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Potential use of electron spin resonance spectroscopy for evaluating the oxidative status of potato flakes

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Abstract

During storage for up to 52 weeks, under mildly accelerated conditions (22 °C, atmospheric air), potato flakes (1% lipid, dried to $a_w = 0.4$) were found to undergo oxidative changes as indicated by a slight decrease in headspace oxygen. The headspace concentration of hydrocarbons (ethane and pentane) steadily increased during storage, and the increase was reduced with added antioxidants. For a product without added antioxidants, three short-chain aldehydes increased slightly, but other secondary oxidation products did not change significantly (including thiobarbituric acid reactive substances). Long chain aldehydes (identified by GC–MS) were abundant in fresh products, but decreased during storage. The level of free radicals, as a marker of early events in oxidation and measured directly by electron spin resonance spectroscopy (ESR), increased significantly during the first 2 weeks of storage, followed by a marked decrease for the period of 2–22 weeks of storage to reach a steady state level. Throughout the period of storage, ESR spectrometry was able to rank products protected by natural antioxidant extracts according to increasing level of free radicals: Unprotected > Coffee > Green tea, Grape skin > Rosemary. Hydrocarbons evolved according to a similar pattern and it can be concluded that ESR spectrometry provides a method for detecting early stages of oxidation in this type of low fat dried products.

Keywords: Potato flakes; Natural antioxidants; Lipid oxidation; Storage experiment; Sensory profiling

1. Introduction

During storage of dried potato flakes, the sensory quality decreases, primarily due to oxidative reactions of the potato lipids. Many factors affect the extent of oxidation in the dried potato flakes (Buttery, Hendel, & Boggs, 1961; Sapers, Panasiuk, Talley, & Osman, 1972; Sapers, Panasiuk, & Talley, 1973; Sapers, Panasiuk, & Talley, 1975; Löliger & Jent, 1983). The most important intrinsic factors have been identified as the water activity of the dried potato flakes (Löliger & Jent, 1983), the potato variety and processing parameters (Sapers et al., 1973), as well as the nature and concentration of added antioxidants (Sapers et al., 1975).

Most experiments on the effect of antioxidants on oxidative stability of dried potato flakes have used synthetic antioxidants, such as butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) and gallates (Sapers et al., 1975). During the last two decades the request for substitution of synthetic antioxidants with natural antioxidants has been increasing, leading to more studies on natural antioxidants, primarily in model systems (Madsen & Bertelsen, 1995). However, in an early study performed by Löliger and Jent (1983) on dried potato flakes, rosemary extract was shown to give the same degree of protection against oxidative changes as BHA and BHT. Several other natural antioxidants may find use for protection of dried food. It was thus recently demonstrated that both tea and coffee extract give some protection against oxidative deterioration during storage of dehydrated chicken meat, although they are less efficient than either rosemary extract or the synthetic antioxidants BHA and octyl gallate (Nissen, Månsson, Bertelsen, Huynh-Ba, & Skibsted, 2000).

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Oxidative deterioration in dried potato flakes during storage has often been monitored by measurement of volatile compounds using headspace gas chromatography (Buttery et al., 1961; Sapers et al., 1972; Sapers et al., 1973; Sapers et al., 1975; Löliger & Jent, 1983). In a recent study of dehydrated chicken meat (Nissen et al., 2000), it was, however, demonstrated that the level of radicals, directly determined by electron spin resonance (ESR) spectrometry, developed similarly to headspace concentrations of ethane, pentane, and hexanal, as well as to oxygen depletion, both in unprotected and protected products (natural and synthetic antioxidants) during storage. As the water activity of potato flakes is as low as dehydrated chicken meat, ESR spectrometry should be explored as a method for predicting oxidative stability of potato flakes by early measurement directly on the product.

The objective of the present study was, thus, to compare direct ESR spectrometry on potato flakes with sensory evaluation as well as various analytical techniques more routinely used for evaluation of oxidative stability of dried foods. The sensitivity of the different methods for measuring oxidative changes, in unprotected as well as protected potato flakes, with incorporation of each of four natural extracts (rosemary, green tea, coffee, and grape skin), was compared.

