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# Oxidative stability of snack and cereal products in relation to moisture sorption

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**Abstract**

A collection of snack and cereal products including peanuts, pork scratchings, a mixture of rolled oat and wheat from muesli and oatmeal have been characterized in terms of the relationship between storage humidity and stability against lipid oxidation. The products were stored above various saturated salt solutions in an atmosphere corresponding to ambient air. The development of free radicals, hexanal and water content was monitored during the storage. For oatmeal, muesli-mixture and pork scratchings an optimal humidity existed at which the oxidation rate constant was minimal. Furthermore, the humidity was concluded to be an important packaging parameter for oatmeal and muesli as a large difference between minimal and maximal oxidation rate constant was observed. The optimal humidity with respect to oxidative stability did not coincide with the BET-monolayer value. The radical content was very dependent of the relative humidity as an increased humidity resulted in decreased radical content.


*Keywords:* Peanuts; Pork scratchings; Oatmeal; Muesli; Water activity; Humidity; Lipid oxidation; Sorption isotherm

## 1. Introduction

Many cereal and snack products are dry foods containing lipids. Having a water activity below 0.6 they are stable against microbial growth, but chemical and enzymatic reactions can occur which results in deterioration (Labuza, 1980). Products like peanuts, pork scratchings and muesli have a high content of unsaturated fatty acids and are therefore very susceptible to lipid oxidation resulting in formation of off-flavours during storage.

From a food packaging perspective the effect of oxygen pressure and humidity on the oxidative stability of snack and cereal products is of major concern and may be decisive of the choice of initial headspace gas composition, initial product water activity and gas and water vapor permeability of the packaging material (Robertson, 1993). From the authors point of view this stresses the importance of further studies on the interrelation between water activity and susceptibility to oxidation for various specific dry products in order to obtain a long shelf life and a high product quality and in order to clarify the still unresolved question of the existence of a general relationship. Furthermore studies must include multiple water activities in order to resolve possible regions of minimal and maximal susceptibility to oxidation.

If foods are dried to too low a moisture content (less than about 2–3%) they may become susceptible to oxidation (Labuza, 1971). For some systems it has been found that an optimal water activity exists, and lipid oxidation reactions proceeded faster below and above this optimal water activity (Labuza, 1980). This relation has been postulated to be a "general scheme" and valid for most kinds of food and has found its way into textbooks of food chemistry (Belitz, Grosch, & Schieberle, 2004; Fennema, 1996). In model systems (methyl linoleate) (Maloney, Labuza, Wallace, & Karel, 1965) and different food products such as peanuts (Baker, Sims, Gorbet, Sanders, & O'Keefe, 2002; Evranuz, 1993; Hill & Rizvi, 1982), walnuts (Rockland, Swarthout, & Johnson, 1961) and potato chips (Quast &

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Karel, 1972), the dependence of the water activity on the rate of oxidation has been shown to agree with this "general scheme"; i.e. minimal oxidation at intermediate humidity and increased rate of oxidation both below and above this humidity. However, in other studies on peanuts (Maté, Saltveit, & Krochta, 1996; Reed, Sims, Gorbet, & O'Keefe, 2002), wheat flour (Arya & Thakur, 1990) and rolled oats (Molteberg, Magnus, Bjørge, & Nilsson, 1996), the degree of oxidation was found to decrease with increasing humidity, whereas in walnuts (Maté et al., 1996), macadamia nuts (Cavaletto, Cruz, Ross, & Yamamoto, 1966) and wheat flour (Cuendet, Larson, Norris, & Geddes, 1954) the oxidation rate increases with increasing humidity (or moisture content). However, these studies often only include a limited number of water activities (typically only two) and may therefore have failed to detect a possible minimum.

