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Cholesterol oxidation in whole milk powders as influenced by processing and packaging

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The effects of various spray-drying processes (direct-fired heating, high levels of oxides of nitrogen (NO_x); direct-fired heating, low NO_x; indirect electrical heating) and packaging systems (polyethylene pouches and crimp-sealed glass vials, with and without oxygen absorbers) on the oxidative stability of lipids in whole milk powders during storage were studied. Lipid oxidation, including the generation of cholesterol oxidation products, was greatest in samples processed by high NO_x direct-fired driers. Oxygen absorbers effectively controlled cholesterol oxidation during the six month storage period, even in those samples from the high NO_x drying system. There was a positive correlation (r = 0·89) between lipid oxidation and the concentration of cholesterol oxides in the samples. It was concluded that the stability of whole milk powders during storage can be improved by using low NO_x drying processes and by packaging in oxygen-impermeable packaging systems containing oxygen absorbers.

INTRODUCTION

Cholesterol, being an unsaturated lipid, readily undergoes oxidation in the presence of oxygen, heat, light and radiation. Some of the cholesterol oxidation products (COPS) have been implicated in a number of adverse biological effects including atherogenesis, cytotoxicity, carcinogenesis and inhibition of cholesterol synthesis (Kumar & Singhal, 1991).

Foods of animal origin may contain varying concentrations of COPS, depending upon the severity of processing and storage (Addis, 1986). Whole milk powders contain about 0·1% cholesterol (USDA, 1976) and when subjected to various thermal treatments and storage at ambient temperature for prolonged periods, may undergo oxidation (Sander *et al.*, 1989). However, cholesterol oxidation in whole milk powders has not been studied to the same extent as it has in egg products (Tsai & Hudson, 1984; Missler *et al.*, 1985; Morgan & Armstrong, 1989, 1992).

The formation of COPS in dried foods of animal origin can be minimized by developing better methods of processing, packaging and storage of the products. For example, the influence of the spray-drying method (direct versus indirect heating) on the formation of cholesterol oxides in egg powders has been examined by a number of investigators including Tsai and Hudson (1984) and Missler *et al.* (1985). They proposed that the greater levels of nitrogen oxides (NO_x) generated during the direct-fired spray-drying process, i.e. the direct heating of the drying air by gas combustion, enhanced the oxidation of cholesterol in egg powders. Morgan and Armstrong (1992) also demonstrated that outlet air temperature and NO_x in the combustion gases were the only conditions that affected COPS levels in egg yolk powders.

The first objective of this study was to examine the influence of three methods of spray drying (indirect

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electrical; direct, low NO_x; direct, high NO_x) on the formation of cholesterol oxides in whole milk powder during storage at 20 and 40°C. A second objective was to evaluate the efficacy of various packaging systems (polyethylene pouches and crimp-sealed glass vials with or without oxygen absorbers) in suppressing lipid oxidation in whole milk powders during storage.

MATERIALS AND METHODS

Reagents

Cholesterol oxide standards, 5α-cholestane, cholestan-5,6α-epoxy-3β-ol(α-epoxide), cholestan-5,6β-epoxy-3β-ol(β-epoxide), 5-cholesten-3β-ol-7-one(7-ketocholesterol), cholestan-3β,5α,6β-triol, 5-cholesten-3β,20α-diol (20α-hydroxycholesterol),5-cholesten-3β,25-diol(25-hydroxycholesterol), 5-cholesten-3β,7α-diol (7α-hydroxycholesterol) and 5-cholesten-3β,7β-diol (7β-hydroxycholesterol) were purchased from Steraloids Inc., Wilton, NH, USA. Cholest-5-en-3β-ol (cholesterol) and 5α-cholestan-3β-ol-6-one, were obtained from Sigma Chemical Co. (St Louis, MO, USA). Pyridine and bis(trimethylsilyl)trifluoroacetamide (BSTFA) were purchased from Pierce Chemical Co., Rockford, IL, USA. All other reagents used in the experiments were of analytical grade.

Packaging materials

Pouched oxygen absorbers were obtained from Multiform Desiccants, Inc., Buffalo, NY, USA. Polyethylene pouches (PE) (Ziploc freezer bags, 5in × 7in, 2-mil (50 μ) thickness) were purchased from a local supermarket. Crimp seal glass vials (100 ml), teflon septa and aluminium crimp-on caps were purchased from Supelco, Inc. (Bellefonte, PA, USA).

