

in okra seed), this value is considerably higher than that of most cereal grains. A representative list of cereal grains where lysine is the first limiting amino acid and the respective chemical scores includes barley 64, cornmeal 49, millet 63, oats 68, polished rice 66, ragi 53, rye 62, sorghum 37, teff 51, wheat bulgur 47, and wheat flour 38 (Jansen, 1977).

Thus, the present data suggest that okra seed meal obtained by the simple process of grinding and sieving is an improvement over ground whole seed and should be of high nutritional value.

LITERATURE CITED

Association of Official Analytical Chemists (AOAC), Washington, D.C., 1975.

Culver, B. R., Lech, J. F., Pradham, N. K., *Food Technol. (Chicago)* 29, 16 (1975).

FAO/WHO (Joint FAO/WHO Ad Hoc Expert Committee on Energy and Protein Requirements), "Energy and Protein Requirements", WHO Technical Report Series No. 522, World Health Organization, Geneva, 1973.

Jansen, G. R., in "Evaluation of Proteins for Humans", Bodwell, C. E., Ed., Avi Publishing Co., Westport, CT, 1977, pp 178-182.

Karakoltsidis, P. A., Constantinides, S. M., *J. Agric. Food Chem.* 23, 1204 (1975).

Martin, F. W., Rubetê, R., *J. Agric. Univ. P. R.* 63, 1 (1979).

Miller, E. L., *J. Sci. Food Agric.* 18, 381 (1967).

Moore, S., *J. Biol. Chem.* 238, 235 (1963).

Sengupta, A., Roychoudhury, S. K., Saka, S., *J. Sci. Food Agric.* 25, 401 (1974).

Tkachuk, R., Irvine, G. N., *Cereal Chem.* 46, 206 (1969).

Woodruff, J. G., Georgia Experimental Station Bulletin No. 145, 1927, pp 164-185.

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Effects of Temperature and Storage on the Iron and Tin Contents of Commercially Canned Single-Strength Orange Juice

Steven Nagy,* Russell Rouseff, and Sik-Vung Ting

The effects of storage time and temperature on the corrosion of commercial cans packed with single-strength orange juice showed that accelerated rates of detinning occurred at higher temperatures. Storage of canned juices over a 12-week period showed the following mean weekly rates of tin uptake (mg of Sn/kg juice-week): 0.4 [21.1 °C (70 °F)], 0.8 [26.7 °C (80 °F)], 1.5 [32.2 °C (90 °F)], 2.4 [37.8 °C (100 °F)], 4.0 [43.3 °C (110 °F)], and 12.5 [48.9 °C (120 °F)]. Iron uptake by juice was minimal and indicated that orange juice was not strongly corrosive to the plain carbon steel plate. Storage of juices below 43 °C should not cause the tin contents to exceed 250 ppm (Codex Alimentarius Commission tolerance limit of tin in canned juice) if the juice is stored for 12 weeks or less.

Extensive packaging of liquid foods in tins is due to the many advantages of this type of container, namely, ease of packing and sterilizing, handling and transporting, and minimizing the loss of vitamin potency in a foodstuff because of the anaerobic environment of the sealed can. These containers are made from plain carbon steel plates with a thin coating of tin (American Can Company, 1973).

In an empty tin can, the tinplate is cathodic and the steel base is anodic. The mode of protection is a mechanical one; i.e., the corrosive medium is kept from the corrosion-susceptible steel base by the corrosion-resistant tin layer. However, in the presence of a corrosive acidic liquid, a reversal of polarity takes place. Tin now becomes the local anode and the steel base the local cathode (Lueck and Blair, 1928; Kohman and Sanborn, 1928). Thus, the protective mode of the tin plate is now via an electrochemical process, and this happens in canned acidic fruit juices such as citrus juices.