In some systems the water activity corresponding to a Brunauer–Emmett–Teller (BET) or Guggenheim–Anderson–de Boer (GAB) monolayer was found to be the optimal with respect to minimizing oxidative damage (Hill & Rizvi, 1982; Labuza, 1980; Labuza, Tsuyuki, & Karel, 1968; Maloney et al., 1965). It was rationalized that at the monolayer the water was tightly bound and the rate of oxidation and other reactions were very slow or almost negligible in relation to food storage stability (Labuza, 1971; Labuza, 1980). However, the water activity (relative humidity) corresponding to BET or GAB monolayer has only been reported in two investigations. In peanut flakes the BET monolayer moisture content provides optimal stability with respect to oxidative damage (Hill & Rizvi, 1982), whereas for peanuts the monolayer value was lower than the water activity at which the oxidation was minimal (Evranuz, 1993).

Oxidative deterioration has often been quantified in terms of the peroxide value or the content of volatile secondary lipid oxidation products, such as hexanal. The common polyunsaturated fatty acid, linoleic acid, is very susceptible to oxidation and during this process hexanal is produced (Belitz & Grosch, 1999; Frankel, 1982; Przybylski & Eskin, 1995). Hexanal is a good indicator of the degree of oxidation and has along with other volatiles been applied in various products to follow the quality deterioration (Erickson, 1993; Jensen, Bertelsen, Danielsen, Skibsted, & Andersen, 2005; Jensen, Sørensen, Brockhoff, & Bertelsen, 2003; Jensen, Sørensen, Engelsen, & Bertelsen, 2001; Jeon & Bassette, 1984; Lennersten & Lingnert, 1998; Molteberg et al., 1996; Molteberg, Solheim, Dimberg, & Frølich, 1996; Molteberg, Vogt, Nilsson, & Frolich, 1995; Nissen, Månson, Bertelsen, Huynh-Ba, & Skibsted, 2000; Reed et al., 2002). Radicals are formed during the oxidation of foods, and can be determined by electron spin resonance (ESR) spectroscopy. In the dried products dehydrated chicken meat, milk powder and potato flakes, the level of free radicals detected by ESR has been shown to be a good indicator of early stages of oxidation, that also correlated well with the content of secondary oxidation products and sensory score at later stages (Nissen, Huynh-Ba, Petersen, Bertelsen, & Skibsted, 2002; Nissen et al., 2000; Stapelfeldt, Mortensen, & Skibsted, 1997; Stapelfeldt, Nielsen, & Skibsted, 1997b). Additionally, the development of radicals and hexanal were found to complement each other in detecting the oxidative changes in oatmeal, muesli, peanuts and pork scratchings stored at ambient temperature (27 °C) and relative humidity (Jensen et al., 2005).

The aim of the present study was to obtain more knowledge about the interrelation between oxidative stability and relative humidity/moisture content for a series of specific snack and cereal products (oatmeal, muesli, roasted salted peanuts and pork scratchings) in order to obtain guidelines for optimal packaging and storage as only few studies have been made in this area. The oxidative stability of the four products quantified as the level of hexanal was followed during a realistic storage period. In addition, the development of free radicals was determined during storage. Another objective was to investigate the existence of an optimal water activity/relative humidity at which the degree of oxidation was minimal and the relationship between monolayer value and oxidative stability. Furthermore, the oxidative stability of muesli (sugar coated rolled oats and wheat flakes) was compared to uncoated oatmeal to investigate how sugar coating affected the oxidative stability.

## 2. Materials and methods

### 2.1. Products

Peanuts and pork scratchings were commercially available products from KiMs A/S (Denmark), oatmeal from Cerealia Foods A/S (Denmark) and muesli from Nutana A/S (Denmark). The muesli contained rolled oats, wheat flakes, extruded rice, raisins, almonds and desiccated coconut. The ingredients were mixed, added refined vegetable oil (4%) and honey and baked. Prior to storage, the rolled oats and wheat flakes were separated from the other ingredients and only these two ingredients were used in the experiment and will in this paper be denoted muesli. The water content of rolled oats and wheat flakes in the muesli was approximately 2% and the oatmeal from Cerealia Foods A/S was accordingly dried to similar water content before the experiment in order to compare the stability of the two cereal products.