Preparation of milk powders

Liquid whole milk was supplied by a local producer in County Cork, Ireland. A pilot-scale Anhydro spray drier, model LAB 3, with pneumatic nozzle atomization (Kelly & Slattery, 1985), was used to dry the milk at the National Dairy Products Research Centre (Moorepark, Fermoy, County Cork, Ireland). The drier was equipped with electrical heating elements for indirect heating. The drier also had the capability of being converted to direct gas-fired heating by attaching a gas burner to the extended air inlet duct (Kelly *et al.*, 1989). Whole milk powder samples were manufactured by direct low and high NO_x gas-fired heating of the drier, with the fitting of a CXA gas burner (Urquhart Engineering Co. Ltd, London, England) and a standard gas burner (Radiant Superjet, model GX 25) to the drier, respectively (Kelly *et al.*, 1989). Powders were produced by the three drying methods in duplicate and packaged in three packaging systems, polyethylene (PE) pouches (5 in × 7in, 2-mil (50 μ) thickness) and crimp seal glass vials (100 ml) with and without oxygen absorbers. After filling, the PE pouches were heat-sealed, while the glass vials were sealed by aluminium crimp-on caps with teflon septa. The samples were stored in the dark for six months at 20 ± 1°C and 40 ± 1°C.

Measurement of lipid oxidation

Lipid oxidation was measured by the 2-thiobarbituric (TBA) method of Tarladgis *et al.* (1964), as modified by Crackel *et al.* (1988). Thiobarbituric acid-reactive substances (TBARS) values were expressed as mg malonaldehyde/kg sample.

Lipid extraction

Total lipids were extracted from the milk powders by the chloroform/methanol procedure of Folch *et al.* (1957). After the removal of the solvent, the lipid extract was redissolved in 5 ml hexane and stored at −20°C until used for cholesterol and cholesterol oxide determinations.

Quantitation of cholesterol in whole milk powders

The cholesterol content of the whole milk powders was determined by the direct saponification procedure of Adams *et al.* (1986). The extracted cholesterol was dissolved in dimethylformamide and quantified using a Hewlett Packard 5840A gas chromatograph (Avondale, PA) equipped with a flame ionization detector and a glass column (2 m × 2 mm i.d.) packed with 1% SE-30 on 100/120 Gas Chrom Q. The carrier gas was helium with a flow rate of 25 ml/min and the chromatograph was operated isothermally at 230°C for 20 min. The injector and detector temperatures were 275°C and 300°C, respectively.

Quantitation of cholesterol oxides in whole milk powders

The procedure used to extract and derivatize the COPS was a slightly modified version of the method of Morgan and Armstrong (1989). The lipid extract (250 mg), along with 15 μg of the internal standard (6-ketocholesterol), was transferred to a Supelclean LC-Si SPE tube (Supelco, Bellefonte, PA) which had been prewashed with 5 ml hexane. The tube was then washed with 10 ml hexane and 15 ml hexane/diethyl ether (95:5 (v/v)) to elute most of the triacylglycerols from the column. The remaining triacyglycerols and cholesterol were eluted by washing the column with 25 ml hexane/diethyl ether (90:10 (v/v)) and 15 ml of hexane/diethyl ether (80:20 (v/v)). The cholesterol oxides were eluted off the column with 10 ml of acetone. The acetone fraction was evaporated to dryness under nitrogen. Trimethylsilyl (TMS) ether derivatives of cholesterol oxides were prepared by redissolving the COPS in 50 μl pyridine and 50 μl BSTFA and holding in the dark at room temperature for 1 h. The TMS

ether sterols were then evaporated to dryness under nitrogen and redissolved in 100 μl of ethyl acetate.

A Hewlett Packard 5890A gas chromatograph equipped with an HP 5673A automatic injector and an HP 3392A integrator was used to quantify the cholesterol oxidation products. COPS were separated on a fused silica capillary column DB-1 (15 m × 0·25 mm i.d., 0·1 μm film thickness; J & W Scientific Inc., Ann Arbor, MI). Carrier gas (helium) was delivered at 27 ml/min and a head pressure of 50 kPa. Oven temperature programming was from 170 to 220°C at a rate of 10°C/min, then increased to 234°C at a rate of 0·4°C/min, held for 5 min, and then increased to 256°C at a rate of 2°C/min. Injector port and detector temperatures were 270 and 300°C, respectively. TMS derivatives of COPS (2 μl) were injected onto the column with a split ratio of 11 : 1.

Headspace oxygen measurement

The headspace oxygen concentrations in the packaged samples were determined using a Carle 2153-B gas chromatograph (GC) (Carle Inc., Anaheim, CA) with a molecular sieve 5A column (60/80 mesh, 2·4 m × 3·2 mm i.d.) and a column (50/80 mesh, 2·4 m × 3·2 mm i.d.) consisting of 20% PPQ (Porapak Q) and 80% PPN (Porapak N). A 500-μl sample of gas was withdrawn from the package or vial with a gas-tight syringe (1 ml) and injected into the sample loop of the GC. Helium was used as the carrier gas. The oven temperature was maintained at 50°C.

