - 1/(294.15)\}} / I.S.$

where:
R_G = G mass-transfer rate [mol·kg^{-1}·hr^{-1}]; $k_{1,-i,G}$ = kinetic constant involved in the mass-transfer of G [kg·h^{-1}·m^{-2}];A= surface area of fruit per unit weight [m^2·kg^{-1}]; H_G = equilibrium constant involved in the mass- transfer of G (mol·kg^{-1}· Pa^{-1}); PG = partial pressure of G in the atmosphere (kPa); [G*] = concentration of G inside the apple at a random time t=t (mol·kg^{-1}); $[G]_{c.s.}$ = concentration of G dissolved in the cellular sap (mol·kg^{-1}); $[G]_{i.s.}$ = concentration of G present in the intercellular space (mol·kg^{-1}); $K_{1,2,G}$ = equilibrium constant calculated on the basis of experimental data and assumptions reported in the literature; $\Delta H°_G$ = activation energy connected with partition equilibrium; R = ideal gas constant [m^3·Pa·mol^{-1}·K^{-1}]; T = temperature [K]; d_p=product density [kg·m^{-3}]; $K_{p,G}$ = equilibrium constant [mol · kg^{-1}· Pa^{-1}]; I.S.= fraction of product volume occupied by the intercellular space.

(Pisa, Viterbo)

(ATO)

6.3 Packaging films

6.3.1 Gas permeability

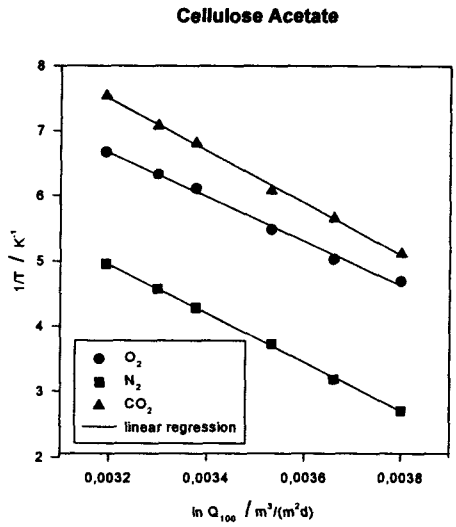


Fig.2: Temperature dependence of gas permeability, normalised to 100 µm film thickness (Q_{100}): Cellulose Acetate ds 2.7

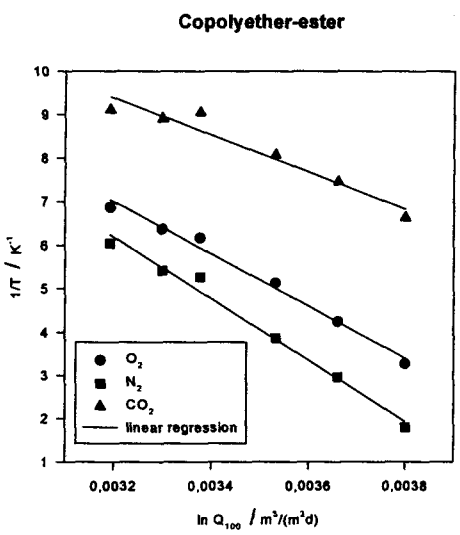


Fig.3: Temperature dependence of gas permeability, normalised to 100 µm film thickness (Q_{100}): Copolyether-ester

6.3.2 Water vapour permeability

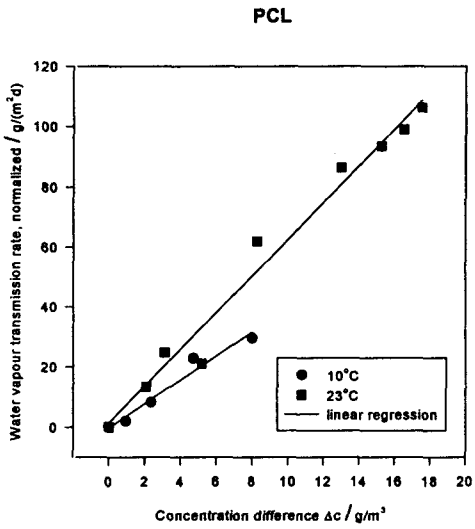


Fig. 6: Water vapour transmission rate, normalised to 100 µm film thickness. Dependence on water vapour concentration difference and temperature: PCL

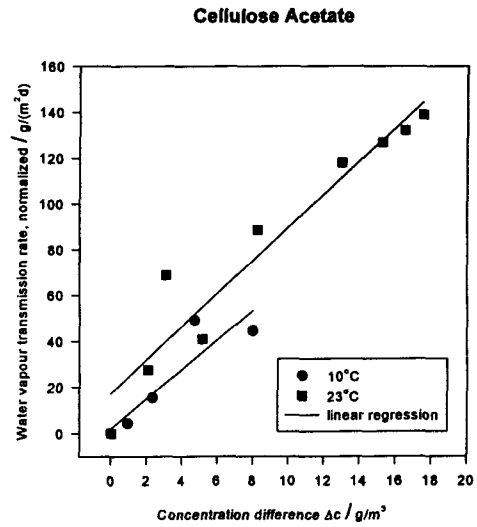


Fig. 7: Water vapour transmission rate, normalised to 100 µm film thickness. Dependence on water vapour concentration difference and temperature: Cellulose Acetate ds 2.7

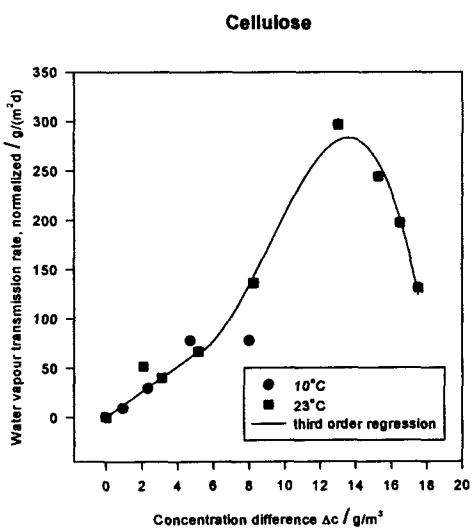


Fig. 8: Water vapour transmission rate, normalised to 100 µm film thickness. Dependence on water vapour concentration difference and temperature: Cellulose

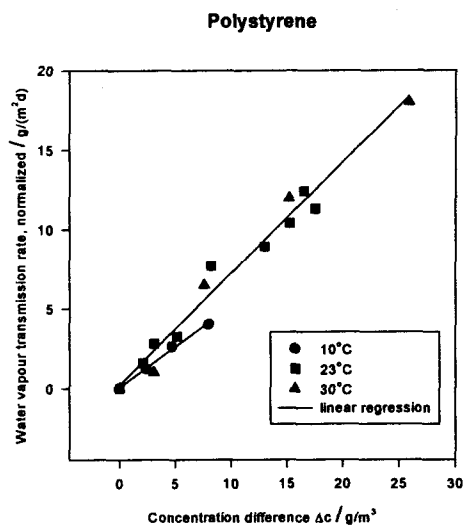


Fig. 9: Water vapour transmission rate, normalised to 100 µm film thickness. Dependence on water vapour concentration difference and temperature: Polystyrene

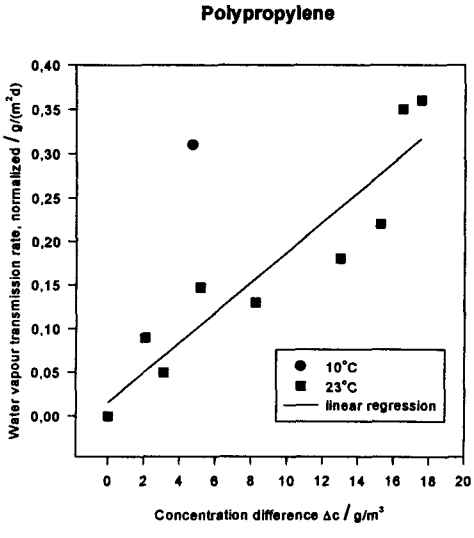


Fig. 10: Water vapour transmission rate, normalised to 100 µm film thickness. Dependence on water vapour concentration difference and temperature: Polypropylene

Table 4: Water vapour transmittances for the different materials at two conditions. Values in g $m^{-2}d^{-1}$ at 23 °C. The right column served for estimating the effect of slight condensation.

Material / thickness in µm	**at 85% → 0% r.h.: Δ c = 17.5 g/ m³**	**at 100% → 50% r.h.: Δ c = 10.3 g/ m³**
PE, 12	14	15
PVC, 16	160	90
EVA/PE, 14	12	7
Copolyether/ester, 9	„2820“[1)] (→3200)	„1800“[1)] (→9000)
Poly (ε-Caprolactone), 15	707	390
Cellulose acetate, 80	174	170
Cellulose, 25	530 ... 700	530 ... 700
Polystyrene, 50	22.6	14
Polypropylene, 20	1.8	1.8
per pore additionally	$2.66 \cdot 10^{-3}$ g/d	

1) Values not very relevant as 5 cm of air also gives 740 g $m^{-2}d^{-1}$ at 23 °C. Values in brackets have been estimated for 2.5 cm of air space

6.4 Packaging experiments

6.4.1 Commercial type of packagings

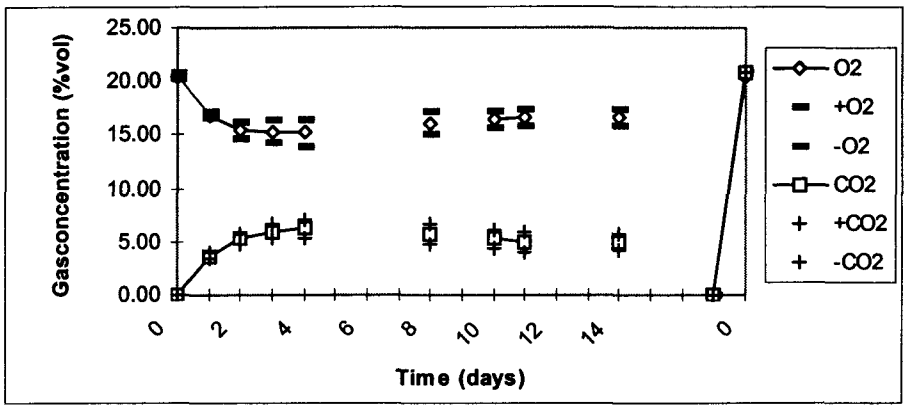


Figure 1: O_2 and CO_2 concentrations in a six pack with tomatoes at 13 °C, packaging foil used: P-plus 10K (polypropylene)

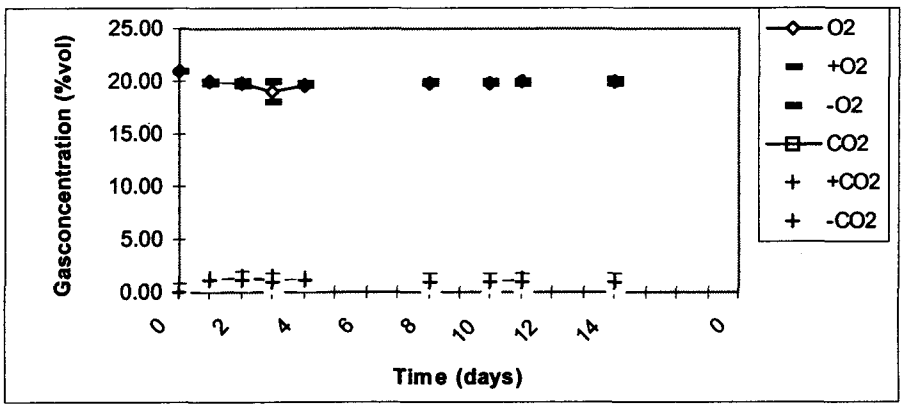


Figure 2: O_2 and CO_2 concentrations in a six pack with tomatoes at 13 °C, packaging foil used: P-plus 100K (polypropylene)

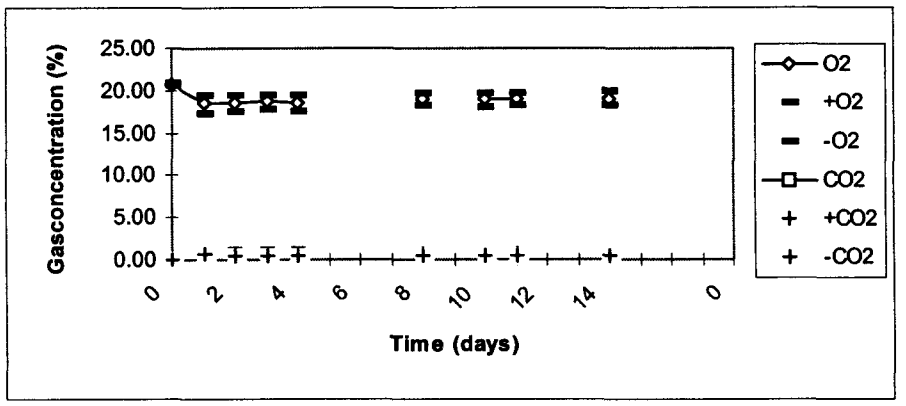


Figure 3: O_2 and CO_2 concentrations in a six pack with tomatoes at 13 °C, packaging foil used: poly-ether/polyester-copolymer

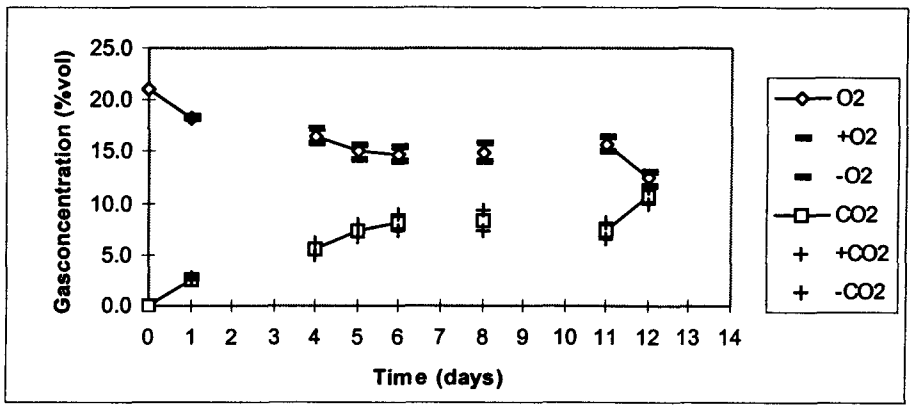


Figure 4: O_2 and CO_2 concentrations in a six pack with tomatoes stored for 4 days at 8 °C, 7 days at 13 °C and 3 days at 23 °C, packaging foil used: P-plus 10K (polypropylene)

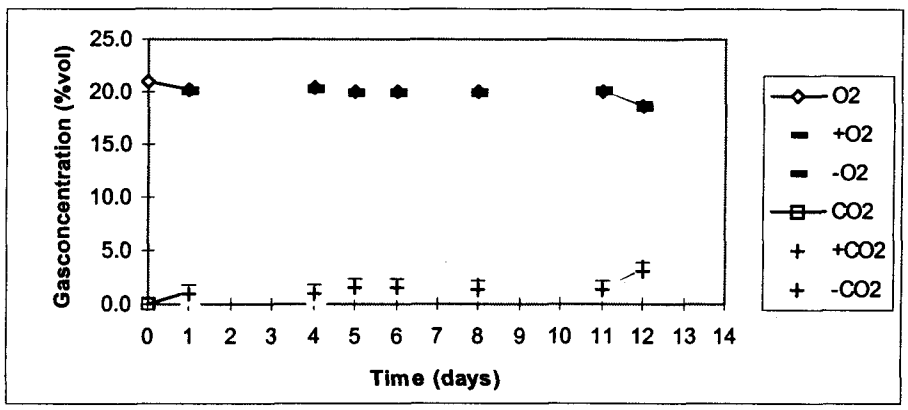


Figure 5: O_2 and CO_2 concentrations in a six pack with tomatoes stored for 4 days at 8 °C, 7 days at 13 °C and 3 days at 23 °C, packaging foil used: P-plus 100K (polypropylene).

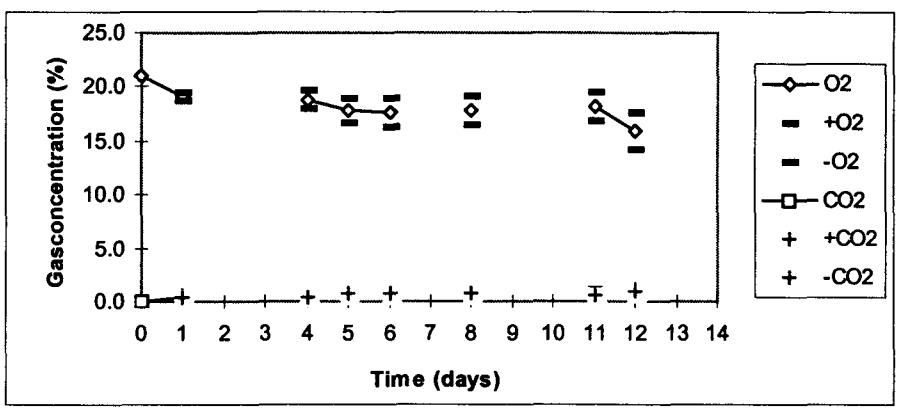


Figure 6: O_2 and CO_2 concentrations in a six pack with tomatoes stored for 4 days at 8 °C, 7 days at 13 °C and 3 days at 23 °C, packaging foil used: polyether/polyester-copolymer

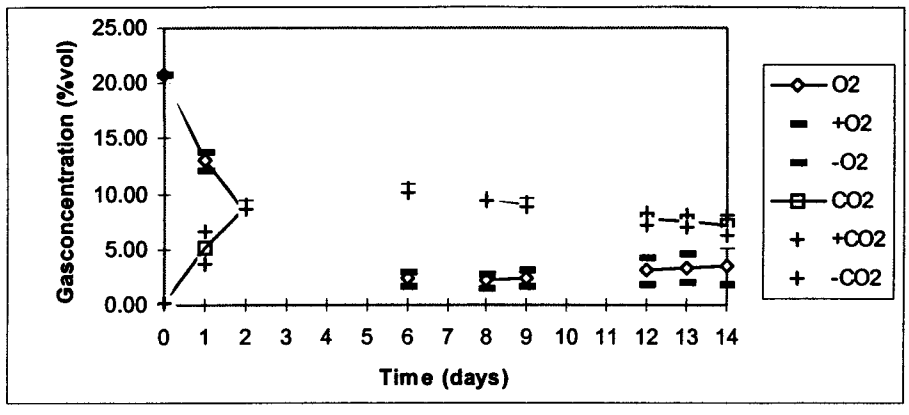


Figure 7: O_2 and CO_2 concentrations in a six pack with apples at 11 °C, packaging foil used: cellulose acetate

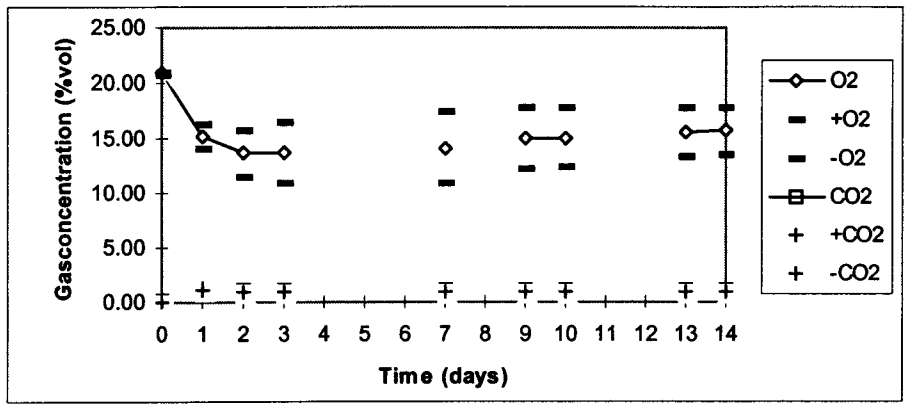


Figure 8: O_2 and CO_2 concentrations in a six pack with apples at 11 °C, packaging foil used: poly-ether/polyester copolymer

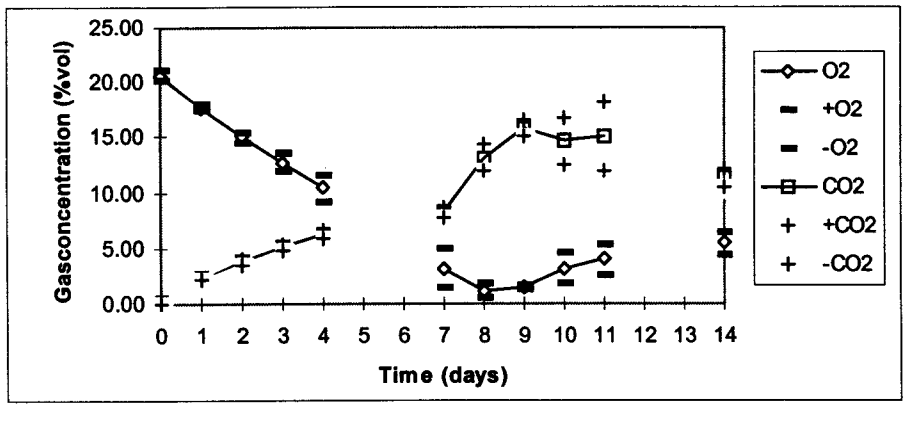


Figure 9: O_2 and CO_2 concentrations in a six pack with apples stored for 7 days at 1 °C, 3 days at 11 °C and 4 days at 21 °C, packaging foil used: cellulose acetate

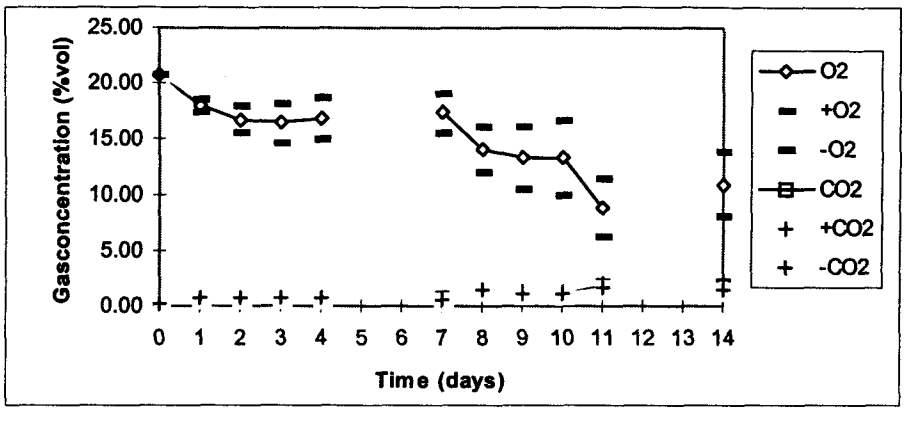
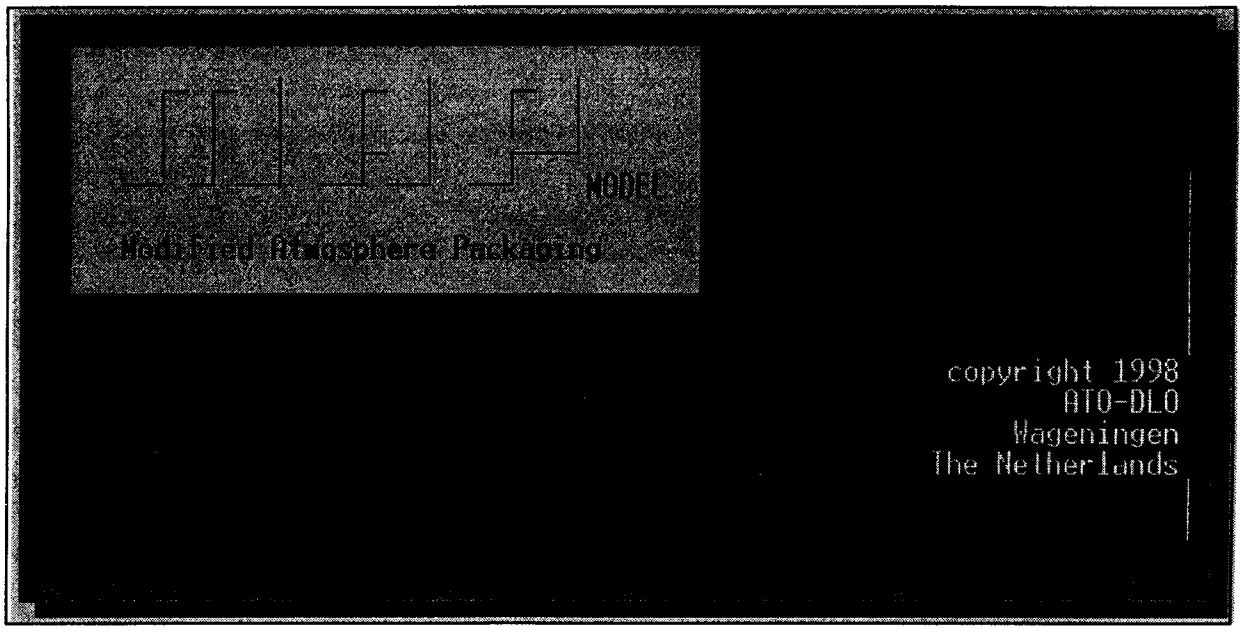


Figure 10: O_2 and CO_2 concentrations in a six pack with apples stored for 7 days at 1 °C, 3 days at 11 °C and 4 days at 21 °C, packaging foil used: polyether/polyester copolymer.