2. Materials and methods

2.1. Chemicals

Analytical grade chemicals and water purified through a Millipore Q-plus purification train (Millipore, Bedford, MA, USA) were used throughout this work. 2-Heptanone (98%) was obtained from Aldrich Chemical Co. (Milwaukee, WI, USA), trichloroacetic acid (TCA) and 2-thiobarbituric acid (TBA) from Merck (Darmstadt, Germany). Extracts of rosemary (Herbor P31), green tea (Licosa-P/The Chinois) and coffee (113–999–01) were provided by Nestlé Research Centre (Lausanne, Switzerland), whereas the grape skin extract (Grape polyphenol powder P2157) was from Unilever (Vlaadingen, Holland). These extracts have been characterized in detail and the composition and content of polyphenols were reported previously (Schwarz et al., 2001).

2.2. Production and storage of potato flakes

The potato flakes were produced at Nestlé R & D Centre Beauvais (France). Bintje potatoes were peeled, pre-blanched, cooled, boiled and mashed, prior to addition of a mix containing glycerol monostearate, acidic sodium pyrophosphate, and citric acid (all food grade) as part of a standard production. No sulphite was added to the product. The natural extracts (rosemary, coffee, grape skin and green tea) were added, together with the emulgator mixture. After mixing, the mashed potato product was drum-dried to reach a water activity (a_w) of approximately 0.4. The concentrations of extracts relative to the final product were 200 ppm (rosemary, coffee, grape skin) and 500 ppm (tea), which were found to be sensorially acceptable by a trained panel.

Potato flakes (125 g) were packed in aluminized sachets, flushed with nitrogen (residual oxygen $<1\%$) and stored at -30 °C. At the beginning of the storage period (week 0) the sachets were opened and left to equilibrate with atmospheric air (12 h). The sachets were then sealed again and stored at 22 ± 4 °C. The storage period lasted for 1 year and throughout this period, sachets were withdrawn and the contents used for sensory evaluation as well as chemical analyses. The content of total fat and the fatty acid composition in potato flakes were determined at the beginning of the storage period (week 0). Sensory evaluation and measurement of the concentration of radicals, TBARS and short-chained aldehydes, were performed after 0, 2, 4, 8, 12, 24, 36 and 52 weeks of storage. Total aroma analyses were carried out after 0 and 12 weeks of storage for reference product and samples containing the rosemary extract. All determinations were made in quadruplicate with analyses on potato flakes from two different sachets. Samples were randomized before analyses. In parallel to aluminized sachets, freshly processed potato flakes were packed under atmospheric air in 425 ml aluminium cans coated with resin and tin oxide (40 g flakes in each can). The cans were stored at 20 ± 2 °C, and the headspace was analyzed after 0, 4, 8, 12, 24, 36 and 59 weeks of storage.

2.3. Fatty acid composition

The lipid fraction of potato flakes (5.0 g) was extracted, transformed into methyl esters and subjected to chromatographic separation as previously described (Nissen et al., 2000), using the techniques given by Nielsen, Sørensen, Skibsted, and Bertelsen (1997), and Jart (1997).

2.4. Volatile compounds in headspace of samples packed in sachets

The content of short chained aldehydes in potato flakes was determined by headspace gas chromatography according to Shahidi and Pegg (1994), with the modifications previously reported (Nissen et al., 2000) using samples of 2.00 ± 0.05 g flakes and 2-heptanone (to yield 100 ppm) as internal standard.

The analyses of total aroma were carried out by simultaneous distillation/extraction, as reported by Jensen, Petersen, Poll and Brockhoff (1999). Samples of 40 g potato flakes and 100 g odourless water, with 4-methyl-1-pentanol (to yield 250 ppb) as internal standard, were

homogenized (Ultra Turrax T25 homogenizer, Janke und Kunkel, IKA-Labor technik, Staufen, Germany). The homogenate was distilled/extracted for 30 min with 6 ml diethyl ether, using a down-scaled Likens–Nickerson method (micro stream distillation-extraction apparatus, Chrompack, Middleburg, Netherlands). The organic phase was dried with sodium sulphate and concentrated to 70 mg. Two microlitres of this concentrated extract were injected into a GC–MS (Hewlett-Packard G1800A GCD, Palo Alto, Ca, USA).

