PROJECT TITLE: Modified Atmosphere Systems in varying TEmperature Regimes
PROJECT NR.: AIR2-CT-1326
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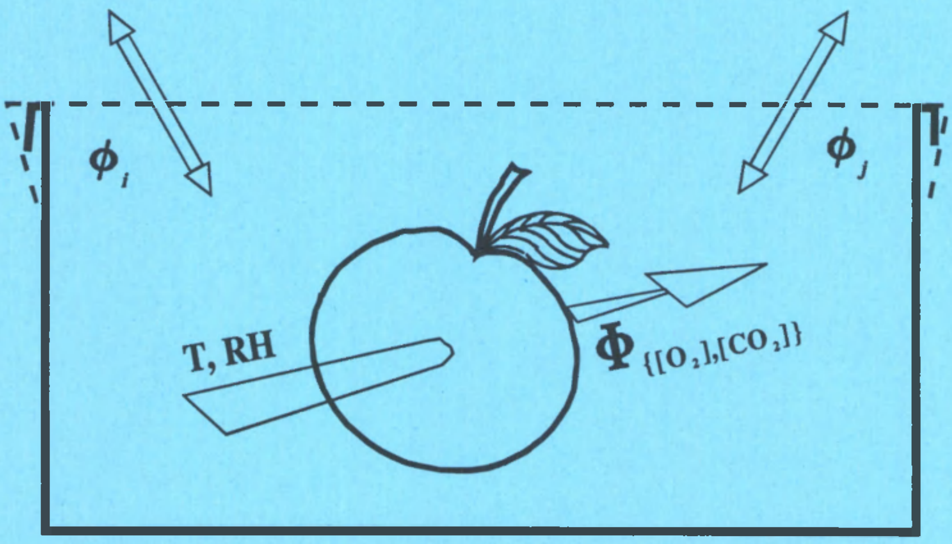
MASTER



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MASTER

Modified Atmosphere Systems in varying TEmperature Regimes

Contract number: AIR 2 / CT 93 1326

Final Synthesis Report

Contractors:

- ATO-DLO (Agrotechnological Research Institute - Agricultural Research Department), NL-6700 AA Wageningen, coordinator
- INRA (Institute National de la Recherche Agronomique), station de Technologie des Produits Végétaux, F-84143 Montfavet
- Istituto di Industrie Agrarie, University of Pisa, I-56124 Pisa
- Fh-IVV (Fraunhofer-Institut für Verfahrenstechnik und Verpackung, till end of 97: Fraunhofer-Institut für Lebensmitteltechnologie und Verpackung, Fh-ILV), D-85354 Freising, project management
- VCBT (Vlaams Centrum voor de Bewaaring van Tuinbouwproducten, till 1997: Verbond van Belgische Tuinbouwveilingen, VBT), B-3001 Heverlee
- Istituto di Tecnologie Agro Alimentari, University of Tuscia, Viterbo, I-01100 Viterbo

Reporting period: 01 January 1994 to 31 December 1997

I Project title:

Modified Atmosphere Systems in varying TEmperature Regimes (MASTER)

II Organisations involved:

P1: ATO-DLO (Agrotechnological Research Institute - Agricultural Research Department), NL-6700 AA Wageningen, coordinator

P2: INRA (Institute National de la Recherche Agronomique), station de Technologie des Produits Végétaux, F-84143 Montfavet

P3: Istituto di Industrie Agrarie, University of Pisa, I-56124 Pisa

P4 Fh-IVV (Fraunhofer-Institut für Verfahrenstechnik und Verpackung), D-85354 Freising, project management

P5: VCBT (Vlaams Centrum voor de Bewaaring van Tuinbouwproducten), B-3001 Heverlee

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III Introduction

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)** was followed in this project. Here, 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.
- Lower temperatures are applied which also have the effect of lowering all reactions of the produce.

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

The technical solution pursued to finally achieve a modified atmosphere was the following:

- 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.

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 abnormal 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 shelf life 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 (selected: Tomato, Chicory, Apples as model products)

→ to determine the respiratory activity of the produce not only under optimum conditions of gas composition and temperature, but also outside this range,

→ to determine the permeability of films, (selected: ***Polyethylene, Polyvinylchloride***, Polystyrene, Ethylene-Vinylacetate-Polyethylene Copolymer, ***Polyester-Polyether Copolymer***, Poly-(ε)-Caprolactone, ***Cellulose acetate***, Cellulose, ***microperforated Polypropylene,*** materials in bold/italics taken for a broader investigation)

in dependence on

gas species

temperature

humidity, humidity difference across the films, condensation conditions,

→ to pre-select a suitable packaging configuration for a given produce

→ and, finally, to model the combined behaviour of produce and packaging - by help of the MASTER 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 or to approach the correct selection of a packaging material and packaging geometry for a given produce application. This sequence was to be performed completely for the exemplary selection of different produces and packaging films to verify the applicability of the model.