6.5 Modelling of experiments



MAP-simulation model

a PROSIM implementation

Version MH3.0
January 1998

User manual

Table of Contents page

1. INTRODUCTION 1. INTRODUCTION 1. INTRODUCTION

Within the framework of the MASTER-project a dynamic model was developed and implemented in PROSIM (Sierenberg en De Gans bv) describing the complete system of M(odified) A(tmosphere) P(ackaging).
The current version of the MAP model was developed for a scientific educated usergroup. Therefore, it was decided to choose for an open design with all the model parameters visible and available for adjustment by the user. As a consequence the user has complete control to define package, film, product and the climate in and surrounding the package. The user has all freedom to adapt the simulation to his desires on the risk of generating rubbish when used in an unauthorised way.

The mathematical description of the processes: The goal was to develop a simulation package as complete as possible, based on the general elements of the MAP-system. Only the general structure of processes are described which, depending on the specific value of the parameters, can result in the typical behaviour of that specific combination of product, film and pack under that specific surrounding air conditions.

Boundary conditions: Although the MAP-model can be used for a broad range of applications, the validity can in some cases be limited.

- X The individual models incorporated are all of them physically or physiologically founded. Still, when using models outside the range where they were validated one runs a certain risk. So the MAP-model should be applied within or around the area validated (0-21% O_2, 0-20% CO_2, 0-21°C).
- X The MAP-model was developed for simulating small size consumer packages assuming a homogeneous temperature inside the package corresponding to the temperature of the environment. When simulating larger packages, or pallets with packages, one should take into account the changed dynamics of heating and cooling and the inhomogeneous heat distribution. To overcome this partly, the possibility is created to feed the model with measured temperatures, for example for the package in the centre of a pile.
- X The model also assumes a homogeneous distribution of O_2, CO_2, N_2, H_2O in the gas phase inside the package. So no diffusion within the package is described. For the small sized consumer packages this is a realistic approach.

Userinterface: The user supplies the simulation package with the appropriate information by filling in the **U**ser **D**efined **F**iles (UDF) and gets the desired results by a dynamic graphic presentation during the simulation and by digital ASCII output which can be analysed afterwards outside the simulation package.

Applications: The developed MAP model can be used to simulate a wide range of situations by manipulating the parameters in the UDF's. The most important are:

MA-packaging: first of all the model is meant to simulate standard MA packages.
Gas-packaging: by manipulating the initial gas conditions of the microclimate (for example 100% N2), gas packaging can be simulated.
Unpacked Product: by setting the foil thickness at zero the unpacked product can be studied

CA-storage:	if the constant gas conditions of the macroclimate are fixed at CA conditions with a foil thickness of zero the product can be studied at CA.
MA under CA:	if the gas conditions of the macroclimate are fixed at CA conditions in combination with a certain foil thickness the MA packed product can be studied at CA conditions.
Empty package:	by setting the mass of the product to zero, the permeability of the film can be studied while changing the gas conditions of the macroclimate and/or the initial gas conditions of the microclimate.
Logistic chains:	a measured profile for temperature or relative humidity can be used as input for the model to simulate at realistic dynamic conditions occurring throughout a logistic chain.
Compound foils:	a compound foil can be defined by defining multiple layers in FOIL.UDF.
Discontinuities:	Temporarily changes in the permeability of the package (like opening of the package) can be simulated.

2. INSTALLATION2. INSTALLATION2. INSTALLATION

The package can easily be installed. After inserting the diskette in the diskdrive type:

A: <ENTER>

Followed by:

INSTALL <ENTER>

The program will be installed in **C:\MAP**. This location may not be changed.

3. INPUT - OUTPUT3. INPUT - OUTPUT3. INPUT - OUTPUT

The user mainly communicates with the program through the so-called user defined ASCII files (UDF=s). These UDF=s should be located in the directory **C:\MAP**. In each of the files certain parts of the simulation can be defined.

Input files:

CLIMATE.UDF	Defining the macroclimate: constant partial pressure (for O_2, CO_2 and N_2) for the surroundings of the package and constant or dynamic T and RH profiles. Defining the microclimate: initial partial pressure (for O_2, CO_2 and N_2) and the initial relative humidity (in %) inside the package Defining the opening and closing of the package including temporary changes in the permeability of the film
PACK.UDF	Defining the package: type and dimensions
FILM.UDF	Defining the film: a film can be constructed consisting of several layers of different materials. For each of the layers the permeability for O_2, CO_2, N_2 and H_2O must be known.
PRODUCT.UDF	The user has to define some general product properties. The more specific product properties on thermodynamics, respiration and Keeping Quality are preset per product. Data from the MASTER project on the gas exchange of Apple, Chicory and Tomato are included here.
INIT.UDF	This file contains some general simulation parameters.
DATA.UDF	Measured data can be incorporated in this file for comparison with the simulation results

Output files:

RESULTS.UDF	This file contains the simulation results
MONCARLO.UDF	This file contains the simulation results in case of Monte Carlo type, multiple simulation runs
PASSWORD.UDF	This file contains the encrypted password belonging to the software package and can be changed by the authorised user.

4. DESCRIPTION OF THE UDF=S4. DESCRIPTION OF THE UDF=S4. DESCRIPTION OF THE UDF=S

Each of the UDF=s can be edited by using your favourite ASCII editor. It is however of the greatest importance to keep the structure of the UDF=s in their original condition as described below. Furthermore, it is not allowed to use TAB stops in the input file. This will cause the program to fail reading the input files. All text in the UDF=s that is in between two @-signs is handled as comments and is ignored during the reading of the files. The subsequent files will now be discussed in more detail.

4.1 CLIMATE.UDF4.1 CLIMATE.UDF4.1 CLIMATE.UDF

```
...
...
                    @------------------------------@
                    @ DEFINING THE MACROCLIMATE:   @
                    @------------------------------@

@---------------------------------@
@ Temperature (C)                 @
@ day    temp                     @
@---------------------------------@
0        25
2        25
3        2
5        2
5.1      10
-1

@---------------------------------@
@ Relative humidity (in %)        @
@ day    RH(%)                    @
@---------------------------------@
  0      90
 -1

@---------------------------------@
@ partial pressures (in Pa)       @
@---------------------------------@
@  pO2_macro: @      .2100E+05
@ pCO2_macro: @      .0010E+05
@  pN2_macro: @      .7900E+05
...
...
```

This file starts with a section to define the conditions of the macroclimate.
First a temperature scenario must be specified by defining the temperature in function of time. The model will interpolate between two successive points.
In the example temperature is constant at 25 °C from day 0 to day 2. Then there is a gradually change to 2 °C from day 2 to day 3. By diminishing the time interval between subsequent points, sharper drops or rises in temperature can be created. Before the first and after the last point given, this first/last temperature is copied. So after 5.1 days the temperature stays constant at 10 °C. The list must be ended with a A-1". The temperature scenario can be 100 points long. So, also real measured data (time, temperature) can be included. In the same way as for temperature, a scenario for relative humidity (RH) can be defined. In the example RH is fixed at 90%. It wil be clear that the absolute moisture content of the air still varies with the varying temperature!
Next the partial pressures for O_2, CO_2 and N_2 (in Pa) in the macroclimate must be given. These values are assumed to be constant during the whole simulation. By setting these values to CA conditions the package can be studied under CA.

```
...
...
                    @------------------------------@
                    @ DEFINING THE MICROCLIMATE:   @
                    @------------------------------@

@---------------------------------@
@ partial pressures (in Pa)       @
@---------------------------------@
@  pO2_micro: @      .2100E+05
@ pCO2_micro: @      .0010E+05
@  pN2_micro: @      .7900E+05
@---------------------------------@
@ relative humidity (in %)        @
@---------------------------------@
@   RH_micro: @      90
...
...
```

```
...
                    @------------------------------@
                    @ OPENING THE PACKAGE AWHILE   @
                    @ OR OTHERWISE CHANGING THE    @
                    @ PERMEABILITY TEMPORARILY     @
                    @------------------------------@

@---------------------------------@
@ will it be changed?      (Y/N): @   y
@ if so:                          @
@ when    how long  perm.incr.    @
@ (days)  (hours)    (factor)     @
@                  >1 : increase  @
@                   1 : no change @
@               0>..<1 : decrease  @
@                   0 : open      @
@---------------------------------@
   2.5      .25      0
   8        24       .3
   -1
```

Subsequently, the microclimate has to be defined. The initial partial pressure (for O_2, CO_2 and N_2) and the initial relative humidity (in %) must be given. So here you get the possibility to introduce gas packaging. The temperature of the microclimate is assumed to follow directly the temperature of the macro-climate.

It is possible to introduce a scenario during which the package is opened or the permeability is changed otherwise. First you must indicate if this option will be used (Y/N). This is of course only possible when a film is present. The discrete events of opening and closing are defined by a starting time (*when*, in days), a duration (*how long*, in hours) and the size of the effect (*perm.inc.*, as a factor relative to the normal situation). When this factor is 1 the permeability is the same as defined in FILM.UDF. When the factor is >1 the permeability increases. When the factor is 0>..<1 the permeability decreases. When the factor is 0, the package is open (no film present). It is possible to define a list with ten such events. The list must be closed using a A-1".

4.2 PACK.UDF4.2 PACK.UDF4.2 PACK.UDF

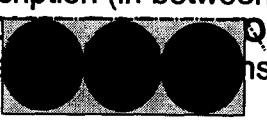
In fact only the first line with a description of a package will be read. The next part of

```
...
...
@ PVC-WRAP          PVC     @ BAG  .21    .14   .002

@-------------------------------------------------------------------------@
@ -DATABASE-DATABASE-DATABASE-DATABASE-DATABASE-DATABASE-DATABASE-DATABASE- @
@-------------------------------------------------------------------------@

@-----------------------------------------------------@
@ description       material type     length width height  @
@-----------------------------------------------------@
@ WIT_PS_BAKJE      PS      @ BOX      .106   .106  .060
@ WIT_PS_BAKJE      PS      @ BOX      .175   .135  .070
@ BLAUW_PS_BAKJE    PS      @ BOX      .123   .104  .065
@ BLAUW_PS_BAKJE    PS      @ BOX      .170   .124  .063

@-----------------------------------------------------@
@ description       material type     volume   diffusion   @
@                                               area        @
@-----------------------------------------------------@
@ GROOT_10,L        RVS     @ MODEL    .014303  0.0620
@ GROOT_3,L         RVS     @ MODEL    .003784  0.0620
...
...
```

the file functions as a kind of database. After the facultative description (in between two @-signs) the type of the package must be specified: **BOX, DISH, BAG or MODEL** (using upper case characters). Depending on the type of package the following dimensions must be specified:

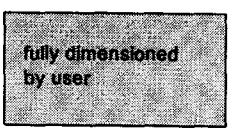
- BOX: length, width and height
  (diffusion area: the upper surface)
- DISH: length, width and height
  (diffusion area: the complete surrounding film)
- BAG: length, width and volume
  (diffusion area: the complete surface of the bag)
- MODEL: volume and diffusion area

The dimensions should be specified in m, m^2, and m^3.


BOX

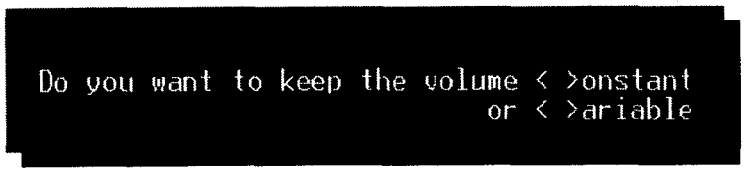

DISH


BAG

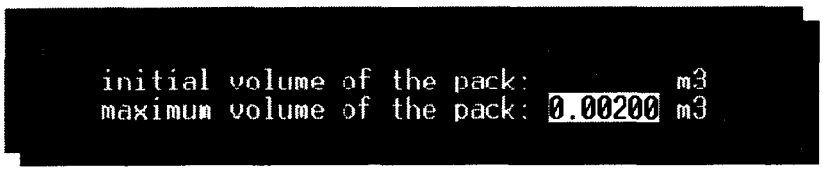


MODEL

In case a flexible bag was specified, the user is asked for additional information at the start of the simulation. First of all he is asked whether he wants to describe the changing volume or whether he wants to assume the volume to stay constant.



In case the user chooses a fully dynamic approach with a varying volume he is asked for the maximum allowable volume of the bag. This value should be equal or larger than the initial volume of the pack.



4.3 FILM.UDF4.3 FILM.UDF4.3 FILM.UDF

The first couple of lines of FILM.UDF contains the definition of the film. The rest of the

```
...
...
@-------------------------------------------------------------------------@
@                        planned  orig.  Trans.rate                       @
@ name, material         thick    thick  at Tref    Ea     Tref   GAS      @
@                        m        m                 J/mol                   @
@-------------------------------------------------------------------------@
type_PS                  10E-06   100E-06      1470   26600  23  @ O2  @
                                               6500   24700  23  @ CO2 @
                                                333   35000  23  @ N2  @
                                                473   15000  23  @ H20 @
-1

@-------------------------------------------------------------------------@
@ -DATABASE-DATABASE-DATABASE-DATABASE-DATABASE-DATABASE-DATABASE-DATABASE- @
@-------------------------------------------------------------------------@
...
...
```

file functions as a database in which the films from the MASTER project are incorporated

The definition of each of the layers consist of a name (a string of maximal 20 characters) followed by the actual thickness of the used film (in m) and the standardized thickness of the film for which the kinetic diffusion constants are valid (also in m). Then an enumeration is given of the kinetic constants of the standard film for the diffusion of O_2, CO_2, N_2 and H_2O. These must be given using the right units:

Transition rate for O_2, CO_2, N_2 at reference temperature:	**ml/m².bar.day**
Transition rate for H_2O at reference temperature:	**g/m².bar.day**
Activation energy:	**J/mol**
reference temperature:	**°C**

When the actual thickness of the film is set to zero this is interpreted as if the product is not packed. Now the respiration can be studied under the conditions of the macroclimate. If the conditions of the macroclimate (see 4.1) are set to CA conditions, the product can be studied at CA conditions.

A compound film can be defined by combining several layers of different materials. The definition of each of the layers is as described above. The list of layer definitions must be ended with a A-1" (even when there is only one layer!). The name of the first layer will be used to address the compound film in the output.

4.4 PRODUCT.UDF4.4 PRODUCT.UDF4.4 PRODUCT.UDF

```
...
...
@--------------------------------------@
@ General product properties:          @
@--------------------------------------@
@ Productname          (in UPPERCASE): @   TOMATO
@ Initial product temperature     (C): @   15
@ Initial mass of the product    (kg): @   .700
@ average weight of one item     (kg): @   .150
@ Standard Temperature for calculating @
@                 Keeping Quality (C): @   14
@--------------------------------------@
...
...
```

The file PRODUCT.UDF contains some general and more specific product properties. At this moment the data from the MASTER project on Apple, Chicory and Tomato are included. First the user has to name the product (using upper case characters) and has to define some general product properties like the initial temperature of the product, the total mass of the packed product and the average weight of the product (per item). When the mass of the product is set to zero, an empty package can be defined to study the film chracteristics. The last parameter is the standard temperature at which the remaining Keeping Quality (under atmospheric conditions) must be calculated. Based on the given product name the specific product properties from the next section is taken. This concerns some physical properties and model parameters on respiration and Keeping Quality. The structure for each of the products is the following:
When new products are added it should be done following this structure. The meaning

```
...
...

@------@
 TOMATO
@------@

@--------------------------------------@
@ Specific weight of product  (kg/m3): @   1005
@ Specific heat of product   (J/kg.K): @   4.0E+03
@ Heat conductivity           (W/m.K): @   .57
@ Specific transpiration (kg/kg.Pa.s): @   .3E-10
@--------------------------------------@

@-------------------------------------------------------------------@
@ Kinetic constants of the Gas Exchange (mmol/kg.h)                 @
@ respiration:           fermentation:              general:        @
@-------------------------------------------------------------------@
@   Vmo2_ref @  .4326     @ Vmco2_ref @  .1489       @ RQ   @  .8971
@    Ea_vmo2 @  67402     @  Ea_vmco2 @  64614       @ Tref @  10
@       kmo2 @  22.55
@     kmcco2 @  26.10      @    kmco2f @  2.712
@     kmuco2 @  7.700      @   kmcco2f @  12.68
@-------------------------------------------------------------------@

@--------------------------------------@
@ Kinetic constants of KEEPING QUALITY:@
@                              T_ref @   10
@                         KQ at T_ref @   26.510
@  k_ref         Ea_ref              @
@--------------------------------------@
   1             77897
   3.15          -421510
-1
...
...
...
END
```

of the model parameters is explained in section *6. Mathematical Background*. Take care that the file is always ended with AEND≅.

4.5 INIT.UDF4.5 INIT.UDF4.5 INIT.UDF

```
...
...
@-------------------------------@
@              runtime  (days): @  4
@ frequency for output (hours): @  4
@            (0 for no output)  @
@                          ID: @  ################
@   time unit used in DATA.UDF  @
@              D(ays), H(ours): @  d
@-------------------------------@
...
...
```

This file contains some general parameters for the simulation. First of all the runtime (in days) can be adapted. However, the graphical display uses a time axes of two weeks. So, if a longer runtime is defined the simulation results are not shown on screen but can still be studied in the output file. The *frequency for output (hours)* determines the frequency for ASCII-output. Furthermore an identification string of 20 characters can be given which is used in the output file. Also the time unit used for the experimental data (in DATA.UDF) can be defined.

```
...
...
@-------------------------------@
@    Monte Carlo simulations    @
@       ** if n_sim > 1 **      @
@-------------------------------@
@        number of simulations: @  1
@                               @
@       - DEVIATIONS (%) -      @
@                               @
@              mass of product: @  15
@                 gas exchange: @  0
@              initial quality: @  0
@                thick of film: @  20
@         size of flexible bag: @  10
@-------------------------------@
```

The second part of this file creates the opportunity to perform so called Monte Carlo simulations.
If the number of simulations is set to 1, a single simulation is performed according the input in the previous described UDF=s. The output is send to the file RESULTS.UDF.
If the number of simulations is set larger than 1, multiple simulations are performed. The output is send to the file MONCARLO.UDF. The multiple simulations are executed using varying values for mass of the packed product, rates of gas exchange, initial quality, thickness of the film and the size of a flexible bag. These values are randomly chosen from normal distributions with their average values as defined in the different UDF=s and standard deviations as defined in this file, INIT.UDF. In this way the effect of variation between packages can be studied. This will enhance the comparison between simulated results and experimental results. The deviations are not allowed to be larger than 30%. Else, the probability to generate negative values becomes too large.

4.6 DATA.UDF4.6 DATA.UDF4.6 DATA.UDF

```
@-------------@
@ t  O2   CO2 @
@-------------@
  0  20   0
  1  16   3
  2  13   4
  3  10   4
...
...
 12   5   3
 13   6   3
 14   7   2
-1
```

The file DATA.UDF can be used to easily compare measured experimental data with simulation results. The data points included in this file (time, O_2, CO_2) are represented in the graphs during the simulation. The time unit can be either hours or days, and should be defined in INIT.UDF. The list of data points should be ended with a A-1".

4.7 RESULTS.UDF4.7 RESULTS.UDF4.7 RESULTS.UDF

```
Simulation results from the MAP-model (version MH3.0)        ATO-DLO 1998
Date:  8 -  2 - 1998                                  ID: ####################

     Product: TOMATO                              film: type_PS
        mass: 0.7000 kg                        thickness: 1.000E-5 m
     Package: BAG Rigid                  Diffusion Area:  0.0588 m2
Total volume:  2.0000 l                      Air volume:  1.3035 l
```

time	t_macro	rh_macr	t_prod	vo2	vco2	anaer	o2_%	co2_%	n2_%	P_tot	rh_micr	p_sat	cond_ml	mass_%	kq_st
0.0000	25.000	90.000	15.000	0.35255	0.32325	0.01515	20.3983	0.0971	76.7366	1.01603	90.000	3166.14	0.00000	100.000	14.364
0.1667	25.000	90.000	24.965	0.71210	0.65857	0.02360	17.2521	2.6179	77.2282	1.00957	93.752	3166.14	0.00000	99.999	13.984
0.3333	25.000	90.000	25.000	0.64940	0.60486	0.03051	14.5053	4.1808	78.3667	0.99490	93.836	3166.14	0.00000	99.991	13.580
...															

rh_macro	relative humidity of macroclimate	%
t_prod	temperature of the product	°C
vo2	oxygen consumption by respiration	mmol/kg.h
vco2	carbondioxide production by respiration	mmol/kg.h
anaer	the ratio fermentative/oxydative respiration	-
o2_%	oxygen concentration of microclimate	%
co2_%	carbondioxide concentration of microclimate	%
n2_%	nitrogen concentration of microclimate	%
P_tot	total air pressure in the package	atmosphere
rh_micr	relative humidity of microclimate	%
p_sat	saturation pressure at t_macro	Pa
cond_ml	formed condensate in the package	ml
mass_%	mass expressed as percentage of the initial mass	%
kq_st	keeping quality at standard conditions	days

4.8 MONCARLO.UDF4.8 MONCARLO.UDF4.8 MONCARLO.UDF

```
Simulation results from the MAP-model (version MH3.0)        ATO-DLO 1998

Date:  8 -  2 - 1998                                  ID: ####################
Product: TOMATO                                     Foil: KNPtomaat

                          Monte Carlo Simulations
```

n	mass	kq	Vm_o2	Vm_co2	thick
1	5.50000	2.2003	0.33369	0.12473	9.99E-5
2	5.50000	2.2003	0.35065	0.12425	9.64E-5
3	5.50000	2.2003	0.35437	0.12603	1.04E-4
...					
...					
198	5.50000	2.2003	0.35133	0.14397	1.05E-4
199	5.50000	2.2003	0.32661	0.12498	1.11E-4
200	5.50000	2.2003	0.32804	0.13244	1.10E-4

TIME	COND_L	COND_A	COND_H	O2_L	O2_A	O2_H	CO2_L	CO2_A	CO2_H	RO2_L	RO2_A	RO2_H	RCO2_L	RCO2_A	RCO2_H	ANAE_L	ANAE_A	ANAE_H	KQ_L	KQ_A	KQ_H
0.0000	0.000	0.000	0.000	20.708	20.708	20.708	0.010	0.010	0.010	0.215	0.276	0.325	0.198	0.253	0.297	0.011	0.014	0.019	2.200	2.200	2.200
0.5000	0.000	0.000	0.000	17.484	17.949	18.447	2.104	2.543	2.970	0.107	0.247	0.387	0.102	0.242	0.382	0.005	0.012	0.019	2.200	2.200	2.200

	lower limit / average / upper limit	
O2_L/A/U	oxygen concentration of microclimate lower limit / average / upper limit	%
CO2_L/A/U	carbondioxide concentration of microclimate lower limit / average / upper limit	%
RO2_L/A/U	oxygen consumption by respiration lower limit / average / upper limit	mmol/kg.h
RCO2_L/A/U	carbondioxide production by respiration lower limit / average / upper limit	mmol/kg.h
ANAE_L/A/U	the ratio fermentative/oxydative respiration lower limit / average / upper limit	-
KQ_L/A/U	keeping quality at standard conditions lower limit / average / upper limit	days

4.9 PASSWORD.UDF4.9 PASSWORD.UDF4.9 PASSWORD.UDF

```
@-------------------------@
@ Your encrypted password @
@       do NOT change     @
@-------------------------@
      -201
```

This file contains the encryption of the password necessary for using the simulation package. Do not change this directly in this file.