In all cases, the concentration of volatile compounds was calculated as peak area of the compound relative to that of the internal standard.

2.5. TBARS content of samples packed in sachets

The method for determination of 2-Thiobarbituric acid reactive substances (TBARS) according to Vyncke (1970) and Vyncke (1975), was modified, as suggested by Sørensen and Jørgensen (1996), and further adapted to the actual product. Potato flakes (1.00 ± 0.05 g) were homogenized with 20.00 ml TCA solution (Ultra Turrax; 45 s; 13500 rpm). The homogenate (5.00 ml) was centrifuged (20 min; 20,000 *g*). An aliquot of the supernatant (3.00 ml) and TBA solution (0.02 M) were mixed to yield a total volume of 6.00 ml, incubated (40 min; 100 °C), and finally cooled to approximately 5 °C. A reagent blank (3.00 ml TCA solution and 3.00 ml TBA solution) was subjected to the same analytical procedure. The samples and the blank were centrifuged again (20 min; 20,000 *g*) immediately before measurement. Absorption spectra (400–820 nm) were recorded for the samples relative to the reagent blank, using an HP 8452A Diode Array Spectrophotometer (Hewlett-Packard, Palo Alto, CA, USA). The content of TBARS in the potato flakes was expressed as absorbance in 1.00 cm cuvettes at 450 nm (A_{450}) and at 532 nm (A_{532}) relative to the weight of the product (g^{-1}).

2.6. ESR spectrometry on samples packed in sachets

Potato flakes (39 ± 1 mg) were transferred to a cylindrical 713–5PQ quartz precision tube (length 200 mm, outer diameter 10 mm; Wilmad Glass Company Inc., Buena, NJ, USA). The tube was gently tapped against the table in order to establish a dense and uniform packing of flakes. ESR measurements were performed using an ECS106 spectrometer (Bruker Analytische Mestechnik GmbH, Karlsruhe, Germany) equipped with an ER 4103TM cavity. The instrument parameters were: sweep width 50 Gauss; receiver gain 1.25 10^5; microwave power 20 mW; modulation frequency 100 kHz; modulation amplitude 7 Gauss; conversion time 81.92 ms; time constant 1311 ms; total scan time 84 s. ESR-signals were converted into peak areas by integration using the PC-programme "Win-EPR" (Bruker Analytiche Mestechnik GmbH) and the results were expressed as area of the signal relative to the amount of potato flakes in the tube (g^{-1}).

2.7. Sensory evaluation

Sensory analysis was carried out as a quantitative sensory profiling by which the intensities of a number of defined descriptors for the smell and taste characteristics of the product were evaluated. The profiling was performed as a Latin square with cross-over design by an assessor panel (eight persons with special training in evaluation of potato flakes). At the sensory evaluation sessions, the assessors were placed separately in a room established according to the international standard ISO8589: 1988 Sensory Analysis—General guidance for the design of test rooms. Potato flakes (125 g) were mixed with boiling water (750 ml) and the mash was placed in an oven (150 °C; 20 min) to reach a temperature of 60 °C. The mash was mixed before portions were transferred to plastic cups labelled with randomized three-digit codes. The portions of mashed potato were served one at a time (centre temperature approximately 55 °C) in a randomized order. Scores for the intensity of descriptors (0: no recognition; 15: high intensity) were given as marks on an unstructured line scale (15 cm) using a computer program (Fizz; BioSysteme, Couternon, France). At each day of analysis, two different sachets of the product were evaluated. Two standards (a reference sample which was stored under nitrogen at −21 °C and a reference sample, stored under atmospheric air at 22 °C for 2 months more than the product being evaluated), were included as standards in order to define the difference in taste/smell between a fresh and an old product.