### 2.2. Experimental design

In the storage experiment, peanuts, pork scratchings, oatmeal and muesli (coated rolled oats and wheat flakes) were stored in colanders in plastic containers (11 l, non-transparent) with airtight lids at 25 °C. The gas composition in the containers corresponded to ambient air. To obtain different relative humidities (RH), saturated salt solutions were placed in the bottom of the containers.

About 3000 g, 1850 g, 1900 g and 2750 g of peanuts, pork scratchings, oatmeal and muesli, respectively, were equilibrated over saturated salt solutions which had the following constant relative humidities at 25 °C: 7% (LiBr), 11% ($LiCl \cdot 2H_2O$), 23% ($CH_3COOK$), 33% ($MgCl_2 \cdot 6H_2O$), 43% ($K_2CO_3$), 53% ($Mg(NO_3)_2 \cdot 6H_2O$) and 65% ($CoCl_2$). In addition, oatmeal and muesli were equilibrated at 31% (KF) and 38% RH (NaI). A part of the experiment was repeated as oatmeal was stored at 31%, 33% and 38% RH with mixtures of glycerol–water instead of saturated salt solutions to obtain the different relative humidities. The storage conditions were the same as previous, except that the storage period was limited to 19 weeks. To avoid modification of the products the experiment was performed as a working isotherm (Bell & Labuza, 2000), i.e. the products were not dried or "wetted" before the experiment but were used as received.

The stability of the products were investigated at the above mentioned relative humidities (7–65%) during a time period of 21 weeks for peanuts, pork scratching and oatmeal and 51 weeks for muesli. During storage 40 g of peanuts and pork scratchings and 30 g of oatmeal and muesli were frequently withdrawn for analysis. After 3–4 weeks the product reached equilibrium at the different relative humidities and the oxidative stability was followed by measuring the content of free radicals and hexanal. In addition, the moisture content of the products was determined to establish a moisture sorption isotherm.

### 2.3. Sample preparation

Before analysis the products were homogenized for 10 s in a household coffee mill (Braun, Germany). Between the analyses the samples were vacuum packed and stored for up to 3 days at 5 °C in darkness, as all the analyses could not be performed on the same day.

### 2.4. Water content

The water content of the products was determined by placing approximately 2.0 g of the homogenized sample on a dry aluminium tray. The sample was dried for 16–18 h at 105 °C and tempered in a desiccator for 30 min before weighing to obtain the water content. The results were expressed as g water/g dry matter and each value presented as a mean of two measurements.

### 2.5. Hexanal content

The content of hexanal was measured by static headspace-GC according to Jensen et al. (2001) with the modification that the aqueous internal standard was added in a glass liner in order to avoid direct contact with and humidification of the sample. The results were expressed as milligram hexanal/kg product and each value as a mean of two measurements.

### 2.6. Free radical content (ESR spectroscopy)

The relative free radical content was measured by electron spin resonance (ESR) spectroscopy. Approximately 0.35, 0.2, 0.17 and 0.25 g (accurately weighed) of homogenized peanuts, pork scratchings, oatmeal and muesli, respectively, were transferred to a cylindrical, thin-walled 702-PQ-7 clear-fused quartz (CFQ) tube (Wilmad Glass Company Inc., Buena, NJ) which was gently tapped against the table to establish a dense and uniform packing. The column height was approximately 2.5 cm for all the products resulting in densities of 0.14, 0.08, 0.07 and 0.1 g/cm for peanuts, pork scratchings, oatmeal and muesli, respectively. The ESR measurements were performed using a JES FR30 Free Radical Monitor (JEOL, Tokyo, Japan) with the following parameters: sweep time 4 min, sweep width 7.5 mT, microwave power 4 mW, modulation width 0.1 mT and time constant 0.3 s. The content of radicals was quantified in relation to a manganese standard as the height of the signal relative to the height of the standard and then normalized by the density (g/cm) of the sample in the tube. Each value was presented as a mean of two measurements.