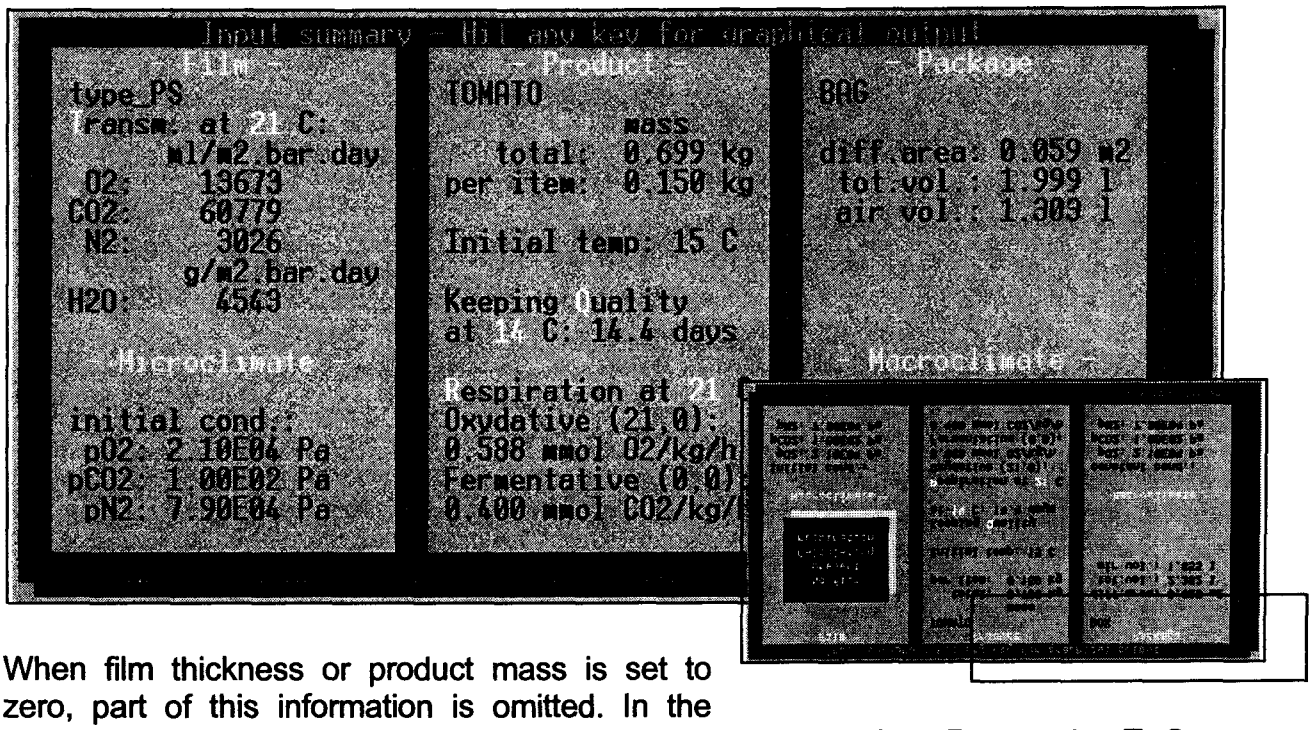
Changing the password can be done in the start up dialogue. After entering the four characters of you password, **don=t** hit the ENTER-key, but hit @. At this moment, an empty input field is given to enter the new password. This password may contain all kind of keystrokes, including spaces and <ENTER>. Furthermore, it is case sensitive. The new password will be encrypted and stored in PASSWORD.UDF and will from now on be your new password.

5. RUNNING THE PROGRAM5. RUNNING THE PROGRAM5. RUNNING THE PROGRAM

After editing the UDF=s in the directory C:\MAP the MAP-model can be started by calling the MAP-model in the same directory.

CD C:\MAP <ENTER>
MAP <ENTER>

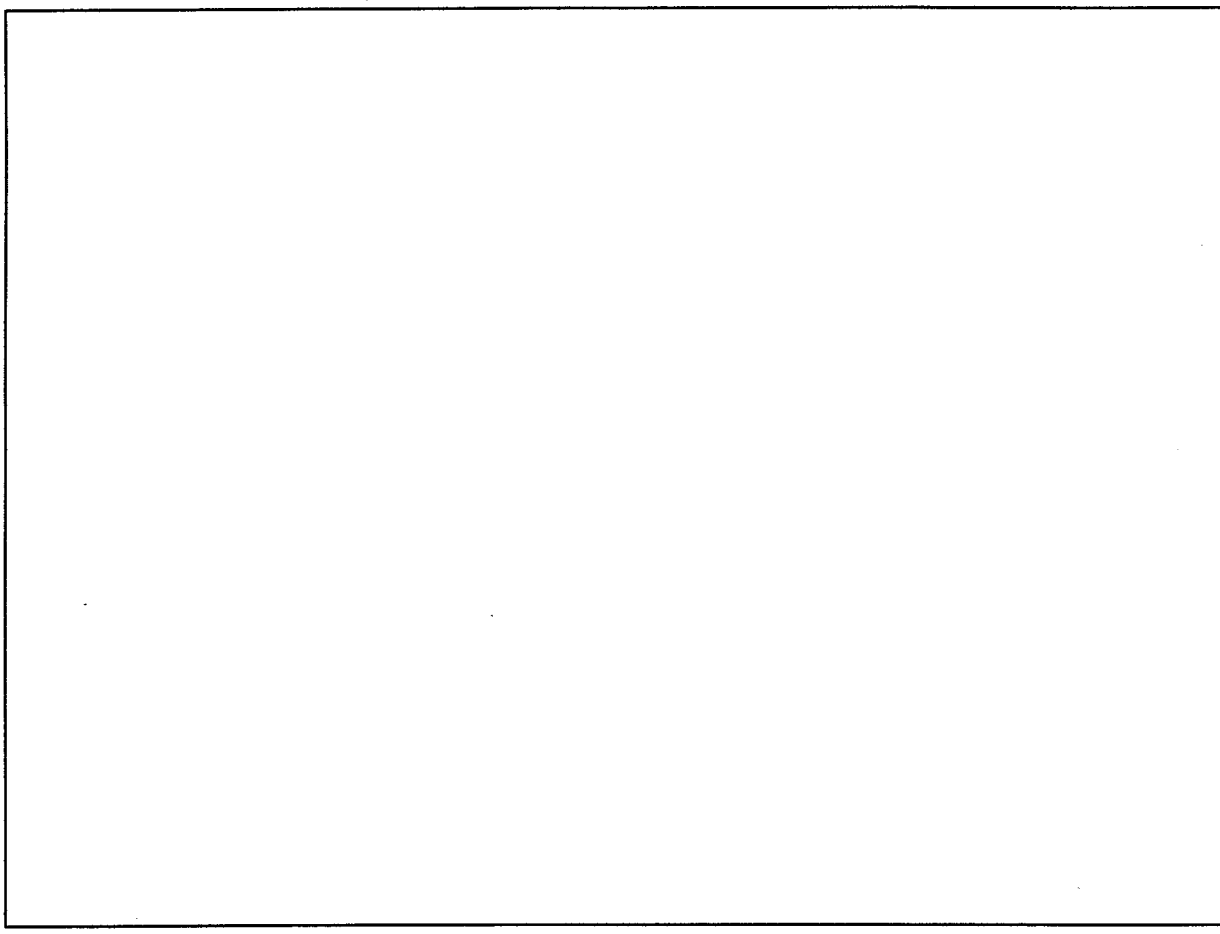
The program will start with an opening screen and subsequently will ask for a password (see 4.9). Then, the UDF=s are read and all model parameters and variables are initiated. If there are some discrepancies in the UDF=s a message will be displayed (see chapter 7). In case a flexible bag was selected as package, an additional dialogue will follow (see 4.2). Then a summary of the input data is displayed on screen.



When film thickness or product mass is set to zero, part of this information is omitted. In the input summary screen some interactive action can be undertaken. By pressing **T**, **Q** or **R** the **T**ransmittance, Keeping **Q**uality or **R**espiration can be calculated at other temperatures than presented at the screen. This can give the user more insight in the concerning processes. The actions taken here are of no influence for the actual simulation.

After hitting any other key, the screen changes to the graphical display screen.

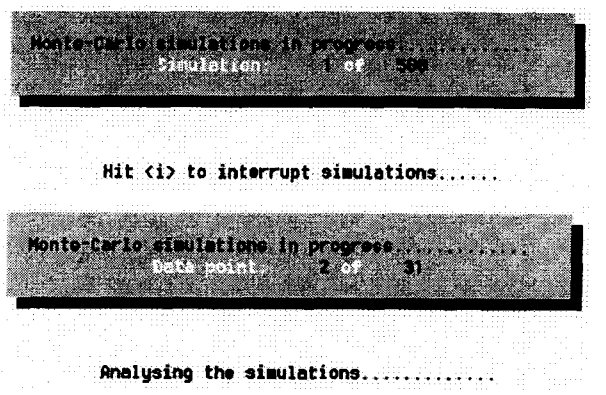
In this screen the most important simulation variables are plotted.



Respiration (mmol/kg.h) red line: O_2 consumption simulated green line: CO_2 production simulated	Temperature (°C) white line: air temperature of the surrounding blue line: product temperature
	Anaerobic activity (ratio) ratio $\frac{\text{fermentative CO2 production}}{\text{total CO2 production}}$
Gas concentrations (%) redline: O_2 concentration simulated red symbols: O_2 concentration measured green line: CO_2 concentration simulated	Condensate (ml) amount of condensate formed
	Keeping Quality (days) Keeping quality remaining at standard conditions (normal air and standard temperature)

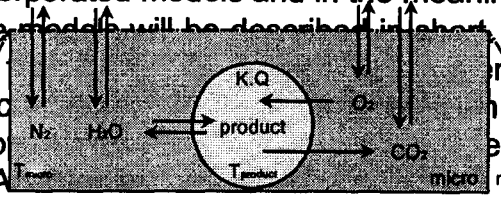
By hitting any key, one can switch between the input summary and the graphical display screen. By hitting **S** one can interrupt the simulation untimely. When the simulation is finished one can exit the program by hitting **X**. The program can always be interrupted by pressing **<SHIFT>F10**. Whenever the input summary is visible one can make use of the interactive possibilities in this screen.

When one uses the option of Monte Carlo simulations the output on screen is a litle different. During the multiple simulations, no graphic output is available. After the input summary one is confronted with a counter, counting the number of simulationans. By hiting **I** the multiple runs can be interrupted at the current one. After completing the simulations, the program has to determine for each time step the average value and the interval containing 95% of the generated data for that time step. After analysing the datapoints of the multiple simulation runs. The average values and the limits enclosing 95% of the simulated values are represented in the graphical display. The corresponding values are saved in the file MONCARLO.UDF.



6. MATHEMATICAL BACKGROUND6. MATHEMATICAL BACKGROUND6. MATHEMATICAL BACKGROUND

To give the user at least some insight in the incorporated models and in the meaning of the different parameters used in the UDF=s the models will be described in short. The system of a MAP can roughly be presented as [illegible] influences the microclimate, which on its turn is in a [illegible] with the surrounding macroclimate. As MAP is develo[illegible]eping quality is one of the major criteria for judging MA[illegible]



6.1 Temperature6.1 Temperature6.1 Temperature

The user defines the temperature of the macroclimate.
The temperature of the microclimate is assumed to follow the macroclimate instantly.
The change of the temperature of the product can be described as:

$$\frac{d\,temp_{prod}}{dt} = \frac{heat_{cond} \bullet area_{prod} \bullet (temp_{micro} - temp_{prod})}{spec_{heat} \bullet mass_{prod} \bullet radi_{prod}}$$

The heat conductivity (better known as ?) and the specific heat (better known as c) are derived from existing data. The area and radius of the product are calculated assuming a spheric body:

$$radi_{prod} = \left(\frac{aver_{wght}}{spec_{wght}} \bullet \frac{3}{4 \bullet \delta} \right)^{1/3}$$

$$area_{prod} = \frac{mass_{prod}}{aver_{wght}} \bullet 4 \bullet \delta \bullet radi_{prod}^{2}$$

The necessary specific weight is also derived from existing data.

6.2 Change of O_2 and CO_2 by Respiration6.2 Change of O_2 and CO_2 by Respiration6.2 Change of O_2 and CO_2 by Respiration

The oxygen production can be described as:

$$vo2 = \frac{vmo2 \bullet po2_{micro} \bullet 0.001}{kmo2 \bullet \left(1 + \frac{pco2_{micro} \bullet 0.001}{kmcco2}\right) + po2_{micro} \bullet 0.001 \bullet \left(1 + \frac{pco2_{micro} \bullet 0.001}{kmuco2}\right)}$$

The factor 0.001 is included because the partial pressures ($po2_{micro}$ and $pco2_{micro}$) in the MAP model are expressed in Pa in contrast to the % used when estimating the parameters for the respiration model. The maximum rate of oxygen production vmo2 depends on temperature of the product according Arrhenius:

$$vmo2 = vmo2_{ref} \bullet e^{\frac{ea_{vmo2}}{R_{gas}} \bullet \left(\frac{1}{tref_{resp}} - \frac{1}{temp_{prod}}\right)}$$

The fermentative part of respiration is responsible for a carbon dioxide production as large as:

$$vco2_{an} = \frac{vmco2}{1 + \frac{po2_{micro} \bullet 0.001}{kmo2f} + \frac{pco2_{micro} \bullet 0.001}{kmco2f}}$$

This descrition includes both an inhibition by O_2 as CO_2. The maximum rate of production (vmco2) depends on temperature:

$$vmco2 = vmco2_{ref} \bullet e^{\frac{ea_{vmco2}}{R_{gas}} \bullet \left(\frac{1}{tref_{resp}} - \frac{1}{temp_{prod}} \right)}$$

Combining this with the oxidative formed amount of carbon dioxide, calculated using the respiration quotient, results in a total CO_2 production rate:

$$vco2 = rq \bullet vo2 + vco2_{an}$$

Because of the relevance of anoxia for quality, an indicators for this is included by the ratio fermentative/oxidative respiration, which is calculated as:

$$anaer = \frac{vco2_{an}}{vco2}$$

6.3 Diffusion through the film6.3 Diffusion through the film6.3 Diffusion through the film

The transmittance of the film is defined in ml/m^2.bar.day for a specific standard film with a standard thickness (100 μm). By multiplying this given transmittance with the standard thickness the diffusion coefficient can be calculated. The diffusion coefficients varies for the different gases and depends on temperature according Arrhenius:

$$Transmittance_{[gas]} = \frac{D_{[gas]}}{d_{foil}}$$

$$D_{[gas]} = D_{ref[gas]} \bullet e^{\frac{ea_{[gas]}}{r_{gas}} \bullet \left(\frac{1}{tref_{[gas]}} - \frac{1}{temp_{macro}} \right)}$$

When using a multi layered film, layers of several materials can be combined. By using an electric analogy the replacement resistance of the compound film can be calculated from the individual layer resistances. The resistance of one single layer is equivalent to the reciproke of its transmittance:

$$R_{layer,i[gas]} = \frac{d_{layer,i}}{D_{i[gas]} \bullet A_{foil}}$$

$$R_{foil[gas]} = R_{layer,1[gas]} + R_{layer,2[gas]} + \ldots.$$

$$= \frac{\sum \frac{d_{layer,i}}{D_{i[gas]}}}{A_{foil}}$$

The way of calculating the diffusion area depends on the shape of the package.
As I=V/R the flux of particles (moles) according to diffusion over the film can now be described as:

$$\frac{dn}{dt} = \frac{p_{macro} - p_{micro}}{R_{foil} \bullet V_{mol}(temp_{macro})}$$

This rate of diffusion was expressed in moles in stead of ml, by use of the molair volume at the macro temperature, to be able to combine it with the respiration flux from/to the product.

6.4 Partial pressure in the microclimate6.4 Partial pressure in the microclimate6.4 Partial pressure in the microclimate

From the general gas law P.V=n.R.T follows that the change of partial pressures in the microclimate can be described by:

$$\frac{dP}{dt} = \frac{R_{gas} \bullet T_{macro}}{V_{micro}} \bullet \frac{dn}{dt}$$

The change of particles (dn/dt) is the total of diffusion through the film and production or consumption through the product. For N_2 it concerns only diffusion. The volume of the microclimate is calculated as difference between package volume and product volume. In case of a flexible package (bag) the pressure inside the package will be constant and the volume will adapt itself to the amount of particles present. Depending on the situation the volume can decrease (shrink to fit the product) or increase up to a maximum allowable volume. From this moment the pressure will change again.

6.5 Transpiration of the product and formation of condensate6.5 Transpiration of the product and formation of condensate6.5 Transpiration of the product and formation of condensate

The water housekeeping is a bit more complicated. The relative humidity of the macroclimate is defined by the user. Water is diffusing through the film and the product transpires. Depending on temperature air can contain more ore less water until a certain saturation level. Beyond this level condensate is formed.
The transpiration of the product is calculated using the given specific transpiration:

$$\frac{dH_2O}{dt} = spec_{mois} \bullet mass_{prod} \bullet (ph2o_{sat}(temp_{prod}) - ph2_{micro})$$

No temperature effect is included. The internal vapour pressure of the product was calculated as a saturated vapour pressure. Diffusion through the film is calculated as described above.
The change of water content of the microclimate is calculated as the summation of diffusion and transpiration. When RH=100% condensate can be formed. When this is the case, no driving force is left for transpiration, unless the product temperature differs from the surrounding temperature. So in other words, the transpiration of the product is zero until all condensate is gone again.

6.6 Mass loss6.6 Mass loss6.6 Mass loss

This is calculated only as water loss because of transpiration.

6.7 Total pressure6.7 Total pressure6.7 Total pressure

The total pressure is calculated as:

$$ptot_{micro} = po2_{micro} + pco2_{micro} + pn2_{micro} + ph2o_{vap}$$

6.8 Keeping quality6.8 Keeping quality6.8 Keeping quality

As MAP is aiming at prolonging shelf life, also a general model on keeping quality is incorporated to give an indication of the success of the MA package in terms of keeping quality. The change of keeping quality is calculated based on the relative respiration in terms of CO_2 production, which is de actual respiration as compared to the respiration under standard atmospheric conditions:

$$rel_{resp} = \frac{vco2}{vco2(\text{atmospheric conditions}, T_{standard})}$$

The initial keeping quality at standard conditions is given by:

$$KQ_{stand,0} = \frac{KQ_{ref}}{k_{st}}$$

The actual decay of quality in MAP is described by the (compound) rate k_{kq}. The rate of decay at given standard conditions is described by the (compound) rate k_{st}. Both of the rates are temperature dependent according to Arrhenius. This results in:

$$\frac{dKQ_{stand}}{dt} = rel_{resp} \bullet \frac{k_{kq}}{k_{st}}$$

7. ERROR MESSAGES AND TROUBLESHOOTING7. ERROR MESSAGES AND TROUBLESHOOTING7. ERROR MESSAGES AND TROUBLESHOOTING

This version has expired, ask for a new update

The lincense for this version has expired, contact ATO-DLO for an updated version

Install MAP in directory >> C:\MAP <<

The program must be installed in this directory

One of the UDF-files not found.
Check C:\MAP for: ########.UDF

All the UDF=s should be present in C:\MAP

Wrong password for this version.....

Restart the program and give the right password. Remember that the password is case sensitive, so check the *Caps Lock*!

Product not found. Check spelling/data in PRODUCT.UDF

Check spelling and the use of UPPERCASE

Package not found. Check spelling/data in PACK.UDF

Check spelling and the use of UPPERCASE

Product does not fit in package. Try again.

Reduce the mass of the produce, or increase the volume of the pack

No film... No product...
So, nothing to simulate!

Check the mass and the foil thickness and give them a value distinct from 0

Deviation given is unrealistic large
This can result in negative values for .....

The deviation for the Monte Carlo simulations may not be larger than 30%

In case of other errors displayed by a yellow box in the lower right corner of the screen:
Contact ATO-DLO and send the text of the error message together with the UDF-s used for the fatal simulation by E-mail to:
M.L.A.T.M.HERTOG@ATO.DLO.NL
You will be assisted as soon as possible.

Two common error messages are:

Conversion error reading file

and

Unexepcted end of file

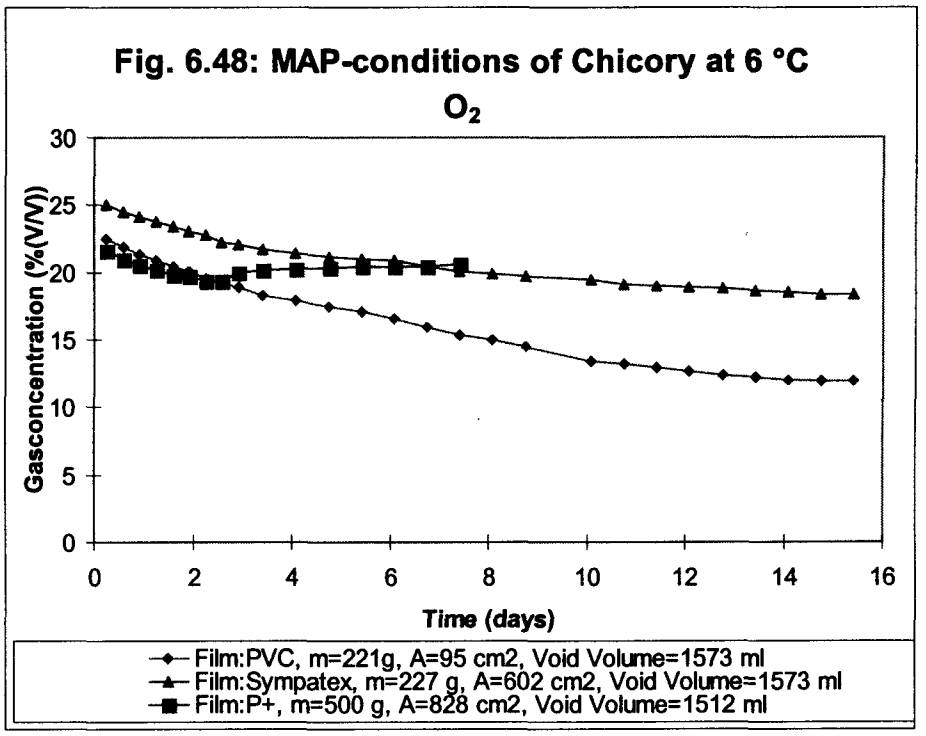
Both can be caused by:

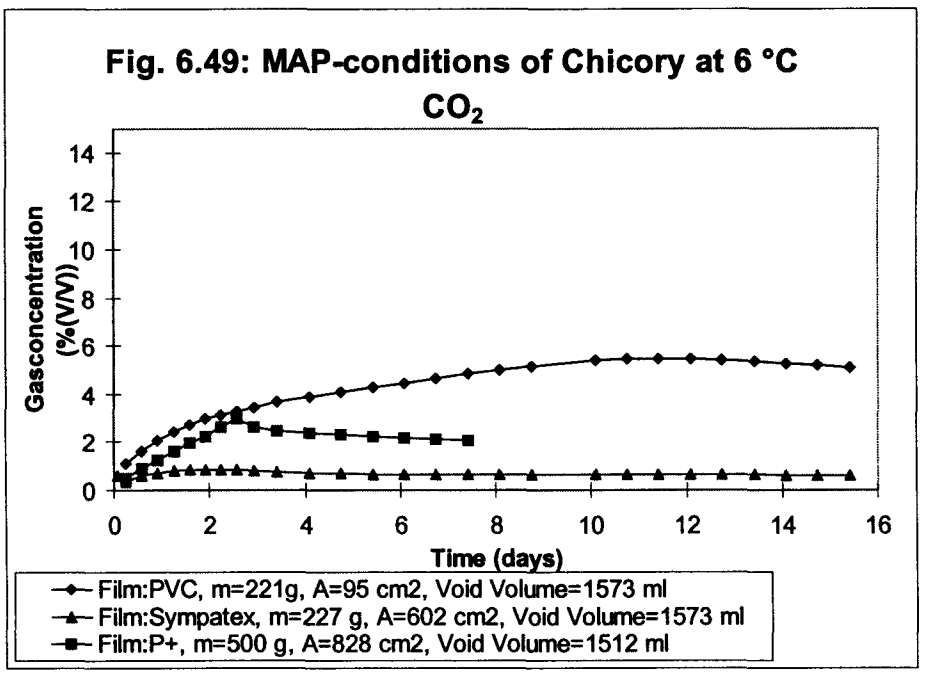
- a missing "-1"
- a missing "END"
- a missing value/string for one of the parameters
- a deleted line from the file
- a TAB stop used instead of spaces
  (This can only be traced by checking all lines using the arrow keys.)

When you are not sure any more about the right structure and layout of your files, you can compare them with the printed versions in this manual.