2.8. Ethane, pentane and residual oxygen in cans

The concentrations of ethane, pentane and residual oxygen were determined directly in the headspace gas above the sample in the can by the static headspace gas chromatography method reported earlier (Nissen et al., 2000). Analyses were performed at least in duplicate.

2.9. Statistical analyses

The applicability of the different chemical methods for measuring oxidative changes in potato flakes in aluminized sachets during storage was evaluated for data obtained on the reference product with no incorporation of extracts. For the methods showing response to oxidative changes during storage, the effect of incorporated antioxidants was further evaluated. The statistical method used was analysis of variance in the procedure ANOVA in SAS 6.12 (SAS Institute, Inc., Cary, North Carolina). Significant storage and treatment effects were further classified by LSD ($P < 0.05$).

3. Results

3.1. Lipid content and fatty acid composition

For both the reference product and for products with added extracts, the lipid fraction of potato flakes (1.0% v/v; SD 0.04) was characterized by a high concentration of saturated fatty acids (82%) in which stearic and palmitic acid were predominant. The unsaturated lipid fraction consisted mainly of linoleic and linolenic acid (Table 1). The high content of saturated fatty acids is, however, due to the addition of glycerol monostearate during production of the flakes as the potato fat itself is dominated by linoleic and linolenic acid, and is, thus, highly unsaturated.

3.2. Oxidative changes in samples packed in aluminized sachets

The chemical methods for measuring oxidative changes in the lipid fraction of potato flakes packed in aluminized sachets during storage were initially evaluated for the reference product (no incorporation of extracts) as this product was supposed to be most vulnerable to oxidation. The chemical markers employed for this evaluation were (1) the level of radicals, (2) headspace short chain aldehydes (acetaldehyde, propanal, isobutanal, isopentanal and hexanal), (3) 2-thiobarbituric acid reactive substances, measured at both absorbance maxima, i.e. 532 nm (TBA_{532}) and at 450 nm (TBA_{450}), and (4) content of characteristic potato aroma compounds. In addition, sensory changes in potato flakes during storage were evaluated by the odour and/or taste descriptors "potato water", "bread", "oatmeal", "dry oak", "mealy", "cardboard", "metal", "potato peel", "wheat bran" and "bitter".

Table 2 shows values for the chemical and sensory markers that changed significantly during storage. The level of radicals was characterized by a significant increase within the first two weeks of storage, followed by a marked decrease for the period of 2–22 weeks of storage to reach a steady level, which lasted during the remaining storage period. TBA_{450} showed a later increase, which was also followed by a decrease, while TBA_{532} was fairly constant throughout the storage period. The concentration of acetaldehyde increased continuously during storage, while the concentration of hexanal and propanal reached steady maxima after 9 weeks of storage. The sensory descriptors did not vary systematically with the time of storage.

Total aroma was analyzed at the beginning of storage and again after 12 weeks of storage. During this time span, concentrations of some compounds increased while others decreased. In general, longer chain compounds (e.g. decadienal), being initially-formed secondary lipid oxidation products, decreased during storage (Table 3), while shorter chain compounds (such as hexanal) from breakdown of compounds, like decadienal, increased.

These methods were further investigated with respect to their capacity to differentiate between products with varying oxidative stability due to incorporation of natural extracts. The procedure employed for this evaluation was analysis of variance and subsequent classification

Table 1
Fat content (% w/w) and fatty acid composition (% of total fatty acid content) in potato flake products used in storage experiment

	Fat content	Myristic	Palmitic	Stearic	Linoleic	Linolenic	Arachidic
Mean	1.04	1.4	24.9	53.3	10.9	5.4	2.0
S.D.	0.04	0.2	1.1	3.7	1.7	0.8	0.2

Table 2
Oxidative changes in unprotected potato flakes during storage (22 °C, packed in aluminized sachets under atmospheric air) as measured directly by ESR spectrometry, by thiobarbituric acid reactive substances on extracts, by headspace-GC aldehydes (acetaldehyde, propanal, hexanal), and by evaluation of the sensory characteristics "wheat bran" and "metal"