### 2.7. Data analysis

The observed rate constants, $k_{obs}$, for the development of hexanal were determined by linear regression in Sigma Plot 2001 (SPSS Inc., Chicago, USA) and compared by a $t$-test ($P \leqslant 0.05$). The monolayer value was determined according to the BET sorption equation, which has been very useful in predicting the monolayer value and was applicable between $a_w$ values of 0 and 0.5. A plot of $a_w/(1 - a_w)$ m versus $a_w$ resulted in a straight line in the range of 0.07–0.43$a_w$ (7–43% RH) and from the slope and intercept the monolayer value was calculated as 1/(slope + intercept) (Bell & Labuza, 2000). The water activity (relative humidity/100) corresponding to the monolayer value was determined using the sorption isotherm.

## 3. Results

### 3.1. General

The development of lipid oxidation (measured by hexanal content) in oatmeal increased linearly with time and varied depending on the relative humidity (Fig. 1). The progress of formation of hexanal in muesli, pork scratchings and peanuts showed similar trends as a function of time and relative humidity. Consequently, for oatmeal, muesli and peanuts the development of hexanal could be described by zero-order kinetics with observed rate constants, $k_{obs}$, which depend on both the product and the relative humidity. However, zero-order kinetics could not describe the development of hexanal in pork scratchings and the rate constants were therefore determined at the end of the storage period as described below.

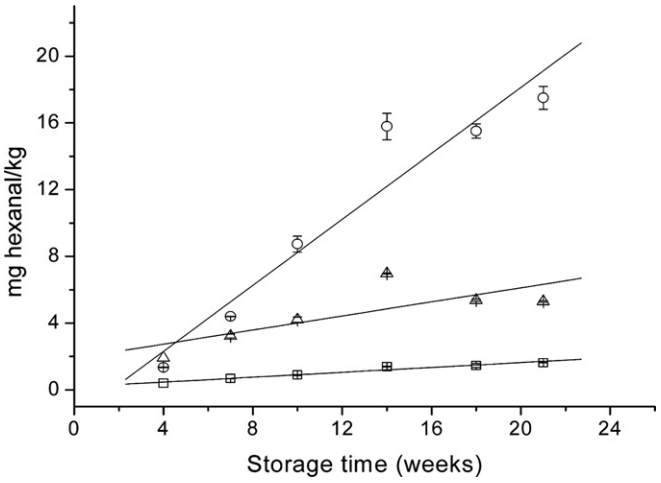


Fig. 1. Development of hexanal for oatmeal stored at 23 (□), 53 (○) and 65% (△) RH. Solid lines show linear regression lines from which the zero-order rate constants are derived.

### 3.2. Moisture sorption

The moisture content of the products increased with increasing relative humidity (Fig. 2A–D). The moisture sorption isotherms were based on measurements from week 18–21 for oatmeal, peanuts and pork scratchings and from week 18–38 for muesli as the water contents were stable in these periods. However, the moisture content at a given RH was different from product to product, indicating different abilities of the products to bind water in a thermodynamic sense. The calculated monolayer values and the corresponding water activities are given in Table 1 together with the natural, initial water activities for the different products. The natural water activity of oatmeal, muesli and peanuts were significantly higher than the monolayer value, whereas for pork scratchings the natural water activity was lower than the monolayer value.

### 3.3. Oxidation rate constant

The oxidation rate in terms of the observed zero-order rate constant for the development of hexanal for oatmeal (A), muesli (B), peanuts (C) and pork scratchings (D) is seen in Fig. 3A–D. Oatmeal and muesli was characterized by a shallow minimum in oxidation rate constant from 23% to 43% RH and generally the rate of oxidation was accelerated considerably at very low and very high humidities. However, storage of oatmeal and muesli above saturated $MgCl_2$ solutions resulted in an apparent maximum at 33% RH (marked by × in Fig. 3A and B) while no dramatic maximum in oxidation rate was observed for oatmeal when using mixtures of glycerol and water to control the humidity. The reason for this apparent interaction between $MgCl_2$ and oatmeal is currently unresolved as the salt is not expected to generate volatile components which can be transferred to the oatmeal. The minimal oxidation rate constants for oatmeal and muesli was observed