During the preservation of acid food products, for example, canned citrus juices, an interaction occurs between the components of the canned food and the material of the can. Corrosion in canned acid products is influenced by the chemical composition of the product (Bombara et al., 1970), character of the tinplate (Mahadeviah et al., 1975), and the presence of corrosion accelerators such as sulfites, sulfur dioxide (Saguy et al., 1973), nitrates (Lambeth et

al., 1967), and oxygen (Kefford et al., 1959; Koehler, 1961). Studies (Vaurio, 1950; Koehler and Canonico, 1957) of the corrosion mechanism have shown that the process entails dissolution of the tin coating, dissolution of the steel base, and evolution of hydrogen.

The object of the present work was to evaluate the influence of temperature and storage on the corrosion (dissolution of iron and tin) of tinplate containers packed with single-strength orange juice (SSOJ).

This experiment should also indicate other factors (pH; titratable acidity; Brix/acid), in addition to time and temperature of storage, that are responsible for enhancing the uptake of tin by the juice, thus limiting the shelf life of the product because the tolerance level of tin (250 mg/kg of juice; Codex Alimentarius Commission, 1978) was exceeded.

EXPERIMENTAL SECTION

Materials. Commercially canned SSOJ was obtained from three processors (A; B; C) during the early (November to January) and mid (January to March) processing seasons and from four processors (A; B; C; D) during the early Valencia (April to May) and late Valencia (May to July) seasons. SSOJ in 46-oz cans was taken directly from the production lines in the processing plants and placed in a laboratory locker at -18 °C. Temperatures of storage lockers were maintained at ±2 °F (about ±1.1 °C).

Instrumentation. A Perkin-Elmer Model 503 atomic absorption spectrophotometer was used with a Perkin-Elmer tin electrode-less discharge lamp set at 8 W or a Perkin-Elmer hollow cathode iron lamp. Tin absorbance

*Florida Department of Citrus, Agricultural Research and Education Center, Lake Alfred, Florida 33850.

Table I. Some Properties of Freshly Canned Commercial Single-Strength Orange Juice

season	plant	pH	% titratable acidity	Brix/acid	mg/kg	
					Fe	Sn
early	A	3.67	0.80	13.4	1.9	17.4
	B	3.69	0.77	13.2	1.2	18.1
	C	3.54	0.98	10.6	0.9	30.6
mid	A	3.67	0.96	13.1	2.1	19.0
	B	3.52	1.11	10.7	1.6	30.5
	C	3.68	0.92	12.6	2.0	14.5
early Valencia	A	3.58	1.02	10.9	0.9	14.2
	B	3.64	0.95	11.6	1.0	11.2
	C	3.63	0.88	12.2	0.8	15.9
	D	3.58	1.01	11.0	1.9	25.2
late Valencia	A	3.79	0.79	14.1	1.7	22.2
	B	3.88	0.77	16.1	1.8	14.4
	C	3.78	0.80	15.3	1.4	12.8
	D	3.83	0.79	14.9	0.9	25.2

was measured at the 286.3-nm line with a 0.7-nm slit width. Iron absorbance was measured at 248.3 nm with a slit width of 0.2 nm.

A single-slot nitrous oxide-acetylene burner head was used for tin measurements and was adjusted to give a fuel rich (reducing) flame. A single-slot air-acetylene burner head adjusted to give a lean (oxidizing) flame was used for iron. Burner head alignment and burner nebulizer aspiration rate were adjusted to give maximum absorption readings in both cases.

The atomic absorption spectrophotometer was operated in the concentration mode by using either a 50 mg/kg tin solution or a 5 mg/kg iron solution as a standard. Blanks containing the same acids, at the same concentrations as the samples, were used to zero the instrument. Three concentration readings taken during a 1-s integration were recorded and averaged for each sample.

