

CHAPTER II

Preventing Oxidation of Dairy Powders Using Oxygen Removal Packaging

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Abstract:

Three types of dried milk (whole, nonfat, and buttermilk) were packaged in a modified atmosphere with a novel palladium-based oxygen removing catalyst and stored for eight weeks at 50°C. Powders stored in air with no catalyst and powders stored with the catalyst in an atmosphere modified to contain 5.7% hydrogen in nitrogen were evaluated by instrumental, chemical, and sensory methods.

Hexanal concentrations were measured weekly using SPME and GC to compare the degrees of oxidation in the powders stored with the catalyst to those stored without it. Color changes were also monitored weekly using Hunter's L-, a-, and b-values. At the end of the eight-week period, a paired comparison sensory test was used to ascertain if the catalyst had an effect on odor. Anisidine values were also measured at this point to determine levels of oxidation in the powders.

No significant difference was found in levels of oxidation between samples packaged with and without the catalyst in the modified atmosphere. At the end of eight weeks, the average hexanal concentration in the whole milk powder stored with the oxygen scavenger was 1.19 ± 0.20 ppm, while the average hexanal concentration in the air-packed whole milk powder was 1.06 ± 0.08 ppm. The average hexanal concentrations for the buttermilk stored with the catalyst and without were 0.84 ± 0.18 and 0.79 ± 0.15 ppm, respectively. In the nonfat milk powder, the sample stored with the catalyst had an average hexanal concentration of 0.91 ± 0.14 ppm and the sample

stored in air without the catalyst had an average hexanal concentration of 0.83 ± 0.20 ppm. Difference testing by volunteer sensory panelists also revealed no significant differences.

It was expected that the milk powders stored with the catalyst in the modified atmosphere would have lower levels of oxidation and off-odors at the end of the eight weeks. However, the treatment ultimately resulted in no chemical or sensory differences. Thus, the catalyst proved ineffective in the given conditions. This could be due to a loss of the hydrogen required for the catalyst to function as time progressed or a lack of significant oxidation under the conditions employed.

Key words: lipid oxidation; powdered milk; oxygen catalyst; modified atmosphere packaging

Introduction:

Dairy powders are extremely useful products and, as this realization grows, so does the demand for a high quality product (IDFA, 2005; USDA-FAS, 2006). Consumers can benefit from the durability, convenience, and stability to microbial spoilage of these products (Shiratsuchi et al., 1994b; Schwambach and Peterson, 2006). The powders are particularly advantageous to those in developing countries because of reduced transport and storage costs.

Unfortunately, since these dairy products have been dried, they are more vulnerable to spoilage via lipid oxidation (Lillard, 1978; Shipe et al., 1978; Forss, 1979; Wills and Cheong, 1979; Heath and Reineccius, 1986; Grosch, 1987; Stapelfeldt et al., 1997). Hydroperoxides, the primary products of lipid oxidation, are decomposed into low molecular weight carbonyls; these compounds are responsible for the off-odor and flavor of oxidized milk (Shiratsuchi et al., 1994a; Andersson and Lingnert, 1998; van Aardt et al., 2001; Karagul-Yuceer et al., 2002). Thus, packaging of milk powders becomes very important. By adding an oxygen catalyst (which works by accelerating an oxygen-consuming reaction) to a sealed package, the problem-causing oxygen can potentially be eliminated before its deleterious effects can take place (Grattan and Gilberg, 1994; Lloyd et al., 2004; Charles et al., 2006; Robertson, 2006). Finding an appropriate oxygen remover to use for a dry product is important, and several systems exist. Absorbers differ from catalysts in that absorbers consume oxygen only until they reach a certain limit. Further, most absorbers and catalysts currently available require moisture to be effective. A catalyst that would work in dry conditions and without a finite capacity would be ideal for extending the shelf life of dairy powders.

The focus of this research is to determine if using a novel palladium catalyst is an effective and reasonable method for slowing or possibly eliminating oxidation in non-permeable packages of various dairy powders. The effectiveness of this unique catalyst is determined by the amount of hydrogen available in the environment. By comparing samples containing the catalyst to samples stored without it, an idea about its functionality can be obtained. If the catalyst is successful, its unique attributes could be applied to various other dried products that are often spoiled by lipid oxidation.

Materials and Methods:

Dairy Powders:

Freshly made samples of nonfat milk powder (NMP) (1% milk fat), buttermilk powder (BMP) (2.4% milk fat), and whole milk powder (WMP) (24.5% milk fat) were obtained from Land O'Lakes, Inc. (St. Paul, MN). Upon receipt, all milk was stored for three weeks in the dark at room temperature until experimentation commenced. Approximately 20 kg of each milk powder were needed for the entire experiment, which was replicated twice.

Oxygen Absorber:

Palladium-based oxygen absorbers were obtained from EMCO Packaging Systems, Ltd. (Kent, UK). The reactive substance is anchored into a non-woven matrix and covered with a gas-permeable membrane. One requirement for activation of the catalyst is an atmosphere modified to contain 5.7% hydrogen in nitrogen. This percentage is the maximum amount permitted by both the United States and United Kingdom in order to ensure safe experimentation and no explosion hazards. When palladium is exposed to the hydrogen and any oxygen in the headspace of the packaged powder, it effectively works to catalyze the formation of water until all the hydrogen or oxygen is used up; thus, the limiting factor is either hydrogen content or the complete removal of oxygen. The small amount of water that is formed reaches equilibrium throughout the system.

