ANALYTICAL METHODS FOR QUALITY CONTROL OF DRIED POTATO FLAKES[1,2]

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Abstract

A set of analytical methods was used for the characterization of the oxidative degradation of dehydrated potato flakes. Headspace gas analysis for straight chain hydrocarbon (Ethane-hexane) and for oxygen was used to directly follow the oxidation. Bleaching was followed by quantitatively determining the carotenoid concentration. Analytical results obtained showed a strong association with taste testing results. The data reported show the effectiveness of natural and synthetic antioxidants for the stabilization of dried potato flakes.

Resumen

Se empleó un grupo de métodos analíticos para caracterizar la degradación oxidativa de las escamas de papa deshidratada. Se hizo el análisis del gas presente sobre la superficie del producto ("Headspace gas analysis") para cadenas lineales de hidrocarburos (Etano-Hexano) y para oxígeno con el fin de seguir directamente la oxidación. La decoloración fue observada mediante la determinación cuantitativa de la concentración de carotenoides. Los resultados de los análisis mostraron una asociación fuerte con los resultados de pruebas de degustación. Los datos presentados muestran la efectividad de los antioxidantes naturales y sintéticos para estabilizar escamas de papa seca.

Introduction

A previous study by Sapers (10) has indicated that the organoleptic quality of dried potato flakes decreases during prolonged storage due to the development of hay-like off-flavors associated with oxidation reactions of the potato lipids. If the potato flakes were stored at 20°C or below, non enzymatic browning reactions did not seem to play a dominant role. The water activity of dried potato flakes, however, influenced the organoleptic keeping quality to such an extent that all other factors were overshadowed.

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KEY WORDS: Potato flakes; keeping quality; headspace gas analysis; hydrocarbon, carotenoid, oxygen absorption, taste testing.

Potato variety, dry matter of potatoes, many processing parameters (11) and antioxidants used (12) were other factors which have been studied in the past. Most of the problems related to the degradation of the organoleptic quality of potato flakes during storage were connected with the development of off-flavors due to the oxidation of the unsaturated lipids in the potatoes. There is sufficient evidence in the literature to support this fact. Buttery (6) and Sapers (10, 11, 12) have clearly shown the correlation of oxidation parameters with taste testing results of potato flakes during storage over periods of up to 12 months at 20°-25°C. These authors were mainly looking at the relatively volatile secondary oxidation products of the lipids. Figure 1 recalls some of the important steps for the lipid radical chain oxidation reaction. It is generally accepted that fat oxidation is initiated by free radicals.

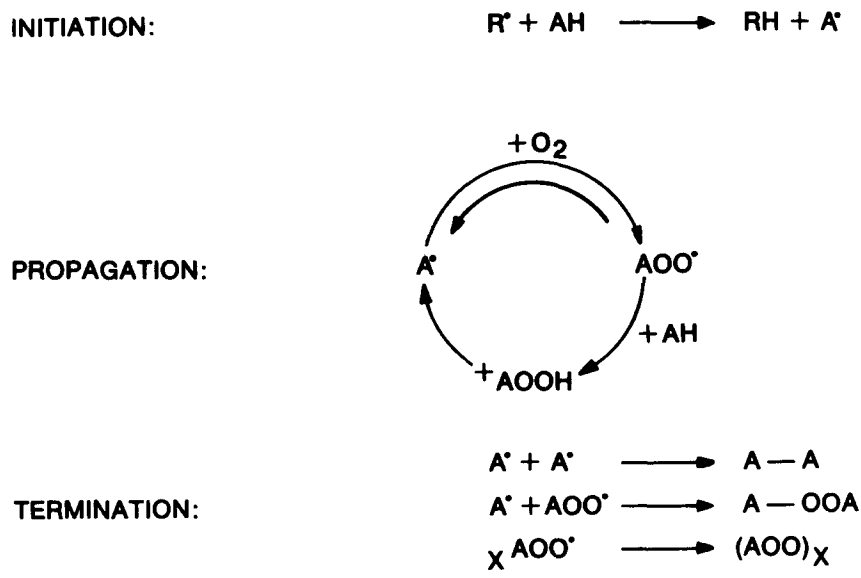


FIG. 1. Simplified pathways of the autoxidation reactions of lipids.

These radicals which can be initiated by many factors (heavy metals, different ions, light, etc.) are reactive intermediates, some of which have been characterized and are well established. During the propagation reaction the concentration of the radicals increases by the formation of other more stable intermediates, the hydroperoxides. Many of the more stable secondary oxidation products like aldehydes, ketones, hydrocarbons, acids, hydroxy acids, etc. have been used as tracers of the oxidation reaction. As primary oxidation product, the hydroperoxides are very often used to establish the state of oxidation of lipids, or the quality of lipids contained in foods.

Hydroperoxides are, however, transient intermediates which are relatively unstable and decompose readily to form the secondary oxidation

products. Peroxides indicate therefore mainly the actual state of oxidation not taking into account the past history of a product; they do not indicate cumulative effects of past oxidation reactions. The most prominent representatives among the secondary oxidation products, derived from the hydroperoxides through many different reaction pathways, are ketones, aldehydes and hydrocarbons. They are the most important chemical species which are found in oxidized lipids. The ketones and aldehydes have always been associated with the "typically rancid off-flavor" of foods after a period of oxidation.