Examples for application of the MASTER model

Chicory





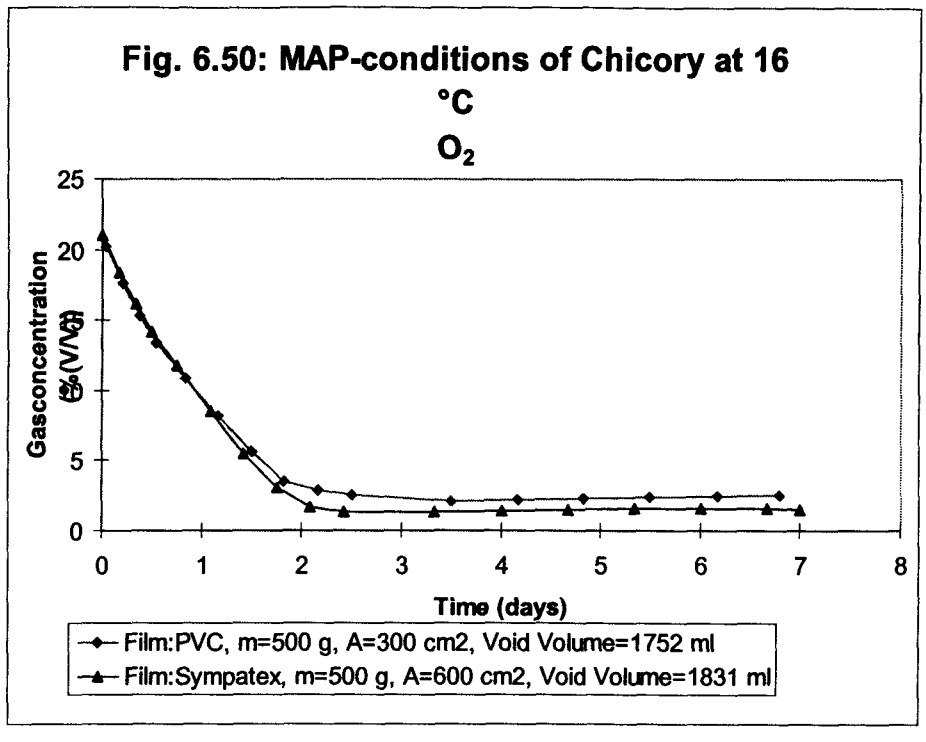


Fig. 6.50: MAP-conditions of Chicory at 16 °C
O_2
Gasconcentration (%(V/V))
25
20
5
0
0 1 2 3 4 5 6 7 8
Time (days)
Film:PVC, m=500 g, A=300 cm2, Void Volume=1752 ml
Film:Sympatex, m=500 g, A=600 cm2, Void Volume=1831 ml

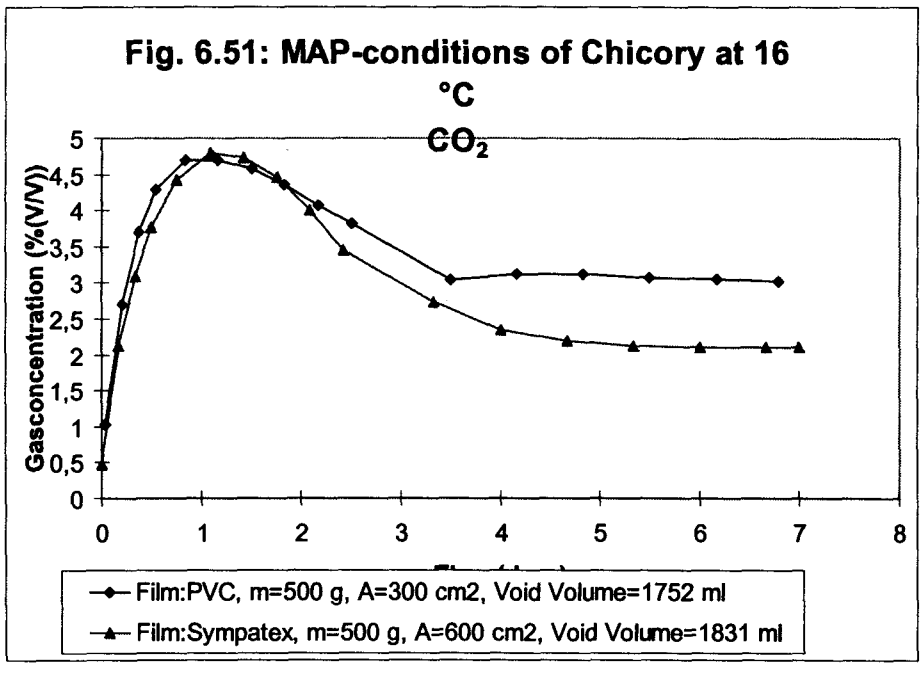


Fig. 6.51: MAP-conditions of Chicory at 16 °C
CO_2
Gasconcentration (%(V/V))
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0
0 1 2 3 4 5 6 7 8
Film:PVC, m=500 g, A=300 cm2, Void Volume=1752 ml
Film:Sympatex, m=500 g, A=600 cm2, Void Volume=1831 ml

Fig. 6.52: MAP-conditions of Chicory at changing temperatures

O_2

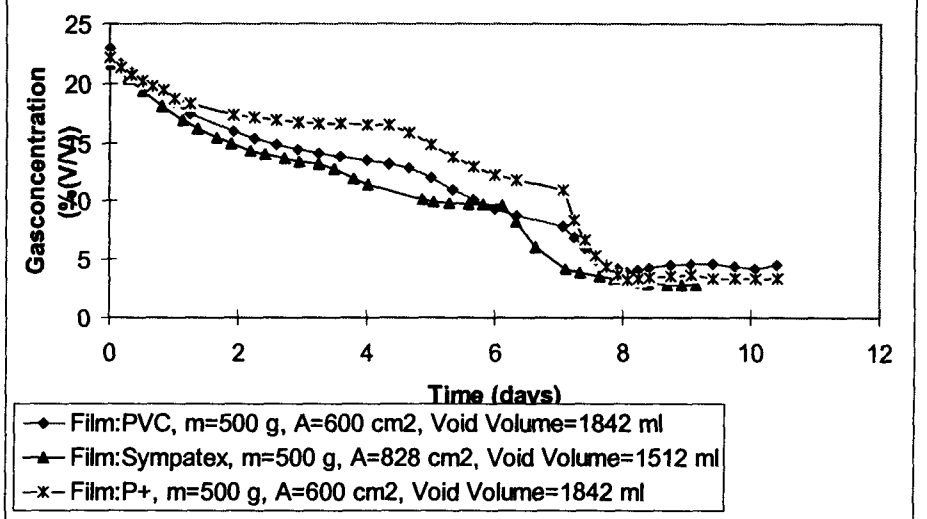
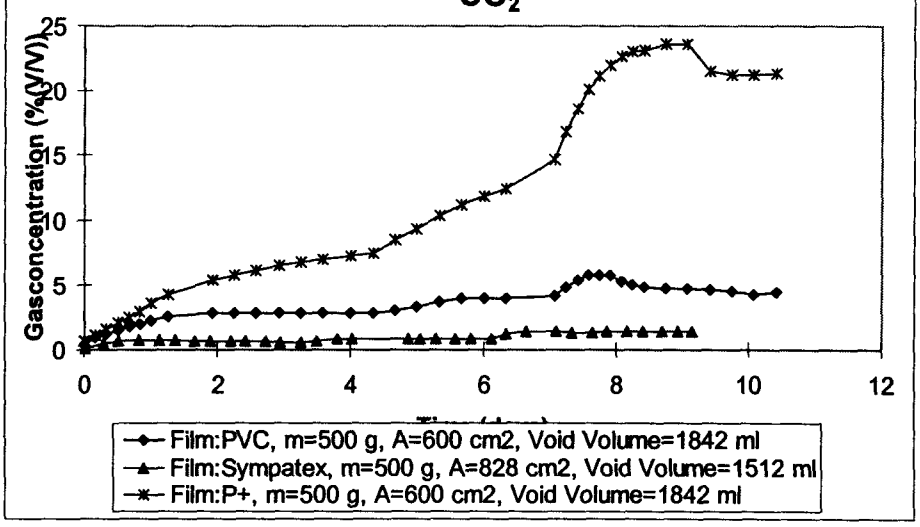


Fig. 6.53:MAP-conditions of Chicory at changing temperatures

CO_2



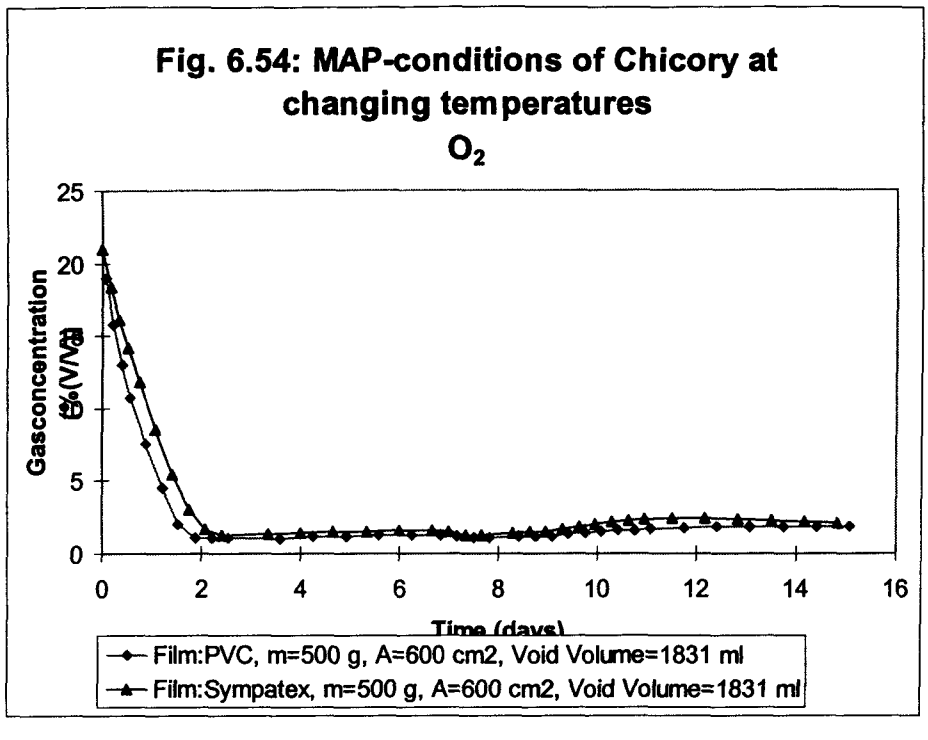


Fig. 6.54: MAP-conditions of Chicory at changing temperatures
O_2
Gasconcentration (%(V/V))
25
20
5
0
0
2
4
6
8
10
12
14
16
Time (days)
Film:PVC, m=500 g, A=600 cm2, Void Volume=1831 ml
Film:Sympatex, m=500 g, A=600 cm2, Void Volume=1831 ml

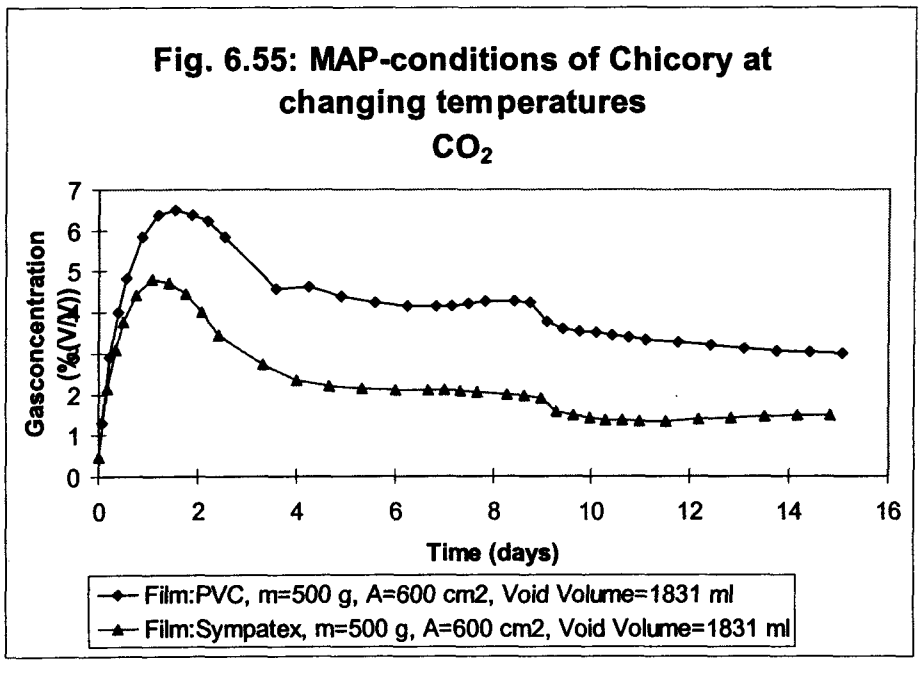


Fig. 6.55: MAP-conditions of Chicory at changing temperatures
CO_2
Gasconcentration (%(V/V))
7
6
5
2
1
0
0
2
4
6
8
10
12
14
16
Time (days)
Film:PVC, m=500 g, A=600 cm2, Void Volume=1831 ml
Film:Sympatex, m=500 g, A=600 cm2, Void Volume=1831 ml

Tomatoes

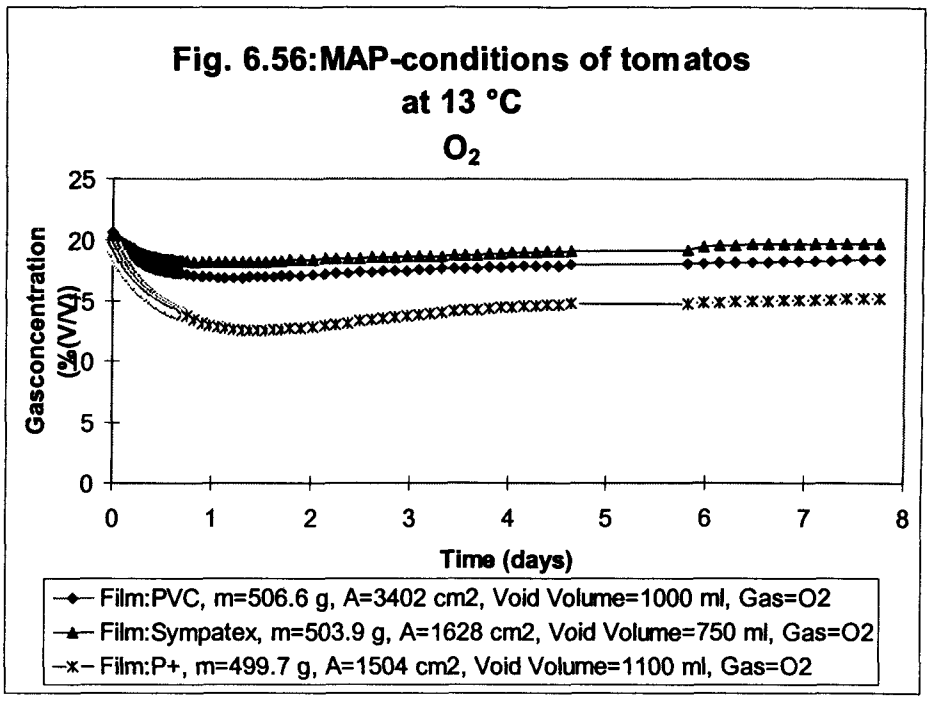


Fig. 6.56:MAP-conditions of tomatos
at 13 °C
O_2
Gasconcentration (%(V/V))
25
20
15
10
5
0
0
1
2
3
4
5
6
7
8
Time (days)
Film:PVC, m=506.6 g, A=3402 cm2, Void Volume=1000 ml, Gas=O2
Film:Sympatex, m=503.9 g, A=1628 cm2, Void Volume=750 ml, Gas=O2
Film:P+, m=499.7 g, A=1504 cm2, Void Volume=1100 ml, Gas=O2

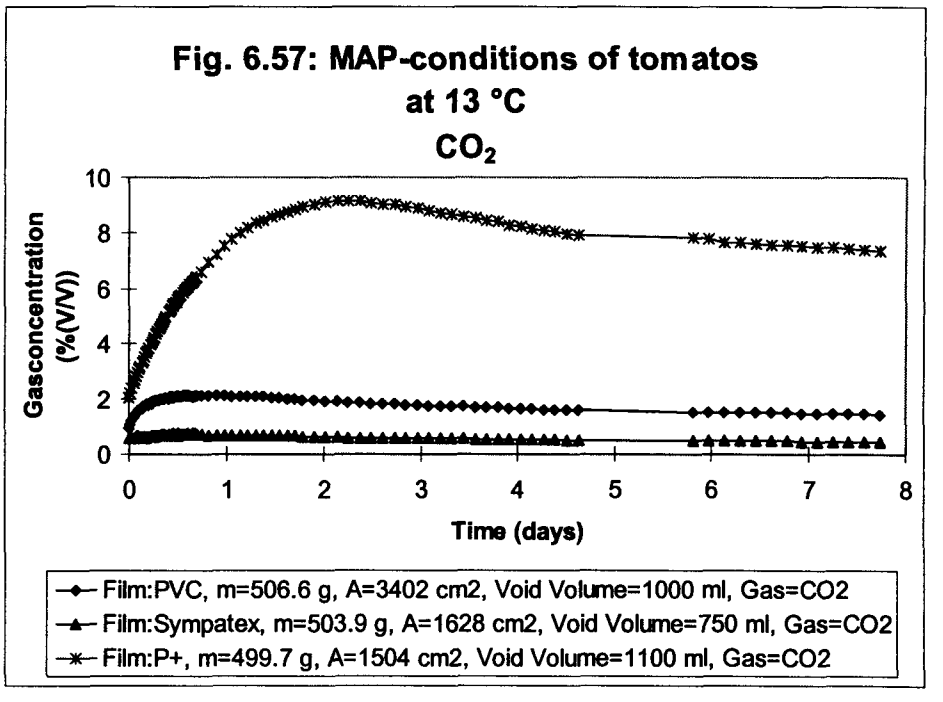


Fig. 6.57: MAP-conditions of tomatos
at 13 °C
CO_2
Gasconcentration (%(V/V))
10
8
6
4
2
0
0
1
2
3
4
5
6
7
8
Time (days)
Film:PVC, m=506.6 g, A=3402 cm2, Void Volume=1000 ml, Gas=CO2
Film:Sympatex, m=503.9 g, A=1628 cm2, Void Volume=750 ml, Gas=CO2
Film:P+, m=499.7 g, A=1504 cm2, Void Volume=1100 ml, Gas=CO2

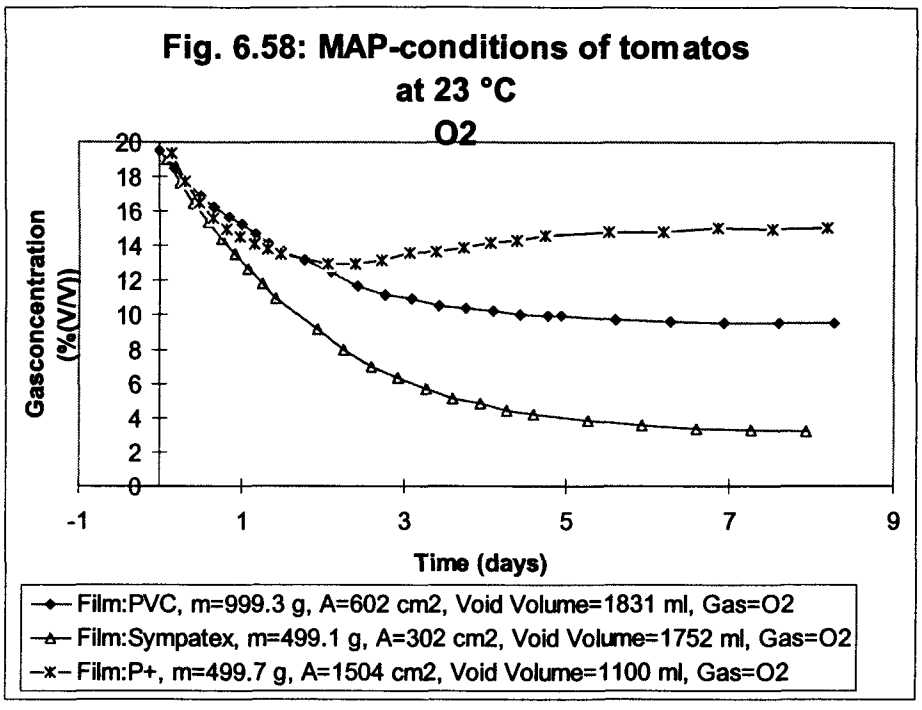


Fig. 6.58: MAP-conditions of tomatos at 23 °C
O2
Gasconcentration (%(V/V))
Time (days)
Film:PVC, m=999.3 g, A=602 cm2, Void Volume=1831 ml, Gas=O2
Film:Sympatex, m=499.1 g, A=302 cm2, Void Volume=1752 ml, Gas=O2
Film:P+, m=499.7 g, A=1504 cm2, Void Volume=1100 ml, Gas=O2

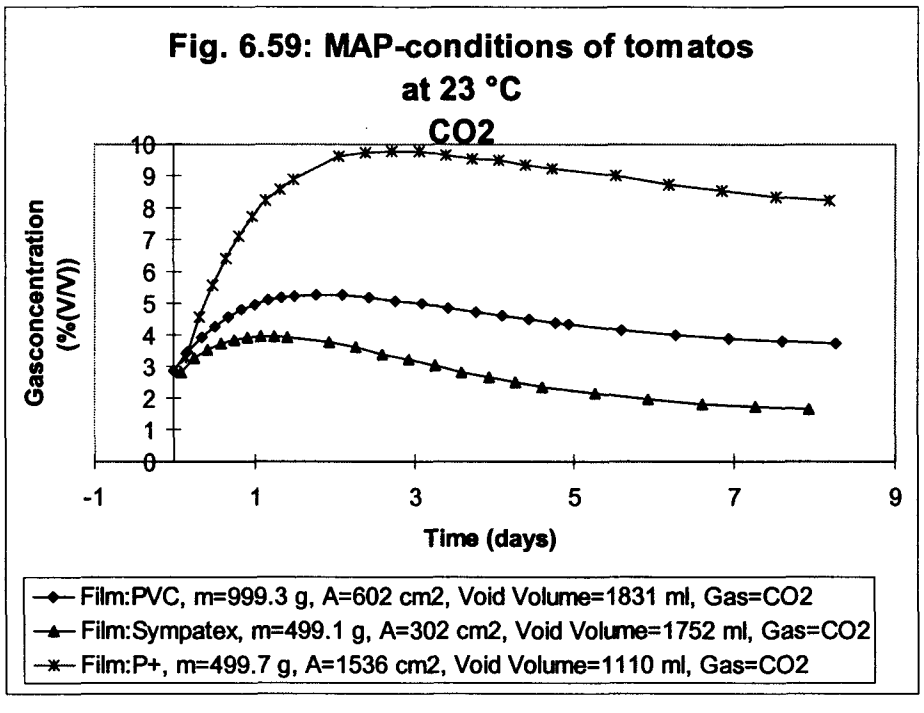


Fig. 6.59: MAP-conditions of tomatos at 23 °C
CO2
Gasconcentration (%(V/V))
Time (days)
Film:PVC, m=999.3 g, A=602 cm2, Void Volume=1831 ml, Gas=CO2
Film:Sympatex, m=499.1 g, A=302 cm2, Void Volume=1752 ml, Gas=CO2
Film:P+, m=499.7 g, A=1536 cm2, Void Volume=1110 ml, Gas=CO2

Annex 6.6: The source code of the MAP-model

Table of contents **page**

DEFINE.MOD

```
@-----+-------------------------+-----+-------------------------------+-----@
@-----|||||||||| M.A.P. ||||||||||-----| M odified                     |-----@
@-----|-------------------------|-----| A tmosphere                   |-----@
@-----|      version MH3.0      |-----| P ackaging                    |-----@
@-----|      January  1998      |-----|                               |-----@
@-----|    Copyright ATO-DLO    |-----| Including: Respiration        |-----@
@-----|-------------------------|-----|            Keeping Quality    |-----@
@-----|    M.L.A.T.M. Hertog    |-----|            Condensation       |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@
```

```
TIMEUNIT:          day

COMPONENT:         macroclimate
                   microclimate
                   film
                   opener
                   product
                   quality
                   data_store
                   watcher
                   screenswitch
                   bag_contr
                   montecarlo
                   worker

CLASS:             layer
                   valueset

QUEUE:             layers
                   values
                   removed

TABLE(100):        temp_tab
                   relh_tab

@-------------------------------------@
 ATTRIBUTES OF MAIN:
@-------------------------------------@

CHARACTER(20):     prod_name
                   film_name
                   search_prod
                   id
                   type
                   time_unit
                   bag

LOGICAL:           ready
                   user
                   multi_run

INTEGER:           i
                   check_date
                   check_data
                   check_film
                   check_prod
                   check_clim
                   check_pack
                   check_pass
                   check_init
                   check_dir
                   check_key
                   checkedfiles
                   n[4]
                   code[5]
                   tijd[4]
                   multirun
                   run_no
                   dat_no
                   n_sim

DOUBLE:            runtime
                   pi
                   r_gas
```

```
                    day_sec
                    day_hour
                    cel_kelv
                    ml_l
                    mmol_mol
                    l_m3
                    kg_g
                    bar_pa
                    p0
                    m_h2o
                    datum
                    key
                    renew_password
                    devi_mass
                    devi_vmax
                    devi_kq
                    devi_film
                    devi_bag

MACRO:              volume
                    pressure
                    vapour

STREAMREFERENCE:    pass_stream
                    carlo_stream

@-------------------------------------@
 ATTRIBUTES OF macroclimate:
@-------------------------------------@

CONTINUOUS(0):      t_macro

DOUBLE:             po2_macro
                    pco2_macro
                    pn2_macro

@-------------------------------------@
 ATTRIBUTES OF microclimate:
@-------------------------------------@

CONTINUOUS(0):      cond_vol
                    o2_perc
                    co2_perc

CONTINUOUS(1):      molo2_micro
                    molco2_micro
                    moln2_micro
                    molh2o_micro
                    moltot_micro

DOUBLE:             max_vol_pack
                    max_vol_air
                    vol_pack
                    extra_vol
                    start_open[10]
                    keep_open[10]
                    perm_open[10]
                    condens_orig

INTEGER:            n_open
                    j

CHARACTER(1) :      open

@-------------------------------------@
 ATTRIBUTES OF film:
@-------------------------------------@

DOUBLE:             thick_film
                    diff_area
                    perm_factor

ATTRIBUTES OF layer:
DOUBLE:             thick
                    dref[5]
                    ea[5]
                    tref[5]
```

```
@-------------------------------------@
 ATTRIBUTES OF product:
@-------------------------------------@

CONTINUOUS(0):     t_prod
                   vo2_out
                   vco2_out
                   anaer

CONTINUOUS(1):     temp_prod
                   mass

DOUBLE:            kmo2
                   kmcco2
                   kmuco2
                   vmo2_ref
                   vmo2_avg
                   ea_vmo2
                   kmo2f
                   kmco2f
                   vmco2_ref
                   vmco2_avg
                   ea_vmco2
                   rq
                   tref_resp
                   vol_prod
                   spec_wght
                   spec_heat
                   heat_cond
                   radi_prod
                   area_prod
                   mass_prod
                   aver_wght
                   spec_mois

@-------------------------------------@
 ATTRIBUTES OF quality:
@-------------------------------------@

CONTINUOUS(1):     kq_st

DOUBLE:            kkq_ref[5]
                   ea_kq[5]
                   tref_kq
                   temp_st
                   k_st
                   kq_ref

INTEGER:           n_proces

@-------------------------------------@
 ATTRIBUTES OF watcher:
@-------------------------------------@

DOUBLE:            freq

@-------------------------------------@
 ATTRIBUTES OF montecarlo:
@-------------------------------------@

CONTINUOUS(0):     tmacro
                   tprod

CONTINUOUS(1):     tempprod

REAL:              time
                   avg[7]
                   sum[7]
                   high[7]
                   low[7]

INTEGER:           outliers
                   c1
                   c2

LOGICAL:           next

ATTRIBUTES OF valueset:
```

```
REAL:              meting[7]

@-------------------------------------@
 ATTRIBUTES OF screenswitch:
@-------------------------------------@

DOUBLE:            mode
                   mode_o

@-------------------------------------@
@             ENVIRONMENT             @
@-------------------------------------@

INPUTSTREAM:       prod_dat
                   film_dat
                   pack_dat
                   clim_dat
                   init_dat
                   expe_dat
                   pass_dat

OUTPUTSTREAM:      results
                   carlo_in
                   carlo_out
                   carlo_normal

RANDOMSTREAM:      rand_mass
                   rand_vmax
                   rand_kq
                   rand_film
                   rand_bag
                   rand_temp

EXTERNAL:          clear_text_box
                   wait_key
                   window_mode
                   get_date
                   erase_file
                   exist_file
                   test_key
                   clear_graph_box
                   gdisplay_string
                   bell
                   sleep
                   open_stream
                   reset_time
                   get_time
```

