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I. Saguy, M. Karel

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Name(s) of investigator(s):

Principal Investigator Israel Saguy

Cooperating investigator(s) Marcus Karel

Name and address of Affiliated institution(s):

Grantee institution Dept. Food Technology, ARO, The Volcani Center, Bet Dagan, Israel

Cooperating institution(s) Department of Nutrition and Food Science, M.I.T., Cambridge, MA 02139, USA

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Principal Investigator

Name Israel Saguy

Signature Israel Saguy

Institution's Authorizing Official

Name Yuval Eshdat

Dr. YUVAL ESHDAT
Head, Div. for Research Projects and Budgets
Agricultural Research Organization

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Kinetics of Oxidation of Dehydrated Food at Low Oxygen, and
Development of Accelerated Tests

ABSTRACT

Israel Saguy¹ and Marcus Karel²

¹ARO, Volcani Center
Bet Dagan, Israel

²M.I.T. Cambridge
Massachusetts, U.S.A.

In dehydrated foodstuffs the main causes of undesirable changes in quality are oxidation and nonenzymatic browning. Factors like water activity, moisture content, oxygen pressure, temperature and light are of fundamental importance in controlling these reactions.

Even though most of the dehydrated food susceptible to oxygen deterioration is packaged under vacuum or under a nitrogen atmosphere, such products are not totally free of molecular oxygen that remains absorbed on, and encapsulated by them. Utilizing the improved method developed in this work for the determination of adsorbed/entrapped gases retained by dehydrated foodstuffs indicated that two general types of behaviour of foods, affecting the amount of gases retained on the powder. Gas volume retained by type I powders reached a plateau and stayed constant regardless of evacuation time. The latter determined the volume of type II.

Kinetic studies were performed to obtain the dependence of rates of beta-carotene decolorization, betanine and vulgaxanthine I degradation and lipid oxidation on oxygen pressure and water activity in systems containing free as well as adsorbed oxygen. Model systems as well as foodstuffs (non-fat milk powder, carrots powder, beet powder, pomegranate juice and potato powder) were investigated. Lipid oxidation followed bimolecular oxidation kinetics with the rate of oxidation more rapid in model system. Oxygen was found also to be a crucial factor in β -carotene and betanine and vulgaxanthine I degradation. Water activity had a protective role in beta-carotene decolorization while an opposite behaviour was observed in beet pigments.

The decolorization of beta-carotene supported a microcrystalline cellulose under reduced oxygen (0-20.9%) and low water activity ("dry" - 0.84) followed a chain radical oxidation and described by a sigmoidal curve.

The kinetic data collected provides the necessary elements required for shelf life prediction and the development of accelerated tests. The expected defect-free shelf life of dehydrated commodities is of great economic advantage.

II. Report

A. Objective of the Research

The overall objective of this research was the development of techniques for predicting of quality deterioration due to oxidation of dehydrated foods. Model and food systems containing β -carotene and lipids were used in an attempt to correlate oxygen uptake with a chemical index of deterioration. Kinetics and the mechanism of β -carotene decoloration and of lipid oxidation were determined under low oxygen concentration. The kinetic models and the data generated can be used in the development of accelerated tests for prediction of shelf life and quality changes in sensitive food system due to oxidation.

1. Objective of Grantee Institution - Volcani Center

The objectives were as follows:

- a. To redesign the oxygen uptake apparatus and the method of determination in order to overcome drawbacks observed in previous work.
- b. To establish the kinetic model of beta-carotene decoloration and oxygen uptake at low oxygen concentration in model and food systems.
- c. Use of the kinetic model in a computer-aided simulation program for predicting changes during storage of dried products.
- d. Development of simplified accelerated tests for the prediction of dried products' shelf life in storage due to oxidation or beta-carotene decoloration.

2. Objectives of the Cooperating Institution - M.I.T.

Kinetics of oxidation at very low oxygen pressures is important in design of packaging and oxygen scavenging systems for foods. The overall aim was to develop and evaluate a technique for measuring the oxidation in food systems at low oxygen pressures, and to use the technique in development of kinetic models of oxidation at low oxygen pressures.

The following specific aims were approached:

- a. To test the validity of previously established kinetic models of oxidation at low oxygen pressures in model systems containing unsaturated fatty acid esters.
- b. To test the validity of previously established kinetic models of oxidation at low oxygen pressures in a food product containing unsaturated fatty acids.
- c. To develop a new or modified kinetic model for lipid oxidation involving unsaturated fatty acids, should the model developed previously prove inadequate.

B. Materials and Methods

Due to the complexity of the methods implemented in this research a detailed description of the materials and methods used are not given herewith. Yet, they are fully described in the various publications which are a direct outcome of the project (see list of publications).

C. Results

Detailed description of the results and discussions are given in the various published papers. The following are a capsuled abstracts.