Sample Preparation:

For each type of powder, samples of 50 g were placed into 240 mL gas-tight Mason jars (Ball, Muncie, IN) with a threaded closure and metal lid and screw cap that were designed to be hermetically sealed. A 2.54 cm x 2.54 cm square of the palladium-based oxygen catalyst was added to half of the jars, with the other half containing samples sealed in air and receiving no catalyst. A hole (0.2 cm) was drilled in the lid of every jar. The jars were covered with aluminum foil to protect from light and those containing the scavenger were sealed with a modified atmosphere of 5.7% hydrogen in nitrogen (Airgas, Inc., Duluth, GA) using a vacuum packaging machine (Koch Supplies, Inc., Model x-200, Kansas City, MO). To flush and seal, four jars with the lids and rings tightly in place were placed in the machine. The holes in the lids were left uncovered so the air in the jars could be flushed. A 99% vacuum was obtained,

followed by a 30% gas flush using the special gas mixture. This was done twice in quick succession, and pieces of aluminum tape were placed over the hole in the lid immediately following the second flushing. The flushing served two purposes—it reduced the amount of oxygen in the headspace and supplied the hydrogen needed for the catalyst to be effective. To ensure that the atmosphere had been adequately modified, two jars were arbitrarily selected for headspace analysis. It was found that oxygen in the jars was lowered to an average of $3.15 \pm 0.5\%$. All samples were randomly positioned and stored in the dark.

Treatments:

On day 0, 32 jars of each type of powder (whole, buttermilk, and nonfat) were filled. Half of the jars for a given milk powder (16) were sealed in air with no oxygen catalyst. The other half received the oxygen catalyst and the modified atmosphere of 5.7% hydrogen in nitrogen. All of the jars were stored at $50 \pm 1^\circ\text{C}$. After some preliminary testing to find an appropriate storage temperature, 50°C was chosen to magnify the treatment effects without causing too much degradation in the powders (Nielsen et al., 1997; van der Merwe et al., 2003).

Testing:

Each week for two months, three randomly selected jars of each product were removed from incubation. A single jar was subjected to only one test—either a measure of the hexanal concentration or an assessment of headspace oxygen was performed. Only one test was done on a single jar because the headspace inside the jar became compromised upon puncture of the aluminum tape. Following analysis, the sample was no longer needed and was discarded. In two of the three jars, hexanal concentration was measured by extracting samples of headspace gas through the pre-drilled hole. The oxygen content in the headspace of the third randomly selected jar from each treatment was tested to ensure that the seal was sufficiently holding and to monitor the effectiveness of the catalyst.

Hexanal Concentration:

Following a modified version of a solid phase microextraction (SPME) technique (Marsili, 2000), a 75 um Carboxen/polydimethylsiloxane (PDMS) SPME fiber (Supelco, Bellefonte, PA) was exposed to the sample headspace through the pre-drilled hole with the end of the fiber about

2 cm above the surface of the milk powder. This fiber was selected for its ability to detect trace levels of volatiles (Fenaille et al., 2001; Perkins et al., 2005). The SPME unit was clamped in this position in the 50°C incubator for 30 minutes before the fiber was transferred to a gas chromatograph (HP 5890, Hewlett-Packard Co., Palo Alto, CA) equipped with a flame ionization detector, using a 25m x 0.32 mm (5% phenyl)-methylpolysiloxane silicone column. This non-polar column was chosen for its low bleed characteristics and inertness. Helium flow was 1.0 mL/min. The oven temperature remained at 100°C for 10 minutes before ramping to 250 °C at 25 °C/minute and remaining at 250 °C for 5 minutes to clean the column. The injector and detector temperatures were 200 and 250 °C, respectively. The hexanal peak was identified using a standard compound (Aldrich Chemical Company, Inc., Milwaukee, WI). Hexanal concentrations were quantified using a calibration curve. Stock solutions consisted of concentration levels of 0.1, 1, 5, 10, and 100 ppm.

Headspace Oxygen:

Headspace oxygen was monitored using a CheckPoint™ gas analyzer (PBI-Dansensor, Glen Rock, NJ). The probe was calibrated and then inserted through the aluminum tape and into the headspace. Readings were immediately taken for each sample. To prevent the probe from clogging, which would compromise the measurements, it was reamed with a thin wire between each sample.

Color:

The Hunter's L-, a-, and b-values for all samples were read using a colorimeter (Minolta CR-300, Konica Minolta Sensing Americas, Inc., Ramsey, NJ). The instrument was calibrated with a white calibration tile before being used each day. Comparisons were made between powders stored with the scavenger and those without.

Anisidine Value:

Anisidine value (AV) is quick, simple, and particularly well-suited for measuring 2-alkenals, which are the major contributors to off-flavors in dairy powders (White, 1995). AV was tested at the end of the two-month period and values for powders packaged with the oxygen absorber were compared to those stored without it.

Following the AOCS Official Method Cd 18-90 for p-anisidine value, 0.5 g of each sample was weighed out into a 25-mL volumetric flask, dissolved, and diluted to volume with isoctane. The absorbance was read at 350 nm using a Shimadzu UV-2101PC Scanning Spectrophotometer (Shimadzu Scientific Instruments, Inc., Columbia, MD). Exactly 5.0 mL of the sample solution was pipetted into one test tube and 5.0 mL of the solvent went into a second test tube. Next, 1.0 mL of a p-anisidine reagent was added to each tube and mixed. After 10 minutes, the absorbance at 350 nm of the solvent in the first test tube was measured, using the solution from the second test tube as a blank. (AOCS, 1998)

Sensory Evaluation:

Using the SIMS 2000 program (Version 6, 2007, Sensory Information Management Systems, Morristown, NJ), a forced paired comparison test was performed. Fifty (50) volunteer panelists were given two samples of powder and asked to identify the sample with the greater oxidized off-odor. Panelists were mostly faculty, staff, and students of Food Science and Technology and were all over 18 years of age. They were screened to ensure that they had an understanding of the characteristics of oxidation and given an informed consent statement to sign.