MAINMOD.MOD

```
@-----+-------------------------+-----+-------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----| Main module from which the    |-----@
@-----|-------------------------|-----| components are initialised    |-----@
@-----|      version MH3.0      |-----| and subsequently activated    |-----@
@-----|      January  1998      |-----|                               |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@

CALL copyright
CALL sleep(2)
CALL wait_key
CALL file_check
   TERMINATE IF checkedfiles ? 7
CALL password
   TERMINATE IF user = FALSE
   CALL password IF renew_password = 64

CALL initsys1

start_run:
```

```
CALL initsys2
CALL initfilm
CALL initproduct
CALL initpack
CALL initbag  IF type = "BAG"
CALL initmacro
CALL initmicro

IF multi_run = FALSE
   CALL initspec
   CALL initexpdata IF check_data = 1
   TERMINATE IF comments = 1
   CALL setscreen
   CALL wait_key
   DISPLAY
"Input summary - Hit <S> to Stop, any other key for graphical output"
AT LINE 1 POSITION 7 COLOUR 7 ON 8 WITH IMAGE A
   CALL window_mode(2) IF multirun ? 1
END

ACTIVATE macroclimate FROM start
ACTIVATE product      FROM start IF mass_prod  > 0
ACTIVATE microclimate FROM start IF thick_film > 0
ACTIVATE quality      FROM start IF mass_prod  > 0
ACTIVATE opener       FROM start IN open_control IF (thick_film > 0)
&       n_open > 0
WAIT 1e-10 SECOND

IF multirun ? 1
   ACTIVATE data_store   FROM start IN auto_store
   ACTIVATE watcher      FROM start IN watch_mod IF (freq > 0)
   ACTIVATE screenswitch FROM start IN scrn_control
END
IF multirun = 1
   ACTIVATE worker       FROM start IN work_mod
   ACTIVATE montecarlo   FROM generate IN monte_carlo IF (freq > 0)
END

WAIT runtime + freq HOURS

CANCEL ALL

multi_run _ TRUE IF multirun = 1

IF multi_run = TRUE
   CALL reset_time
   run_no _ run_no + 1
   REMOVE EACH layer IN layers FROM layers
   GOTO start_run IF run_no = n_sim
   WRITE "-1" TO carlo_out WITH IMAGE a
   ACTIVATE montecarlo FROM analyse IN monte_carlo IF (freq > 0)
END
IF multi_run = FALSE
   ready _ TRUE
   CALL bell
   DISPLAY
"Input summary - Hit <X> to eXit, any other key for graphical output"
AT LINE 1 POSITION 7 COLOUR 7 ON 8 WITH IMAGE A
   CALL window_mode(2) IF mode_o = 1
   ACTIVATE screenswitch FROM start IN scrn_control
END

TERMINATE

start:
INTEGRATE runtime
```

INITSYS1.MAC

```
@-----+-------------------------+-----+------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----|                              |-----@
@-----|-------------------------|-----|  Initializing parameters for  |-----@
```

```
@-----|       version MH3.0       |-----|  redimensioning from and to   |-----@
@-----|       January  1998       |-----|  S.I. units                   |-----@
@-----|     Copyright ATO-DLO     |-----|                               |-----@
@-----|---------------------------|-----|                               |-----@
@-----|     M.L.A.T.M. Hertog     |-----|                               |-----@
@-----|         R.G. Evelo        |-----| INPUTSTREAM: init_dat         |-----@
@-----+---------------------------+-----+-------------------------------+-----@

runtime     _ READ FROM init_dat
freq        _ READ FROM init_dat
id          _ CHREAD FROM init_dat
time_unit   _ CHREAD FROM init_dat
n_sim       _ READ FROM init_dat

IF n_sim > 1
   multirun _ 1
   devi_mass  _ ABS(0.01*READ FROM init_dat)
   devi_vmax  _ ABS(0.01*READ FROM init_dat)
   devi_kq    _ ABS(0.01*READ FROM init_dat)
   devi_film  _ ABS(0.01*READ FROM init_dat)
   devi_bag   _ ABS(0.01*READ FROM init_dat)
END

CALL randomize

pi          _ ARCCOS(-1)
day_sec     _ 86400
day_hour    _ 24
cel_kelv    _ 273.15
r_gas       _ 8.3143
ml_l        _ 1E-03
mmol_mol    _ 1E-03
kg_g        _ 1000
l_m3        _ 1E-03
bar_pa      _ 1E+05
p0          _ 1.01325E+05
m_h2o       _ 18.02

RETURN
```

INITSYS2.MAC

```
@-----+---------------------------+-----+-------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----|  Initializing variables for   |-----@
@-----|---------------------------|-----|  each monte carlo simulation  |-----@
@-----|       version MH3.0       |-----|  again                        |-----@
@-----|       January  1998       |-----|                               |-----@
@-----|     Copyright ATO-DLO     |-----|                               |-----@
@-----|---------------------------|-----|                               |-----@
@-----|     M.L.A.T.M. Hertog     |-----|                               |-----@
@-----|         R.G. Evelo        |-----|                               |-----@
@-----+---------------------------+-----+-------------------------------+-----@

ready       _ FALSE
pressure    _ var_press
volume      _ con_vol
perm_factor_ 1

RETURN
```

INITSPEC.MAC

```
@-----+---------------------------+-----+-------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----| Defining all the continuous   |-----@
@-----|---------------------------|-----| variables in order of subject |-----@
@-----|       version MH3.0       |-----|                               |-----@
@-----|       January  1998       |-----|                               |-----@
@-----|     Copyright ATO-DLO     |-----|                               |-----@
@-----|---------------------------|-----|                               |-----@
```

```
@-----|    M.L.A.T.M. Hertog    |-----|                                |-----@
@-----|        R.G. Evelo       |-----|                                |-----@
@-----+-------------------------+-----+--------------------------------+-----@

@-------------------------------------------------------------------------@
@ TEMPERATURE:                                                            @
@                 T_product: modelling the heat-exchange with the         @
@                            surrounding, taking the product as spheres   @
@-------------------------------------------------------------------------@

SPECIFY temp_prod
PRECEPT(temp_prod' _ (heat_cond*area_prod*(temp_macro-temp_prod))/
(spec_heat*mass_prod*radi_prod))
ABSERROR(1e-6) RELERROR(1e-6)

@-------------------------------------------------------------------------@
@ GAS DIFFUSION INTO THE MICROCLIMATE in terms of MOLES                    @
@-------------------------------------------------------------------------@

SPECIFY molo2_micro  PRECEPT(molo2_micro' _ flux_gas(po2_macro ,
pressure(molo2_micro ), filmresist(1), vo2 , -1, molo2_micro))
ABSERROR(1e-6) RELERROR(1e-6)
SPECIFY molco2_micro PRECEPT(molco2_micro'_ flux_gas(pco2_macro,
pressure(molco2_micro), filmresist(2), vco2, +1, molco2_micro))
ABSERROR(1e-6) RELERROR(1e-6)
SPECIFY moln2_micro  PRECEPT(moln2_micro' _ flux_gas(pn2_macro ,
pressure(moln2_micro ), filmresist(3), 0   ,  0, moln2_micro))
ABSERROR(1e-6) RELERROR(1e-6)

SPECIFY molh2o_micro PRECEPT(molh2o_micro'_ flux_h2o)
ABSERROR(1e-6) RELERROR(1e-6)

SPECIFY moltot_micro PRECEPT(moltot_micro' _ molo2_micro' + molco2_micro'
+ moln2_micro' + (molh2o_micro'*(cond_vol=0)))

@-------------------------------------------------------------------------@
@ FORMATION OF CONDENS AS A RESULT OF SATURATION OF THE AIR                @
@-------------------------------------------------------------------------@

SPECIFY cond_vol PRECEPT(cond_vol _ (molh2o_micro-vapour)*m_h2o)

@-------------------------------------------------------------------------@
@ MASS LOSS BECAUSE OF TRANSPIRATION                                       @
@                                                                         @
@ spec_mois : kg/kg.Pa.s                                                  @
@ resist_h2o: mol/m2.dag.Pa                                               @
@-------------------------------------------------------------------------@

SPECIFY mass PRECEPT(mass'    _ 0-spec_mois*mass_prod*day_sec*
(ph2o_sat(temp_prod)-pressure(vapour)))

@-------------------------------------------------------------------------@
@ KEEPING QUALITY of the produkt at a standard temperature (Temp_st) after @
@ opening the package                                                     @
@-------------------------------------------------------------------------@

SPECIFY kq_st PRECEPT(kq_st' _ 0-loss_kq)

@-------------------------------------------------------------------------@
@ VARIABLES, USED ONLY FOR OUTPUT                                         @
@-------------------------------------------------------------------------@

   SPECIFY t_macro  PRECEPT(t_macro  _ temp_macro-cel_kelv)

IF mass_prod  > 0
   SPECIFY t_prod   PRECEPT(t_prod   _ temp_prod -cel_kelv)
   SPECIFY vo2_out  PRECEPT(vo2_out  _ vo2)
   SPECIFY vco2_out PRECEPT(vco2_out _ vco2)
   SPECIFY anaer    PRECEPT(anaer    _ (vco2-rq*vo2)/vco2)
END

IF thick_film > 0
   SPECIFY o2_perc  PRECEPT(o2_perc  _ 100*pressure(molo2_micro )/ptot_micro)
   SPECIFY co2_perc PRECEPT(co2_perc _ 100*pressure(molco2_micro)/ptot_micro)
END
RETURN
```

INITMACRO.MAC

```
@-----+-------------------------+-----+------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----| Reading temp. and RH profile |-----@
@-----|-------------------------|-----| of the macroclimate in arrays|-----@
@-----|      version MH3.0      |-----| for dynamic use.             |-----@
@-----|      January  1998      |-----|                              |-----@
@-----|    Copyright ATO-DLO    |-----| pO2/pCO2/pN2 are assumed to  |-----@
@-----|-------------------------|-----| be constants                 |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                              |-----@
@-----|       R.G. Evelo        |-----| INPUTSTREAM: clim_dat        |-----@
@-----+-------------------------+-----+------------------------------+-----@

LOCAL:
   DOUBLE: m_t

REWIND clim_dat

m_t_READ FROM clim_dat
WHILE m_t =0
   TABULATE cel_kelv+READ FROM clim_dat IN temp_tab AT m_t
   m_t_READ FROM clim_dat
END

m_t_READ FROM clim_dat
WHILE m_t =0
   TABULATE READ FROM clim_dat IN relh_tab AT m_t
   m_t_READ FROM clim_dat
END

 po2_macro _ READ FROM clim_dat
pco2_macro _ READ FROM clim_dat
 pn2_macro _ READ FROM clim_dat

RETURN
```

INITMICRO.MAC

```
@-----+-------------------------+-----+------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Defining the microclimate    |-----
@
@-----|-------------------------|-----|                              |-----@
@-----|      version MH3.0      |-----|                              |-----@
@-----|      January  1998      |-----|                              |-----@
@-----|    Copyright ATO-DLO    |-----|                              |-----@
@-----|-------------------------|-----|                              |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                              |-----@
@-----|       R.G. Evelo        |-----| INPUTSTREAM: clim_dat        |-----@
@-----+-------------------------+-----+------------------------------+-----@
LOCALS:
   DOUBLE: ph2o_micro
           po2_micro
           pco2_micro
           pn2_micro
           t0
           volume
           origpackvol
IF type="BAG"
   origpackvol _ vol_pack
   sample:
   vol_pack _ ABS(rand_bag*origpackvol)
   REPEAT FROM sample IF vol_pack = vol_prod
IF bag="Flexible"
   REPEAT FROM sample IF vol_pack > max_vol_pack
END
END
t0       _ VALUE OF temp_tab AT(0)
volume   _ vol_pack-vol_prod
```

```
@-----------------@ IF thick_film = 0@-----------------@   po2_micro    _
po2_macro   pco2_micro   _ pco2_macro   pn2_micro    _ pn2_macro   vapour
_ vapour_out
END

@-----------------@ IF thick_film > 0@-----------------@   po2_micro    _
READ FROM clim_dat   pco2_micro   _ READ FROM clim_dat   pn2_micro    _ READ
FROM clim_dat   vapour        _ vapour_in   molh2o_micro _
ph2o_sat(t0)*.01*READ FROM clim_dat*volume/t0*r_gas
END
   molo2_micro  _ po2_micro *volume/t0*r_gas
   molco2_micro _ pco2_micro*volume/t0*r_gas
   moln2_micro  _ pn2_micro *volume/t0*r_gas
   moltot_micro _ molo2_micro + molco2_micro + moln2_micro + molh2o_micro

@-----------------@
 IF thick_film > 0@-----------------@   open _ CHREAD FROM clim_dat   n_open
_ 0   IF (open = "Y") | (open = "y") | (open = "J") |(open = "j")   n_open _
1      start_open[n_open] _ READ FROM clim_dat      WHILE start_open[n_open]
> -1
         keep_open[n_open]   _ READ FROM clim_dat
         perm_open[n_open]   _ READ FROM clim_dat
         n_open _ n_open+1
         start_open[n_open] _ READ FROM clim_dat
      END
      n_open _ n_open-1
   END
END
RETURN
```

INITPRODUCT.MAC

```
@-----+-------------------------+-----+--------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Defining product dimensions    |-----
@@-----|-------------------------|-----|                                |-----
@
@-----|      version MH3.0      |-----|                                |-----@
@-----|      January  1998      |-----|                                |-----@
@-----|    Copyright ATO-DLO    |-----|                                |-----@
@-----|-------------------------|-----|                                |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                                |-----@
@-----|        R.G. Evelo       |-----| INPUTSTREAM: prod_dat          |-----@
@-----+-------------------------+-----+--------------------------------+-----@

REWIND prod_dat

@--------------------------------@
@ choosing the product           @
@ and general product properties @
@--------------------------------@

prod_name _ CHREAD FROM prod_dat
temp_prod _ cel_kelv + READ FROM prod_dat
mass_prod _ ABS(rand_mass*READ FROM prod_dat)
mass      _ mass_prod
aver_wght _ READ FROM prod_dat
temp_st   _ cel_kelv + READ FROM prod_dat

@--------------------------------@
@ searching the product          @
@--------------------------------@

search_prod _ CHREAD FROM prod_dat
WHILE search_prod ? prod_name
   search_prod _ CHREAD FROM prod_dat
   IF search_prod="END"
      RETURN
   END
END


@----------------------------------------@
@ specific initial dimensions of the product @
```

```
@-----------------------------------------@

spec_wght _ READ FROM prod_dat
spec_heat _ READ FROM prod_dat
heat_cond _ day_sec*READ FROM prod_dat        @ W=J/s !! secs >> days @
spec_mois _ READ FROM prod_dat
vol_prod  _ mass_prod/spec_wght

@-------------------------------@
@ product interpreted as spheres @
@-------------------------------@

radi_prod _ ((aver_wght/spec_wght)*.75/pi)_(1/3)
area_prod _ (mass_prod/aver_wght)*4*pi*radi_prod_2

@--------------------------------------@
@ parameters describing O2 consumption @
@ and                    CO2 production @
@--------------------------------------@

vmo2_avg  _ READ FROM prod_dat
vmo2_ref  _ ABS(rand_vmax*vmo2_avg)
vmco2_avg _ READ FROM prod_dat
vmco2_ref _ ABS(rand_vmax*vmco2_avg)
rq        _ READ FROM prod_dat
ea_vmo2   _ READ FROM prod_dat
ea_vmco2  _ READ FROM prod_dat
tref_resp _ cel_kelv+READ FROM prod_dat
kmo2      _ READ FROM prod_dat
kmcco2    _ READ FROM prod_dat
kmo2f     _ READ FROM prod_dat
kmuco2    _ READ FROM prod_dat
kmco2f    _ READ FROM prod_dat

@-----------------------------------------------@
@ innitializing parameters for keeping quality @
@-----------------------------------------------@

tref_kq  _ cel_kelv + READ FROM prod_dat
kq_ref   _ ABS(rand_kq*READ FROM prod_dat)

n_proces _ 1
kkq_ref[n_proces] _ READ FROM prod_dat
WHILE kkq_ref[n_proces] > 0
   ea_kq[n_proces]   _ READ FROM prod_dat
   n_proces _ n_proces+1
   kkq_ref[n_proces] _ READ FROM prod_dat
END
n_proces _ n_proces-1

k_st_0

FOR i_1 TO n_proces
   k_st  _ k_st + arrh(kkq_ref[i],ea_kq[i],tref_kq,temp_st)
END

kq_st _ kq_ref/k_st

RETURN
```

INITFILM.MAC

```
@-----+-------------------------+-----+-------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----| Dimensions the constants for  |-----@
@-----|-------------------------|-----| all layers of the film. The   |-----@
@-----|      version MH3.0      |-----| layers are joined to the queue|-----@
@-----|      January  1998      |-----| layers. Total number of       |-----@
@-----|    Copyright ATO-DLO    |-----| layers is given by n_layer    |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----| INPUTSTREAM: film_dat         |-----@
@-----+-------------------------+-----+-------------------------------+-----@
LOCALS:
```

```
   DOUBLE: thick_temp
           thick_orig
           trans1 ea1 tref1
           trans2 ea2 tref2
           trans3 ea3 tref3
           trans4 ea4 tref4
   CHARACTER(20): filmname

REWIND film_dat

thick_film _ 0
film_name  _ CHREAD FROM film_dat

WHILE filmname ? "-1"
   thick_temp _ READ FROM film_dat
   thick_orig _ READ FROM film_dat
       trans1 _ READ FROM film_dat
          ea1 _ READ FROM film_dat
        tref1 _ READ FROM film_dat
       trans2 _ READ FROM film_dat
          ea2 _ READ FROM film_dat
        tref2 _ READ FROM film_dat
       trans3 _ READ FROM film_dat
          ea3 _ READ FROM film_dat
        tref3 _ READ FROM film_dat
       trans4 _ READ FROM film_dat
          ea4 _ READ FROM film_dat
        tref4 _ READ FROM film_dat

@-------------@
@ gas 1 : O2  @
@ gas 2 : CO2 @
@ gas 3 : N2  @
@ gas 4 : H2O @
@-------------@

      THIS layer _ NEW layer
           thick _ ABS(rand_film*thick_temp)
         dref[1] _ trans1*thick_orig*ml_l*l_m3/bar_pa
           ea[1] _ ea1
         tref[1] _ cel_kelv+tref1
         dref[2] _ trans2*thick_orig*ml_l*l_m3/bar_pa
           ea[2] _ ea2
         tref[2] _ cel_kelv+tref2
         dref[3] _ trans3*thick_orig*ml_l*l_m3/bar_pa
           ea[3] _ ea3
         tref[3] _ cel_kelv+tref3
         dref[4] _ trans4*thick_orig/(m_h2o*bar_pa)
           ea[4] _ ea4
         tref[4] _ cel_kelv+tref4
      JOIN THIS layer TO layers
      thick_film _ thick_film+thick

        filmname _ CHREAD FROM film_dat
END

RETURN
```

INITPACK.MAC

```
@-----+------------------------+-----+------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Defining dimensions of the    |-----
@@-----|------------------------|-----| package                      |-----
@@-----|      version MH3.0     |-----|   BOX:length, width and height|-----
@
@-----|      January  1998     |-----|  DISH:length, width and height|-----@
@-----|    Copyright ATO-DLO   |-----|       including the product   |-----@
@-----|------------------------|-----|   BAG:length, width and volume|-----@
@-----|    M.L.A.T.M. Hertog   |-----| MODEL:volume and diff. area   |-----@
@-----|        R.G. Evelo      |-----| INPUTSTREAM: pack_dat         |-----@
@-----+------------------------+-----+------------------------------+-----@

LOCALS:
```

```
   DOUBLE:  h
            w
            l

REWIND pack_dat

type _ CHREAD FROM pack_dat

@---------------@
 IF type="BOX"
@---------------@
   l _ READ FROM pack_dat
   w _ READ FROM pack_dat
   h _ READ FROM pack_dat
   vol_pack  _ l*w*h
   diff_area _ l*w
   RETURN
END

@---------------@
 IF type="DISH"
@---------------@
   l _ READ FROM pack_dat
   w _ READ FROM pack_dat
   h _ READ FROM pack_dat
   vol_pack  _ l*w*h
   diff_area _ (2*l*w)+2*h*(w+l)
   RETURN
END

@---------------@
 IF type="BAG"
@---------------@
   l _ READ FROM pack_dat
   w _ READ FROM pack_dat
   vol_pack  _ READ FROM pack_dat
   diff_area _ 2*l*w
   RETURN
END

@---------------@
 IF type="MODEL"
@---------------@
   vol_pack  _ READ FROM pack_dat
   diff_area _ READ FROM pack_dat
   RETURN
END

vol_pack _ -999

RETURN
```

INITBAG.MAC

```
@-----+-------------------------+-----+-------------------------------+-----
@@-----|||||||||| M.A.P.|||||||||||-----|  Dialog to initiate the use   |-----
@
@-----|-------------------------|-----|  of either a constant or      |-----@
@-----|      version MH3.0      |-----|  variable volume of a BAG.    |-----@
@-----|      January  1998      |-----|                               |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@

GOTO constant IF thick_film=0

IF multi_run = TRUE
   GOTO constant IF bag = "Rigid"
   GOTO variable2 IF bag = "Flexible"
END
```

```
CALL clear_text_box(1,19,5,76,8,0)
CALL clear_text_box(8,12,19,63,1,14)
DISPLAY "A flexible BAG was selected as package."
AT LINE 9  POSITION 21 COLOUR 14 ON 1 WITH IMAGE a
DISPLAY "Do you want to keep the volume < >onstant"
AT LINE 10 POSITION 21 COLOUR  7 ON 1 WITH IMAGE A
DISPLAY "                            or < >ariable"
AT LINE 11 POSITION 21 COLOUR  7 ON 1 WITH IMAGE A
DISPLAY "C" AT LINE 10 POSITION 53 COLOUR  4 ON 1 WITH IMAGE A
DISPLAY "V" AT LINE 11 POSITION 53 COLOUR  4 ON 1 WITH IMAGE A

key:
key _ wait_key
GOTO constant IF (key=67) | key=99
GOTO variable IF (key=86) | key=118
REPEAT FROM key

constant:
   pressure _ var_press
   volume   _ con_vol
   bag      _ "Rigid"
RETURN

variable:
   CALL clear_text_box(8,12,17,66,1,14)
   DISPLAY "Give the maximum inflatable volume of the bag:"
AT LINE 9  POSITION 19 COLOUR 14 ON 1 WITH IMAGE a
   DISPLAY "initial volume of the pack:         m3"
AT LINE 10 POSITION 23 COLOUR  7 ON 1 WITH IMAGE A
   DISPLAY "maximum volume of the pack:         m3"
AT LINE 11 POSITION 23 COLOUR  7 ON 1 WITH IMAGE A
   DISPLAY vol_pack AT LINE 10 POSITION 51 COLOUR  4 ON 1 WITH IMAGE x.xxxxx

   input:
   DISPLAY vol_pack AT LINE 11 POSITION 51 COLOUR  4 ON 1 WITH IMAGE x.xxxxx
   CAPTURE max_vol_pack AT LINE 11 POSITION 51 FIELDLENGTH 7
   REPEAT FROM input IF (max_vol_pack < vol_pack)
   max_vol_air _ max_vol_pack-vol_prod
variable2:
   pressure    _ con_press
   volume      _ var_vol
   bag         _ "Flexible"
   pressure    _ con_press

RETURN
```