1. Decolorization of beta-carotene in model systems simulating dehydrated foods. Mechanism and kinetic principles.

The mechanism and kinetic principles of β -carotene decolorization under reduced oxygen (0-20.9%) low water activity ("dry - 0.84) and 35°C were investigated in a model system. Oxygen was found to be a crucial factor in β -carotene degradation. Rate of decolorization due to oxygen was found to be influenced by the amount of oxygen adsorbed. This amount was influenced by oxygen partial pressure and the physical and chemical structure of the adsorbent. β -Carotene decolorization was found to be strongly affected by the presence of free radical initiators. On the other hand, degradation was

slowed down when an antioxidant was added. β -Carotene retention curves were sigmoidal with three regions, namely, an induction period, a fast "main" period, and a retardation period-typical of an autocatalytic radical reaction. Water activity was found to play a protective role in β -carotene decolorization (Goldman, Horev and Saguy, 1983).

2. Thermal stability of pomegranate juice

This investigation was aimed primarily at determining the color stability of pomegranate juice under high-temperature conditions, representative of processing conditions such as pasteurization, evaporation and dehydration. Results indicate that the red pomegranate anthocyanins are sufficiently stable. Browning is a significant problem requiring further investigation (Mishkin and Saguy, 1982).

3. Kinetics of beta-carotene degradation at temperatures typical of air drying of foods

Degradation of β -carotene was studied in a model system at temperatures between 60 and 80°C in order to formulate a kinetic model useful in the optimization of air drying processes. Two previously reported kinetic analyses were used: a first order model and a simplified free radical reaction model. In both cases the models fit the experimental data but neither is entirely satisfactory since the kinetic parameters reflected an initial concentration dependence. This dependence disappeared at high carotene initial concentrations and also when the thickness of the lipid layer was increased either by using a support with a lower specific surface area or by adding a saturated fatty acid. These results indicate that at high concentrations oxygen diffusion becomes a limiting factor.

When using food systems, a first order model seemed a better choice for the simulation of the carotene degradation. Results could not be directly

related to those of the model system, probably because the model was too simple, and did not contain the pro- and anti-oxidant components naturally occurring in foods (Stefanovich and Karel, 1982).

4. The effect of oxygen retained on beet powder on the stability of betanine and vulgaxanthine I

The effect of oxygen retained on beet powder on the stability of betanine and vulgaxanthine I was studied at 35°C as a function of a_w ("dry"-0.75), moisture content, added aluminium oxide powder and head-space gases (N_2 , air). Limited degradation was observed under N_2 or air and $a_w < 0.41$. Deterioration was accelerated at $a_w > 0.52$ and the presence of added Al_2O_3 . This was interpreted as a lack of liquid phase mobility which governed the reaction up to $\sim 0.5a_w$. Above $0.5a_w$ the transition in the mechanism was related to the concentration of the dissolved O_2 in the liquid phase, which controlled the deterioration rate. The latter was strongly affected by the added Al_2O_3 . In the presence of aluminium oxide, the very fast pigment oxidation suggested a catalytic reaction and the participation of active oxygen species (Saguy, Goldman, Bord and Cohen, 1983).

5. An improved method for the determination of adsorbed/entrapped gases in dehydrated foodstuffs

An improved method for the determination of the volume and composition (oxygen, carbon dioxide and nitrogen) of adsorbed/entrapped gases retained by dehydrated foodstuffs was described. The coefficient of variation of the method for a typical skimmed dried milk powder was 2.6. Two general types of behaviour of foods, affecting the amount of entrapped/adsorbed gases retained by the powder upon evacuation were observed. Gas volume retained by type I powders after reaching a plateau, stayed constant regardless

of evacuation time, which determined the retained gas volume in type II powders (Saguy, Goldman, Horev and Karel, 1983).

6. Kinetics of oxidation of dehydrated food at low oxygen pressures

Kinetic studies were performed to obtain the dependence of rates of lipid oxidation on oxygen pressure, in a system containing free as well as adsorbed oxygen. The model system consisted of methyl linoleate dispersed on either microcrystalline cellulose or on non-fat milk powder. Oxidations were carried out at 37°C, and with headspace concentrations of oxygen ranging from 0.52% to 10.7%. These concentrations were maintained approximately constant by periodically resupplying oxygen to replace the amount reacted with the lipid.

Bimolecular oxidation kinetics were found in both systems with the rate of oxidation more rapid (by a factor of 5 to 6) in the cellulose system. The dependence of oxidation on oxygen pressure was of a form previously found for oxidizing lipids by other investigators, and is consistent with theoretical considerations. The slower oxidation in the milk system appeared to be due to two factors: encapsulation of part of the lipid in the milk solids, and the lower internal surface area of the milk solids compared to the cellulose support. (Kacyn, Saguy and Karel, 1983).

7. Prediction of beta-carotene decolorization under static and dynamic conditions of reduced oxygen

A mathematical/kinetic model was established to predict beta-carotene decolorization under dynamic conditions. This model may be applicable in simulating shelf life of dehydrated foodstuffs.