Short chain hydrocarbons are formed parallel with the formation of the aldehydes (1, 6). They do not have any particular flavor and do not influence the shelf-life of foods as such. From an analytical point view, however, they are of enormous interest as an indication of the state of oxidation.

The termination reactions lead to nonreactive oxidation products which normally combine two radicals and therefore often reach high molecular weights. Figure 2 is a characteristic representation of the oxidation reaction versus time. A fat is oxidized at 100°C by blowing air through it at a constant rate. At intervals the hydroperoxides are determined (2).

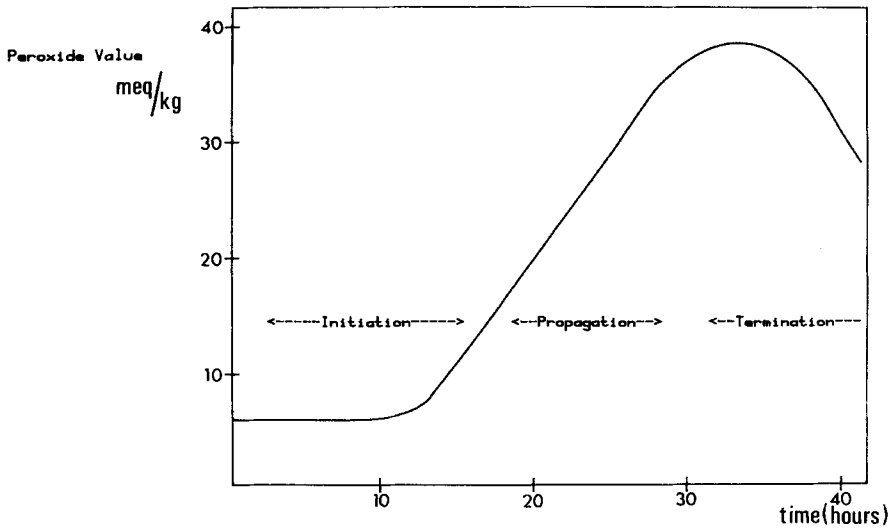


FIG. 2. The influence of time on the formation of peroxides during autoxidation of lipids.

The initiation period is characterized by a very slow increase of the hydroperoxide concentration. The second phase, characterized by a rapid increase of the oxidation reaction, is typical for a radical reaction. The termination phase is characterized by the slow decay of the concentration of the hydroperoxides.

The last general remark on autoxidation concerns the role of antioxidants. In Figure 3 some typical chemical formulas of the important antiox-

idants are given. They all are of phenolic type and are characterized by the fact that they form relatively stable radicals. Their role in slowing down the oxidation reaction is primarily the destruction of the highly reactive primary radicals during the initiation phase of the autoxidation. They are consumed during the initiation phase. It can be easily understood from Figure 4, which represents the fast autoxidation of different oils with 500 ppm of the natural rosemary antioxidants (2), that the presence of antioxidants increases the induction time of the fat.

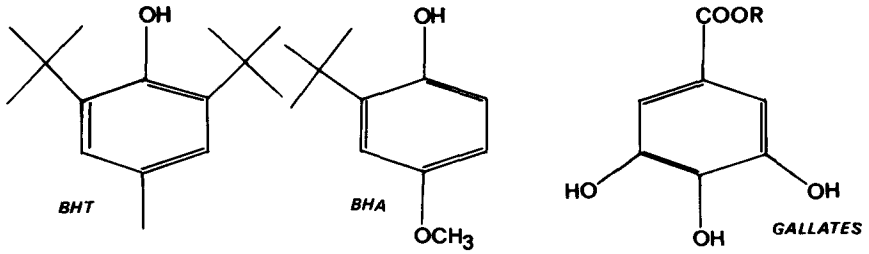


FIG. 3. Chemical structure of typical food grade antioxidants.

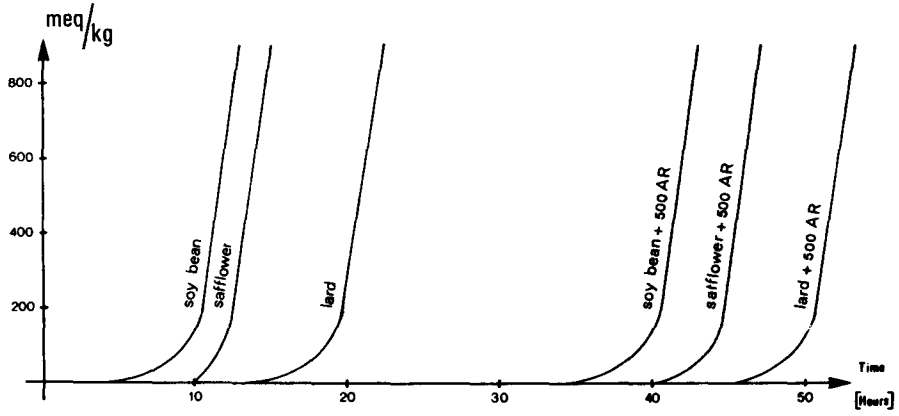


FIG. 4. Response of rosemary antioxidants (AR) during fast induction time determination for different oils.

The antioxidant radicals are of such low energy that they cannot react with the lipids any more. Autoxidation is not inhibited but the initiation period is extended. Antioxidants are therefore consumed during the induction period. Once they are eliminated, the ordinary autoxidation starts.