	Time of storage (weeks)							
	0	2	4	9	12	22	36	52
ESR (peak area/density)	3.3d[a]	11.3a	8.8bc	9.3ab	9.3ab	6.8c	7.5bc	6.8c
TBA_{532} ($Abs^{1\,cm}_{532}$/g flakes)	0.081e	0.105ab	0.085e	0.095cd	0.110a	0.102abc	0.087de	0.099bc
TBA_{450} ($Abs^{1\,cm}_{450}$ /g flakes)	0.149d	0.183c	0.149d	0.203b	0.177c	0.256a	0.265a	0.213b
Acetaldehyde (ppm)	1.02c	1.20bc	1.23b	1.32ab	1.39ab	1.47a	1.49a	1.51a
Propanal (ppm)	0.18c	0.35b	0.32b	0.48a	0.44ab	0.39ab	0.43ab	0.41ab
Hexanal (ppm)	0.07c	0.31bc	0.28bc	0.61a	0.51ab	0.40ab	0.51ab	0.44ab
Sensory: "wheat bran" (arb. unit 0–15)	4.08d	5.08cd	6.31ab	5.70abc	5.39bc	5.22c	4.00d	6.58a
Sensory: "metal" (arb. unit 0–15)	5.4ab	4.6bc	5.7ab	5.3ab	6.4a	5.3ab	3.5c	6.1a

[a] Classification obtained by analysis of variance. Different letters in the same row indicate significant differences at $P < 0.05$ level.

Table 3
The concentrations (ppb) of hexanal, nondienal and decadienal in potato flakes during storage (22 °C, packed in aluminized sachets under atmospheric air) and threshold values (ppb) of these compounds in mashed potatoes and in water

Compound	Time of storage (weeks)		Threshold values in	
	0	12	Mashed potatoes[a]	Water[a]
Hexanal	163	248	3	47
(E,E)-2,4-Nonadienal	2.9	1.6	0.0017	–
(E,E)-2,4-Decadienal	88	33	0.045	63

[a] Reference: Jensen et al. (1999).

Table 4
Level of significance for treatment effect resulting from incorporation of natural extracts in potato flakes at each day of testing during storage (22 °C, packed in aluminized sachets under atmospheric air)

Time of storage (weeks)	0	2	4	8	12	24	36	52
ESR	**	*	*	**	***	**	***	**
TBA_{532}	ns[a]	ns	**	ns	ns	ns	ns	ns
TBA_{450}	*	ns	**	ns	*	*	*	ns
Acetaldehyde	*	***	*	ns	ns	ns	**	ns
Propanal	**	ns	**	ns	ns	*	ns	*
Hexanal	*	**	***	ns	ns	***	ns	**
Sensory: "wheat bran"	ns	ns	ns	ns	ns	ns	ns	ns
Sensory: "metal"	ns	ns	ns	ns	ns	ns	ns	ns

* $P<0.05$.
** $P<0.01$.
*** $P<0.001$.
[a] ns, Non-significance.

($P<0.05$) of significant treatment effects for data obtained at the individual days of testing (Table 4). TBA_{450} and hexanal showed significant treatment effects for five of the eight testing days, whereas significant effects for acetaldehyde, propanal and TBA_{532} were found at four, three and one testing days, respectively. For the sensory descriptors, no significant effect of treatment was observed. Only the ESR method was consistently found to distinguish between treatments (Fig. 1), and throughout the period of storage the following pattern of ESR signal intensity was found:

reference > coffee > tea, grapeskin > rosemary

3.3. Oxidative changes in samples packed in cans

For potato flakes packed in cans, oxidative changes were determined as residual oxygen content and by the concentration of ethane and pentane using gas headspace-GC. In all samples, the residual oxygen content showed a slight decreasing trend during the period of storage. However, the decrease was not significant, due to a large standard deviation for the measurement. On the other hand, the concentrations of the two hydrocarbons were found to increase continuously throughout the storage and the increase was reduced when antioxidant extracts were added. The antioxidant efficacy of different extracts could be distinguished with statistical significance and the same ranking as above was observed as with the ESR method, except for the coffee extract, which seemed to have a slight pro-oxidative effect when measured by this method (Fig. 2).