INITEXPDATA.MAC

```
@-----+-------------------------+-----+------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----|                              |-----
@@-----|-------------------------|-----|  Reading and storing         |-----
@
@-----|      version MH3.0      |-----|  experimental data for       |-----@
@-----|      January  1998      |-----|  comparison.                 |-----@
@-----|    Copyright ATO-DLO    |-----|                              |-----@
@-----|-------------------------|-----|       time: days or hours    |-----@
@-----|    M.L.A.T.M. Hertog    |-----|    O2_micro: %               |-----@
@-----|        R.G. Evelo       |-----|   CO2_micro: %               |-----@
@-----+-------------------------+-----+------------------------------+-----@

LOCAL:
   DOUBLE: tijd
   DOUBLE: o2
   DOUBLE: co2
tijd  _ READ FROM expe_dat DAYS  IF (time_unit="d") | time_unit="D"
tijd  _ READ FROM expe_dat HOURS IF (time_unit="h") | time_unit="H"

WHILE tijd = 0
   o2  _ READ FROM expe_dat
   co2 _ READ FROM expe_dat
   STORE o2  VERSUS tijd AS "o2_dat"
   STORE co2 VERSUS tijd AS "co2_dat"
   tijd  _ READ FROM expe_dat DAYS  IF (time_unit="d") | time_unit="D"
```

```
   tijd  _ READ FROM expe_dat HOURS IF (time_unit="h") | time_unit="H"
END

RETURN
```

FLUX_GAS.MAC

```
@-----+-------------------------+-----+------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Defining the flux into the    |-----
@@-----|-------------------------|-----| microclimate because of:     |-----
@
@-----|      version MH3.0      |-----|                              |-----@
@-----|      January  1998      |-----| * diffusion through the film |-----@
@-----|    Copyright ATO-DLO    |-----|   according Fick             |-----@
@-----|-------------------------|-----| * respiration of the product |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                              |-----@
@-----|        R.G. Evelo       |-----| Both expressed in mol/day    |-----@
@-----+-------------------------+-----+------------------------------+-----@

PARAMETERS:
   DOUBLE: p_macro
   DOUBLE: p_micro
   DOUBLE: resist
   DOUBLE: v_resp
   DOUBLE: sign
   DOUBLE: act_val
LOCAL:
   DOUBLE: flow

flow _ ((p_macro-p_micro)/(resist*r_gas*temp_macro/p0))
+ sign*(v_resp*mmol_mol*mass_prod*day_hour)

RETURN flow * (ABS(flow) > 0.001*act_val)

@-------------------------------------------------------------------------@@
V_RESP: mmol/kg/h adjusting to mol/day by means of: mmol > mol          @
@                                                    mass of the product @
@                                                    hour > day          @
@ FLUX: m3/day      adjusting to mol/day by means of the molair volume    @
@ SIGN: +1 in case of CO2 production                                      @
@       -1 in case of O2 consumption                                      @
@        0 in case of N2                                                  @
@-------------------------------------------------------------------------@
```

FLUX_H20.MAC

```
@-----+-------------------------+-----+------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Defining the flow of water   |-----
@
@-----|-------------------------|-----| as a result of diffusion and |-----@
@-----|      version MH3.0      |-----| transpiration                |-----@
@-----|      January  1998      |-----|                              |-----@
@-----|    Copyright ATO-DLO    |-----|                              |-----@
@-----|-------------------------|-----|                              |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                              |-----@
@-----|        R.G. Evelo       |-----|                              |-----@
@-----+-------------------------+-----+------------------------------+-----@

LOCAL:
   DOUBLE: flow

flow _ ((ph2o_macro-pressure(vapour))/filmresist(4))
- mass'*kg_g/m_h2o

RETURN flow * (ABS(flow)>.1*ph2o_sat(temp_macro)*volume/r_gas*temp_macro)
```

PH2O_SAT.MAC

```
@-----+-------------------------+-----+-------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Calculates saturated vapour   |-----
@
@-----|-------------------------|-----| pressure given the temperature|-----@
@-----|      version MH3.0      |-----|                               |-----@
@-----|      January  1998      |-----|                               |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@

PARAMETER:
  DOUBLE: temp

LOCAL:
  DOUBLE: hulp

temp _ temp-cel_kelv

hulp _ 7.5*temp/(237.3+temp)
hulp _ 9.5*temp/(265.5+temp) IF (temp) <0

RETURN 10_(2.7857+hulp)
```

PH2O_MACRO.MAC

```
@-----+-------------------------+-----+-------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Vapour pressure of the macro- |-----
@@-----|-------------------------|-----| climate                       |-----
@
@-----|      version MH3.0      |-----|                               |-----@
@-----|      January  1998      |-----|                               |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@

RETURN ph2o_sat(temp_macro)*0.01*VALUE OF relh_tab AT(CT)
```

VAPOUR_IN.MAC

```
@-----+-------------------------+-----+-------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Amount of vapour of the       |-----
@
@-----|-------------------------|-----| microclimate                  |-----@
@-----|      version MH3.0      |-----|                               |-----@
@-----|      January  1998      |-----|                               |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@

RETURN MIN(molh2o_micro,ph2o_sat(temp_macro)*volume/r_gas*temp_macro)
```

VAPOUR_OUT.MAC

```
@-----+-------------------------+-----+-------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Amount of vapour of the       |-----
```

```
@@-----|-------------------------|-----| macroclimate                  |-----
@
@-----|      version MH3.0      |-----|                               |-----@
@-----|      January  1998      |-----|                               |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@

RETURN ph2o_macro*volume/temp_macro*r_gas
```

CON_VOL.MAC

```
@-----+-------------------------+-----+-------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----|                               |-----
@
@-----|-------------------------|-----|  Defining a constant volume   |-----@
@-----|      version MH3.0      |-----|  (based on the initial vol.)  |-----@
@-----|      January  1998      |-----|                               |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@

RETURN vol_pack-vol_prod
```

VAR_VOL.MAC

```
@-----+-------------------------+-----+-------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----|                               |-----@
@-----|-------------------------|-----| Defining a variable volume    |-----@
@-----|      version MH3.0      |-----| based on the total amount of  |-----@
@-----|      January  1998      |-----| moles present taking into     |-----@
@-----|    Copyright ATO-DLO    |-----| account the maximum possible  |-----@
@-----|-------------------------|-----| volume                        |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@
LOCALS:
   DOUBLE: act_vol

act_vol _ moltot_micro*r_gas*temp_macro/ptot_macro

RETURN MIN(max_vol_air, act_vol)
```

CON_PRESS.MAC

```
@-----+-------------------------+-----+-------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----|                               |-----
@@-----|-------------------------|-----| Defining a partial pressure   |-----
@
@-----|      version MH3.0      |-----| for use with a flexible bag.  |-----@
@-----|      January  1998      |-----| Either a constant or a        |-----@
@-----|    Copyright ATO-DLO    |-----| variable volume is used       |-----@
@-----|-------------------------|-----| depending on the actual       |-----@
@-----|    M.L.A.T.M. Hertog    |-----| volume in relation to the     |-----@
@-----|        R.G. Evelo       |-----| maximum volume.               |-----@
@-----+-------------------------+-----+-------------------------------+-----@

PARAMETER:
   DOUBLE: mol_micro

LOCALS:
```

```
   DOUBLE: pcon
           pvar
           switch

switch _ (volume=max_vol_air)
pcon   _ ptot_macro*mol_micro/moltot_micro
pvar   _ r_gas*temp_macro*mol_micro/volume

RETURN (pcon*(1-switch))+pvar*switch
```

VAR_PRESS.MAC

```
@-----+-------------------------+-----+-------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----|                               |-----
@
@-----|-------------------------|-----| Defining a variable partial   |-----@
@-----|      version MH3.0      |-----| pressure based on the amount  |-----@
@-----|      January  1998      |-----| of moles present of that      |-----@
@-----|    Copyright ATO-DLO    |-----| specific gas                  |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@

PARAMETER:
   DOUBLE: mol_micro

RETURN r_gas*temp_macro*mol_micro/volume
```

PTOT_MICRO.MAC

```
@-----+-------------------------+-----+-------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Defining the total pressure   |-----
@@-----|-------------------------|-----| in the microclimate           |-----
@@-----|      version MH3.0      |-----|                               |-----
@
@-----|      January  1998      |-----|                               |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@

RETURN  pressure(molo2_micro)+pressure(molco2_micro)
+pressure(moln2_micro)+pressure(vapour)
```

PTOT_MACRO.MAC

```
@-----+-------------------------+-----+-------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Defining the total pressure   |-----
@
@-----|-------------------------|-----| in the macroclimate           |-----@
@-----|      version MH3.0      |-----|                               |-----@
@-----|      January  1998      |-----|                               |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@

RETURN po2_macro+pco2_macro+pn2_macro+ph2o_macro
```

ARRH.MAC

```
@-----+-------------------------+-----+------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Temperature dependency       |-----
@@-----|-------------------------|-----| according Arrhenius          |-----
@@-----|      version MH3.0      |-----|                              |-----
@
@-----|      January  1998      |-----|                              |-----@
@-----|    Copyright ATO-DLO    |-----|                              |-----@
@-----|-------------------------|-----|                              |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                              |-----@
@-----|        R.G. Evelo       |-----|                              |-----@
@-----+-------------------------+-----+------------------------------+-----@

PARAMETERS:
   DOUBLE: kref
   DOUBLE: ea
   DOUBLE: tref
   DOUBLE: temp

RETURN kref*EXP((ea/r_gas)*((1/tref)-1/temp))
```

LOSS_KQ.MAC

```
@-----+-------------------------+-----+------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----|                              |-----@
@-----|-------------------------|-----|   Keeping Quality according: |-----@
@-----|      version MH3.0      |-----|                              |-----@
@-----|      January  1998      |-----|        L.M.M. Tijskens       |-----@
@-----|    Copyright ATO-DLO    |-----|                              |-----@
@-----|-------------------------|-----|                              |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                              |-----@
@-----|        R.G. Evelo       |-----|                              |-----@
@-----+-------------------------+-----+------------------------------+-----@

LOCALS:
   DOUBLE: k_kq

@-------------------------------------------------@
@ Calculating sum of the k's of the separate      @
@ processe responsible for the quality decay      @
@-------------------------------------------------@
k_kq_0
FOR i_1 TO n_proces
   k_kq  _ k_kq + arrh(kkq_ref[i],ea_kq[i],tref_kq,temp_prod)
END
@-------------------------------------------------@
@ Decay of keeping quality in function of the     @
@ relative respiration                            @
@-------------------------------------------------@

RETURN (rel_resp*k_kq/k_st) * (kq_st = 0)
```

FILMRESIST.MAC

```
@-----+-------------------------+-----+------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Defining the resistance of   |-----
@@-----|-------------------------|-----| a compound film for the      |-----
@
@-----|      version MH3.0      |-----| different gasses             |-----@
@-----|      January  1998      |-----|                              |-----@
@-----|    Copyright ATO-DLO    |-----|                              |-----@
@-----|-------------------------|-----|                              |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                              |-----@
@-----|        R.G. Evelo       |-----|                              |-----@
@-----+-------------------------+-----+------------------------------+-----@
PARAMETER:
   INTEGER: gas_nr
```

ARRH.MAC

```
@-----+-------------------------+-----+-------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Temperature dependency        |-----
@@-----|-------------------------|-----| according Arrhenius           |-----
@@-----|      version MH3.0      |-----|                               |-----
@
@-----|      January  1998      |-----|                               |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@

PARAMETERS:
   DOUBLE: kref
   DOUBLE: ea
   DOUBLE: tref
   DOUBLE: temp

RETURN kref*EXP((ea/r_gas)*((1/tref)-1/temp))
```

LOSS_KQ.MAC

```
@-----+-------------------------+-----+-------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----|                               |-----@
@-----|-------------------------|-----|   Keeping Quality according:  |-----@
@-----|      version MH3.0      |-----|                               |-----@
@-----|      January  1998      |-----|        L.M.M. Tijskens        |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@

LOCALS:
   DOUBLE: k_kq

@-------------------------------------------------@
@ Calculating sum of the k's of the separate      @
@ processe responsible for the quality decay      @
@-------------------------------------------------@
k_kq_0
FOR i_1 TO n_proces
   k_kq  _ k_kq + arrh(kkq_ref[i],ea_kq[i],tref_kq,temp_prod)
END
@-------------------------------------------------@
@ Decay of keeping quality in function of the     @
@ relative respiration                            @
@-------------------------------------------------@

RETURN (rel_resp*k_kq/k_st) * (kq_st = 0)
```

FILMRESIST.MAC

```
@-----+-------------------------+-----+-------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Defining the resistance of    |-----
@@-----|-------------------------|-----| a compound film for the       |-----
@
@-----|      version MH3.0      |-----| different gasses              |-----@
@-----|      January  1998      |-----|                               |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@
PARAMETER:
   INTEGER: gas_nr
```

```
LOCAL:
    DOUBLE: film_resist

THIS layer _ FIRST OF layers
FOR i_1 TO LENGTH OF layers
   film_resist_film_resist+
thick/arrh(perm_factor*dref[gas_nr],ea[gas_nr],tref[gas_nr],temp_macro)
   GOTO ready IF i = LENGTH OF layers
   THIS layer _ SUCC OF THIS layer IN layers
END

ready:

film_resist _ film_resist/diff_area

RETURN film_resist
```

REL_RESP.MAC

```
@-----+-------------------------+-----+------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----|   Relative Respiration       |-----
@@-----|-------------------------|-----|   based on CO2 production    |-----
@
@-----|    .   version MH3.0    |-----|                              |-----@
@-----|        January  1998    |-----|                              |-----@
@-----|     Copyright ATO-DLO   |-----|                              |-----@
@-----|-------------------------|-----|                              |-----@
@-----|     M.L.A.T.M. Hertog   |-----|                              |-----@
@-----|         R.G. Evelo      |-----|                              |-----@
@-----+-------------------------+-----+------------------------------+-----@

LOCALS:
   DOUBLE: k_kq
           vmo2
           vmco2

@-------------------------------------------------@
@ Calculating relative respiration in terms of CO2 @
@-------------------------------------------------@

vmo2     _ arrh(vmo2_avg,ea_vmo2,tref_resp,temp_prod)
vmco2    _ arrh(vmco2_avg,ea_vmco2,tref_resp,temp_prod)

RETURN   vco2/(rq*vmo2*21/kmo2+21)+(vmco2/(1+21/kmo2f))
```

VO2.MAC

```
@-----+-------------------------+-----+------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Respiration according        |-----
@@-----|-------------------------|-----| Peppelenbos 1996 extended    |-----
@
@-----|      version MH3.0      |-----| with a temperature dependence |-----@
@-----|      January  1998      |-----| according Arrhenius (Hertog   |-----@
@-----|    Copyright ATO-DLO    |-----| 1996)                        |-----@
@-----|-------------------------|-----|                              |-----@
@-----|    M.L.A.T.M. Hertog    |-----| O2 CONSUMPTION (in mmol/kg/h) |-----@
@-----|        R.G. Evelo       |-----|                              |-----@
@-----+-------------------------+-----+------------------------------+-----@

LOCAL:
   DOUBLE: vmo2
           perc_o2
           perc_co2

vmo2     _ arrh(vmo2_ref,ea_vmo2,tref_resp,temp_prod)
perc_o2  _ (100*pressure(molo2_micro )/ptot_micro)
perc_co2 _ (100*pressure(molco2_micro)/ptot_micro)
```

```
RETURN  vmo2*perc_o2/
((kmo2*(1+perc_co2/kmcco2))+ perc_o2*(1+perc_co2/kmuco2))
```

VCO2.MAC

```
@-----+-------------------------+-----+------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----| Respiration according         |-----@
@-----|-------------------------|-----| Peppelenbos 1996 extended    |-----@
@-----|      version MH3.0      |-----| with a temperature dependence|-----@
@-----|      January  1998      |-----| according Arrhenius (Hertog  |-----@
@-----|    Copyright ATO-DLO    |-----| 1996)                        |-----@
@-----|-------------------------|-----|                              |-----@
@-----|    M.L.A.T.M. Hertog    |-----| CO2 PRODUCTION (in mmol/kg/h)|-----@
@-----|        R.G. Evelo       |-----|                              |-----@
@-----+-------------------------+-----+------------------------------+-----@

LOCAL:
   DOUBLE: vmco2
           perc_o2
           v_co2_an
           v_co2

vmco2     _ arrh(vmco2_ref,ea_vmco2,tref_resp,temp_prod)
perc_o2   _ 100*pressure(molo2_micro )/ptot_micro
v_co2_an  _ vmco2/(1+(perc_o2/kmo2f)+(perc_co2/kmco2f))
v_co2     _ (rq*vo2)+v_co2_an

RETURN v_co2
```

TEMP_MACRO.MAC

```
@-----+-------------------------+-----+------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----| Defining the temperature     |-----@
@-----|-------------------------|-----| of the macroclimate          |-----@
@-----|      version MH3.0      |-----|                              |-----@
@-----|      January  1998      |-----|                              |-----@
@-----|    Copyright ATO-DLO    |-----|                              |-----@
@-----|-------------------------|-----|                              |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                              |-----@
@-----|        R.G. Evelo       |-----|                              |-----@
@-----+-------------------------+-----+------------------------------+-----@

RETURN VALUE OF temp_tab AT(CT)
```

MONTE_CARLO.MOD

```
@-----+-------------------------+-----+------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Generating output from       |-----
@@-----|-------------------------|-----| Monte-Carlo simulations      |-----
@
@-----|      version MH3.0      |-----| and calculating 95%          |-----@
@-----|      January  1998      |-----| confidence limits            |-----@
@-----|    Copyright ATO-DLO    |-----|                              |-----@
@-----|-------------------------|-----|                              |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                              |-----@
@-----|        R.G. Evelo       |-----|                              |-----@
@-----+-------------------------+-----+------------------------------+-----@

@----------@
 generate:
@----------@

carlo_stream _ carlo_out

IF run_no = 1
```

```
   @-------------------------------------@
   @ preparing layout of screen and file @
   @-------------------------------------@
   CALL clear_text_box(1,19,5,76,8,0)
   CALL clear_text_box(8,11,14,67,1,14)
   DISPLAY "Monte-Carlo simulations in progress..... "
AT LINE 9  POSITION 16 COLOUR 14 ON 1 WITH IMAGE a
   DISPLAY "            Simulation:       of"
AT LINE 10 POSITION 16 COLOUR  7 ON 1 WITH IMAGE A
   DISPLAY n_sim
AT LINE 10 POSITION 49 COLOUR  4 ON 1 WITH IMAGE xxxxx
   DISPLAY "Hit <i> to interrupt simulations..... "
AT LINE 15 POSITION 23 COLOUR 12 ON 8 WITH IMAGE a

   REWIND carlo_in
   WRITE "+-------------------------------------------------------------------
---------+" TO carlo_in WITH IMAGE |a
   WRITE "| Simulation results from the MAP-model (version MH3.0)        ATO-
DLO 1998 |" TO carlo_in WITH IMAGE a
   WRITE "| Date: " TO carlo_in WITH IMAGE a
   WRITE n[3]  TO carlo_in WITH IMAGE |xx
   WRITE " - " TO carlo_in WITH IMAGE |a
   WRITE n[2]  TO carlo_in WITH IMAGE |xx
   WRITE " - " TO carlo_in WITH IMAGE |a
   WRITE n[1]  TO carlo_in WITH IMAGE |xxxx
   WRITE "                              ID: " TO carlo_in WITH IMAGE |a
   WRITE id    TO carlo_in WITH IMAGE |a20
   WRITE "  |" TO carlo_in WITH IMAGE |a
   WRITE "| Product: " TO carlo_in WITH IMAGE a
   WRITE prod_name TO carlo_in WITH IMAGE |a20
   WRITE "                    Film: " TO carlo_in WITH IMAGE |a
   WRITE film_name TO carlo_in WITH IMAGE |a20
   WRITE "  |" TO carlo_in WITH IMAGE |a
   WRITE "+----------------------| Monte Carlo Simulations |---------------
---------+" TO carlo_in WITH IMAGE a
   WRITE "" TO carlo_in WITH IMAGE a
   WRITE "n      " TO carlo_in WITH IMAGE  ????a2
   IF mass_prod  > 0
      WRITE "   mass" TO carlo_in WITH IMAGE |?a7
      WRITE "     kq" TO carlo_in WITH IMAGE |?a7
      WRITE "  Vm_o2" TO carlo_in WITH IMAGE |?a7
      WRITE " Vm_co2" TO carlo_in WITH IMAGE |?a7
   END
   IF thick_film > 0
      WRITE "  thick" TO carlo_in WITH IMAGE |?a7
   END
   IF type = "BAG"
      WRITE " volume" TO carlo_in WITH IMAGE |?a7
   END

   REWIND carlo_stream
   WRITE "@ n_run" TO carlo_stream WITH IMAGE  a7
   WRITE "  n_dat" TO carlo_stream WITH IMAGE |?a7
   IF thick_film > 0
      WRITE "   cond" TO carlo_stream WITH IMAGE |?a7
      WRITE " o2 (%)" TO carlo_stream WITH IMAGE |?a7
      WRITE "co2 (%)" TO carlo_stream WITH IMAGE |?a7
   END
   IF mass_prod > 0
      WRITE "    vo2" TO carlo_stream WITH IMAGE |?a7
      WRITE "   vco2" TO carlo_stream WITH IMAGE |?a7
      WRITE "  anaer" TO carlo_stream WITH IMAGE |?a7
      WRITE "     kq" TO carlo_stream WITH IMAGE |?a7
   END
      WRITE "@      " TO carlo_stream WITH IMAGE |?a7
END

DISPLAY run_no
AT LINE 10 POSITION 40 COLOUR  4 ON 1 WITH IMAGE xxxxx

WRITE run_no          TO carlo_in WITH IMAGE  xxxxx
IF mass_prod  > 0
   WRITE mass_prod       TO carlo_in WITH IMAGE |??x.xxxxx
   WRITE kq_st*(kq_st>0) TO carlo_in WITH IMAGE |?xx.xxxx
   WRITE vmo2_ref        TO carlo_in WITH IMAGE |?x.xxxxx
   WRITE vmco2_ref       TO carlo_in WITH IMAGE |?x.xxxxx
END
IF thick_film > 0
```

```
   WRITE thick_film      TO carlo_in WITH IMAGE |?xxxxExx
END
IF type = "BAG"
   WRITE vol_pack/l_m3   TO carlo_in WITH IMAGE |??x.xxxx
END

dat_no _ 1

@----------@
 writedata:
@----------@

   WRITE run_no          TO carlo_stream WITH IMAGE  ??xxxxx
   WRITE dat_no          TO carlo_stream WITH IMAGE |?xxxxxxx
IF thick_film > 0
   WRITE cond_vol        TO carlo_stream WITH IMAGE |?x.xxxxx
   WRITE o2_perc         TO carlo_stream WITH IMAGE |?xx.xxxx
   WRITE co2_perc        TO carlo_stream WITH IMAGE |?xx.xxxx
END
IF mass_prod > 0
   WRITE vo2_out         TO carlo_stream WITH IMAGE |?x.xxxxx
   WRITE vco2_out        TO carlo_stream WITH IMAGE |?x.xxxxx
   WRITE anaer           TO carlo_stream WITH IMAGE |?x.xxxxx
   WRITE kq_st*(kq_st>0) TO carlo_stream WITH IMAGE |?xx.xxxx
END

WAIT freq HOURS
dat_no _ dat_no + 1
REPEAT FROM writedata
TERMINATE

@----------@
 analyse:
@----------@

@-------------------------------------------------------------------------@
@ generating temperature profiles macroclimate and product                @
@-------------------------------------------------------------------------@

CALL initproduct
CALL initmacro
IF mass_prod  > 0
   SPECIFY tempprod PRECEPT(tempprod' _
(heat_cond*area_prod*(temp_macro-tempprod))/
(spec_heat*mass_prod*radi_prod))
ABSERROR(1e-6) RELERROR(1e-6) INIT(temp_prod)
   SPECIFY tprod   PRECEPT(tprod   _ tempprod -cel_kelv)
END
SPECIFY tmacro  PRECEPT(tmacro  _ temp_macro-cel_kelv)
INTEGRATE 1e-10 SECOND
AUTOSTORE tmacro    AS "T_macro   "
AUTOSTORE tprod     AS "T_prod    " IF mass_prod  > 0
INTEGRATE runtime

@-------------------------------------@
@ preparing layout of screen and file @
@-------------------------------------@

DISPLAY "            Data point:       of                   "
AT LINE 10 POSITION 16 COLOUR  7 ON 1 WITH IMAGE A
DISPLAY 1 + runtime/freq HOURS
AT LINE 10 POSITION 49 COLOUR  4 ON 1 WITH IMAGE xxxxx
DISPLAY "Analysing the simulations..... "
AT LINE 15 POSITION 23 COLOUR 12 ON 8 WITH IMAGE a

WRITE " "       TO carlo_in WITH IMAGE a
WRITE "  TIME" TO carlo_in WITH IMAGE ?a6
IF thick_film > 0
   WRITE "COND_L" TO carlo_in WITH IMAGE |?a6
   WRITE "COND_A" TO carlo_in WITH IMAGE |?a6
   WRITE "COND_U" TO carlo_in WITH IMAGE |?a6
   WRITE "  O2_L" TO carlo_in WITH IMAGE |?a6
   WRITE "  O2_A" TO carlo_in WITH IMAGE |?a6
   WRITE "  O2_U" TO carlo_in WITH IMAGE |?a6
   WRITE " CO2_L" TO carlo_in WITH IMAGE |?a6
   WRITE " CO2_A" TO carlo_in WITH IMAGE |?a6
   WRITE " CO2_U" TO carlo_in WITH IMAGE |?a6
END
```

```
IF mass_prod > 0
   WRITE " RO2_L" TO carlo_in WITH IMAGE |?a6
   WRITE " RO2_A" TO carlo_in WITH IMAGE |?a6
   WRITE " RO2_U" TO carlo_in WITH IMAGE |?a6
   WRITE "RCO2_L" TO carlo_in WITH IMAGE |?a6
   WRITE "RCO2_A" TO carlo_in WITH IMAGE |?a6
   WRITE "RCO2_U" TO carlo_in WITH IMAGE |?a6
   WRITE "ANAE_L" TO carlo_in WITH IMAGE |?a6
   WRITE "ANAE_A" TO carlo_in WITH IMAGE |?a6
   WRITE "ANAE_U" TO carlo_in WITH IMAGE |?a6
   WRITE "  KQ_L" TO carlo_in WITH IMAGE |?a6
   WRITE "  KQ_A" TO carlo_in WITH IMAGE |?a6
   WRITE "  KQ_U" TO carlo_in WITH IMAGE |?a6
END

time _ 1e-10 SECOND
dat_no _ 1
carlo_stream _ carlo_out
CALL open_stream("carlo_out",0,"carloout")
outliers _ .5*.05*n_sim
IF thick_film > 0
   c1_1
   c2_3
END
IF mass_prod > 0
   c1_4 IF thick_film = 0
   c2_7
END

@--------------@
 scroll_values:
@--------------@

REWIND carlo_stream
DISPLAY dat_no
AT LINE 10 POSITION 40 COLOUR  4 ON 1 WITH IMAGE xxxxx
FOR i _ c1 TO c2
   sum[i] _ 0
   avg[i] _ 0
END
next _ TRUE

@-------------------------------------------------------------------@
@ reading simulations and calculating mean and 95% confidence limits @
@-------------------------------------------------------------------@
THIS valueset _ NEW valueset
CALL read_carlo(<meting>)
WHILE next=TRUE
   FOR i _ c1 TO c2
      sum[i] _ sum[i]+meting[i]
   END
   JOIN THIS valueset TO values
   THIS valueset _ NEW valueset
   CALL read_carlo(<meting>)
END

WRITE time TO carlo_in WITH IMAGE xx.xxxx
FOR i _ c1 TO c2
   FOR j_1 TO outliers
      JOIN   FIRST valueset IN values WITH GREATEST meting[i] TO   removed
      REMOVE FIRST valueset IN values WITH GREATEST meting[i] FROM values
      JOIN   FIRST valueset IN values WITH SMALLEST meting[i] TO   removed
      REMOVE FIRST valueset IN values WITH SMALLEST meting[i] FROM values
   END
   THIS valueset _ FIRST valueset IN values WITH GREATEST meting[i]
   high[i]_ meting[i]
   THIS valueset _ FIRST valueset IN values WITH SMALLEST meting[i]
   low[i] _ meting[i]
   avg[i] _ sum[i]/n_sim
   STORE low[i]  VERSUS time AS "LOW   "|i
   STORE avg[i]  VERSUS time AS "MEAN  "|i
   STORE high[i] VERSUS time AS "HIGH  "|i
   WRITE low[i]  TO carlo_in WITH IMAGE |?xx.xxx
   WRITE avg[i]  TO carlo_in WITH IMAGE |?xx.xxx
   WRITE high[i] TO carlo_in WITH IMAGE |?xx.xxx
   FOR EACH valueset IN removed
      JOIN   THIS valueset TO   values
      REMOVE THIS valueset FROM removed
```

```
   END
END

time _ time + (freq HOURS)
dat_no _ dat_no + 1
GOTO ready IF time > runtime + 1 MINUTE
REMOVE EACH valueset IN values FROM values
REPEAT FROM scroll_values

ready:

ready _ TRUE
CALL bell
CALL initfilm
CALL initmacro
CALL initmicro
CALL setscreen
DISPLAY
"Input summary - Hit <X> to eXit, any other key for graphical output"
AT LINE 1 POSITION 7 COLOUR 7 ON 8 WITH IMAGE A
CALL window_mode(2)

CALL clear_graph_box(1,1,1,80,0)
CALL gdisplay_string("Product:                          Hit <X> to eXit, any
other key for INPUT summary",80,1,1,9)
CALL gdisplay_string(prod_name,10,1,10,9)
CALL clear_graph_box(13,19,26,56,8)
CALL clear_graph_box(14,18,28,54,1)
CALL gdisplay_string("        RESULTS          ",25,13,30,15)
CALL gdisplay_string("Monte Carlo Simulations ",25,15,30,15)
CALL gdisplay_string("    Mean values and     ",25,16,30,5)
CALL gdisplay_string("       95% limits       ",25,17,30,5)
CALL gdisplay_string("   Hit any key.....     ",25,19,30,15)
CALL wait_key
CALL window_mode(2)

CALL erase_file("C:\MAP\CARLOOUT.UDF")

ACTIVATE screenswitch FROM start IN scrn_control

TERMINATE
```