The list of tasks is shown in the following table (table 1).

Table 1: Time schedule of the work plan, as originally planned, and allocation of the resources

Task	Title	1st year	2nd year	3rd year	4th year
1	Survey and selection of agricultural produce	P2, P5, P6			
2	Gas transport in the produce	P3	P3	P3	P3
3	Respiration rate as a function of the surrounding gas composition and temperature	P2, P3, P5	P2, P3, P5	P3, P5	P3, P5
4	Modelling of the respiration rate	P1	P1, P6	P1, P6	P1, P6
5	Survey and selection of the packaging materials	P4			
6	Temperature dependent gas and water permeability constants	P4	P4	P4	
7	Modelling the diffusion process through the packaging material	P1	P1	P1	P1
8	Building databases		P4	P4	P4
9	Evaluation of the whole system, for selected packaging and product	P1, P5	P1, P5	P1, P2, P5	P1, P2, P4, P5
10	Maturity effects on the respiration rate		P5	P5	
11	Project management	P4	P4	P4	P4

IV Results

- Measurements on the behaviour of products (respiration, internal gas transport characteristics) at various temperatures have been performed.

An example of the respiration characteristics of chicory endives is given in figures 1 to 3, showing

⇒ the different respiration rates of oxygen consumption (RRO_2) and carbon dioxide production ($RRCO_2$) at 11 °C

⇒ and the dependence of the respiration rate on temperature which can be obtained by comparing figure 1 with figure 3 (oxygen consumption rate at 21 °C).

The total range of values obtained for the 3 model products covers

⇒ the temperature range from 1 °C to 21 °C (apples, chicory endives) respectively from 8 °C to 28 °C (tomatoes)

⇒ and the gas concentration range from 0% to 21% of atmospheric pressure (oxygen) respectively from 0% to 20% at atmospheric pressure (carbon dioxide).

A total number of 574 respiration rates could be implemented into the produce data base of the MAP program. Moreover, the gas transport properties of the plant tissues of the three model products could be described quantitatively.

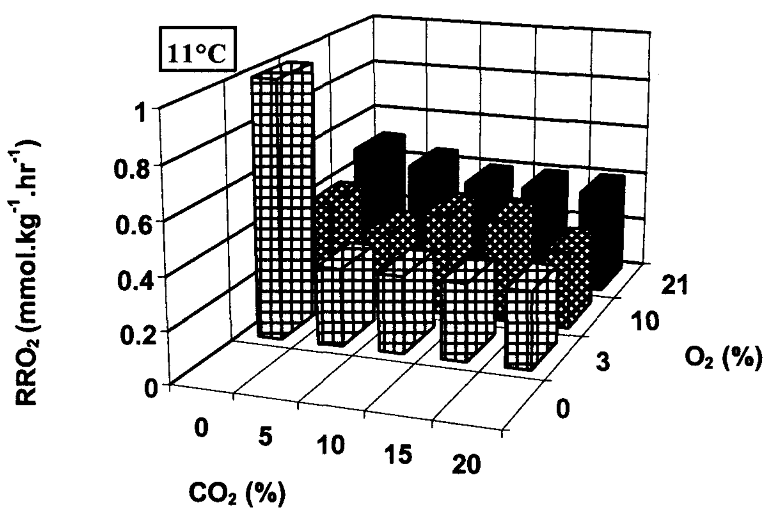

Figure1: RO_2 of endive shoots as a function of atmosphere composition at 11 °C.