4. Discussion

Potato flakes have low lipid contents and, although oxidation in potato flakes has been recognized as important for quality deterioration (Löliger & Jent, 1983), a sensitive method for detection of oxidative changes in this product is still not available. In the present study, two aspects of lipid oxidation in potato flakes were investigated: (1) development of oxidation during storage, and (2) detection of differences in oxidation in products protected by different natural antioxidants.

Sensory evaluation was found to be inconclusive, as a non-significant variation with storage time was seen for the unprotected product. This finding could be the consequence of a high starting concentration of off-flavours in the product, due to lipoxygenase-catalyzed oxidation of linoleic and linolenic acids in membrane lipids during preblanching of potatoes. Even though the lipoxygenase is quickly inactivated by a high processing temperature, the enzymatic oxidation is fast and leads to the formation of hexanal, nonadienal and decadienal. These compounds have previously been demonstrated to be of great importance to off-flavour in boiled potatoes (Petersen & Poll, 1999). In this study they were found in concentrations above threshold values in water (all three aldehydes) as well as in mashed potatoes (only hexanal) at the beginning of the period of storage (Jensen et al., 1999). The observed increase of the concentration of hexanal (163–248 ppb) during storage does not necessarily reflect a marked sensory change, especially as the concentration of nonadienal and decadienal were simultaneously decreasing, leaving the net change in concentration of off-flavours uncertain.

The level of radicals, however, changed with storage time with a pattern characteristic for a marker of early events. Following exposure to atmospheric air, the level

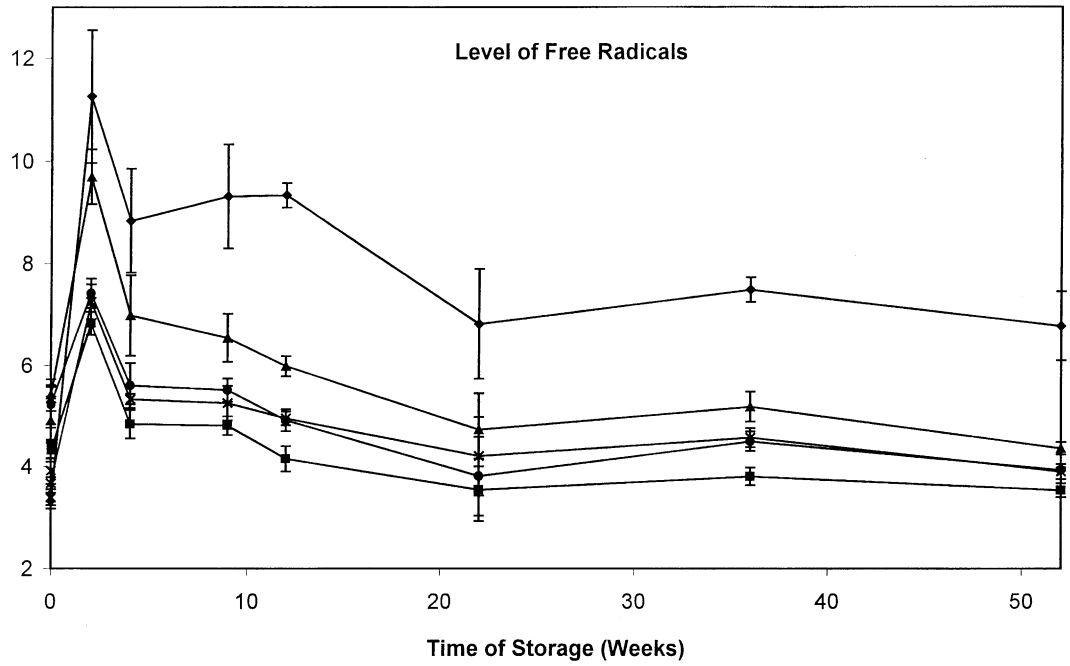

Fig. 1. Radicals in protected and unprotected potato flakes during 52 weeks of storage (22 °C, packed in aluminized sachets under atmospheric air) as measured by ESR spectrometry (peak area in spectra relative to product density). ◆: Non-protected reference product; ■: Rosemary; ●: Tea; ▲: Coffee; ×: Grape skin.