The testing was performed in the sensory laboratory of the Food Science and Technology building on the Virginia Tech campus. The final samples of each type of milk receiving similar treatments were combined, giving six different groups of powder. For the evaluation, one-ounce sample cups received one tablespoon of powder and were covered with a lid. Each sample tray held six randomly coded samples, with the two samples containing a particular powder being placed side by side. The order of presentation was executed as instructed by the SIMS 2000 program. SAS Version 9.1 (2007, SAS Institute, Inc., Cary, NC) was used to analyze the data. A two-tailed analysis was used to determine the p-value based on number of correct responses.

Statistical Analysis:

To determine the effect of the oxygen catalyst on oxidation of the milk powders, results were analyzed as a split-plot design using the type of milk (whole, nonfat, or buttermilk) as the whole plot, and treatment (air headspace with no catalyst or modified atmosphere with catalyst) and week of storage (1-6) as subplots. The General Linear Model (GLM) procedure prepared by SAS was used to determine the effect of the catalyst on hexanal content in the headspace. Means

were compared using the least significant difference test. Significant differences were defined at $P < 0.05$ (SAS Version 9.1, 2007, SAS Institute, Inc., Cary, NC).

Results & Discussion:

If an appropriate atmosphere was obtained and held in the headspace of the jars containing the palladium oxygen catalyst, it was expected that the level of oxidation would be lower than in the powders with no modifications. This would be indicated by the amount of hexanal formation as determined by SPME/GC testing. Further, increased development of other secondary lipid oxidation products would be seen using anisidine values. Also, if the catalyst worked as expected, testing of the headspace oxygen in the treated jars should reveal progressively lower measurements until all the oxygen reacted with the hydrogen in the modified atmosphere and became converted into water.

Color change is a good indicator of degradation due to the Maillard reaction and is expected with the temperature abuse to which the powders were subjected. Also, as human threshold for odor is often the best test for rancidity, using a sensory panel should also reveal any differences between the air headspace samples and those receiving the modified atmosphere and oxygen catalyst.

Statistical analysis of the data obtained in the experiment revealed that there was no significant difference due to repetition ($p = 0.27$). Data from the replications were combined and the results expressed as the mean and standard deviation.

Headspace Oxygen:

In order to ensure that a proper seal was being maintained and that the altered environment remained as it should, jars were pulled for headspace oxygen testing. A low oxygen content verified that the seal was indeed holding. **Figure 2** shows that the jars receiving the modified atmosphere packaging did retain low levels of oxygen in the headspace. The averages for the headspaces in the jars containing the catalyst were 6.5% for the whole milk powder, 8.3% for the buttermilk powder, and 9.3% for the nonfat milk powder. There were occasional leaks. It is also seen that the jars packed in air kept an oxygen content of around 20.9%, which is to be expected. Interestingly, the headspace above the whole milk powder stored without the oxygen catalyst decreased in oxygen content at the beginning of the test period and stayed at that somewhat lower level. This indicates that some oxygen was consumed in the oxidation reactions occurring

in the whole milk powder. This consumption was not observed in the buttermilk or nonfat milk powders, which is most likely due to the different lipid profiles of the various types of milk powder (deMan, 1999; Commission, 2007).