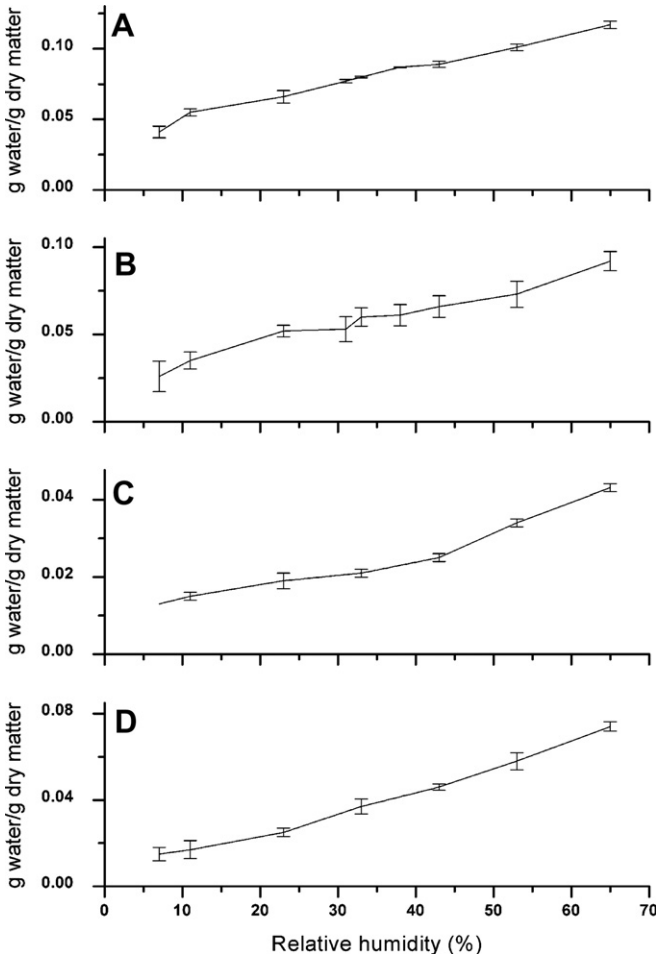


Fig. 2. Moisture content (g water/g dry matter) of oatmeal (A), muesli (B), peanuts (C), and pork scratchings (D). Bars indicate the standard deviation.

at somewhat higher humidities than corresponding to the monolayer value, at 11% and 15% RH, respectively. However, for muesli the natural water activity (25% RH) was in the region of minimal oxidation. The maximal oxidative rate constant for muesli was about half the observed rate constant found for oatmeal and could be considered as slightly more oxidative stable, most likely because sugar coating reduced the susceptibility to oxidation.

The progress of the oxidative rate constants was quite different for peanuts as compared to oatmeal. Peanuts seemed to oxidize at a rate which was less dependent of the humidity. The minimal oxidation rate constant found at 43% RH increased significantly at 23% RH by a factor of about 2. Considering the errors associated with the rate constant it was not possible to define humidity corresponding to maximal and minimal oxidation rate. This product was considerable less sensitive to humidity variation than oatmeal and muesli.

The development of hexanal in pork scratchings could not be described by zero-order kinetics (data not shown) as the product showed a complex time development of hexanal at some water activities. The oxidation rate constants

Table 1
Natural, initial $a_w$, calculated monolayer value and the corresponding $a_w$ for the four products

| Product | Natural $a_w$ | Monolayer value (g water /g dry matter) | Corresponding $a_w$ to monolayer value |
|---|---|---|---|
| Oatmeal | 0.16 | 0.055 | 0.11 |
| Muesli | 0.25 | 0.041 | 0.15 |
| Peanuts | 0.22 | 0.015 | 0.11 |
| Pork scratchings | 0.17 | 0.029 | 0.27 |