Methods and Materials

a) *Raw Material and Process*

The potato variety Bintje grown in sandy soil was used. Potatoes were stored under controlled temperature and humidity for 3 months after har-

vest prior to processing. The potato flakes were produced on the Venreco (Venreco B.V., Witte Venneweg 6, Venray-Oostrum, Holland) pilot line using an ordinary process for potato flake production as described by Willard and Kluge (13). The emulsion containing the conventional additives (13) contained enough sodium bisulfite to maintain the flakes at about 40 ppm ± 10 ppm residual sulfur dioxide and had a pH of 6.5. The water content of the final product was adjusted to 8 ± 1% by varying roller speed and steam pressure accordingly.

b) *Storage and Evaluation*

One hour after production the potato flakes were conditioned in tins of 400 ml volume containing each 80 g of potato flakes. They were stored at 20°C for the conservation test. Some samples for reference use were stored under nitrogen and kept at 4°C.

Antioxidants used in the different samples are summarized in Table 1. The relative activity of the antioxidants was determined using a modified active oxygen method (8). To evaluate the concentration of the antioxidants in potato flakes, special care was taken for the extraction/evaporation of the solvent as described (12). The dried extract was taken up in toluene/ethanol and the quantitative determination performed by differential pulse polarography on a glassy carbon working electrode (9).

TABLE 1. — *The additive recovery of various antioxidants in potato flakes.*

Antioxidants	concentration (ppm) added	recovered
BHA	100	26
BHT	100	24
BHA/BHT	50/50	12/12
dl-α-Tocopherol	400	310
Rosemary extract AR[1]	300	n.d.[2]
TBHQ	50	22
Deodorized Rosemary extract (5)	900	n.d.[2]
Tempeh	1200	n.d.[2]

[1]Food ingredient Specialties Inc., CH-1618 Châtel St. Denis, Switzerland.
[2]n.d. = not detected.

Taste testing was performed in red light to prevent influences from color changes due to oxidative deterioration. Two standard samples were given to the taster and samples were rated 1 or 8, best or poorest taste. The sample submitted for tasting had to be situated between these two standards, making tasting scores between 1 and 8.

The determination of carotenoids in dried flakes was done according to the following procedure: 5 g potato flakes were added to 50 ml of boiling

water and left shaking during 15 min., 200 ml 96% ethanol was added with further 30 min. shaking. The solution was filtered through filter paper, the residue on the filter was washed twice with 50 ml hexane/methanol 1:1 and the filtrate was washed twice with 200 ml 2.5% aqueous sodium chloride solution. The dried organic phase (sodium sulfate) was evaporated at 40°C. The residue was taken up in 10 ml hexane and cooled for 30 min. to 0°C (for precipitations of lipids). This solution was filtered and directly measured in a spectrophotometer. The absorption maximum between 440 and 450 nm was used for the calculation of the quantity of carotenoids present. As standard for the calculations pure β-carotene (E. Merck AG, Darmstadt, Germany) was used.

The determination of the concentration of the residual oxygen and the determination of the volatile hydrocarbons were done directly using the headspace gas above the dry sample. The experimental set-up consists essentially of a vacuum pump, manometer, gas sampling valve, oxygen concentration determination device and a gas chromatograph. The set-up used is illustrated in Figure 5. Any two stage oil vacuum pump (10 mm Hg) can be used.

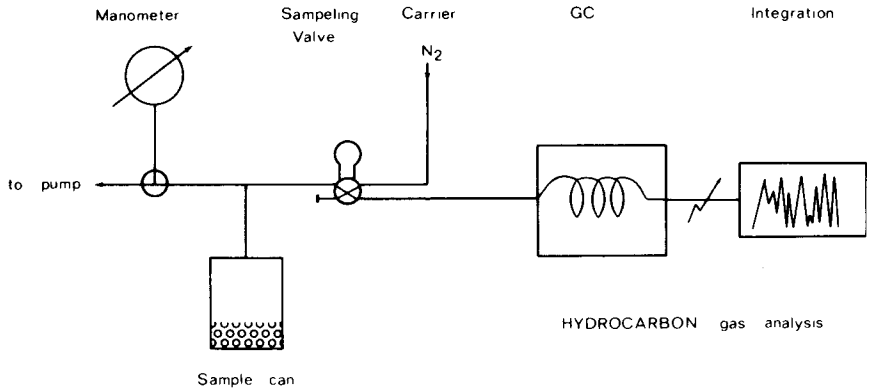


FIG. 5. Experimental design for headspace gas analysis.

The manometer used was a Micro Manometer from Thommen CH-4437 Waldenburg, Switzerland 19A2.200.01, 0 to 2'000 mbar. The oxygen analyzer was a Taylor Servomex model 0A570 supplied by Omni Ray CH-5008 Zurich, Switzerland. The gas sampling valve was mounted on the gas chromatograph (Rheodyne 6 port gas sampling valve, with 5 ml sample loop). All the connections were made with 1/8" stainless steel tubing. The gas sampling unit was essentially composed of a stainless steel plunger for puncturing the tins and an 0-ring rubber sealer. For normal operation, the system was evacuated to about 0 to 1 mbar, the tin was punctured and the gas left to reach equilibrium. The manometer reading was utilized to calculate the integration values of the determination of the hydrocarbons and the residual dual oxygen content to normal pressure (gas law: $p_1v_1 = p_2v_2$). The difference of

residual oxygen content after storage was converted to the amount of the linoleic acid which could be oxidized due to the molar reaction of oxygen with the poly-unsaturated fat of the potato flakes. It can be seen from Figure 6 that up to a fraction of 0.7 (70%) of the linoleic acid present was oxidized during the 9 month storage time.