Statistical analysis

The experiment was conducted as a four-factor (drying method × packaging × temperature × time) split-plot design with two replications. Statistical analyses of the data for cholesterol oxides and TBARS values were performed using a Bonferroni *t*-test to analyze specific contrasts among temperature treatments and Duncan's multiple comparisons test for drying methods and packaging systems (Ott, 1988). The analyses of variance were performed using the MSTAT-C microcomputer statistical program (Michigan State University, East Lansing, MI, 1989).

RESULTS AND DISCUSSION

Headspace oxygen content

The oxygen concentrations in the headspaces of the PE pouches, and the glass vials without and with the oxygen absorbers, were 20·1, 20·2 and 0·03%, respectively, three hours after package closure. The headspace oxygen contents of whole milk powders packaged in PE pouches were similar to the percent oxygen in air, and remained constant during the entire storage period. Headspace oxygen concentrations in the glass vials without oxygen absorbers decreased to 18·8

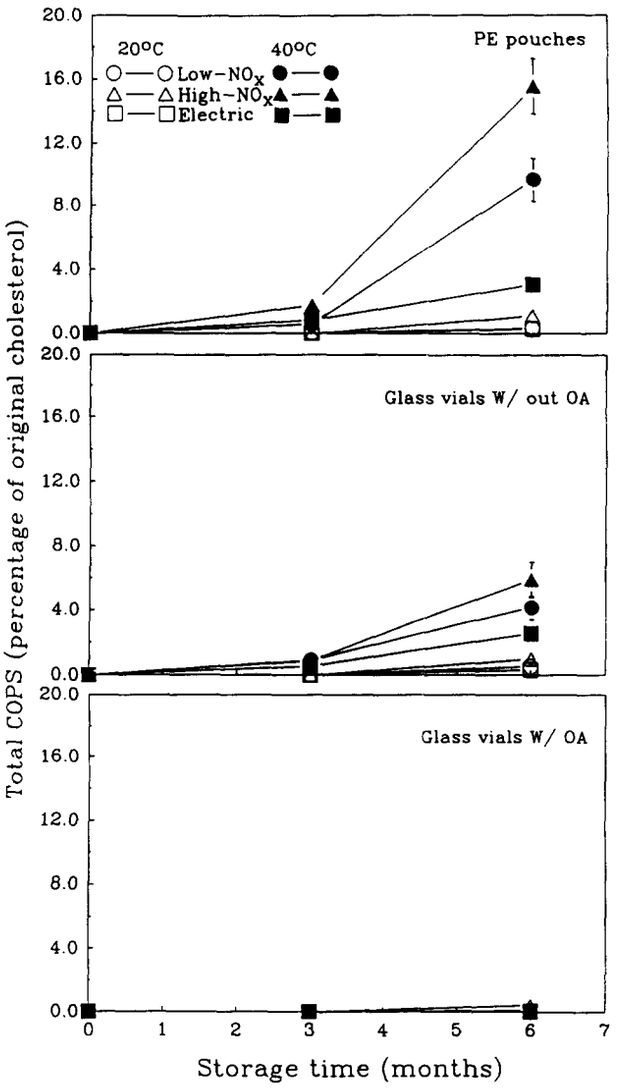

Fig. 1. Total cholesterol oxidation products (COPS) (expressed as a percentage of total cholesterol) in whole milk powders packaged in PE pouches and glass vials, with and without oxygen absorbers (OA), as influenced by storage time and temperature.

and 6·8% after 6 months at 20 and 40°C, respectively. It is likely that the oxygen in the headspace reacted with the whole milk powders and the reaction rate was accelerated by the higher temperature. On the other hand, the headspace oxygen in the glass vials with the oxygen absorbers remained relatively constant during the storage period. The slight increase to 0·24% after 6 months could be attributed to a small leak in the seals of the vials.

Cholesterol oxidation in whole milk powders

Cholesterol oxide formation in whole milk powders during storage, as influenced by packaging and processing, is summarized in Figs 1, 2 and 3. Treatment (processing, packaging, temperature and storage time) effects, as well as significant interactions among treatments, were found ($p < 0·01$). The effect of each individual treatment on COPS formation is discussed as follows.