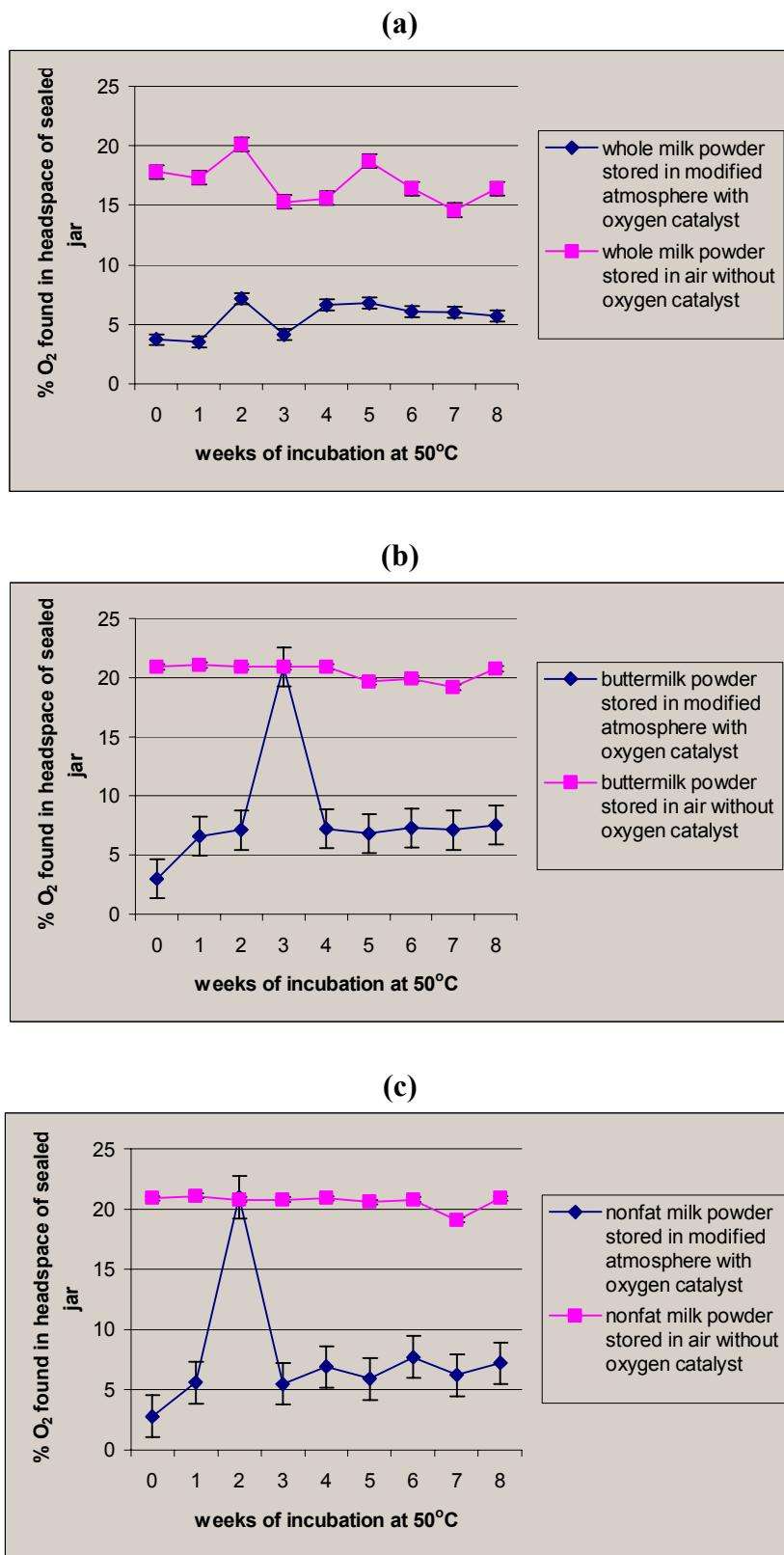


Figure 2. Headspace oxygen content in (a) WMP, (b) BMP, and (c) NMP sealed in 240 mL glass jars for 8 weeks

Hexanal Concentrations:

Since hexanal has been proven to have a strong correlation with oxidative rancidity in milk powders, its formation was monitored to give an indication of the degree of lipid oxidation (Barrefors et al., 1995; Ulberth and Roubicek, 1995; Andersson and Lingnert, 1997; Berenzon and Saguy, 1998; Karagul-Yuceer et al., 2002). Further, based on previous research, SPME using a Carboxen/PDMS fiber has been found to exhibit the greatest sensitivity for low molecular weight analytes, such as hexanal (MW=100 g/mol). Amounts of hexanal in jars of each treatment were measured weekly for eight weeks. No real trends emerged over the eight weeks, and it is obvious that the hexanal levels in the air headspace samples did not differ greatly from levels in the active-packaged samples, as was expected. **Figure 3** seems to show a decrease in hexanal with time, which would indicate that the gas was somehow escaping from the jar or reacting with proteins present in the dried milk. However, this is refuted by the headspace oxygen readings taken on the final week. Since the oxygen levels were still at relatively low levels, it can be concluded that there was not a leak in the system. A better explanation for the disappearance of hexanal would be that it became bound to the proteins present in the milk powders.

Another explanation for the amount of oxygen remaining in the headspace in spite of the presence of the catalyst is an insufficient amount of hydrogen in the headspace. The initial oxygen content measurements indicate that the percent oxygen in the headspace at the beginning of the experiment was consistently reduced to $3.15 \pm 0.5\%$. This means that the headspace mixture was about one part oxygen and four parts special hydrogen-nitrogen gas mixture. Estimating that the headspace was around 118.28 mL and knowing that the special mixture was 5.7% hydrogen in nitrogen, simple calculations lead to a measurement of 5.39 mL (240.5 umol) of hydrogen in the headspace, around 4.85%. Similar calculations lead to a measurement of 4.73 mL (211 umol) of oxygen contained in the headspace. Thus, there should be more than enough hydrogen in the headspace to react with the oxygen and form water.

Therefore, barring flaws in the sampling procedure or analysis, the remaining justification for the continued presence of oxygen in the headspace of the treated samples is that the catalyst is insufficient in these conditions.

Using the GLM to analyze the resulting data, no significant difference was found in the powders (WMP, BMP, and NMP) stored in air with no oxygen catalyst and those stored in the modified atmosphere with the catalyst ($p = 0.08$).