The quantitative determination of hydrocarbons in the headspace was done by gas solid chromatography on activated alumina (4). A 2 m column (1/8" ∅ filled with F-1, 60/80 mesh Alumina on a HP-5840 chromatograph fitted with FID (Flame Ionization Detector) was used. The temperature was programmed from 50° to 250° at 12°C/min. and then held isothermally at 250°C for 15 min. Nitrogen was used as carrier gas at a flow rate of 30 ml/min. Quantitative results were obtained using the calculating integrator of the HP-5840 gas chromatograph, calibrating the individual responses for the hydrocarbons ethane, propane, butane, pentane and hexane using a tailor-made standard containing 1 ppm of each (plus methane) in helium (Matheson Gas Products, 2431 Oevel Belgium). The fatty acid composition was determined by using the A.O.C.S. official method (3) with a 2 m ¼ inch O.D. filled column.

Results and Discussion

All the results were given in respect to two standard potato flakes. Potato flakes containing BHA-BHT as standard of good resistance towards oxidation and potato flakes without antioxidants which were readily oxidized. It can be seen that C_2-C_6 hydrocarbons are lowest in potato flake samples with BHA-BHT (Fig. 6). The sample not containing antioxidants (blank) showed significantly higher values for the hydrocarbons. The absorption of oxygen was also much higher for the non-protected flakes. The bleaching as measured by the concentration of carotenoids was far more pronounced for the non-stabilized flakes than for the flakes stabilized with BHA-BHT. For the organoleptic evaluation, stabilized flakes made much better taste testing scores than non-stabilized flakes.

The potato flakes stabilized with the natural rosemary extract gave values for the oxidized linoleic acid, the hydrocarbons and the bleaching which were situated within the boundaries obtained for the flakes stabilized with BHA-BHT and the non-stabilized flakes. The taste testing scores were also between the two extremes. The results obtained with the potato flakes stabilized with tempeh extract (Fig. 7) showed that tempeh, in this context, is no antioxidant. The bleaching of the flakes containing tempeh was as rapid as was the bleaching of stabilized flakes, the development of hydrocarbons and the oxidation of the linoleic acid as well. The taste testing scores showed that tempeh was not showing any antioxidant effect in these potato flakes. Tempeh was however an antioxidant in the chicken fat model (Table 2).