READ_CARLO.MAC

```
@-----+-------------------------+-----+------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----|  Reading the generated data  |-----@
@-----|-------------------------|-----|  from Monte Carlo simulations|-----@
@-----|      version MH3.0      |-----|  to calculate mean and 95%   |-----@
@-----|      January  1998      |-----|  confidence intervals        |-----@
@-----|    Copyright ATO-DLO    |-----|                              |-----@
@-----|-------------------------|-----|                              |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                              |-----@
@-----|        R.G. Evelo       |-----|                              |-----@
@-----+-------------------------+-----+------------------------------+-----@

PARAMETER:
    < REAL: data[#] >
LOCAL:
      REAL: serie_in
            point_in
   INTEGER: k

serie_in _ READ FROM carlo_stream

WHILE serie_in > 0
      point_in    _ READ FROM carlo_stream
      FOR k _ c1 TO c2
         data[k] _ READ FROM carlo_stream
      END
      RETURN IF point_in = dat_no
      serie_in _ READ FROM carlo_stream
END
```

```
next _ FALSE

RETURN
```

RANDOMIZE.MAC

```
@-----+-------------------------+-----+------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Generating random values for  |-----
@
@-----|-------------------------|-----| Monte-Carlo simulations       |-----@
@-----|      version MH3.0      |-----|                               |-----@
@-----|      January  1998      |-----|                               |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+------------------------------+-----@

run_no _ 1

CALL get_time(<tijd>)

SEED OF rand_mass _ tijd[3]*tijd[4]
SEED OF rand_vmax _ tijd[3]*tijd[4]
SEED OF rand_kq   _ tijd[3]*tijd[4]
SEED OF rand_film _ tijd[3]*tijd[4]
SEED OF rand_bag  _ tijd[3]*tijd[4]

RESHAPE rand_mass AS SAMPLED FROM DISTRIBUTION NORMAL WITH PARAMETERS
MEAN(1) DEVIATION(devi_mass)
RESHAPE rand_vmax AS SAMPLED FROM DISTRIBUTION NORMAL WITH PARAMETERS
MEAN(1) DEVIATION(devi_vmax)
RESHAPE rand_kq   AS SAMPLED FROM DISTRIBUTION NORMAL WITH PARAMETERS
MEAN(1) DEVIATION(devi_kq)
RESHAPE rand_film AS SAMPLED FROM DISTRIBUTION NORMAL WITH PARAMETERS
MEAN(1) DEVIATION(devi_film)

RESHAPE rand_bag  AS SAMPLED FROM DISTRIBUTION NORMAL WITH PARAMETERS
MEAN(1) DEVIATION(devi_bag )
```

WORK_MOD.MOD

```
@-----+-------------------------+-----+------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Just a worker to stimulate    |-----
@@-----|-------------------------|-----| the integration process and   |-----
@
@-----|      version MH3.0      |-----| to registrate the interrupt   |-----@
@-----|      January  1998      |-----| of Monte Carlo simulations    |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+------------------------------+-----@

start:
WHILE test_key = 0
   WORK 1 HOUR
END
key _ wait_key
GOTO stop IF ((key=105) | key=73)
REPEAT FROM start

stop:
n_sim _ run_no
DISPLAY n_sim
AT LINE 10 POSITION 49 COLOUR  4 ON 1 WITH IMAGE xxxxx
DISPLAY "       Interrupted, wait.....          "
AT LINE 15 POSITION 23 COLOUR 12 ON 8 WITH IMAGE a
REPEAT FROM start
```

PASSWORD.MAC

```
@-----+-------------------------+-----+-------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----| Checking and setting password |-----@
@-----|-------------------------|-----|                               |-----@
@-----|      version MH3.0      |-----|                               |-----@
@-----|      January  1998      |-----|                               |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@

LOCALS:
   INTEGER: char
      REAL: sleutel
            check


sleutel     _ 1
pass_stream _ pass_dat

CALL clear_text_box(1,19,5,76,8,0)
CALL clear_text_box(8,10,26,55,1,14)
DISPLAY "Your password please: "
AT LINE 9 POSITION 28 COLOUR 14 ON 1 WITH IMAGE a
CALL clear_text_box(9,9,50,53,4,1)
FOR char _ 1 TO 5
   rekey:
   key _ wait_key
   IF key=26
      char _ char-1
      char _ 1 IF char < 1
      DISPLAY " " AT LINE 9 POSITION 49+char COLOUR 14 ON 4 WITH IMAGE a
      REPEAT FROM rekey
   END
   code[char] _ key
   DISPLAY "*" AT LINE 9 POSITION 49+char COLOUR 14 ON 4
WITH IMAGE a if char < 5
END

FOR char _ 1 TO 4
   sleutel _ sleutel + SIN(sleutel)*code[char]
END

IF renew_password ? 64
   renew_password _ code[5]
   sleutel        _ FLOOR(sleutel*10)
   check          _ READ FROM pass_dat @ IF check_pass = 1
   IF sleutel = check
      user _ TRUE
      RETURN
   END
   CALL clear_text_box(1,19,5,76,8,0)
   CALL clear_text_box(8,10,19,59,1,14)
   DISPLAY "Wrong password for this version....."
AT LINE 9 POSITION 21 COLOUR 14 ON 1 WITH IMAGE a
   user _ FALSE
   CALL exit
END
IF renew_password = 64
   CALL open_stream("PASS_DAT",1,"PASSWORD")
   REWIND pass_stream
   WRITE "@-------------------------@" TO pass_stream WITH IMAGE |a
   WRITE "@ Your encrypted password @" TO pass_stream WITH IMAGE a
   WRITE "@       do NOT change     @" TO pass_stream WITH IMAGE a
   WRITE "@-------------------------@" TO pass_stream WITH IMAGE a
   WRITE FLOOR(sleutel*10) TO pass_stream WITH IMAGE xxxxxxxxxx
   CALL open_stream("PASS_DAT",0,"PASSWORD")
   RETURN
END
```

COPYRIGHT.MAC

```
@-----+-------------------------+-----+-------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----| Copyright information         |-----@
@-----|-------------------------|-----|                               |-----@
@-----|      version MH3.0      |-----|                               |-----@
@-----|      January  1998      |-----|                               |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@
```

```
CALL clear_text_box(1,19,5,76,8,0)
CALL clear_text_box(2,9,8,45,7,0)
DISPLAY "   +- +-  |    +-  |    +-  |"
AT LINE 3 POSITION 10 COLOUR 1 ON 7 WITH IMAGE a
DISPLAY "   | |  |    |   |    |   |"
AT LINE 4 POSITION 10 COLOUR 1 ON 7 WITH IMAGE a
DISPLAY "   | |  |    +-  |    +---+"
AT LINE 5 POSITION 10 COLOUR 1 ON 7 WITH IMAGE a
DISPLAY " --+ -+ --+  --+ --+  --+    MODEL"
AT LINE 6 POSITION 10 COLOUR 1 ON 7 WITH IMAGE a
DISPLAY "  odified  tmosphere  ackaging"
AT LINE 8 POSITION 10 COLOUR 4 ON 7 WITH IMAGE a
DISPLAY "M" AT LINE 8 POSITION 11 COLOUR 1 ON 7 WITH IMAGE a
DISPLAY "A" AT LINE 8 POSITION 20 COLOUR 1 ON 7 WITH IMAGE a
DISPLAY "P" AT LINE 8 POSITION 31 COLOUR 1 ON 7 WITH IMAGE a
DISPLAY "Developed within the framework of the EC MASTER project: AIR2-CT-
1326" AT LINE 19 POSITION 6 COLOUR 1 ON 8 WITH IMAGE a
DISPLAY "               |" AT LINE 6  POSITION 60 COLOUR 14 ON 8 WITH IMAGE a
DISPLAY "               |" AT LINE 7  POSITION 60 COLOUR 14 ON 8 WITH IMAGE a
DISPLAY "               |" AT LINE 8  POSITION 60 COLOUR 14 ON 8 WITH IMAGE a
DISPLAY "               |" AT LINE 9  POSITION 60 COLOUR 14 ON 8 WITH IMAGE a
DISPLAY "               |" AT LINE 10 POSITION 60 COLOUR 14 ON 8 WITH IMAGE a
DISPLAY "               |" AT LINE 11 POSITION 60 COLOUR 14 ON 8 WITH IMAGE a
DISPLAY " copyright 1998 " AT LINE 12 POSITION 60 COLOUR 14 ON 8 WITH IMAGE a
DISPLAY "        ATO-DLO " AT LINE 13 POSITION 60 COLOUR 14 ON 8 WITH IMAGE a
DISPLAY "     Wageningen " AT LINE 14 POSITION 60 COLOUR 14 ON 8 WITH IMAGE a
DISPLAY "The Netherlands " AT LINE 15 POSITION 60 COLOUR 14 ON 8 WITH IMAGE a
DISPLAY "               |" AT LINE 16 POSITION 60 COLOUR 14 ON 8 WITH IMAGE a
DISPLAY "               |" AT LINE 17 POSITION 60 COLOUR 14 ON 8 WITH IMAGE a
```

DATE_CHECK.MAC

```
@-----+-------------------------+-----+-------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----| Checks for the date           |-----@
@-----|-------------------------|-----| n[1] = year           (yyyy)  |-----@
@-----|      version MH3.0      |-----| n[2] = month          (mm)    |-----@
@-----|      January  1998      |-----| n[3] = day            (dd)    |-----@
@-----|    Copyright ATO-DLO    |-----| n[4] = day of the week        |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@
```

```
LOCAL:
   REAL:    yyyy
            mm
            dd

CALL get_date(<n>)

@-------------------------------@
@ This version will last till:  @
@-------------------------------@

              @-------@
yyyy _ 1999   @ year  @
```

```
mm   _ 1       @ month @
dd   _ 1       @ day   @
               @-------@

RETURN -1 IF n[1] > yyyy
RETURN  0 IF n[1] < yyyy
RETURN -1 IF n[2] > mm
RETURN  0 IF n[2] < mm
RETURN -1 IF n[3] > dd
RETURN  0 IF n[3] = dd
```

KEY_CHECK.MAC

```
@-----+-------------------------+-----+-------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----| Check keys hit for            |-----@
@-----|-------------------------|-----| recalculating input summary   |-----@
@-----|      version MH3.0      |-----| screen                        |-----@
@-----|      January  1998      |-----|                               |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@

CALL interact("qual") IF ((key=81) | key=113) & mass_prod > 0
CALL interact("resp") IF ((key=82) | key=114) & mass_prod > 0
CALL interact("film") IF ((key=84) | key=116) & thick_film > 0

RETURN 1 IF ((key=81) | key=113) & mass_prod > 0
RETURN 1 IF ((key=82) | key=114) & mass_prod > 0
RETURN 1 IF ((key=84) | key=116) & thick_film > 0

RETURN 0
```

FILE_CHECK.MAC

```
@-----+-------------------------+-----+-------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----| Checking the presence of the  |-----@
@-----|-------------------------|-----| UDF-files in directory        |-----@
@-----|      version MH3.0      |-----| C:\MAP\                       |-----@
@-----|      January  1998      |-----|                               |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@

check_dir    _ exist_file("C:\MAP\MAP.MNT")
check_data   _ exist_file("C:\MAP\DATA.UDF")
check_init   _ exist_file("C:\MAP\INIT.UDF")
check_film   _ exist_file("C:\MAP\FILM.UDF")
check_prod   _ exist_file("C:\MAP\PRODUCT.UDF")
check_clim   _ exist_file("C:\MAP\CLIMATE.UDF")
check_pack   _ exist_file("C:\MAP\PACK.UDF")
check_pass   _ exist_file("C:\MAP\PASSWORD.UDF")
check_date   _ date_check
checkedfiles _ check_dir  + check_init + check_film
+ check_prod + check_clim + check_pack + check_pass

CALL clear_text_box(1,19,5,76,8,0)

@-----------------@
 IF check_date = -1
@-----------------@
      CALL clear_text_box(8,10,14,63,1,14)
      DISPLAY "This version has expired, ask for a new update"
AT LINE 9 POSITION 16 COLOUR 14 ON 1 WITH IMAGE a
      CALL erase_file("C:\MAP\MAP.MNT")
      GOTO back
```

```
END

RETURN IF checkedfiles = 7
@-----------------@
 IF check_dir = 0
@-----------------@
      CALL clear_text_box(8,10,19,61,1,14)
      DISPLAY "Install MAP in directory >> C:\MAP <<"
AT LINE 9 POSITION 21 COLOUR 14 ON 1 WITH IMAGE a
      GOTO back
END

@--------------------@
@ IF *.UDF NOT FOUND @
@--------------------@
CALL clear_text_box(7,10,24,58,1,14)
DISPLAY "One of the UDF-files not found."
AT LINE 8 POSITION 26 COLOUR 14 ON 1 WITH IMAGE a
DISPLAY "Check C:\MAP for: "
AT LINE 9 POSITION 26 COLOUR 7 ON 1 WITH IMAGE a
DISPLAY "INIT.UDF" AT LINE 9 POSITION 44 COLOUR 4 ON 1 WITH IMAGE a
IF check_init = 0
DISPLAY "FILM.UDF" AT LINE 9 POSITION 44 COLOUR 4 ON 1 WITH IMAGE a
IF check_film = 0
DISPLAY "PACK.UDF" AT LINE 9 POSITION 44 COLOUR 4 ON 1 WITH IMAGE a
IF check_pack = 0
DISPLAY "CLIMATE.UDF" AT LINE 9 POSITION 44 COLOUR 4 ON 1 WITH IMAGE a
IF check_clim = 0
DISPLAY "PRODUCT.UDF" AT LINE 9 POSITION 44 COLOUR 4 ON 1 WITH IMAGE a
IF check_prod = 0
DISPLAY "PASSWORD.UDF" AT LINE 9 POSITION 44 COLOUR 4 ON 1 WITH IMAGE a
IF check_pass = 0

back:
CALL exit
RETURN
```

COMMENTS.MAC

```
@-----+-------------------------+-----+-------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----|  Some comments in case of      |-----
@@-----|-------------------------|-----|  conflicting input             |-----
@
@-----|      version MH3.0      |-----|                               |-----@
@-----|      January  1998      |-----|                               |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@

CALL clear_text_box(1,19,5,76,8,0)

@----------------------@
 IF search_prod = "END"
@----------------------@
      CALL clear_text_box(8,11,12,68,1,14)
      DISPLAY "Product not found. Check spelling/data in PRODUCT.UDF"
AT LINE 9  POSITION 14 COLOUR 14 ON 1 WITH IMAGE a
      DISPLAY "Name of the product:"
AT LINE 10 POSITION 25 COLOUR  7 ON 1 WITH IMAGE A
      DISPLAY prod_name
AT LINE 10 POSITION 46 COLOUR  4 ON 1 WITH IMAGE a
      GOTO back
END

@------------------@
 IF vol_pack = -999
@------------------@
      CALL clear_text_box(8,11,14,67,1,14)
      DISPLAY "Package not found. Check spelling/data in PACK.UDF"
AT LINE 9  POSITION 16 COLOUR 14 ON 1 WITH IMAGE a
```

```
      DISPLAY "Name of the package:"
AT LINE 10 POSITION 27 COLOUR  7 ON 1 WITH IMAGE A
      DISPLAY type
AT LINE 10 POSITION 48 COLOUR  4 ON 1 WITH IMAGE a
      GOTO back
END

@----------------------@
 IF vol_pack = vol_prod
@----------------------@
      CALL clear_text_box(8,12,18,64,1,14)
      DISPLAY "Product does not fit in package. Try again."
AT LINE 9  POSITION 20 COLOUR 14 ON 1 WITH IMAGE a
      DISPLAY "   volume of the pack:       l"
AT LINE 10 POSITION 27 COLOUR  7 ON 1 WITH IMAGE A
      DISPLAY "volume of the product:       l"
AT LINE 11 POSITION 27 COLOUR  7 ON 1 WITH IMAGE A
      DISPLAY vol_pack/1_m3
AT LINE 10 POSITION 50 COLOUR  4 ON 1 WITH IMAGE x.xxx
      DISPLAY vol_prod/1_m3
AT LINE 11 POSITION 50 COLOUR  4 ON 1 WITH IMAGE x.xxx
      GOTO back
END

@-------------------------------------@
 IF (thick_film = 0) & (mass_prod = 0)
@-------------------------------------@
      CALL clear_text_box(8,11,26,53,1,14)
      DISPLAY "No film... No product..."
AT LINE 9  POSITION 28 COLOUR 14 ON 1 WITH IMAGE a
      DISPLAY "So, nothing to simulate!"
AT LINE 10 POSITION 28 COLOUR 14 ON 1 WITH IMAGE a
      GOTO back
END

@-----------------------------------------------------------@
 IF (devi_mass > 0.3) | (devi_vmax > 0.3) | (devi_bag > 0.3)
| (devi_film > 0.3) | (devi_kq  > 0.3)
@-----------------------------------------------------------@
      CALL clear_text_box(6,12,20,65,1,14)
      DISPLAY "Deviation given is unrealistic large"
AT LINE 7  POSITION 22 COLOUR 14 ON 1 WITH IMAGE a
      DISPLAY "This can result in negative values for"
AT LINE 8 POSITION 22 COLOUR 7 ON 1 WITH IMAGE a
      DISPLAY "Mass of the Product"
AT LINE 9 POSITION 28 COLOUR 4 ON 1 WITH IMAGE a IF devi_mass > 0.3
      DISPLAY "Gas Exchange"
AT LINE 9 POSITION 28 COLOUR 4 ON 1 WITH IMAGE a IF devi_vmax > 0.3
      DISPLAY "Volume of the flexible BAG"
AT LINE 9 POSITION 28 COLOUR 4 ON 1 WITH IMAGE a IF devi_bag  > 0.3
      DISPLAY "Film Thickness"
AT LINE 9 POSITION 28 COLOUR 4 ON 1 WITH IMAGE a IF devi_film > 0.3
      DISPLAY "Keeping Quality"
AT LINE 9 POSITION 28 COLOUR 4 ON 1 WITH IMAGE a IF devi_kq   > 0.3
      DISPLAY "Please check INIT.UDF"
AT LINE 11 POSITION 28 COLOUR 7 ON 1 WITH IMAGE a
      GOTO back
END

@---------------@
@ everything OK @
@---------------@
RETURN 0

@---------------@
@ on error      @
@---------------@

back:
CALL exit

RETURN  1
```

OPEN_CONTROL.MOD

```
@-----+-------------------------+-----+------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----| Control module regulating    |-----@
@-----|-------------------------|-----| the opening and closing of   |-----@
@-----|      version MH3.0      |-----| the package. If opened gas   |-----@
@-----|      January  1998      |-----| conditions of the microclimate|-----@
@-----|    Copyright ATO-DLO    |-----| are copied from the macro-   |-----@
@-----|-------------------------|-----| climate                      |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                              |-----@
@-----|        R.G. Evelo       |-----|                              |-----@
@-----+-------------------------+-----+------------------------------+-----@
```

```
start:

FOR j _ 1 TO n_open

   WAIT WHILE CT = start_open[j]

   IF perm_open[j] = 0
      condens_orig _ cond_vol
      volume  _ con_vol
      vapour  _ vapour_out

      SPECIFY cond_vol PRECEPT(cond_vol _ 0)             IF keep_open[j] > 0.5
      SPECIFY cond_vol PRECEPT(cond_vol _ condens_orig) IF keep_open[j] = 0.5
      SPECIFY molh2o_micro PRECEPT(molh2o_micro _ (cond_vol/m_h2o) + vapour)
      SPECIFY molo2_micro  PRECEPT(molo2_micro  _
po2_macro *volume/temp_macro*r_gas)
      SPECIFY molco2_micro PRECEPT(molco2_micro _
pco2_macro*volume/temp_macro*r_gas)
      SPECIFY moln2_micro  PRECEPT(moln2_micro  _
pn2_macro *volume/temp_macro*r_gas)
      SPECIFY moltot_micro PRECEPT(moltot_micro _ vapour + molo2_micro
+ molco2_micro + moln2_micro)
   END
   IF perm_open[j] > 0
      perm_factor _ perm_open[j]
   END

   WAIT keep_open[j] HOURS

   IF perm_open[j] = 0
      CALL initspec
      vapour _ vapour_in
      volume _ var_vol IF max_vol_pack > 0
   end
   IF perm_open[j] > 0
      perm_factor _ 1
   END

   start_open[j] _ runtime IF runtime < start_open[j]

END

TERMINATE
```