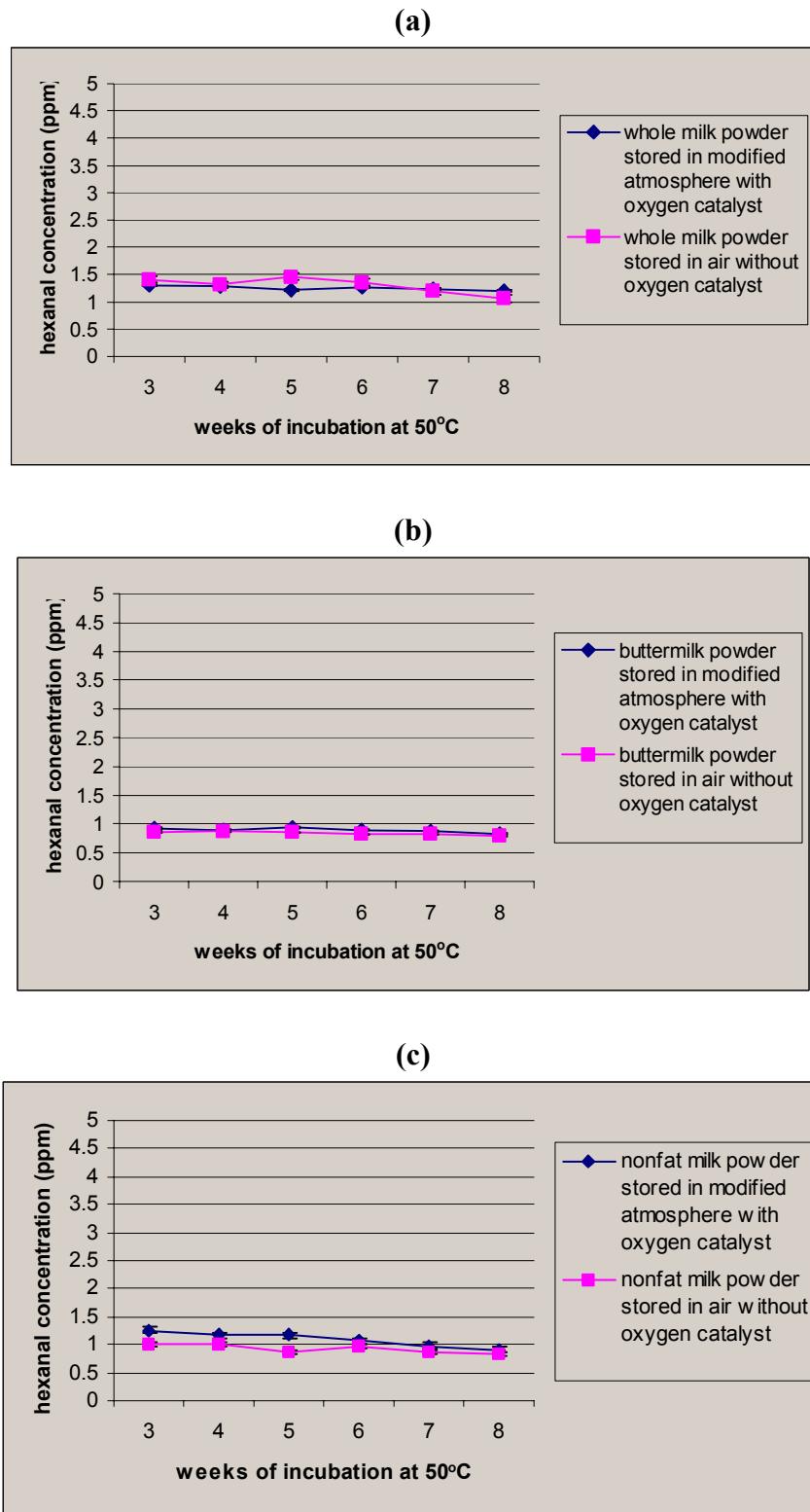


Figure 3. Headspace hexanal concentration in (a) WMP, (b) BMP, and (c) NMP sealed in 240 mL glass jars for 8 weeks

Anisidine Values:

The formation of secondary lipid oxidation products was measured using anisidine values. Not only were the values extremely minute, but there was also little to no difference between samples stored with the oxygen catalyst and those stored without it (see **Figure 4**).

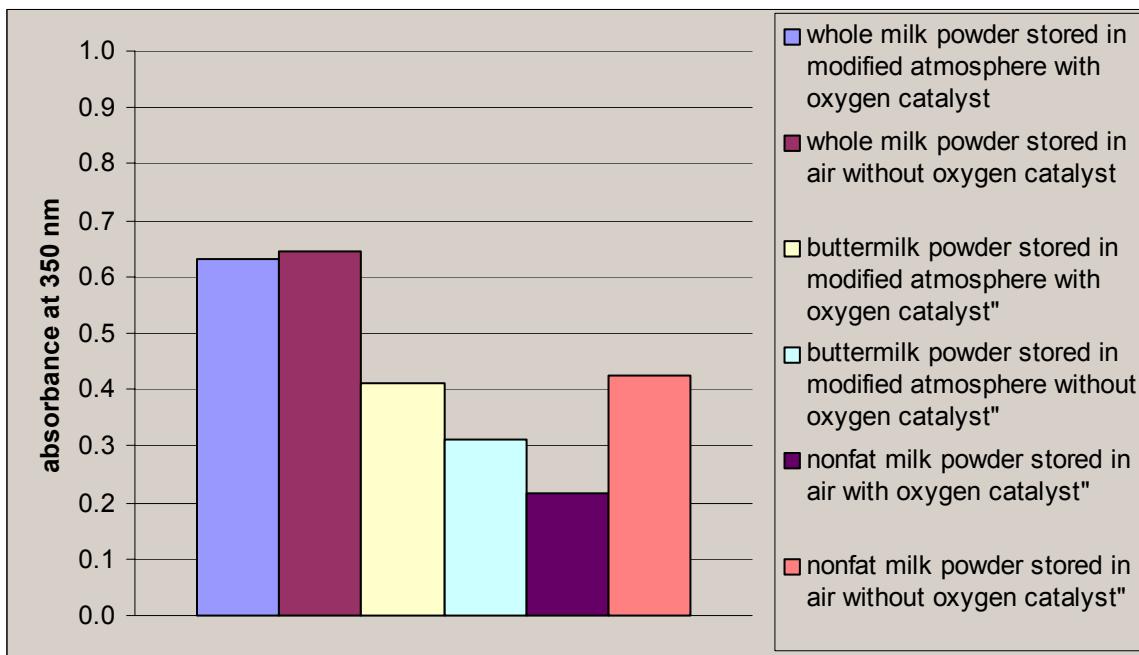


Figure 4. Anisidine values of milk powders sealed in 240 mL glass jars at 8 weeks of storage at 50°C

Color Testing:

No real trends were seen in Hunter L, a, or b values for the samples. **Figures 5-7** show the weekly measurements. Samples stored with the catalyst showed no blatant differences from those stored without.