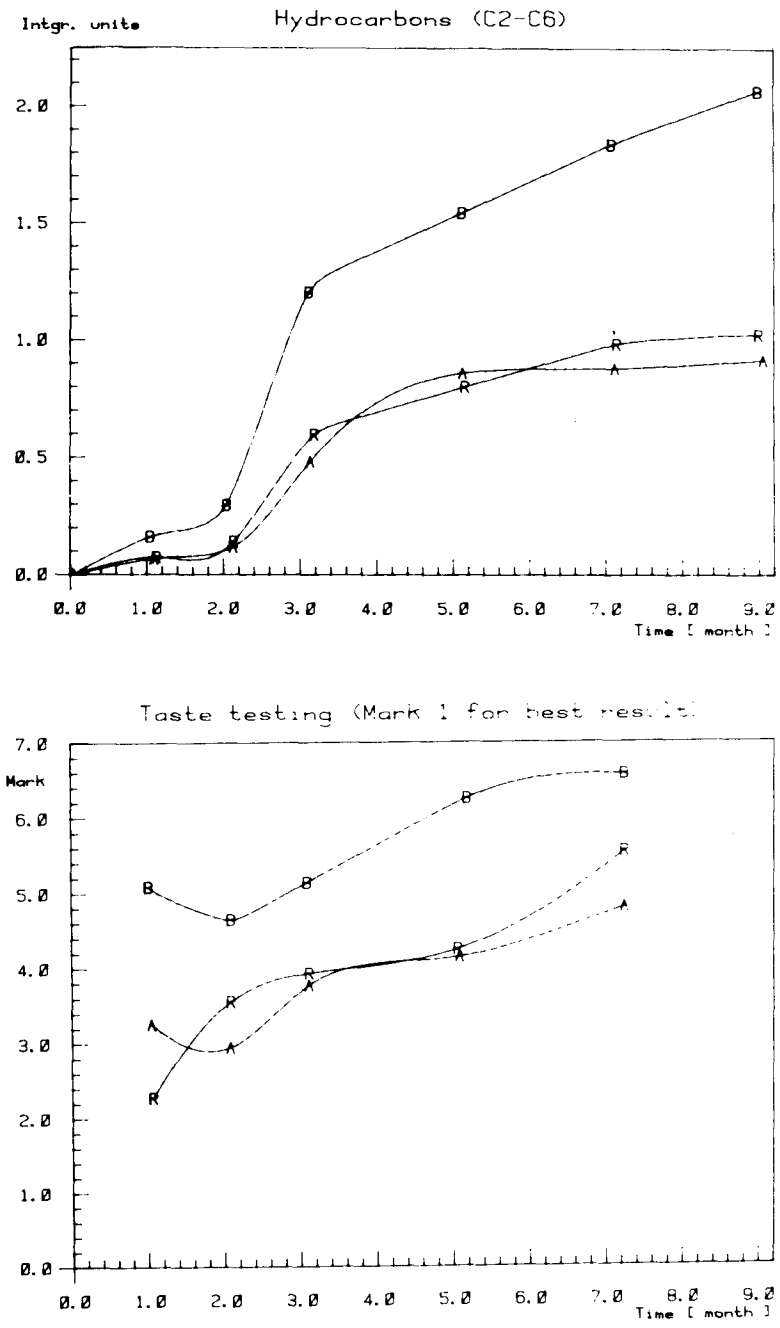
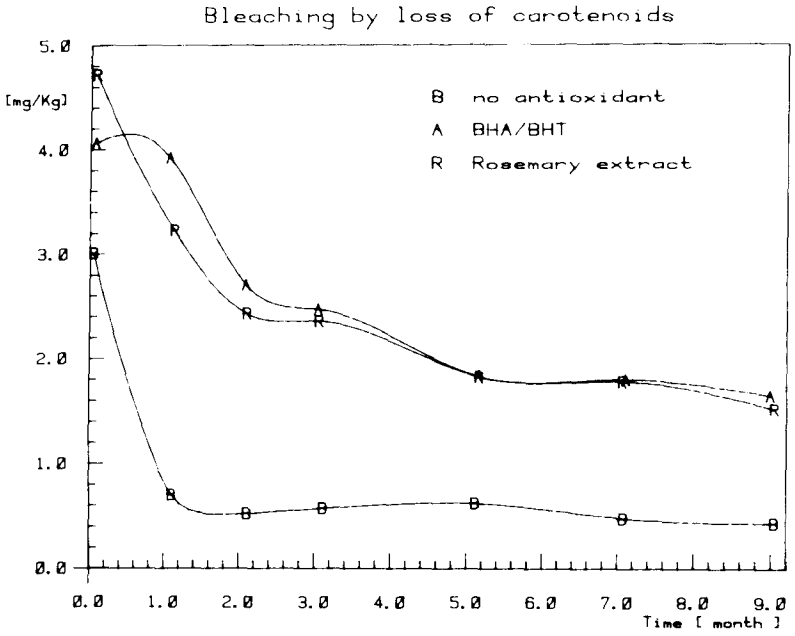
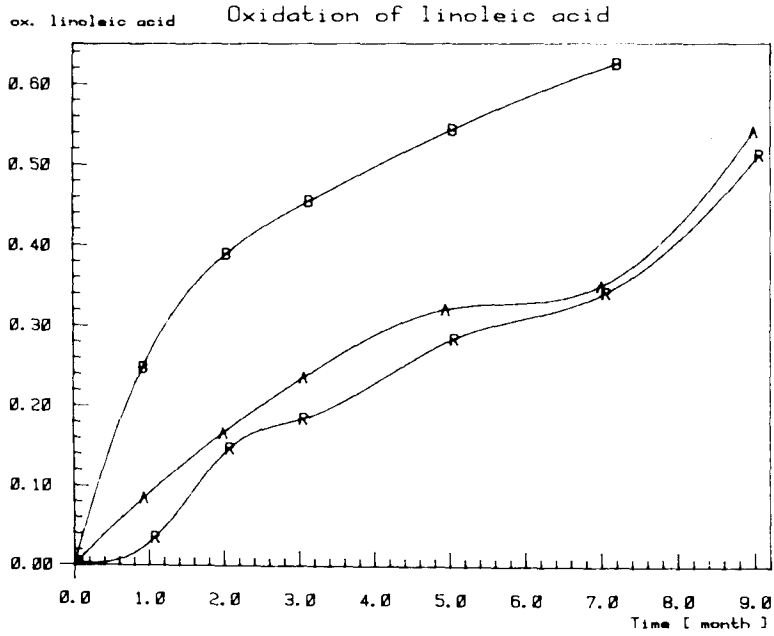


FIG. 6. Influence of BHA-BHT and rosemary spice extract on bleaching by loss of carotenoids, volatile hydrocarbon production, oxidation of linoleic acid and taste testing.


Bleaching by loss of carotenoids
[mg/Kg]
5.0
4.0
3.0
2.0
1.0
0.0
B no antioxidant
A BHA/BHT
R Rosemary extract
0.0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0
Time [month]


ox. linoleic acid
Oxidation of linoleic acid
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0.0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0
Time [month]