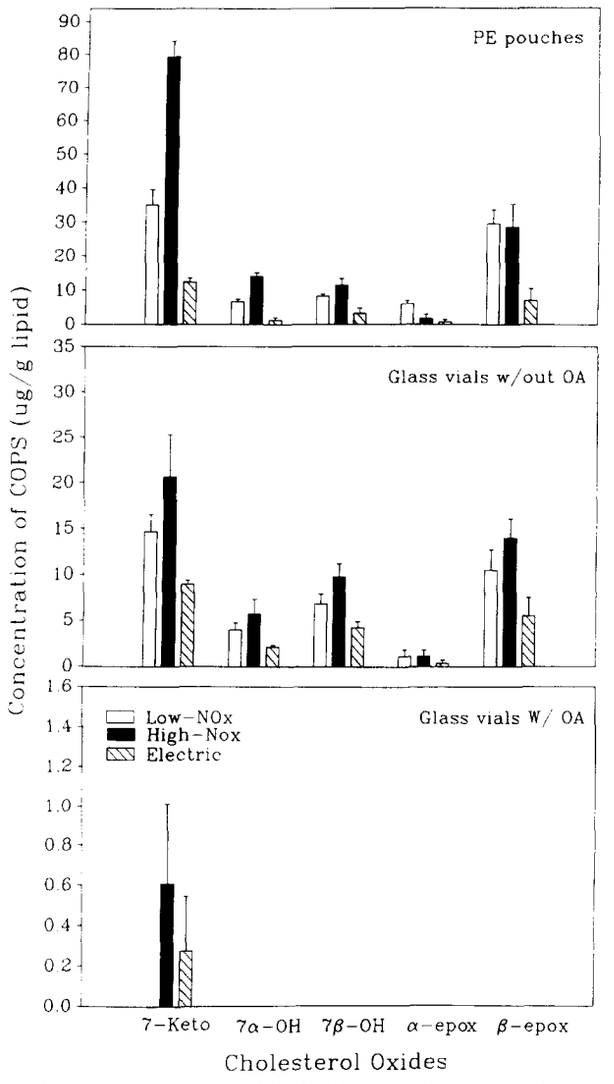

Fig. 2. Concentrations of individual cholesterol oxidation products (COPS) in 6-month old whole milk powders processed by different drying methods, packaged in various packaging systems, and stored at 40°C.

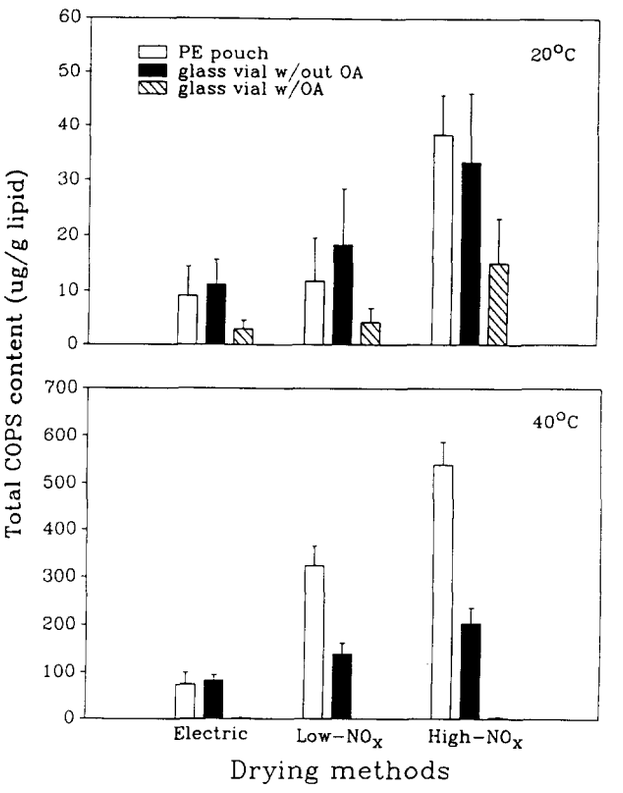

Fig. 3. Total cholesterol oxide concentrations in whole milk powders processed by different drying methods, packaged in various packaging systems, and stored at 20°C and 40°C for 6 months.

Effect of storage conditions

The development of COPS in whole milk powders during storage is shown in Fig. 1. COPS were not detected in freshly processed whole milk powder samples, regardless of drying procedure. These results are consistent with those obtained by Nourooz-Zadeh and Appelqvist (1988). Several COPS were detected in samples stored for 3 months at 40°C, 7-ketocholesterol and the epimeric 7-hydroxycholesterols being the major oxidation products, followed by the isomeric 5,6-epoxycholestanols. After 6 months at 20 and 40°C, all samples showed increased concentrations of COPS.

The predominant COP was 7-ketocholesterol (Fig. 2), an observation similarly reported by Nourooz-Zadeh and Appleqvist (1988). The concentrations of 7β-hydroxycholesterol and β-epoxide were higher than those of 7α-hydroxycholesterol and α-epoxide, respectively. Side-chain hydroxylated cholesterol oxides and 5α-cholestane,3β,5,6β-triol were not detected in the samples. A similar finding was reported by Nourooz-Zadeh and Appleqvist (1988).