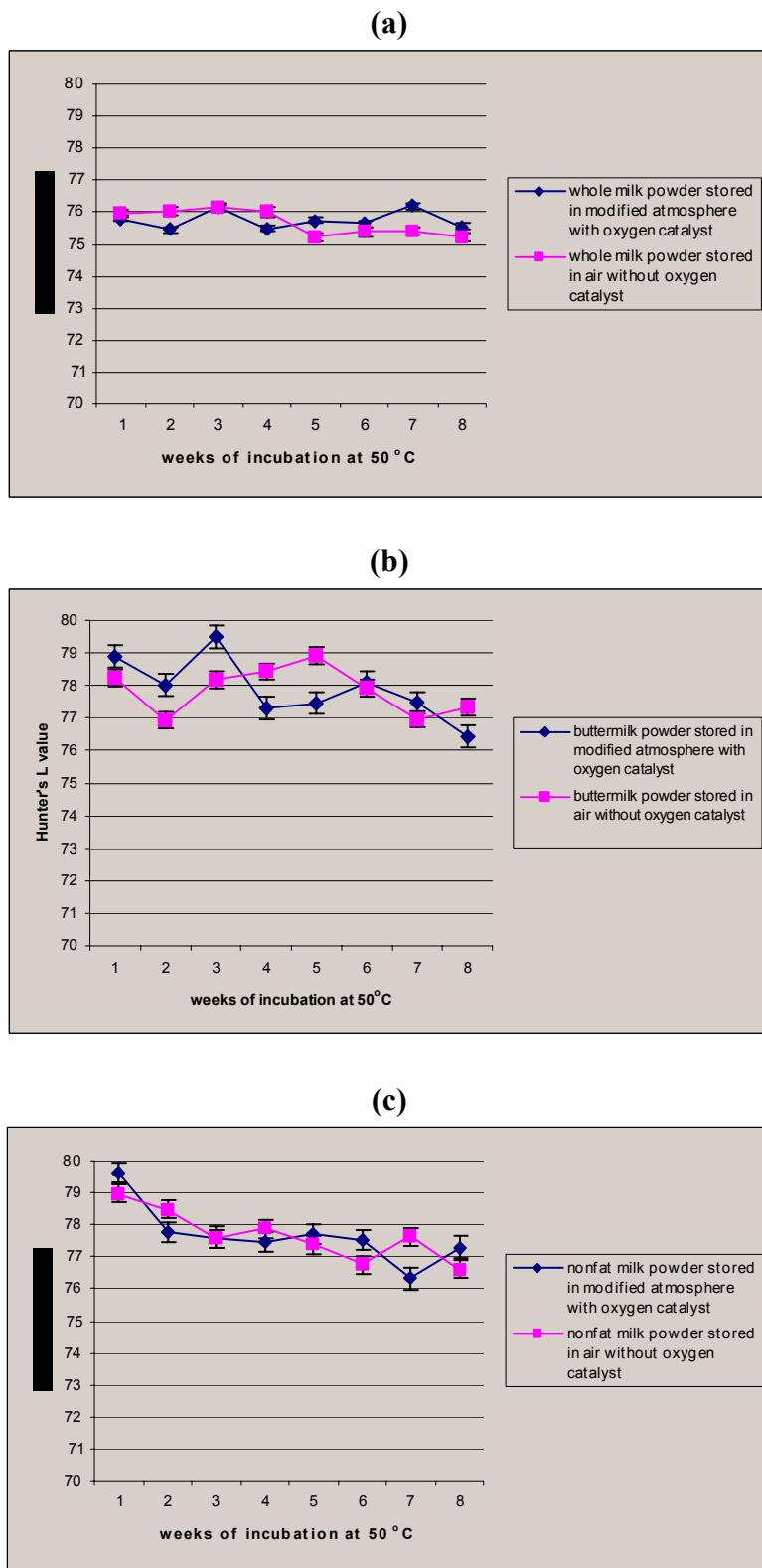


Figure 5. Hunter L value of (a) WMP, (b) BMP, and (c) NMP sealed in 240 mL glass jars for 8 weeks