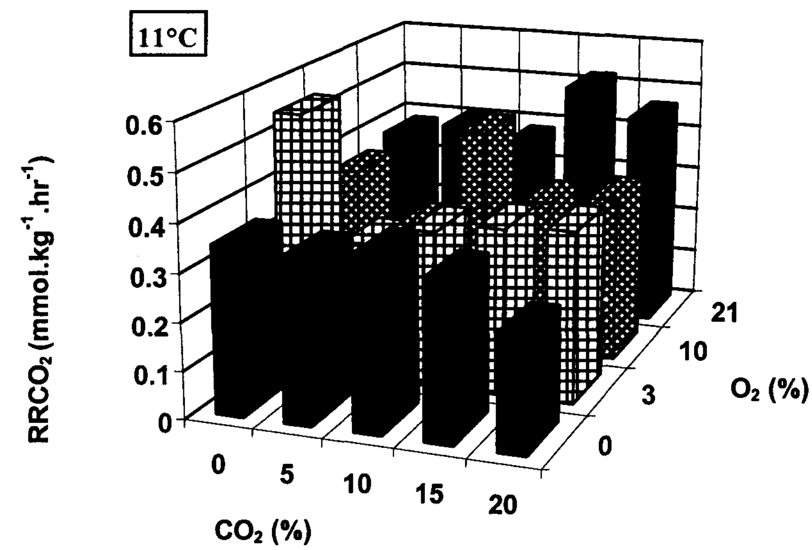

Figure 2: $RRCO_2$ of endive shoots as a function of atmosphere composition at 11 °C.

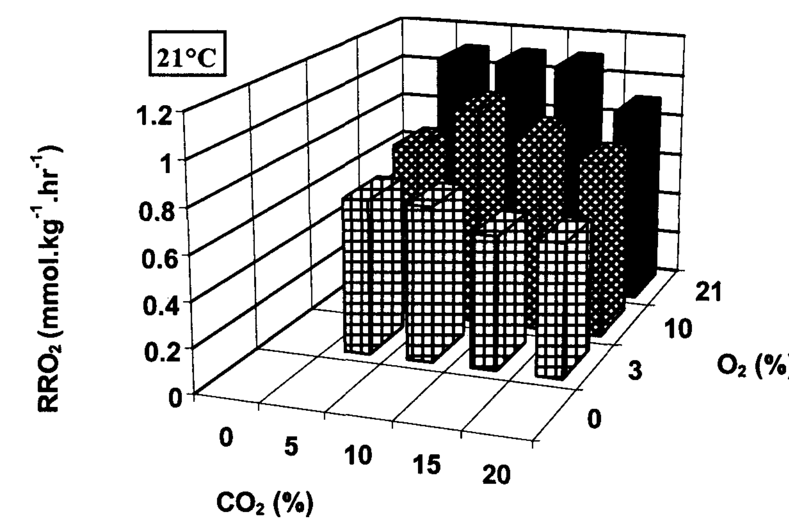

Figure 3: RRO_2 of endive shoots as a function of atmosphere composition at 21 °C.

- Measurements of packaging films (gas and water transport characteristics) at different temperature and relative humidity conditions have been performed for 9 different materials. Among these, 5 materials have been investigated in more detail, thus allowing for a better assessment of limitations of the accuracy of the measurements, of individual differences of the samples and of the influence of condensation.

As examples,

⇒ the gas permeability in terms of temperature is demonstrated in figure 4, for Polyether-ester-copolymer, a highly transmitting material,

⇒ the water vapour permeability in dependence of temperature and on the humidity gradient across the film is shown for the same material in figure 5.

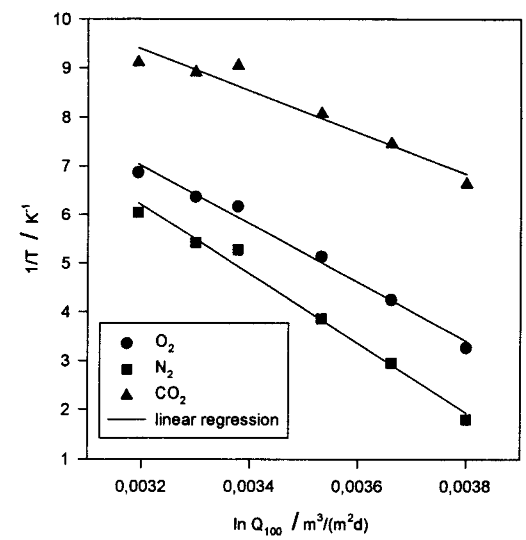

Fig.4: Temperature dependence of gas permeability, normalised to 100 µm film thickness (Q_{100}) in an Arrhenius graph: Copolyether-ester