The concentrations of C_7 oxidation products represented 0·63 and 2·57% of the cholesterol present in whole milk powders stored for 3 and 6 months, respectively. On the other hand, the concentration of secondary cholesterol oxides accounted for only 0·15 and 1·05% of the original cholesterol in samples stored for 3 and 6 months, respectively. These results suggest that COPS at the allylic position, i.e. C_7, are formed more abundantly than those at the double bond itself, i.e. positions 5 and 6. Smith (1981) noted that this is probably because epoxidation is a secondary process which is dependent upon the presence of 7-hydroxycholesterols. It was observed that 7-ketocholestrol was formed more extensively than any other cholesterol oxide throughout the storage period, especially when the samples were stored at 40°C. This COP represented 39·6% and 48·2% of the total cholesterol oxide concentrations for samples stored at 20 and 40°C, respectively. According to Smith *et al.* (1973), thermal decomposition of C_7 hydroperoxides results in the formation of 7α- and 7β-hydroxycholesterol and 7-ketocholesterol. Therefore, it is assumed that at the higher temperature or in the absence of water, the decomposition of the 7-hydroperoxides via dehydration to 7-ketocholesterol is more likely than the formation of epimeric 7-hydroxycholesterols. Moreover, the concentration of 7β-hydroxycholesterol was predominant over the 7α-hydroxycholesterol, as was β-epoxide over α-epoxide. The ratio of β-epoxide to α-epoxide was approximately 2·9:1, while the ratio of 7β-hydroxy to

7α-hydroxycholesterol was 1·5:1. These data are somewhat similar to the findings of Nourooz-Zadeh and Appelqvist (1988), who reported ratios of 1·6:1 and 1·9:1 for β-epoxide/α-epoxide and 7β-hydroxy/7α-hydroxycholesterol, respectively, in whole milk powders stored for 12 months. These results can be explained by the greater thermodynamic stability of the equatorial conformation over that of the axial conformation (Smith, 1981).

The data presented in Figs 1 and 3 indicate that exposure to the higher temperature (40°C) during storage increased the concentrations of COPS in whole milk powders. The difference between means of temperature treatments was significant ($P < 0·05$). When the samples were packaged in PE pouches or in glass vials without oxygen absorbers, the average concentrations of COPS in samples stored at 40°C for 6 months were approximately twelve times greater than those in samples stored at 20°C. Furthermore, the quantities of secondary cholesterol oxides were increased at 40°C. The rate of formation of 7β-hydroxycholesterol was greater than that of the β-epoxide at 20°C; however, β-epoxide was formed in higher quantities than 7β-hydroxycholesterol when the samples were stored at 40°C. Because β-epoxide is a secondary oxidation product of cholesterol, it is apparent that the elevated temperature accelerated the oxidative process. Smith (1981) indicated that the exposure of cholesterol to high temperatures for a relatively long period in the presence of oxygen may initiate the allylic free-radical reaction at C_7. Following the formation of C_7 peroxy radicals, a series of free-radical reactions take place which results in the formation of stable oxidative products. Thus, storage of samples at 40°C leads to a more intense oxidative degradation of cholesterol than when stored at 20°C.

Effect of drying method

The absence of COPS in freshly processed whole milk powder samples indicated that the drying method initially had no influence on the presence of COPS in fresh products. Similar results were found for samples stored for 3 months at 20°C. Although COPS were detected in the samples stored at 40°C for 3 months, the drying methods did not show any significant effect ($P < 0·05$) on COPS formation. After 6 months at 20°C, powders prepared by direct high NO_x gas-fired heating had the greatest COPS content, followed by samples produced by the direct low NO_x gas-fired and indirect electrical heating systems. Nevertheless, there was no significant difference among the means. The methods of drying, however, did significantly ($P < 0·05$) affect the concentrations of COPS in whole milk stored at 40°C for 6 months (Figs 1 and 2). Total COPS in powders manufactured by the direct high NO_x gas-fired heating process increased rapidly from 59·5 μg/g lipid after 3 months to 540 μg/g lipid after 6 months for samples packaged in PE pouches. COPS concentrations in samples packaged in glass vials without oxygen absorbers increased from 29·7 to 204 μg/g lipid over the same time period at 40°C. Powders prepared by the direct low NO_x gas-fired heating process followed a similar pattern but had smaller concentrations of COPS. There was only a relatively small change in the total cholesterol oxide contents of powders produced by indirect electrical heating compared to those from direct gas-fired heating.