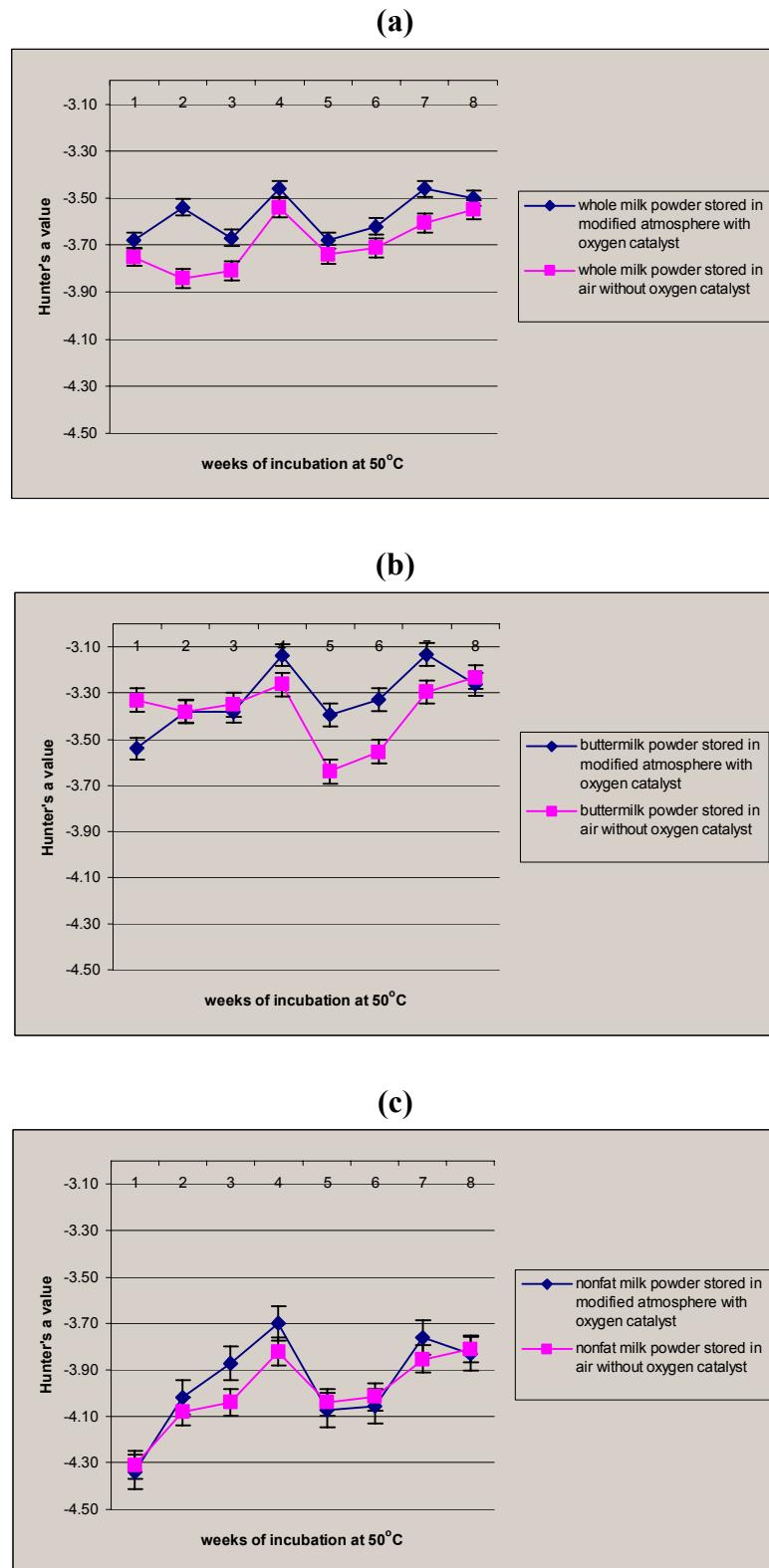


Figure 6. Hunter a value of (a) WMP, (b) BMP, and (c) NMP sealed in 240 mL glass jars for 8 weeks

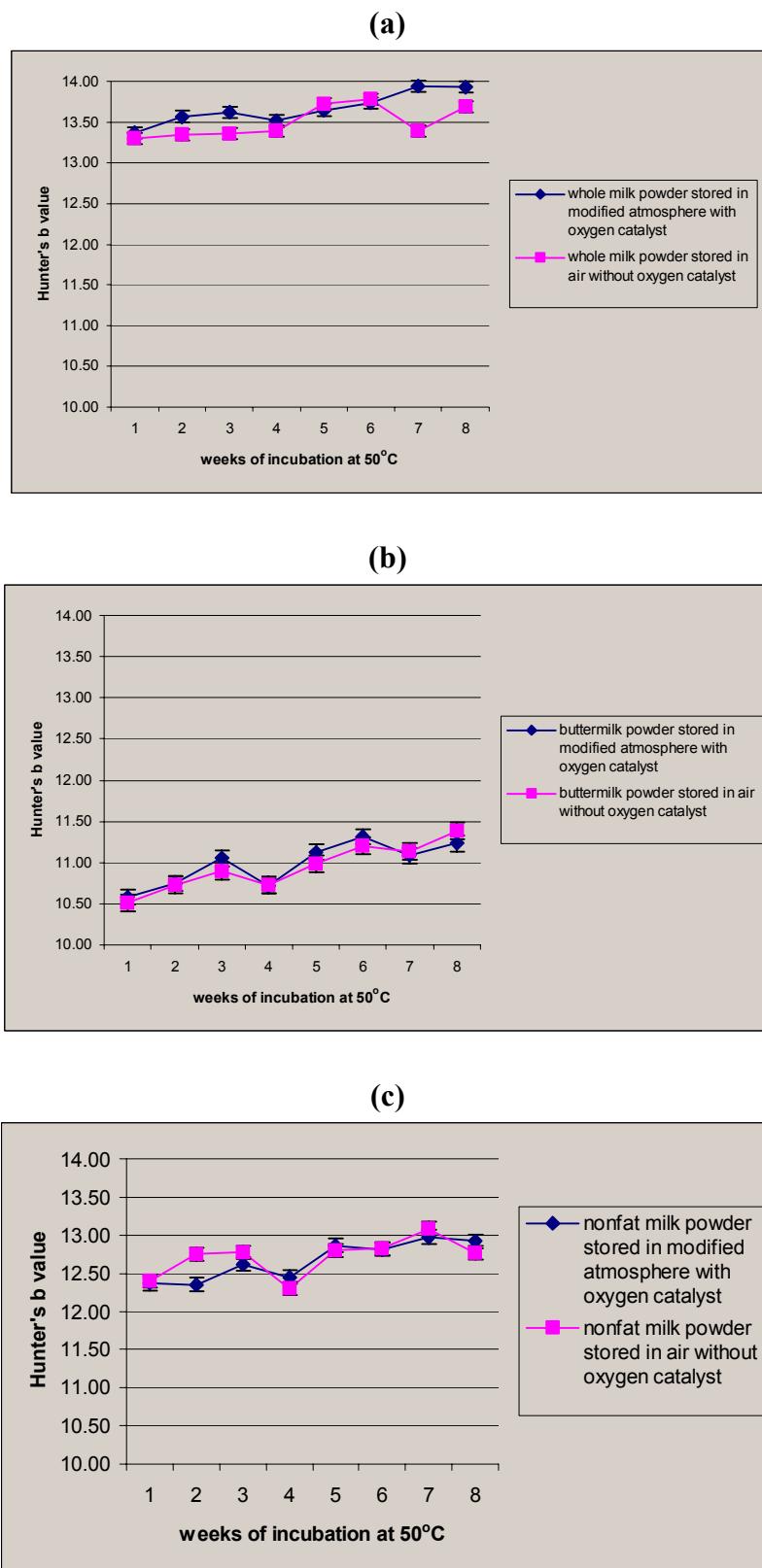


Figure 7. Hunter b value of (a) WMP, (b) BMP, and (c) NMP sealed in 240 mL glass jars for 8 weeks

Sensory Testing:

There was no significant difference ($p < 0.05$) in oxidation off-odor intensity in the samples stored with the oxygen catalyst and those stored without it. Since the sensory testing was being performed in a building frequented by students and faculty of the Food Science and Technology department, it was assumed that each panelist would recognize an oxidized sample. Most volunteer panelists commented that no difference could be detected, especially in the samples of nonfat milk powder. Thus, sensory testing, which is often more reliable and sensitive than instrumental testing, reveals that there is no discernible difference between powder stored with the catalyst and powder stored without it.