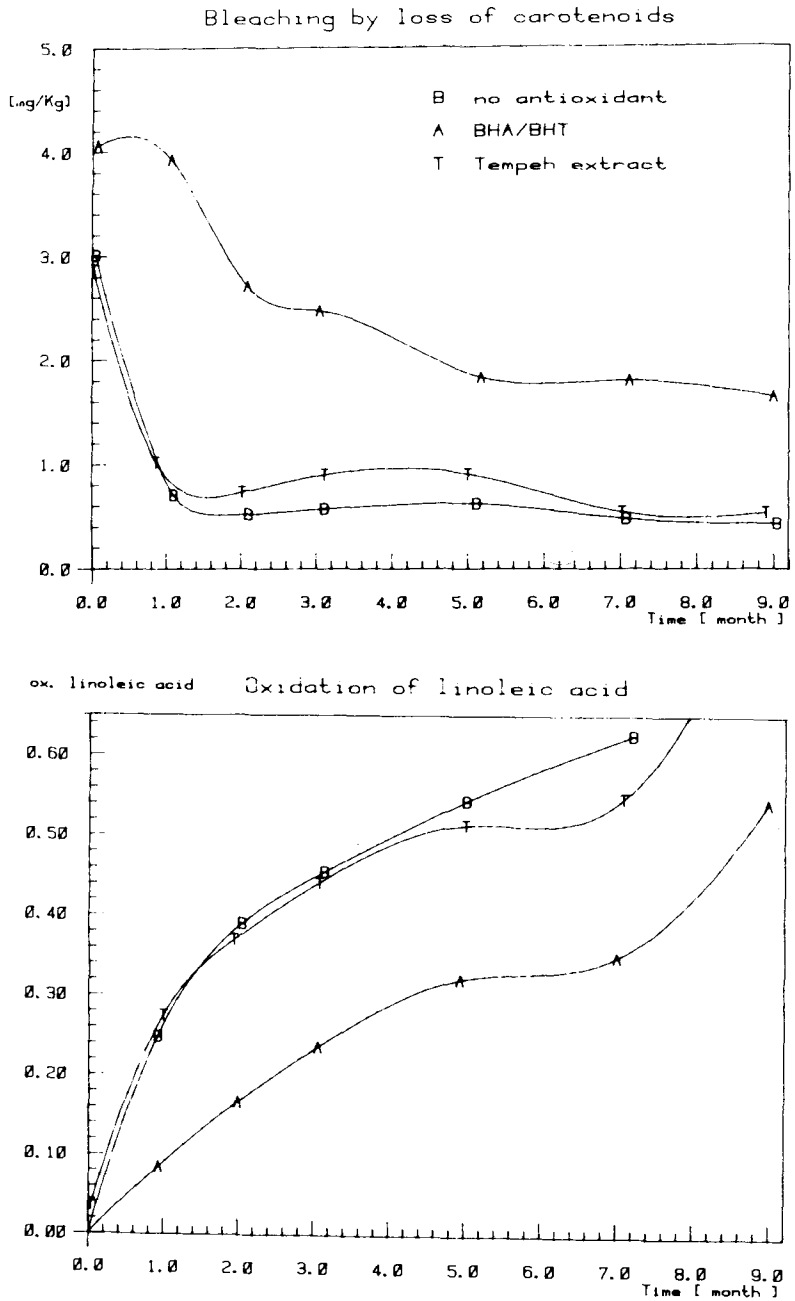
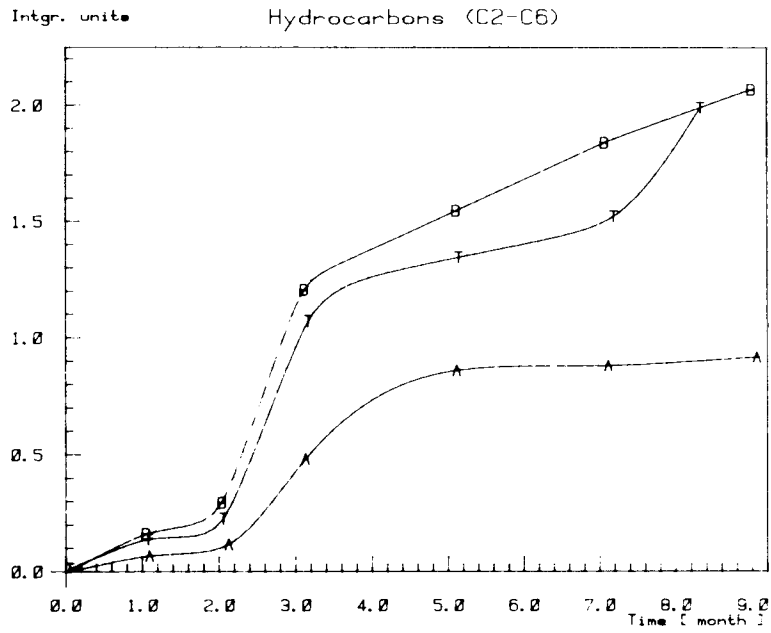


FIG. 7. Influence of BHA-BHT and tempeh on bleaching by loss of carotenoids, volatile hydrocarbon production, oxidation of linoleic acid and taste testing.


Intgr. units
Hydrocarbons (C2-C6)
2.0
1.5
1.0
0.5
0.0
0.0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0
Time [month]

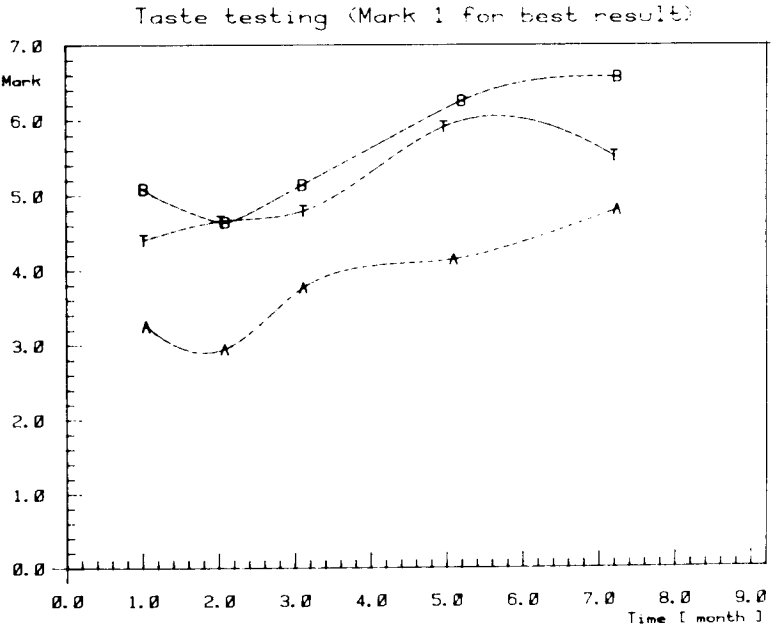

Taste testing (Mark 1 for best result)
Mark
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0
Time [month]

TABLE 2. — Induction time for deodorized chicken fat stabilized with different antioxidants.