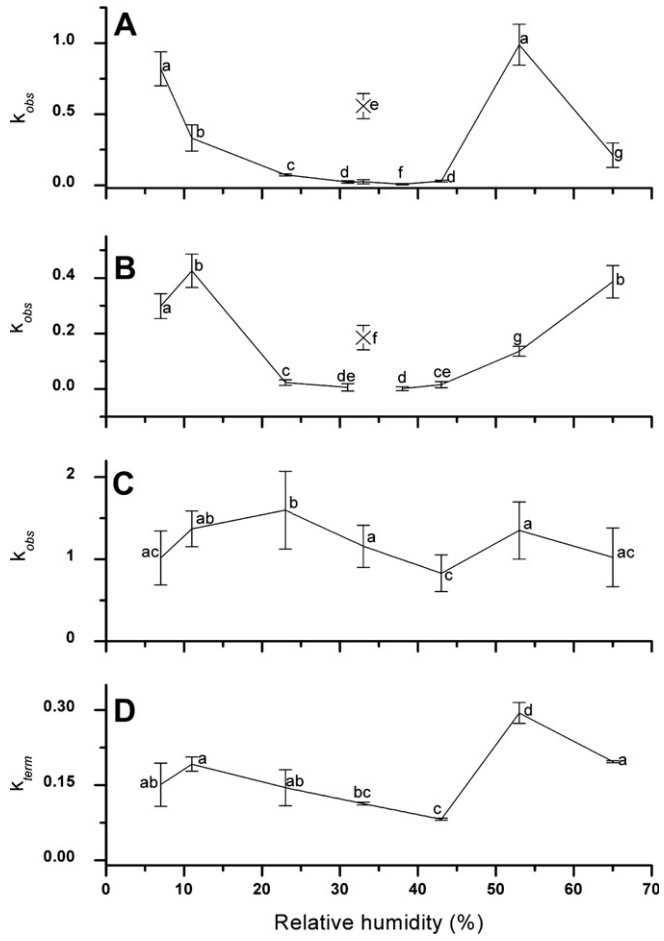


Fig. 3. Observed zero-order rate constant, $k_{obs}$ (mg hexanal/(kg week)) of oatmeal (A), muesli (B), peanuts (C) and pork scratchings (D). Bars indicate the standard deviation. Samples with different letters (a, b, c, or d) are significantly different ($P < 0.05$).

of pork scratchings are therefore calculated as the hexanal content measured at the end of the storage period (after 21 weeks) divided by the duration of the storage time interval. This quantity, which we denote $k_{\text{term}}$, has the same dimension as an observed zero-order rate constant and it can therefore be compared to the rate constants obtained from the other products storage experiments. Pork scratchings showed a narrow increase in the oxidation rate constant at relative humidities below 43% as seen in Fig. 3D. Above this humidity the oxidation rate constant increased by a factor of about 2. The oxidation rate constant at the highest humidity (65%) was apparently lower. However, this humidity was not realistic for storage of pork scratchings as they became soft at these higher humidities. For pork scratchings a minimal oxidation rate constant was observed at a significantly higher relative humidity (43% RH) as the monolayer value (27% RH) and the natural water activity (17% RH).

### 3.4. Free radical content

During storage the development of free radicals was also followed. The content of radicals was found to be constant throughout the storage period; the results are hence presented as an average of the radical content taken over the entire storage period at the respective relative humidities (Fig. 4A–D). The results showed a clear dependence of the relative humidity – the radicals became unstable at higher humidities due to larger mobility of the radicals. This mobility is due to that no development in the radical content during time was seen for any of the products.