The greater concentrations of COPS in direct gas-fired whole milk powders is related to the processing conditions which generated greater quantities of NO_x, known initiators of lipid oxidation. During processing of the milk powder samples, NO_x levels were quantitated using Draeger tubes (Kelly, P. M. pers. comm.). For the low NO_x gas burner, the levels of NO_x in the flue gases at the burner throat were between 1 and 1·65 parts per million (ppm). Following dilution with drying air, the levels of NO_x were between 0·13 and 0·23 ppm (Kelly *et al.*, 1989). For the high NO_x burner, the levels of NO_x were 8 ppm in the air at the inlet of the dryer. For the electrical heated system, the level of NO_x was 0·5 ppm. Thus, the concentration of NO_x in the drying air and the resultant concentrations of nitrite and nitrate (data not presented) in powders prepared by the different drying processes tended to be parallel to lipid oxidation as measured by TBARS and the formation of cholesterol oxides.

Effect of packaging

The extent of cholesterol oxidation in whole milk powders was related to the packaging conditions (Fig. 3). The interactions between packaging and processing, temperature and storage time were significant ($P < 0·01$). Samples packaged in PE pouches had the greatest concentrations of COPS, while those in the glass vials with oxygen absorbers had the smallest concentrations. Total COPS in milk powders processed by direct high NO_x gas-fired heating and packaged in PE pouches increased from 1·7% of the original cholesterol content after 3 months at 40°C, to 15·6% after 6 months (Fig. 1). In the glass vials without oxygen absorbers, the milk powders processed by the same drying procedure had COPS concentrations of 0·86 and 5·9% of the original cholesterol after 3 and 6 months of storage, respectively (Fig. 1). In the packaging system with oxygen absorbers, the cholesterol oxidation products accounted for only 0·07% of the total cholesterol content after 6 months of storage at 40°C (Fig. 1).

Considering the interaction of packaging and processing, powders produced by direct gas-fired heating and packaged in PE pouches contained the greatest concentrations of COPS, followed by the samples packaged in glass vials without oxygen absorbers (Fig. 3). Moreover, samples produced by the direct high NO_x gas-fired heating system had greater concentrations of cholesterol oxides than those from the direct low NO_x gas-fired heating system. Samples prepared by indirect electrical heating and packaged in PE pouches or in the system without oxygen absorbers achieved moderate levels of oxidation of cholesterol, but there was no

significant difference between the mean values at the 95% confidence level. In the packaging systems with the oxygen absorbers, samples showed the least extent of cholesterol oxidation, irrespective of the drying method used.

As discussed above, COPS started to appear in detectable concentrations in samples packaged in PE pouches and glass vials without oxygen absorbers after 3 months, and the amounts increased substantially over the next 3 months. On the other hand, the oxygen absorbers effectively prevented oxidative changes in cholesterol during the entire storage period. Thus, the oxygen content in the headspace plays an important role in determining the susceptibility of cholesterol to oxidation, and the formation of cholesterol oxides could be significantly minimized by packaging whole milk powders in gas-impermeable packaging systems including oxygen absorbers.

Lipid oxidation in whole milk powders during storage

Many methods have been developed to measure lipid oxidation in food products, including the TBA test, peroxide value, carbonyl measurement, oxygen absorption and sensory assessment. Tuohy (1987) evaluated several methods for quantitating lipid oxidation in milk powders and concluded that the TBARS values was a better index of milkfat oxidation than the measurement of other oxidation parameters. Based on these results, only the TBA procedure was used to measure lipid oxidation in this study.

Effect of storage conditions

The accelerating effect of temperature on lipid oxidation in whole milk powders packaged in PE pouches and in glass vials with and without oxygen absorbers was reflected in the development of TBARS (Fig. 4). The initial TBARS values of whole milk powder samples produced by indirect electrical heating, direct low NO_x gas-fired and direct high NO_x gas-fired heating were 0·11, 0·12 and 0·13, respectively. These results generally agree with the values reported by Mettler (1973).

The change in TBARS values of the milk powders with storage time was very distinct. During storage, the TBARS values increased in a linear manner for the sample packaged in PE pouches and glass vials without oxygen absorbers. Significant correlations of 0·87 and 0·96 were found between TBARS values and storage time at 20 and 40°C, respectively. However, a poor correlation (r = 0·55) between TBARS values and storage time was found in the samples packaged in glass vials with oxygen absorbers.