Sample	concentration ppm	induction time hours
BHA	50	14
BHT	50	12
BHA/BHT	25/25	17
dl-α-Tocopherol	400	13
Rosemary Extract AR[1]	300	12
TBHQ	50	16
Deodorized Rosemary Extract (5)	900	13
Tempeh	1200	12

[1]Food ingredient Specialties Inc., CH-1618 Châtel St. Denis, Switzerland

All of the samples prepared with the antioxidants shown in Table 1 were analyzed as was shown in detail here by headspace gas analysis for hydrocarbons and oxidation of linoleic acid, the bleaching by loss of carotenoids, and taste testing. The concentration of the antioxidants was chosen for obtaining roughly the same induction time in an accelerated oxidation test (8). The results reported in Table 2 show the induction times found.

The results were all within the boundaries given by the two standard potato flakes (potato flakes with BHA-BHT and the blank not containing any antioxidant), with one exception: TBHQ which showed better results in all tests than the standard sample containing BHA-BHT. The results of the sample stabilized with dl-α-tocopherol were very similar to the results of the sample containing no antioxidant. Tocopherol was therefore no antioxidant in this context (as was found for tempeh). The induction times reported in Table 2 reflect only to a certain degree the antioxidant properties of the additives used in the stabilization of potato flakes. BHA and BHT separately were slightly less efficient as antioxidant in the chicken fat model than the synergistic mix of BHA-BHT. The potato flakes prepared with the two antioxidants individually also showed lower results for their oxidation indicators and for the taste testing than the sample containing the synergistic mix. The deodorized rosemary extract showed one important advantage over the non-deodorized extract in respect to its flavor neutrality, but this was only revealed by a taste testing asking for discerning specific off flavors due to rosemary extracts!

In comparing the 4 different types of analysis performed: headspace gas analysis for hydrocarbon, oxidation of linoleic acid, bleaching of carotenoids and taste testing, an association is apparent. The results show a potential use for chemical evaluation to replace taste testing. The end of the induction period is determined with much more precision, taste testing re-

sults having always a certain dispersion due to the inhomogeneity of the taste testers' performance. Analytical results are available after not more than 3 months' storage time; the organoleptic evaluation, however, only gives reliable results after a much longer storage period.

It is certain that long time storage trials still have an important role to play for the evaluation of definitive storage life. The short time evaluation has its main advantage in the fact that improvements of technological parameters and the potential effect of new additives in the keeping quality can be evaluated in a relatively short time.

The headspace gas analysis, as proposed, is an analytical method which measures as secondary oxidation products the volatile hydrocarbons and oxygen present in the headspace. Some years ago, Sapers (10) presented a method which is much more closely related to the actual oxidation products which cause flavor deterioration. The headspace gas analysis for volatile hydrocarbons is a simplistic derivative of the more complete method of analyzing all the secondary oxidation products.

The method presented here has a sound chemical background. The analysis of the chemical composition of the total potato lipids for their individual fatty acids revealed (6, 7) that more than 75% of these were composed of linoleic and linolenic acids. Both of them are poly-unsaturated fatty acids which oxidize readily. Figure 8 represents the headspace gas analysis of oxidized methyl lineolate. It can be seen that the major part of the oxidation product is pentane and hexane. It is clear as the analysis is done on an alumina column, that all of the more polar constituents of the volatile oxidation products were absorbed on the column and only non polar compounds like hydrocarbons could be detected. These hydrocarbons are the secondary oxidation products which were also found in the headspace gas analysis of the potato flakes. It was therefore not surprising that the oxidation of the potato flakes could be followed by the quantitative hydrocarbon (C_2-C_6) analysis. Figure 9 represents a sample chromatogram of the headspace gas for potato flakes not containing any antioxidants stored for 3 months at 20°C in a sealed tin. It can be seen that, predominantly, pentane is detected by the chromatographic procedure utilized.

Discussion

The practical utility of these analyses has been clearly shown by a large series of trials with many more different antioxidants not shown here and many different technological treatments of the potatoes right from the beginning of the conditioning of the potatoes to the storage of the potato flakes at different temperatures for example: the strong association of the analytical results and the organoleptic evaluations is very promising for rapidly obtaining sound results on the keeping quality of potato flakes. A correlation of the chemical analysis and taste testing can not yet be estab-