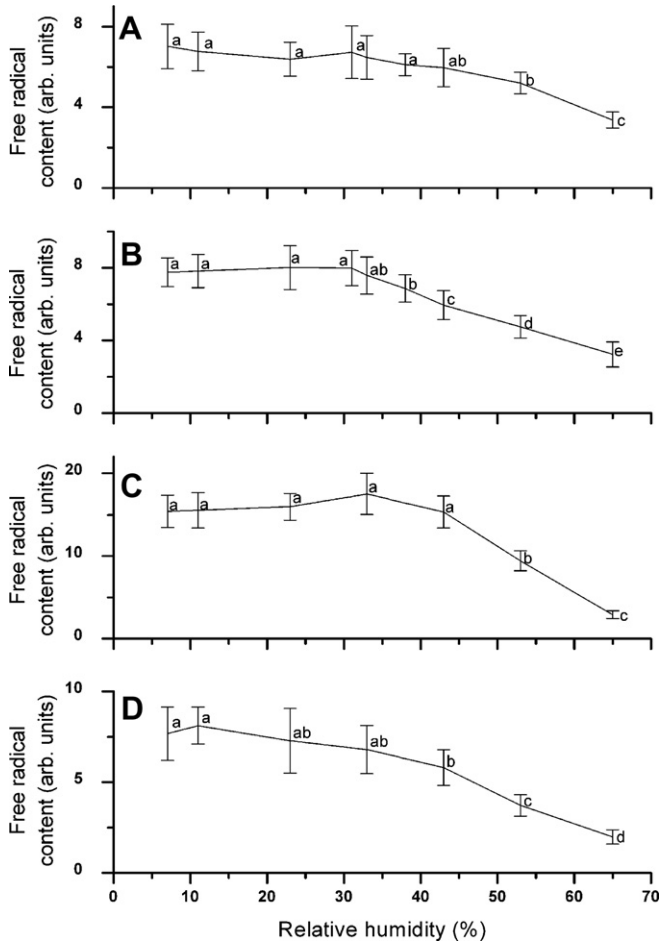


Fig. 4. Free radical content (arbitrary units) of oatmeal (A), muesli (B), peanuts (C) and pork scratchings (D). Bars indicate the standard deviation. Samples with different letters (a, b, c, d, e, f, or g) are significantly different ($P < 0.05$).

Additionally, the figure shows that the steady state radical content for oatmeal and peanuts was within statistical accuracy independent of humidity below 43% RH, whereas a constant level of free radicals was observed for muesli and pork scratchings below 33% RH. Above these humidities the radical content decreased significantly to a lower value.

## 4. Discussion

The oxidative stability was successfully quantified by hexanal content and hence the oxidation rate constants were determined. The progress of oxidation of oatmeal and muesli was quite similar – both having minimal oxidation rate constants from 23% to 43% RH. Pork scratchings have minimal oxidation rate constant at 43% RH whereas no minimal/maximal oxidation rate can be determined for peanuts.

The content of free radicals quantified by ESR spectroscopy has previously shown to correlate with the oxidative stability (quantified by e.g. volatiles and thiobarbituric acid reactive substances) of dry lipid containing foods (Jensen et al., 2005; Nissen et al., 2002; Stapelfeldt, Nielsen, & Skibsted, 1997a; Stapelfeldt et al., 1997b). The results presented in this paper did not seem to support such a relation for the products under investigation as the oxidation rate profiles of measurements of hexanal content (Fig. 3A–D) and radical content (Fig. 4A–D) did not parallel each other. It was noteworthy that all the products contained a high level of radicals at dry conditions followed by a significantly decrease in the radical content at higher humid conditions. Presumably the radical content is a balance between the formation and decay of radicals. The latter could very well be thought to be accelerated by an increased mobility at higher humidity and thus giving rise to a lower radical content. However, it is still possible that in case of comparison of related systems stored at same humidity and thus having the same conditions for radical stability, the radical content will reflect the rate of radical generation and thereby the rate of oxidation. The findings of this study are therefore not necessary contradictory to the previous studies (Jensen et al., 2005; Nissen et al., 2002; Stapelfeldt et al., 1997a; Stapelfeldt et al., 1997b), but rather reflect another experimental setup.

The rate of oxidation was observed to accelerate both at dry and humid conditions with a minimal oxidation rate at an intermediate humidity (Baker et al., 2002; Evranuz, 1993; Hill & Rizvi, 1982; Labuza, 1980; Maloney et al., 1965; Matz et al., 1955; Quast & Karel, 1972; Rockland et al., 1961). The results presented for hexanal in this study showed that oatmeal, muesli and pork scratchings also had a minimum of this kind and thus supported the general observation postulated by Labuza (1980). A closer study of the oxidation rate constant in the literature for a variety of products revealed that the difference between minimal and maximal oxidation rate constant was in the order of magnitude of 2–10 and thus comparable to the modest difference in rate constants presented for pork scratchings. On the contrary, the variation for oatmeal and muesli was much greater (125 and 355, respectively) and these products were therefore much more affected by changes of the humidity. This finding constitutes an important new result with respect to storage of these products.