Table 1. Summary of data yielded from sensory evaluation

Attribute	Trials	Successes needed for significance	Successes obtained	Two-tailed p -value	Significance
WMP	50	33	23	0.7601	NS
BMP	50	33	24	0.6641	NS
NMP	50	33	28	0.2399	NS

Conclusion:

The final hexanal concentrations jars treated with a modified atmosphere and oxygen catalyst were not significantly different from those of the jars packaged in air without the catalyst, with averages ranging from 1.19 to 1.06 ppm in the whole milk powder, from 0.84 to 0.79 ppm in the buttermilk powder, and from 0.91 to 0.83 in the nonfat milk powder. So, the palladium-based catalyst requires some adjustments before it can be used to decrease or cease oxidation in powdered milks. The continued formation of hexanal at a rate equal to that of samples stored in its absence indicates that perhaps a refined sampling or analysis procedure and technique are needed to optimize the performance of the catalyst.

The oxygen in the headspace of the treated jars did not decrease at all, much less become completely eliminated as hypothesized. The average percentages of headspace oxygen for the whole milk, buttermilk, and nonfat milk powders stored with the catalyst were 6.5%, 8.3%, and 9.3%, respectively. This suggests that perhaps 4.85% was not a sufficient amount of hydrogen retained in the headspace atmosphere to react with the oxygen already present or formed from lipid oxidation. More meticulous control of the modified atmosphere may be needed in order to ensure the proper amount of hydrogen is present in the headspace. The addition of a step to directly measure the amount of hydrogen in the headspace using thermal conductivity gas chromatography might also be helpful.

Sensory panelists could not determine a difference between powders stored with the catalyst and those stored without. This indicates that the levels of off-odors in both were similar and that the catalyst did nothing to reduce the rate of oxidation in the given environment. A description of the term “oxidized” may prove useful for future studies to make certain that the volunteer panelists have all the information needed to make an educated assessment.

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APPENDIX A: Human Subjects Consent Form

**Virginia Polytechnic Institute and State University
Informed Consent for Participation in Sensory Evaluation**

Title of Project: Preventing Oxidation of Dairy Powders Using Oxygen Removal Packaging

Principal Investigator: Adria Mannon

I. THE PURPOSE OF THIS PROJECT

You are invited to participate on a sensory evaluation panel involving dairy powders. This study is being conducted in order to test the ability of an innovative oxygen scavenger to slow, if not stop, the adverse effects (mainly odor) of oxidation of dairy powders. Approximately fifty subjects are needed. The only sense involved is smell. If your sense of smell is impaired, please excuse yourself from this study. Further, you must be 18 years or older to participate.

II. PROCEDURES

There will be only one session involving about 15 minutes of your time. You will be presented with approximately six samples at each session. Should you find a sample unpalatable or offensive, you may choose to move on to other samples.

Certain individuals are sensitive to some foods such as **milk**, eggs, wheat gluten, strawberries, chocolate, artificial sweeteners, etc. If you are aware of any food or drug allergies, list them here:

III. BENEFITS/RISKS OF THE PROJECT

Your participation in the project will provide the following information that may be helpful: you will be giving an overall idea about consumer response to powders stored with the scavenger. You may receive the results or summary of the panel when the project is completed. Some risk may be involved if you have an unknown food allergy. However, since only smelling is involved, risks are minimal. Some discomfort may occur in smelling certain samples.

IV. EXTENT OF ANONYMITY AND CONFIDENTIALITY

The results of your performance as a panelist will be kept strictly confidential. Individual panelists will be referred to by code for analyses and in any publication of the results. Names will not be taken, so complete anonymity and confidentiality are ensured.

VI. FREEDOM TO WITHDRAW

It is essential to sensory evaluation projects that you complete each session in so far as possible. However, there may be conditions preventing your completion of all sessions. If after reading and becoming familiar with the sensory project, you decide not to participate as a panelist, you may withdraw at any time without penalty.

VII. APPROVAL OF RESEARCH

This research project has been approved by the Institutional Review Board for projects involving human subjects at Virginia Polytechnic Institute and State University and by the human subjects review of the Department of Food Science and Technology.

VIII. SUBJECT'S RESPONSIBILITIES

I know of no reason I cannot participate in this study.

Signature/Date

Please provide address and phone number so investigator may reach you in case of emergency or schedule changes.

Address _____

Phone _____

-----(tear off)-----

IX. SUBJECT'S PERMISSION (provide tear off for human subject to keep)

I have read the information about the conditions of this sensory evaluation project and give my voluntary consent for participation in this project.

I know of no reason I cannot participate in this study.

Signature/Date

Should I have any questions about this research or its conduct, I should contact:

Adria Mannon (agmannon@vt.edu)
Investigator/E-mail

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Faculty/E-mail

APPENDIX B: Questionnaire for Sensory Evaluation of Milk Powders

PAIRED COMPARISON TEST

Type of Sample: (whole milk powder, buttermilk powder, or nonfat milk powder)

Characteristic Studied: off-odor due to oxidation

Instructions:

Smell each pair from left to right and enter your verdict below.

If no difference is apparent, enter your best guess, however uncertain.

Test Pairs:

Which sample smells more oxidized?

Comments: _____

CURRICULUM VITA:

Adria Grace Mannon was born and raised in Floyd, VA. She received her Bachelor of Science degree from Roanoke College in May 2005, where she focused her studies on chemistry and math. Her experiences included an internship with the Division of Forensic Science Toxicology Laboratory and a summer research project involving pepper spray. Adria then pursued her Master of Science in Life Sciences degree at Virginia Tech in Blacksburg, VA. She studied Food Science and Technology and obtained her degree in December 2007. While at Virginia Tech, she was a graduate student assistant, helping in various laboratories. Her main focus was her thesis project, which centered around preventing oxidation in dairy powders using oxygen removal packaging. She worked temporarily as a lab technician at Chateau Morrisette Winery in Meadows of Dan, VA, where her duties included lab testing, yeast wrangling, and bottling. She is now employed as a food technologist by Beech Nut Nutrition Corporation in Canajoharie, NY.