The model derived was:

$$\ln[1+E]/(1-E)] = k_e t$$

where: $E = \sqrt{1-C/Co}$

C - concentration at time t

Co - initial concentration

k_e - reaction rate constant

t - time

The reaction rate constant was a function of oxygen partial pressure

$$k_e = 2.98 \cdot 10^{-2} + 1.656 \cdot 10^{-2} PO_2$$

where: PO_2 - oxygen concentration ($0 \leq PO_2 \leq 20.9\%$)

in systems where water activity changed the final model derived was

$$k_e = (2.98 \cdot 10^{-2} + 1.656 \cdot 10^{-2} PO_2) e^{-0.4833 a_w}$$

where: a_w - water activity ($0 \leq a_w \leq 0.84$)

PO_2 - oxygen content ($0 \leq PO_2 \leq 2\%$)

Comparison between experimental and predicted data showed excellent agreement, thus indicating that shelf life prediction is feasible (Saguy, Goldman and Karel, 1984).

III. Description of the Cooperation

The collaboration of the two Institutes enabled us to focus the efforts on vital problems of beta-carotene degradation and mechanism. In order to gain necessary data required for the development of accelerated tests. These efforts were aimed at different topics and avenues which were defined in the original proposal. For instance, the effect of oxygen and water activity at low temperature was investigated at the Volcani Center, while the effect of high temperatures was derived at MIT. Thus, furnishing the whole range of environmental factors simulating dehydration and storage of foodstuffs.

Also the collaboration supported (in part) the occupation of Dr. M. Mishkin (at that time a Ph.D. candidate at M.I.T.) for a month in January 1982, and hence sustained an important collaboration (the paper by Mishkin and Saguy is a direct outcome of this collaboration).

Furthermore, two master's theses were completed at M.I.T. as part of this work:

a. Ana Stefanovich, S.M. May 1982.

Thesis Title: Kinetics of beta-carotene degradation at temperatures typical of air drying of foods.

b. Louis J. Kacyn, S.M. June 1983.

Thesis Title: Kinetics of oxidation of dehydrated food at low oxygen pressures.

Finally the cooperation furnish the avenue for frequent exchange of data and ideas by correspondence, and annual meeting, with the location alternated between U.S. and Israel.

IV. Contribution of the research to the U.S.A. and Israel

Loss of quality in storage, with attendant development of organoleptic defects, deterioration of nutrient quality and potential development of harmful or obnoxious products limits the utilization of dehydrated foods stored for prolonged periods. When such foods must be withdrawn from the market because of defects this leads to economic losses, and the consumer awareness of occasional occurrence of such defects limits their willingness to utilize dehydrated products. Dehydrated foods are, however, very useful, energy-efficient and versatile form of supplying foods over large distances and for storing them for prolonged periods. They are thus a major potential mechanism for export and import of foods.

Both the United States and Israel export dehydrated foods to each other and to other countries. It is of great economic advantage to be able to accurately specify the expected shelf life. Based on the kinetic data obtained, the methodologies established and the advanced determination methods developed, accelerated tests and models for shelf life prediction of foodstuffs stored under reduced water activity and oxygen may be obtained. Furthermore, the feasibility and the applicability of these methods were proven in model and actual foodstuff systems.

V. List of Publications

1. Goldman, M., Horev, B. and Saguy, I. 1983.
Decolorization of β -carotene in model systems simulating dehydrated foods. Mechanism and kinetic principles. J. Food Sci. 48 : 751-754.
2. Kacyn, L.J., Saguy, I., and Karel, M. 1983.
Kinetics of oxidation of dehydrated foods at low oxygen pressures.
J. Food Process. Preserv. (In press).
3. Mishkin, M. and Saguy, I. 1982.
Thermal stability of pomegranate juice.
Z. Lebensm. U. Forsch 175 : 410-412.
4. Saguy, I., Goldman, M., Horev, B. and Karel, M. 1983.
An improved method for the determination of adsorbed/entrapped gases in dehydrated foodstuff.
Z. Lebensm! U. Forsch. (In press).
5. Saguy, I., Goldman, M., Bord, A. and Cohen, E. 1983.
The effect of oxygen retained on beet powder on the stability of betanine and vulgaxanthine I.
J. Food Science. (In press).

6. Saguy, I., Goldman, M. and Karel, M. 1984.

Prediction of β -carotene decolorization under static and dynamic conditions of reduced oxygen environment. (In preparation; will be submitted upon completeness).

7. Stefanovich, A.F., and Karel, M. 1982.

Kinetics of beta-carotene degradation, at temperatures typical of air-drying of foods.

J. Food Process. Preserv. 6 : 227.

VI. List of Papers Presented at International Meetings

1. Stefanovich, A., Saguy, I., Mishkin, M. and Karel, M. 1982.

Kinetics of beta-carotene degradation at temperature typical of air-drying of foods. Presented at the American Institute of Chemical Engineers 1982 Winter Meeting, Orlando, FL.

2. Goldman, M., Horev, B. and Saguy, I. 1982.

Effect of oxygen and water activity on the decolorization of beta-carotene in model system simulating dehydrated foods. Presented at the 42nd National I.F.T. Meeting, Las Vegas, NV.

3. Saguy, I., Goldman, M. and Cohen, E. 1983.

The effect of oxygen retained by beet powder on the stability of betanine and vulgaxanthine I. Presented at the 43rd Annual Meeting, Institute of Food Technologists, New Orleans, Louisiana, June 19-22.