increased (2 weeks of storage), indicating the initiation of oxidation. The level of radicals in the product declined subsequently over the next weeks of storage to reach a steady state value after less than half a year. A similar pattern was previously observed for dried chicken meat, another low water-activity product, for which the developments of secondary lipid oxidation products, such as hexanal, were found to correlate with the level of radicals (Nissen et al., 2000). For the present product, secondary lipid oxidation products developed with a delay compared to the level of radicals. This is most clearly seen for hexanal and propanal, both reaching a maximum after 9 weeks of storage. This pattern can be understood on the basis of the autocatalytic nature of lipid oxidation, where radicals precede cleavage of lipid to yield volatiles.

As for protection of potato flakes by antioxidants, a similar pattern was seen. Sensory evaluation was difficult and (for sensory descriptors) no significant effect of treatment was seen. Only measurement of levels of radicals and hydrocarbons (ethane and pentane), obtained with the ESR and the static headspace-GC methods, respectively, showed a significant influence of extracts in protecting potato flakes against lipid oxidation. Furthermore, these three chemical markers all indicated that rosemary extract had the highest antioxidative efficacy, followed by the tea and grape skin extracts. For the coffee extract, however, a discrepancy between methods could be observed as the results of the headspace-GC method indicated a pro-oxidative effect of this extract, whereas the ESR method resulted in an antioxidative effect. This difference is not yet fully understood but could relate to a different mechanism for the antioxidants present in coffee compared to other plant extracts (Schwarz et al., 2001).

The applicability of the headspace hydrocarbons method to evaluate and distinguish the effects of antioxidant extracts on lipid oxidation of food has previously been demonstrated (Löliger, 1990; Prior & Löliger, 1994), whereas the use of the electron spin resonance (ESR) method for this purpose is relatively new. Studies on whole milk powder (Stapelfeldt, Nielsen, & Skibsted, 1997a; Stapelfeldt, Nielsen, & Skibsted, 1997b), as well as a study on dehydrated chicken meat (Nissen et al., 2000), did, however, show the potential of the ESR method to measure and predict oxidative changes in food products with low water activity.

In studying oxidative changes in chicken meat (Nissen et al., 2000), the same extracts as used in the present study were incorporated in the product. Comparing the results of these two studies, it is worth noting that the amounts of both ethane and pentane developed in potato flakes are much smaller than the levels found in dehydrated chicken meat. This difference can be explained by a smaller content of fat (1 vs. 25%) and smaller amounts of PUFA (16 vs. 27% of total lipids) in potato flakes than in dehydrated chicken meat. Also, in contrast to dehydrated chicken meat, the small PUFA content in potato flakes could explain the failure of most of the analytical methods employed to measure