SCRN_CONTROL.MOD

```
@-----+-------------------------+-----+------------------------------+-----
@@-----|||||||||| M.A.P.||||||||||-----| Module for switching between  |-----
@@-----|-------------------------|-----| graphic and text screen.      |-----
@
@-----|      version MH3.0      |-----|                              |-----@
@-----|      January  1998      |-----|                              |-----@
@-----|    Copyright ATO-DLO    |-----|                              |-----@
@-----|-------------------------|-----|                              |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                              |-----@
@-----|        R.G. Evelo       |-----|                              |-----@
@-----+-------------------------+-----+------------------------------+-----@
```

```
start:
```

```
            @-----------------------------------------@
mode_o _ 2  @ Current graphical mode, initially graphic @
mode   _ 1  @ Future  graphical mode, initially text    @
            @-----------------------------------------@

restart:
IF mode_o=2
   IF ready=FALSE
      CALL clear_graph_box(1,1,1,60,0)
      CALL gdisplay_string("Product:            <S>top, any other key for
INPUT summary",60,1,1,9)
   END
   IF ready=TRUE
      CALL clear_graph_box(1,1,1,80,0)
      CALL gdisplay_string("Product:                        Hit <X> to eXit,
any other key for INPUT summary",80,1,1,9)
   END
   CALL gdisplay_string(prod_name,10,1,10,9)
END

wait_again:
@---------------------- WAITING FOR KEY ---------------------------@
                      WHILE test_key = 0
                         WORK 1 HOUR IF ready=FALSE
                      END
@----------------------------------------------------------------@

key _ wait_key
GOTO exit IF ((key=88) | key=120) & ready=TRUE
GOTO stop IF ((key=83) | key=115) & ready?TRUE
IF mode_o=1
   check_key _ key_check
   REPEAT FROM wait_again IF check_key=1
END

CALL window_mode(mode)

mode_o _ mode
mode _ 1 IF mode_o=2
mode _ 2 IF mode_o=1

REPEAT FROM restart

exit:
CALL exit
TERMINATE

stop:
CANCEL watcher      IF watcher      IS ACTIVE
CANCEL quality      IF quality      IS ACTIVE
CANCEL opener       IF opener       IS ACTIVE
CANCEL microclimate IF microclimate IS ACTIVE
CANCEL film         IF film         IS ACTIVE
CANCEL product      IF product      IS ACTIVE
CANCEL macroclimate

REPEAT FROM restart
```

SETSCREEN.MAC

```
@-----+-------------------------+-----+------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----| Module for constructing the  |-----@
@-----|-------------------------|-----| text summary screen.         |-----@
@-----|      version MH3.0      |-----|                              |-----@
@-----|      January  1998      |-----|                              |-----@
@-----|    Copyright ATO-DLO    |-----|                              |-----@
@-----|-------------------------|-----|                              |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                              |-----@
@-----|        R.G. Evelo       |-----|                              |-----@
@-----+-------------------------+-----+------------------------------+-----@

LOCAL:
```

```
   DOUBLE: resist
           vmo
           resp
           resp_an
           temp_act
  INTEGER: gasnr

temp_act _ 21

CALL clear_text_box(1,19,5,76,8,0)
DISPLAY " Input summary - Hit any key for graphical output "
AT LINE 1 POSITION 15 COLOUR 7 ON 8 WITH IMAGE A
CALL clear_text_box(2,18,7,27,7,0)
CALL clear_text_box(2,18,30,50,7,0)
CALL clear_text_box(2,18,53,73,7,0)
DISPLAY "- Film -"    AT LINE 2  POSITION 13 COLOUR 14 ON 7 WITH IMAGE A
DISPLAY "- Product -" AT LINE 2  POSITION 35 COLOUR 14 ON 7 WITH IMAGE A
DISPLAY "- Package -" AT LINE 2  POSITION 58 COLOUR 14 ON 7 WITH IMAGE A
DISPLAY "- Microclimate -" AT LINE 12 POSITION  9 COLOUR 14 ON 7 WITH IMAGE A
DISPLAY "- Macroclimate -" AT LINE 12 POSITION 55 COLOUR 14 ON 7 WITH IMAGE A

@---------@
@  film   @
@---------@

IF thick_film = 0
   CALL clear_text_box(5,10,10,24,1,14)
   DISPLAY "  No film  " AT LINE 6  POSITION 12 COLOUR 14 ON 1 WITH IMAGE A
   DISPLAY "  present  " AT LINE 7  POSITION 12 COLOUR 14 ON 1 WITH IMAGE A
   DISPLAY "Calculating" AT LINE 8  POSITION 12 COLOUR 14 ON 1 WITH IMAGE A
   DISPLAY "respiration" AT LINE 9  POSITION 12 COLOUR 14 ON 1 WITH IMAGE A
END

IF thick_film > 0

DISPLAY film_name AT LINE 3 POSITION 8 COLOUR 4 ON 7 WITH IMAGE A19
DISPLAY " ransm. at    C: " AT LINE 4  POSITION 8  COLOUR 1 ON 7 WITH IMAGE A
DISPLAY "T"                AT LINE 4  POSITION 8  COLOUR 15 ON 7 WITH IMAGE A
DISPLAY temp_act  AT LINE 4 POSITION 19 COLOUR 15 ON 7 WITH IMAGE xx
DISPLAY "    ml/m2.bar.day" AT LINE 5  POSITION 10 COLOUR 1 ON 7 WITH IMAGE A
DISPLAY " O2:"              AT LINE 6  POSITION 8  COLOUR 1 ON 7 WITH IMAGE A
DISPLAY "CO2:"              AT LINE 7  POSITION 8  COLOUR 1 ON 7 WITH IMAGE A
DISPLAY " N2:"              AT LINE 8  POSITION 8  COLOUR 1 ON 7 WITH IMAGE A
DISPLAY "     g/m2.bar.day" AT LINE 9  POSITION 10 COLOUR 1 ON 7 WITH IMAGE A
DISPLAY "H2O:"              AT LINE 10 POSITION 8  COLOUR 1 ON 7 WITH IMAGE A

FOR gasnr_1 TO 4
   resist _ 0
   THIS layer _ FIRST OF layers
   FOR i_1 TO LENGTH OF layers
      resist _ resist+
thick/arrh(dref[gasnr],ea[gasnr],tref[gasnr],temp_act+cel_kelv)
      GOTO ready IF i = LENGTH OF layers
      THIS layer _ SUCC OF THIS layer IN layers
   END
   ready:
   resist_bar_pa/(resist*ml_l*l_m3) IF gasnr<4
   resist_bar_pa*m_h2o/resist IF gasnr=4

   DISPLAY resist AT LINE (5+gasnr)
POSITION 14 COLOUR 4 ON 7 WITH IMAGE xxxxxxx IF gasnr<4
   DISPLAY resist AT LINE 10
POSITION 14 COLOUR 4 ON 7 WITH IMAGE xxxxxxx IF gasnr=4
END
END

@---------@
@ PRODUCT @
@---------@

IF mass_prod = 0
   CALL clear_text_box(6,12,33,47,1,14)
   DISPLAY " No product " AT LINE 7  POSITION 35 COLOUR 14 ON 1 WITH IMAGE A
   DISPLAY "  present   " AT LINE 8  POSITION 35 COLOUR 14 ON 1 WITH IMAGE A
   DISPLAY "Calculating " AT LINE 9  POSITION 35 COLOUR 14 ON 1 WITH IMAGE A
   DISPLAY " diffusion  " AT LINE 10 POSITION 35 COLOUR 14 ON 1 WITH IMAGE A
   DISPLAY "through film" AT LINE 11 POSITION 35 COLOUR 14 ON 1 WITH IMAGE A
END
```

```
IF mass_prod  > 0

DISPLAY "           mass"     AT LINE 4 POSITION 31 COLOUR 1 ON 7
WITH IMAGE A
DISPLAY "   total:        kg" AT LINE 5 POSITION 31 COLOUR 1 ON 7
WITH IMAGE A
DISPLAY "per item:        kg" AT LINE 6 POSITION 31 COLOUR 1 ON 7
WITH IMAGE A
DISPLAY "Initial temp:    C " AT LINE 8 POSITION 31 COLOUR 1 ON 7
WITH IMAGE A
DISPLAY "Keeping  uality"     AT LINE 10 POSITION 31 COLOUR 1 ON 7
WITH IMAGE a
DISPLAY "Q" AT LINE 10 POSITION 39 COLOUR 15 ON 7 WITH IMAGE a
DISPLAY "at    C:      days"  AT LINE 11 POSITION 31 COLOUR 1 ON 7
WITH IMAGE a
DISPLAY " espiration at    C" AT LINE 13 POSITION 31 COLOUR 1 ON 7
WITH IMAGE a
DISPLAY "R" AT LINE 13 POSITION 31 COLOUR 15 ON 7 WITH IMAGE a
DISPLAY "Oxydative (21,0):  " AT LINE 14 POSITION 31 COLOUR 1 ON 7
WITH IMAGE a
DISPLAY "      mmol O2/kg/h " AT LINE 15 POSITION 31 COLOUR 1 ON 7
WITH IMAGE a
DISPLAY "Fermentative (0,0):" AT LINE 16 POSITION 31 COLOUR 1 ON 7
WITH IMAGE a
DISPLAY "      mmol CO2/kg/h" AT LINE 17 POSITION 31 COLOUR 1 ON 7
WITH IMAGE a

vmo     _ arrh(vmo2_ref,ea_vmo2,tref_resp,21+cel_kelv)
resp    _ vmo*21/(kmo2+21)
resp_an _ arrh(vmco2_ref,ea_vmco2,tref_resp,21+cel_kelv)


DISPLAY prod_name AT LINE 3 POSITION 31 COLOUR 4 ON 7 WITH IMAGE A19
DISPLAY mass_prod AT LINE 5 POSITION 41 COLOUR 4 ON 7 WITH IMAGE xx.xxx
DISPLAY aver_wght AT LINE 6 POSITION 41 COLOUR 4 ON 7 WITH IMAGE xx.xxx
DISPLAY temp_prod-cel_kelv AT LINE 8  POSITION 45 COLOUR 4 ON 7 WITH IMAGE xx
DISPLAY temp_st-cel_kelv  AT LINE 11 POSITION 34 COLOUR 15 ON 7 WITH IMAGE xx
DISPLAY kq_st     AT LINE 11 POSITION 40 COLOUR 4  ON 7 WITH IMAGE xx.x
DISPLAY temp_act  AT LINE 13 POSITION 46 COLOUR 15 ON 7 WITH IMAGE xx
DISPLAY resp      AT LINE 15 POSITION 31 COLOUR 4  ON 7 WITH IMAGE x.xxx
DISPLAY resp_an   AT LINE 17 POSITION 31 COLOUR 4  ON 7 WITH IMAGE x.xxx
END

@---------@
@ PACKAGE @
@---------@

DISPLAY "diff.area:       m2"AT LINE 5 POSITION 54 COLOUR 1 ON 7 WITH IMAGE A
DISPLAY " tot.vol.:       l" AT LINE 6 POSITION 54 COLOUR 1 ON 7 WITH IMAGE A
DISPLAY " air vol.:       l" AT LINE 7 POSITION 54 COLOUR 1 ON 7 WITH IMAGE A
DISPLAY type            AT LINE 3 POSITION 54 COLOUR 4 ON 7 WITH IMAGE A7
DISPLAY diff_area       AT LINE 5 POSITION 65 COLOUR 4 ON 7 WITH IMAGE x.xxx
DISPLAY vol_pack/l_m3   AT LINE 6 POSITION 65 COLOUR 4 ON 7 WITH IMAGE x.xxx
DISPLAY (vol_pack-vol_prod)/l_m3  AT LINE 7 POSITION 65 COLOUR 4 ON 7 WITH
IMAGE x.xxx

@---------@
@ CLIMATE @
@---------@

DISPLAY "constant cond.: " AT LINE 14 POSITION 54 COLOUR 1 ON 7 WITH IMAGE A
DISPLAY " pO2:          Pa" AT LINE 15 POSITION 54 COLOUR 1 ON 7 WITH IMAGE A
DISPLAY "pCO2:          Pa" AT LINE 16 POSITION 54 COLOUR 1 ON 7 WITH IMAGE A
DISPLAY " pN2:          Pa" AT LINE 17 POSITION 54 COLOUR 1 ON 7 WITH IMAGE A
DISPLAY po2_macro  AT LINE 15 POSITION 60 COLOUR 4 ON 7 WITH IMAGE xxxxExx
DISPLAY pco2_macro AT LINE 16 POSITION 60 COLOUR 4 ON 7 WITH IMAGE xxxxExx
DISPLAY pn2_macro  AT LINE 17 POSITION 60 COLOUR 4 ON 7 WITH IMAGE xxxxExx

DISPLAY "initial cond.:  " AT LINE 14 POSITION 8 COLOUR 1 ON 7 WITH IMAGE A
DISPLAY " pO2:          Pa" AT LINE 15 POSITION 8 COLOUR 1 ON 7 WITH IMAGE A
DISPLAY "pCO2:          Pa" AT LINE 16 POSITION 8 COLOUR 1 ON 7 WITH IMAGE A
DISPLAY " pN2:          Pa" AT LINE 17 POSITION 8 COLOUR 1 ON 7 WITH IMAGE A
DISPLAY pressure(molo2_micro ) AT LINE 15 POSITION 14 COLOUR 4 ON 7 WITH
IMAGE xxxxExx
DISPLAY pressure(molco2_micro) AT LINE 16 POSITION 14 COLOUR 4 ON 7 WITH
IMAGE xxxxExx
```

```
DISPLAY pressure(moln2_micro ) AT LINE 17 POSITION 14 COLOUR 4 ON 7 WITH
IMAGE xxxxExx


RETURN
```

INTERACT.MAC

```
@-----+-------------------------+-----+-------------------------------+-----@
@-----|||||||||| M.A.P.|||||||||||-----| Updating temperatures to      |-----@
@-----|-------------------------|-----| calculate respiration,        |-----@
@-----|      version MH3.0      |-----| transmittance and keeping     |-----@
@-----|      January  1998      |-----| quality in the input          |-----@
@-----|    Copyright ATO-DLO    |-----| summary screen                |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@
PARAMETER:
   CHARACTER(10): proces

LOCALS:
   DOUBLE: vmo
           resp
           resp_an
           temp_act
           resist
           kqst
           kst
           kref

  INTEGER: gasnr


@----------------@
 IF proces="resp"
@----------------@

CAPTURE temp_act AT LINE 13 POSITION 46 FIELDLENGTH 2

vmo     _ arrh(vmo2_ref,ea_vmo2,tref_resp,temp_act+cel_kelv)
resp    _ vmo*21/(kmo2+21)
resp_an _ arrh(vmco2_ref,ea_vmco2,tref_resp,temp_act+cel_kelv)

DISPLAY resp      AT LINE 15 POSITION 31 COLOUR 4 ON 7 WITH IMAGE x.xxx
DISPLAY resp_an   AT LINE 17 POSITION 31 COLOUR 4 ON 7 WITH IMAGE x.xxx

END

@----------------@
 IF proces="film"
@----------------@

CAPTURE temp_act  AT LINE 4 POSITION 19 FIELDLENGTH 2

FOR gasnr_1 TO 4
   resist _ 0
   THIS layer _ FIRST OF layers
   FOR i_1 TO LENGTH OF layers
      resist _ resist+
thick/arrh(dref[gasnr],ea[gasnr],tref[gasnr],temp_act+cel_kelv)
      GOTO ready IF i = LENGTH OF layers
      THIS layer _ SUCC OF THIS layer IN layers
   END
   ready:
   resist_bar_pa/(resist*ml_l*l_m3) IF gasnr<4
   resist_bar_pa*m_h2o/resist IF gasnr=4

   DISPLAY resist AT LINE (5+gasnr)
POSITION 14 COLOUR 4 ON 7 WITH IMAGE xxxxxxx IF gasnr<4
   DISPLAY resist AT LINE 10
POSITION 14 COLOUR 4 ON 7 WITH IMAGE xxxxxxx IF gasnr=4
```

```
END
END

@----------------@
 IF proces="qual"
@----------------@

CAPTURE temp_act AT LINE 11 POSITION 34 FIELDLENGTH 2

FOR i_1 TO n_proces
   kst _ kst + arrh(kkq_ref[i],ea_kq[i],tref_kq,temp_act+cel_kelv)
END

kqst _ kq_ref/kst
DISPLAY kqst AT LINE 11 POSITION 40 COLOUR 4  ON 7 WITH IMAGE xx.x

END

RETURN
```

WATCH_MOD.MOD

```
@-----+-------------------------+-----+-------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----| Generating ascii output to    |-----@
@-----|-------------------------|-----| outputstream RESULTS with     |-----@
@-----|      version MH3.0      |-----| frequency FREQ                |-----@
@-----|      January  1998      |-----|                               |-----@
@-----|    Copyright ATO-DLO    |-----|                               |-----@
@-----|-------------------------|-----|                               |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                               |-----@
@-----|        R.G. Evelo       |-----|                               |-----@
@-----+-------------------------+-----+-------------------------------+-----@

start:
REWIND results
WRITE "+-------------------------------------------------------------------------
------+" TO results WITH IMAGE |a
WRITE "| Simulation results from the MAP-model (version MH3.0)        ATO-DLO
1998 |" TO results WITH IMAGE a
WRITE "| Date: " TO results WITH IMAGE a
WRITE n[3]  TO results WITH IMAGE |xx
WRITE " - " TO results WITH IMAGE |a
WRITE n[2]  TO results WITH IMAGE |xx
WRITE " - " TO results WITH IMAGE |a
WRITE n[1]  TO results WITH IMAGE |xxxx
WRITE "                              ID: " TO results WITH IMAGE |a
WRITE id    TO results WITH IMAGE |a20
WRITE "  |" TO results WITH IMAGE |a
WRITE "|-------------------------------------------------------------------------
------¶" TO results WITH IMAGE a
WRITE "|       Product: " TO results WITH IMAGE a
WRITE prod_name TO results WITH IMAGE |a20
WRITE "            Film: " TO results WITH IMAGE |a
WRITE film_name TO results WITH IMAGE |a20
WRITE "  |" TO results WITH IMAGE |a
WRITE "|          Mass: " TO results WITH IMAGE a
WRITE mass_prod TO results WITH IMAGE |x.xxxx
WRITE " kg" TO results WITH IMAGE |a
WRITE "                 Thickness: " TO results WITH IMAGE |a
WRITE thick_film TO results WITH IMAGE |xxxxxExx
WRITE " m            |" TO results WITH IMAGE |a
WRITE "|       Package: " TO results WITH IMAGE a
IF type?"BAG"
   WRITE type TO results WITH IMAGE |a20
END
IF type="BAG"
   WRITE type TO results WITH IMAGE |a4
   WRITE bag  TO results WITH IMAGE |a16
END
WRITE " Diffusion Area: " TO results WITH IMAGE |a
WRITE diff_area TO results WITH IMAGE |xx.xxxx
WRITE " m2           |" TO results WITH IMAGE |a
WRITE "|  Total Volume: " TO results WITH IMAGE a
```

```
WRITE vol_pack/l_m3 TO results WITH IMAGE |xx.xxxx
WRITE " l                Air Volume: " TO results WITH IMAGE |a
WRITE (vol_pack-vol_prod)/l_m3 TO results WITH IMAGE |xx.xxxx
WRITE " l             |" TO results WITH IMAGE |a
WRITE "+-------------------------------------------------------------------------
------+"  TO results WITH IMAGE a
WRITE " " TO results WITH IMAGE  a

   WRITE "time    " TO results WITH IMAGE  ?a7
   WRITE "t_macro" TO results WITH IMAGE |?a7
   WRITE "rh_macr" TO results WITH IMAGE |?a7
IF mass_prod  > 0
   WRITE "t_prod " TO results WITH IMAGE |?a7
   WRITE "vo2    " TO results WITH IMAGE |?a7
   WRITE "vco2   " TO results WITH IMAGE |?a7
   WRITE "anaer  " TO results WITH IMAGE |?a7
END
IF thick_film > 0
   WRITE "o2_%   " TO results WITH IMAGE |?a7
   WRITE "co2_%  " TO results WITH IMAGE |?a7
   WRITE "n2_%   " TO results WITH IMAGE |?a7
   WRITE "P_tot  " TO results WITH IMAGE |?a7
   WRITE "rh_micr" TO results WITH IMAGE |?a7
   WRITE "air_vol" TO results WITH IMAGE |?a9 IF max_vol_pack > 0
   WRITE "p_sat  " TO results WITH IMAGE |?a7
   WRITE "cond_ml" TO results WITH IMAGE |?a7
END
IF mass_prod  > 0
   WRITE "mass_% " TO results WITH IMAGE |?a7
   WRITE "kq_st  " TO results WITH IMAGE |?a7
END

@----------@
 writedata:
@----------@

   WRITE CT                       TO results WITH IMAGE  xx.xxxx
   WRITE t_macro                  TO results WITH IMAGE |??xx.xxx
   WRITE VALUE OF relh_tab AT(CT) TO results WITH IMAGE |?xxx.xxx

IF mass_prod  > 0
   WRITE t_prod                   TO results WITH IMAGE |??xx.xxx
   WRITE vo2_out                  TO results WITH IMAGE |??x.xxxxx
   WRITE vco2_out                 TO results WITH IMAGE |?x.xxxxx
   WRITE anaer                    TO results WITH IMAGE |?x.xxxxx
END
IF thick_film > 0
   WRITE o2_perc                  TO results WITH IMAGE |?xx.xxxx
   WRITE co2_perc                 TO results WITH IMAGE |?xx.xxxx
   WRITE 100*pressure(moln2_micro)/ptot_micro
TO results WITH IMAGE |?xx.xxxx
   WRITE ptot_micro/p0            TO results WITH IMAGE |?x.xxxxx
   WRITE 100*pressure(vapour)/ph2o_sat(temp_macro)
TO results WITH IMAGE |?xxx.xxx
   WRITE volume/l_m3              TO results WITH IMAGE |?xx.xxxxxx
IF max_vol_pack > 0
   WRITE ph2o_sat(temp_macro)     TO results WITH IMAGE |?xxxx.xx
   WRITE cond_vol                 TO results WITH IMAGE |?x.xxxxx
END
IF mass_prod  > 0
   WRITE 100*mass/mass_prod       TO results WITH IMAGE |?xxx.xxx
   WRITE kq_st*(kq_st>0)          TO results WITH IMAGE |?xxx.xxx
END

WAIT freq HOURS
REPEAT FROM writedata
```

AUTO_STORE.MOD

```
@-----+-------------------------+-----+-------------------------------+-----
@@-----|||||||||| M.A.P. ||||||||||-----|                               |-----
@
```

```
@-----|-------------------------|-----|                                |-----@
@-----|      version MH3.0      |-----|   Generating output for        |-----@
@-----|      January  1998      |-----|   graphical presentation       |-----@
@-----|    Copyright ATO-DLO    |-----|                                |-----@
@-----|-------------------------|-----|                                |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                                |-----@
@-----|        R.G. Evelo       |-----|                                |-----@
@-----+-------------------------+-----+--------------------------------+-----@

start:

   AUTOSTORE t_macro    AS "T_macro   "
IF mass_prod  > 0
   AUTOSTORE t_prod     AS "T_prod    "
   AUTOSTORE vo2_out    AS "O2_CONS   "
   AUTOSTORE vco2_out   AS "CO2_PROD  "
   AUTOSTORE anaer      AS "ANAER_PERC"
   AUTOSTORE kq_st      AS "kq        "
END
IF thick_film > 0
   AUTOSTORE o2_perc    AS "O2_PERC   "
   AUTOSTORE co2_perc   AS "CO2_PERC  "
   AUTOSTORE cond_vol   AS "ML_COND   "
END
```

EXIT.MAC

```
@-----+-------------------------+-----+--------------------------------+-----@
@-----|||||||||| M.A.P.||||||||||-----| Shutting down.....             |-----@
@-----|-------------------------|-----|                                |-----@
@-----|      version MH3.0      |-----|                                |-----@
@-----|      January  1998      |-----|                                |-----@
@-----|    Copyright ATO-DLO    |-----|                                |-----@
@-----|-------------------------|-----|                                |-----@
@-----|    M.L.A.T.M. Hertog    |-----|                                |-----@
@-----|        R.G. Evelo       |-----|                                |-----@
@-----+-------------------------+-----+--------------------------------+-----@

IF READY=FALSE
   DISPLAY "Hit any key to continue....."
AT LINE 16 POSITION 28 COLOUR 12 ON 8 WITH IMAGE a
   CALL bell
   CALL wait_key
END

CALL window_mode(1)
CALL COPYRIGHT
CALL sleep(3)
CALL clear_text_box(1,19,5,76,8,0)
DISPLAY "Bye.." AT LINE 10 POSITION 38 COLOUR 14 ON 8 WITH IMAGE a
CALL sleep(1)

RETURN
```

7 Literature

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