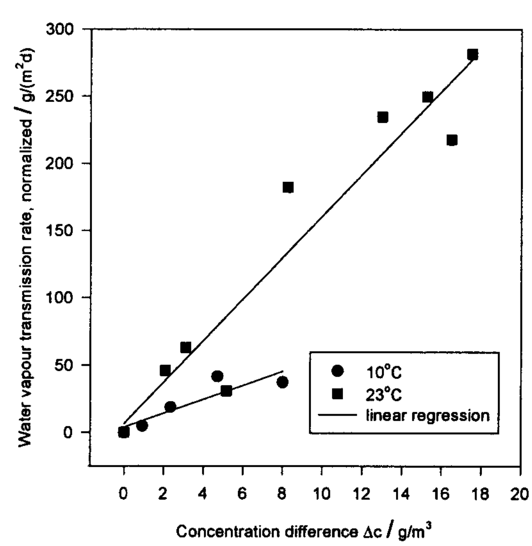

Fig. 5: Water vapour transmission rate, normalised to 100 µm film thickness. Dependence on water vapour concentration difference and temperature: Copolyether-ester

- Measurements on Modified Atmosphere Packages stored at various conditions have been performed to improve the statistical basis and to demonstrate that

  the Michaelis Menten description for the respiration is generally valid,

  the systems under study are accessible to numerical modelling,

  the envisaged software program is generally applicable

  and to collect a substantial number of data for the data base on product and packaging material associated with the modelling software.

Figures 6 and 7 show the different atmospheres inside the packaging of tomatoes in two different types of films: A microperforated film (P Plus) with a nominal permeability of 25000 cm^3/m^2d bar both for oxygen and carbon dioxide at 23 °C and a PVC film showing a nominal permeability of 11000 cm³/m²d bar for oxygen and of 52000 cm³/m²d bar for carbon dioxide.

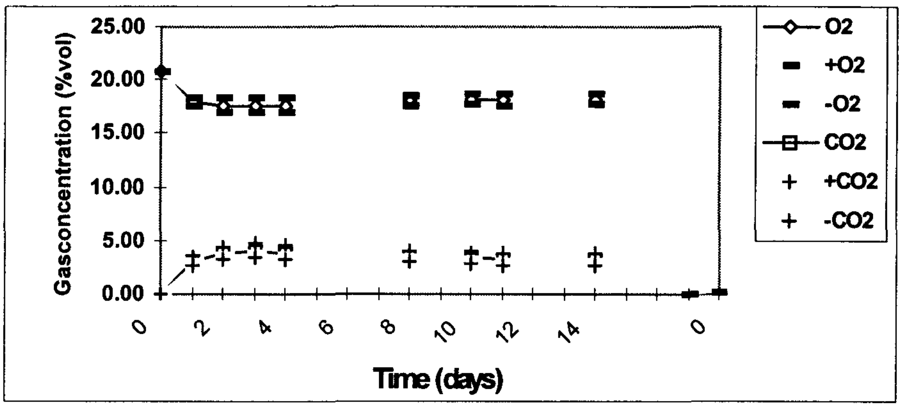

Figure 6: O_2 and CO_2 concentrations in a six pack with tomatoes at 13 °C, packaging foil used: P-plus 25K (polypropylene)

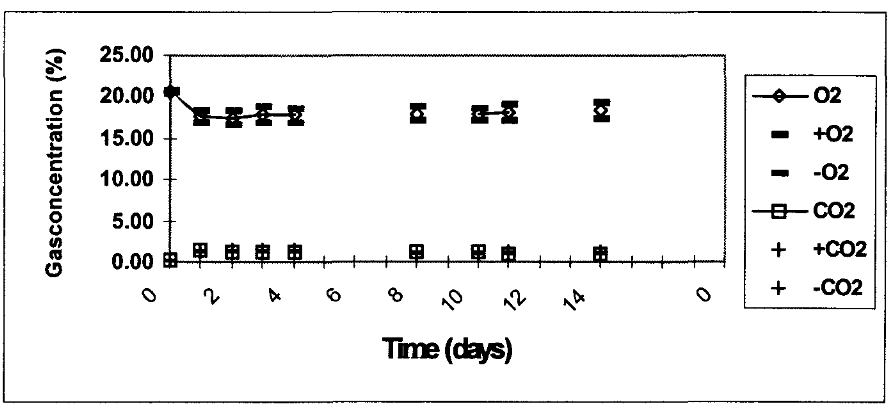

Figure 7: O_2 and CO_2 concentrations in a six pack with tomatoes at 13 °C, packaging foil used: PVC

Under realistic conditions, however, deviations from an ideal temperature occur. The effects of a typical temperature profile which may be observed under conditions of decreasing quality of temperature control are shown for the same packaging materials in figures 8 and 9. Apparently, the higher permeability of the PVC film leads to a lower concentration of carbon dioxide inside the package.