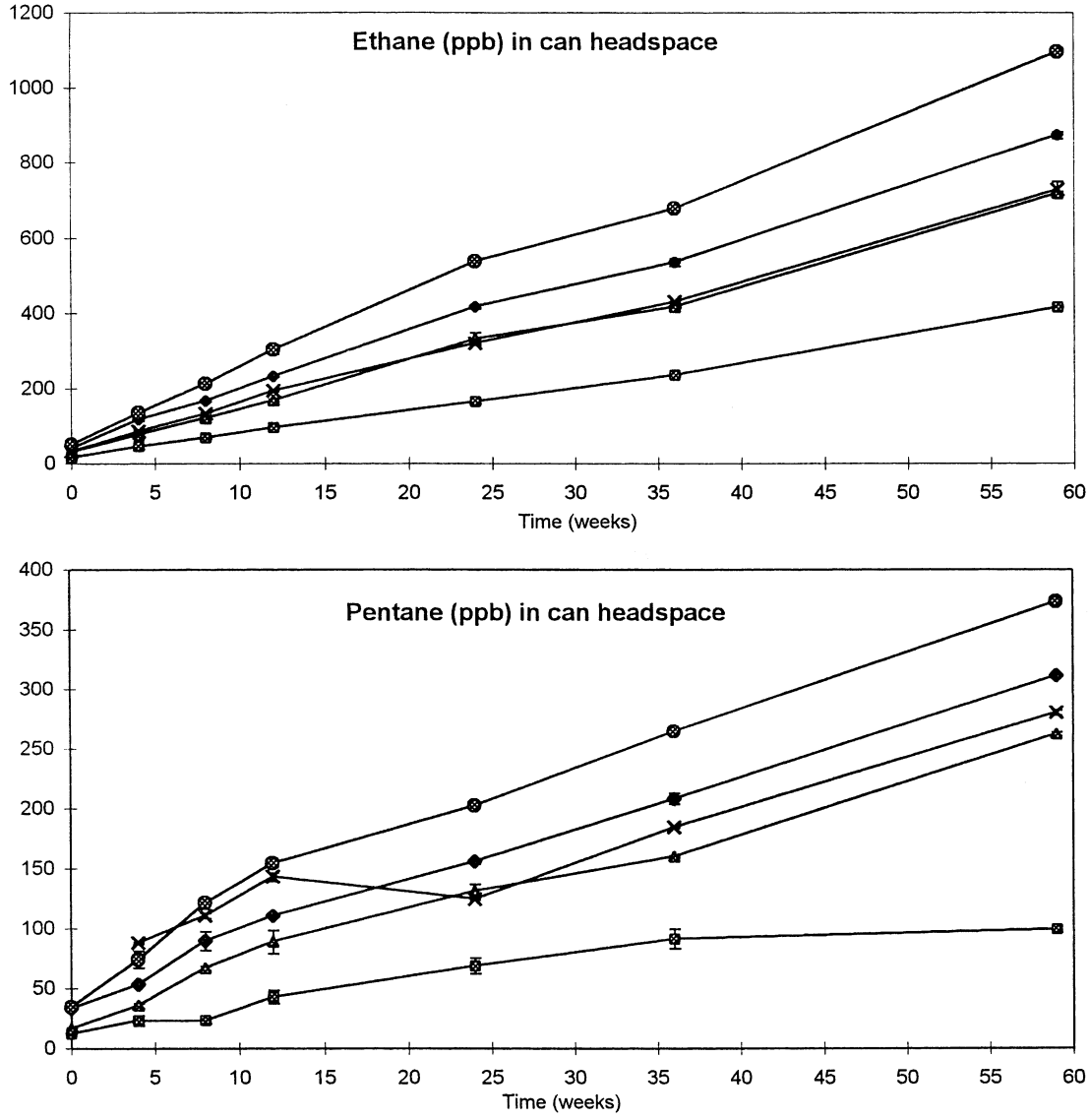

Fig. 2. The concentrations (ppb) of ethane and pentane in protected and unprotected potato flakes during 59 weeks of storage (20 °C, in cans under atmospheric air) as measured by static headspace-GC. ◆: Non-protected reference product; ■: Rosemary; ●: Coffee; ▲: Tea; ×: Grape skin.

oxidative changes in potato flakes. Comparison of the efficacy ranking of extracts found in potato flakes (rosemary > tea≈grape skin > coffee) to that found in dehydrated chicken meat (rosemary > tea≈coffee > grape skin) by Nissen et al. (2001) further indicate that the food matrix can influence the antioxidative efficacy of extracts incorporated in the foods.

In conclusion, direct measurement of free radicals in dried food products by ESR spectrometry is a promising technique both for early detection of oxidative changes during storage and for evaluation of the protection obtained by different antioxidants. The static headspace hydrocarbon method was the most sensitive technique among those commonly used to assess oxidative changes in food via the changes in volatile secondary lipid oxidation products.

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