As expected, TBARS values of the powders stored at 40°C increased more rapidly than those of samples stored at 20°C (Fig. 4). The means were significantly different (P < 0·01). However, the higher temperature did not influence TBARS development in powders packaged in glass vials with oxygen absorbers (Fig. 4). After 6 months, the TBARS values of powders manufactured by direct high NO_x gas-fired heating, packaged

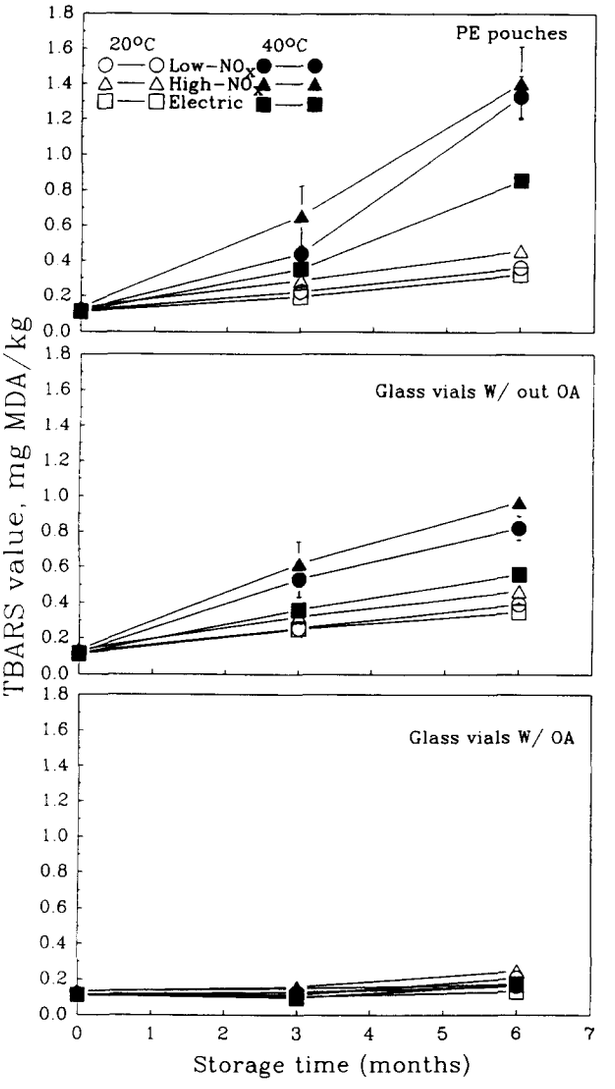

Fig. 4. Development of TBARS (expressed as malonaldehyde (MDA)/kg sample) in whole milk powders during storage as influenced by method of drying, packaging system and storage temperature.

in PE pouches, and stored at 20 and 40°C, were 0·45 and 1·41, respectively. When the same powders were packaged in glass vials without oxygen absorbers, similar results were observed. On the other hand, there was only a slight decrease in TBARS values when the samples were packaged in glass vials with oxygen absorbers and stored at 40°C, compared to samples stored at 20°C.

General rates of lipid oxidation were obtained by comparing the TBARS values of samples stored at 40°C to those at 20°C. An average factor of 1·64 per 10°C was estimated for TBARS development in the samples packaged in PE pouches over the storage period. However, a mean value of 1·01 per 10°C was found for the samples packaged in glass vials without oxygen absorbers. An average value of 0·48 per 10°C was observed for samples packaged in glass vials containing oxygen absorbers. Because the oxygen absorbers reduced the oxygen content of the headspace to a limiting amount of oxygen, the rate of lipid oxidation in whole milk powder was considerably reduced.

Influence of drying method

The initial TBARS values of whole milk powder samples produced by the three drying methods were not significantly different from each other. However, during the subsequent storage of the powders, it was observed that the drying method had a significant effect ($P < 0.05$) on TBARS development. In addition, the interactions between drying method and temperature of storage, drying method and packaging, drying method and storage time, were also pronounced.

Whole milk powder produced by direct high NO_x gas-fired heating deteriorated at a faster rate than powders from direct low NO_x gas-fired and indirect electrical heating systems (Fig. 4). Powders manufactured by direct high NO_x gas-fired heating and stored at 40°C had the highest TBARS values. Alternatively, samples produced by indirect electrical heating and stored at 20°C showed the least increase in TBARS values over the storage period. After 6 months at 40°C, samples produced by direct high NO_x gas-fired heating and packaged in PE pouches had an average TBARS value of 1·41 compared to values of 1·33 and 0·86 for the direct low NO_x gas-fired and indirect electrical heating powders, respectively. These data were significantly different ($P < 0.05$). When the samples were packaged in glass vials without oxygen absorbers, the development of TBARS showed a similar pattern, although the values were somewhat lower. However, there was only a relatively small change in TBARS values for powders packaged in the glass vials with oxygen absorbers. In these cases, the influence of drying methods was not significant ($P < 0.05$), even in those samples stored at 40°C.