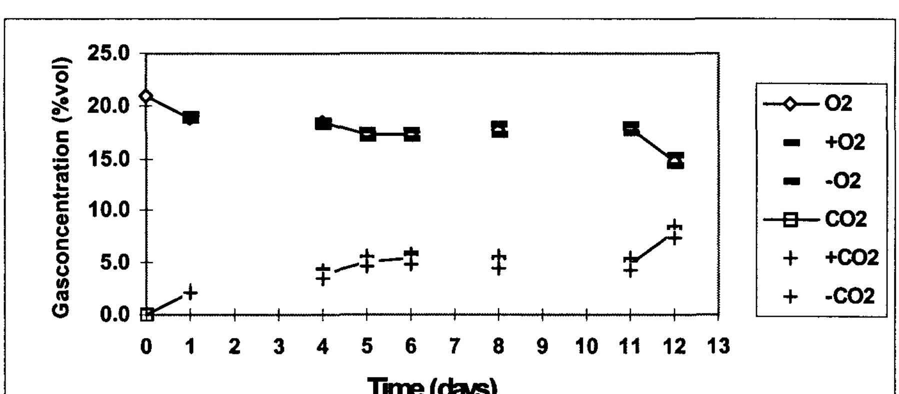

Figure 8: O_2 and CO_2 concentrations in a six pack with tomatoes stored for 4 days at 8 °C, 7 days at 13 °C and 3 days at 23 °C, packaging foil used: P-plus 25K (polypropylene)

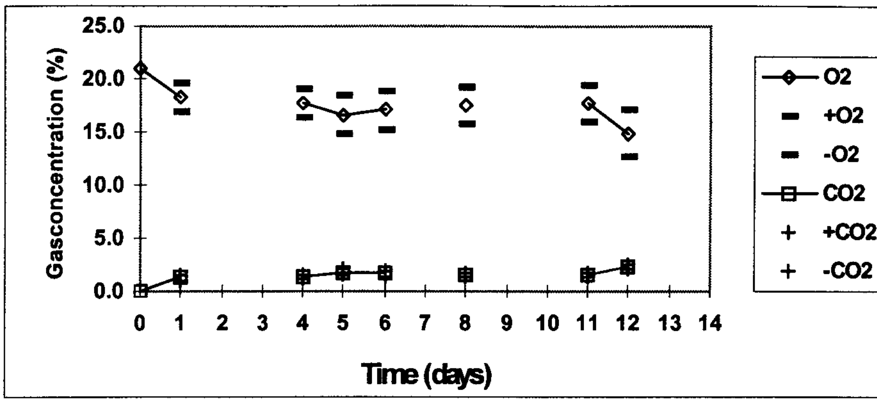

Figure 9: O_2 and CO_2 concentrations in a six pack with tomatoes stored for 4 days at 8 °C, 7 days at 13 °C and 3 days at 23 °C, packaging foil used: PVC

V Discussion

The results for the products show and prove that

* the best normalisation parameters of the individually different products are their initial respiration rate at standard atmospheric conditions and at anoxic (0 % O2, 0 % CO2 and 100 % N2) conditions
* maximum observed respiration rates show an Arrhenius type of temperature dependence for aerobic respiration (about 50 KJ mol-1 activation energy) and for alcoholic fermentation (about 25 kJ mol-1 activation energy),
* respiration rates in dependence of oxygen partial pressure can be described by Michaelis Menten kinetics,
* skin permeability of chicory, apples and tomatoes are in the same order of magnitude for the three produces, but very high compared to all packaging materials concerned.

The results for the packaging films:

* Gas permeabilities generally show an Arrhenius type of temperature behaviour,
* but relatively high variations occur even within the same batch of film material
* and a marked increase of permeability is to be observed at very high relative humidity conditions. Even higher values are measured upon contact of films with liquid water. This is in line with the observation that the permeability of films under realistic, i.e. condensation conditions is at least higher by factor 2 over values obtained under standard dry or moderate humid conditions.

For available measurement equipment, difficulties were higher than expected both for respiration and gas permeation measurement equipment, especially for those parts of the equipment which were not commercially available.

Differences between different measurement methods of gas permeability have been traced back to their origins and show to be a combination of differences between detection principles, of individual properties of material samples and of humidity conditions.

If these differences are properly taken into account, the results overall show a good agreement.

The results for the MA packages show that

* The gas conditions inside a package can be measured with sufficient accuracy.
* The Master model is in principle be able to describe the oxygen and carbon dioxide concentrations vs. time inside MAP at various temperatures, if the observed large individual variation of the properties of produce and packaging materials are taken into account..

VI Conclusions

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 consistently 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 gradient 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 statistical 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 packaging systems with relatively low effort.