Some studies claimed that the humidity at which the best oxidative stability was obtained coincided with the humidity corresponding to the monolayer value according to BET or GAB isotherms (Hill & Rizvi, 1982; Labuza, 1980; Labuza et al., 1968; Maloney et al., 1965). In contrast, the results found in our study for oatmeal and muesli showed that the humidities corresponding to the monolayer values were considerably lower than the optimal humidity with respect to oxidation. A discrepancy of this kind was also found for peanuts and freeze-dried salmon (Evranuz, 1993; Martinez & Labuza, 1968). The conflicting results raised the question of the validity of monolayer values.

The monolayer value could be assessed from two viewpoints, a basic scientific viewpoint and a practical viewpoint. From the basic scientific viewpoint the relationship between monolayer values and oxidative stability might only be valid for a specific product at a specific condition, i.e. when changing parameters such as temperature or product composition it may result in a change in the monolayer value or of the relative humidity at which the product is oxidative stable. Whether this relationship still exists for the new conditions or product formulation must be investigated. From a more practical viewpoint, it must be considered if construction of the moisture sorption isotherm and calculation of the monolayer value is a more applicable method compared to measurements of lipid oxidation. Based on the findings of no relationship between monolayer value and oxidative stability for oatmeal, muesli and pork scratchings, we recommend establishing the oxidative stability by means of direct measurements of lipid oxidation.

Previously, the relationship between relative humidity and oxidative stability in roasted peanuts had been investigated. Using quantification of hexanal it was found that the oxidation rate was lower at high relative humidity (53% or 60%) compared to low relative humidity (23%) (Maté et al., 1996; Reed et al., 2002). This is in agreement with our results where a significantly higher rate of oxidation is observed at a humidity of 23% than at 43%. On the contrary, our data could not confirm the increased oxidation at low humidities (about 12%) observed using PV measurements (Baker et al., 2002; Evranuz, 1993; Hill & Rizvi, 1982). However, it is a possibility that the observed oxidative stability was strongly influenced by chemical detection method; i.e. detection of primary or secondary oxidation products. Further studies using combinations of methods, such as detection of both primary and secondary oxidation products and sensory analysis using a great range of water activities, will answer this question.

The development of hexanal in oats showed a decreased oxidation at 30% RH compared to 55% RH (Molteberg

et al., 1995), which was in agreement with our study of oatmeal and muesli. Comparing the natural water activity and the observed minimum of oxidation of oatmeal and muesli it is worth considering increasing the water activity of the products to obtain an improved oxidative stability. However, the effect of the increased humidity on the texture has to be investigated.

For muesli and oatmeal the development of hexanal is 355 and 125 times larger, respectively, at maximum oxidation rate compared to minimum oxidation rate, whereas peanuts and pork scratchings only differ by a factor of 2 and 3, respectively. A practical implication of this finding is that water activity is an important parameter with respect to packaging and product formulation. Oatmeal is a typical low-cost product and controlling oxygen availability by applying a packaging film with high oxygen barrier properties might contribute to an unrealistic high cost. Alternatively the oxidative stability might be controlled through the initial moisture content of the product or from moisture migration from the surroundings through the packaging materials or from moist food components such as raisins in the case of muesli (Risbo, 2003a; Risbo, 2003b; Sapru & Labuza, 1996).

In conclusion, for the products under investigation the relationship between humidity and oxidative stability was found to more diverse than the "general scheme" (Belitz et al., 2004; Fennema, 1996; Labuza, 1980). The variation of oxidative stability of peanuts was modest whereas the oxidation rate of oatmeal lipid was highly dependent on humidity. The content of radical did not reflect oxidative stability when the humidity was varied.

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