Using the TBARS value as an index of lipid oxidation, it is apparent that whole milk powder manufactured by electrical heating had the best oxidative stability, followed by powders produced by direct low NO_x and high NO_x gas-fired heating. It is assumed that the levels of nitrogen oxides generated during the drying processes are mainly responsible for the difference in lipid oxidation in the powders (Lightsey, 1982; Missler *et al.*, 1985). The initiation of oxidation in model systems of lipids and cholesterol by oxides of nitrogen has been demonstrated by Kamel *et al.* (1971), Rhoem *et al.* (1971) and Smith (1981). Thus, the difference in the levels of nitrogen oxides formed during processing seems to be an important factor influencing the oxidative stability of the whole milk powders during storage.

Influence of packaging

The effect of packaging on the development of TBARS in whole milk powders produced by the various drying methods was significant ($P < 0.05$). TBARS values were greatest in samples packaged in PE pouches, followed by the samples packaged in glass vials without and with oxygen absorbers. When whole milk powder was packaged in PE pouches and stored at 40°C, a large increase in TBARS value was noted, irrespective of the drying method used (Fig. 4). A similar pattern

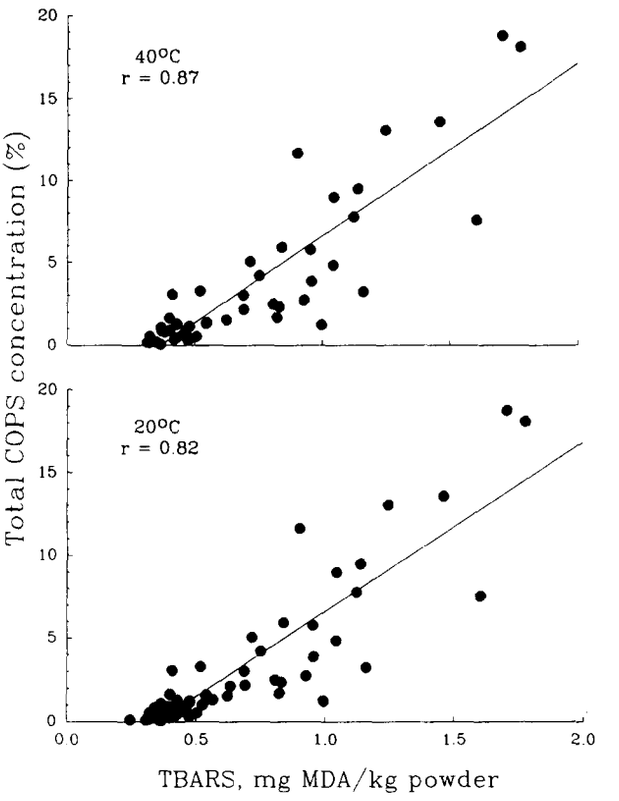

Fig. 5. Relationship between TBARS and total COPS formation (expressed as a percentage of total cholesterol) in whole milk powders processed by different drying methods when packaged in various packaging systems and stored at 20°C and 40°C for 6 months.

was observed for powders packaged in glass vials without oxygen absorbers, although the extent of oxidation was not as great as in powders packaged in PE pouches (Fig. 4). This difference was attributed to a lower oxygen content in the headspace of the glass vials. As discussed earlier, the connection of oxygen in the headspace of PE pouches was almost equal to that in the atmosphere. Therefore, powders packaged in PE pouches were continuously exposed to oxidative attack by atmospheric oxygen. In glass vials, however, the oxidative reaction could be attributed to the oxygen incorporated in the powder particles and the residual oxygen in the headspace. Furthermore, the larger surface area of the PE pouches could provide more access for the interaction of headspace oxygen and the powered milk samples (Nawar, 1985). On the other hand, TBARS development in samples in the packaging system containing the oxygen absorbers did not show the same trend as in those samples packaged in the other two systems (Fig. 4). These results demonstrated that oxygen absorbers effectively retard or delay lipid oxidation in whole milk powders during storage, regardless of the processing method used.

Correlation of TBARS values and cholesterol oxide concentrations

Generally, the changes in cholesterol oxide content during storage agreed with those for the TBARS values

for all treatments, except for the samples packaged in glass vials with oxygen absorbers (Fig. 5). Correlations of 0·86, 0·82 and 0·79 were found between the TBARS values and the total cholesterol oxide contents in whole milk powders manufactured by direct high and low NO_x gas-fired heating and indirect electrical heating, respectively. These results indicate that the rate of cholesterol oxidation in whole milk powder is proportional to milkfat oxidation under storage and packaging conditions with sufficient headspace oxygen.

CONCLUSION

This study has revealed that the oxidation of cholesterol in whole milk powders can be minimized by the use of oxygen-impermeable packaging systems containing oxygen absorbers, or by using drying processes that generate low levels of NO_x. Studies are needed to further evaluate rigid packaging systems with oxygen absorbers as a method of reducing lipid oxidation, including cholesterol oxidation, in whole milk powders during manufacture and distribution.

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