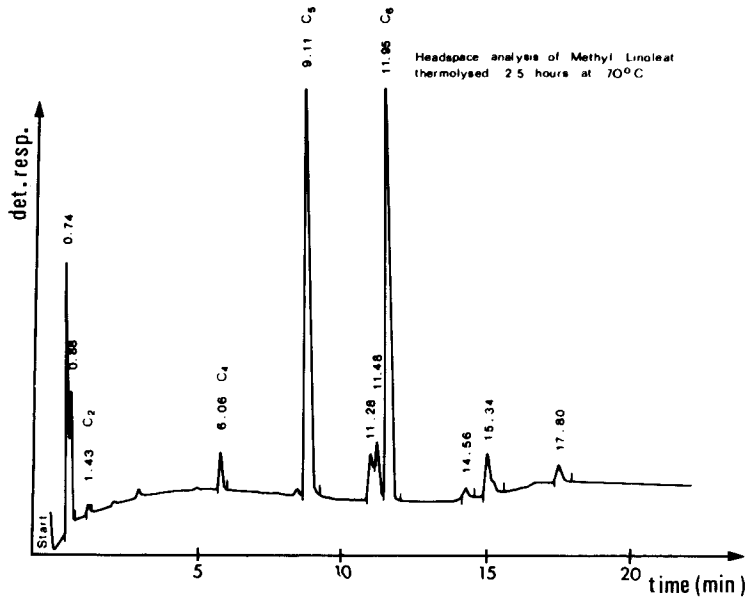


FIG. 8. Headspace gas analysis of linoleic acid methyl ester oxidized for 3 hours at 70°C in a closed flask. F-1 Alumina (60/80 mesh), 2 m S.S (1/8" ∅), 30 ml/min. N_2 carrier, FID, T = 50-250°C, 12°C/min., than 15 min. isocratic at 250. C_2, C_3, C_4, C_5, C_6 are the straight chain hydrocarbons ethane, propane, butane, pentane and hexane.

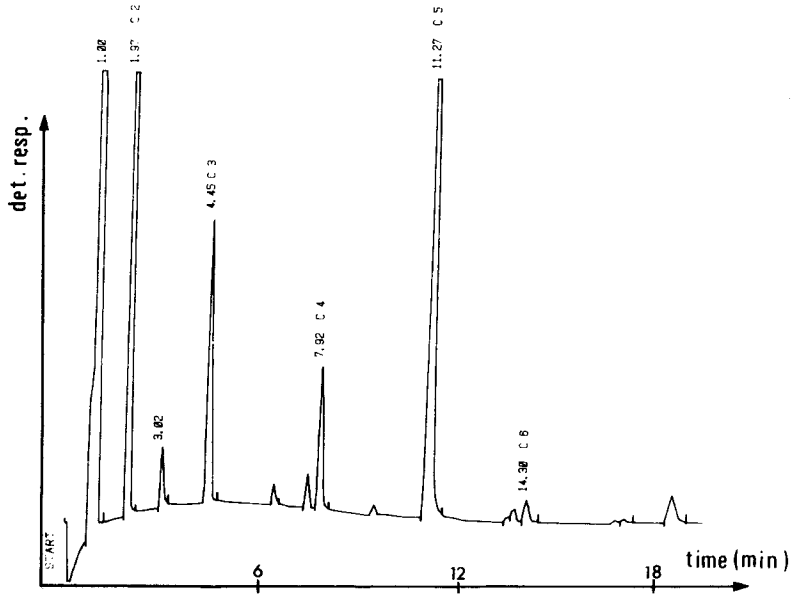


FIG. 9. Headspace gas analysis of oxidized potato flakes (conditions for chromatography as for Fig. 8).

lished as not enough data were accumulated for a rigorous mathematical analysis.

Acknowledgments

The very active collaboration of the Venreco staff (Venreco B.V., Witte Veuneweg 6, Venray-Oostrum, Holland) in the preparation of the potato flakes samples is very much appreciated.

Literature Cited

1. Arnaud, M. and J.J. Wuhrmann. 1974. IV International Congress of Food Science and Technology, Madrid 23-27 September.
2. A.O.C.S. Official Method Cd 12-57, reapproved 1973: Active Oxygen Method.
3. A.O.C.S. Official Method Ce 1-62, reapproved 1975: Fatty Acid Composition by Gas Chromatography.
4. Bigalli, G. 1977. Determination of pentane formed during autoxidation of oils contained in solid samples. J Amer Oil Chem Soc 54:229.
5. Bracco, U., J. Löliger and J.L. Viret. 1981. Production and Use of Natural Antioxidants. J Amer Oil Chem Soc 58:686.
6. Buttery, R.G., C.E. Hendel and M.M. Boggs. 1961. Autoxidation of Potato Granules. Agric Food Chem 9:245.
7. Galliard, T. 1968. Aspects of lipid metabolism in higher plants. I. Identification and quantitative determination of the lipids in potato tubers. Phytochem 7:1907.
8. Hadorn, H. and K. Zürcher. 1974. Zur Bestimmung der Oxidationsstabilität von Oelen und Fetten. Dtsch Lebensm-rundsch 70:57.
9. Löliger, J. and F. Saucy. 1980. Rapid Determination of Antioxidants with an Electrochemical Micro Flow-Through Detector. Z Lebensm Unters Forsch 170:413.
10. Sapers, G.M., O. Panasiuk, F.B. Talley and F. Osman. 1972. Flavor Quality and Stability of Potato Flakes. J Food Sci 37:579.
11. Sapers, G.M., O. Panasiuk and F.B. Talley. 1973. Flavor Quality and Stability of Potato Flakes: Effects of Raw Material & Processing. J Food Sci 38:586.
12. Sapers, G.M., O. Panasiuk and F.B. Talley. 1975. Flavor Quality and Stability of Potato Flakes: Effects of Antioxidant Treatment. J Food Sci 40:797.
13. Willard, M. and G. Kluge. 1975. Chapter 13 in Potato Processing, W.F. Talburt & O. Smith editor 3rd edition, Westport, Connecticut, THE AVI Publishing Company.