Methods. Fifty grams of SSOJ was removed from a 46-oz can and transferred to a tared platinum crucible. The sample was placed on a steam bath for 4–5 h to vaporize most of the water. Following this treatment, the sample was removed and carefully heated with a Bunsen burner to remove any residual water and to char the juice's solids. The sample was subsequently placed in a muffle furnace set at 300 °C for 1–2 h. The temperature was gradually increased to an upper temperature limit of 525 °C and kept at this limit for 18 h. The ashed sample was dissolved in 5 mL of 1:1 concentrated HCl, made up to a 50-mL volume with distilled water, and transferred to a polyethylene bottle. Replicate samples were run at each storage temperature.

RESULTS AND DISCUSSION

Fourteen processed SSOJ samples (Table I) from four processing plants showed the following property ranges: pH (3.52–3.88), percent titratable acidity (0.77–1.11), Brix/acid (10.6–16.1), Fe (0.8–2.1 mg/kg), and Sn (11.2–30.6 mg/kg). No attempt was made to determine the mineral contents of these juices prior to canning. The Fe contents of noncanned orange juice have been reported at 2–4 mg/kg (Birdsall et al., 1961), 0.73–2.45 mg/L (McHard et al., 1976), and 0.2–5 mg/L (Nagy, 1977), whereas in noncanned grapefruit juice a range of 0.6–1.9 mg/kg has been reported (Nagy, 1977). In commercially canned single-strength grapefruit juice, Ting (1977) reported iron contents to range from 0.7 to 7.6 mg/L with a mean of 2.3 mg/L. The Fe values of canned SSOJ (Table I) were similar to those of noncanned orange juices and suggested that iron dissolution of the base plate during canning was minimal.

Information on the Sn contents of noncanned SSOJ is limited but McHard et al. (1979, 1980) recently reported a range of 0.001–0.422 mg/L for Florida single-strength orange juice. The large amounts of Sn found in freshly canned SSOJ (Table I) when contrasted to noncanned juices showed that corrosion of the tinplate took place during the canning operation. At this point, it is necessary to offer a brief explanation as to why the tin levels of juice increased because of canning. During one of the processing stages, orange juice from a pasteurizer is pumped to a filler bowl (juice temperature ~85 °C) and filled directly into tinplated cans. The cans are closed automatically and inverted for ~20 s so that the closing lid is sterilized by the heat of the juice. Live steam injected into the headspace as the cans are closed replaces most of the air and helps create a vacuum during closure. The product next passes to a roller conveyer where they are rapidly cooled to ~39 °C by the can's spinning action under sprays of cold water. It is important that the cans emerging from this cooling operation retain some residual heat to facilitate drying and prevent subsequent rusting. Although every use of modern technology is made to exclude oxygen from the final product (deaeration-deoiling equipment; injection of live steam to create a vacuum; maximum filling of the can to reduce head space), some oxygen still remains dissolved in the juice and entrapped within the small headspace of the can (Kefford et al., 1959). The hot temperature of the juice coupled with the presence of oxygen causes an initial rapid detinning of the can.

Oxygen, dissolved within the juice and entrapped with the headspace of the can, readily reacts with tin to form stannous ions. After dissolved oxygen and headspace oxygen are exhausted, hydrogen gas is produced in the acidic juice medium. Tin is oxidized forming stannous ions while hydrogen ions are reduced to molecular hydrogen (Frankenthal et al., 1959).

Investigations have shown that higher tin contents are found in juice packed in plain cans than in enamel-lined cans shortly after processing (Riester et al., 1945). In addition, several studies (Riester et al., 1945; Curl, 1949; Moore et al., 1951) have shown that the loss of vitamin C in enamel-lined cans was greater than in plain tin cans because residual oxygen reacted with the tin in one case and with vitamin C in the other. Since oxygen accelerates the corrosion of the tin coating and is detrimental to many important nutrients, it is no wonder that current industrial practice is to keep oxygen levels as low as possible during the processing of citrus juices (Veldhuis, 1971).

Canned SSOJ from plant C (late Valencia season) was monitored over a 12-week period to determine the levels of iron and tin. Figure 1 shows the mode of uptake of iron and tin in juices stored at 29.4, 37.8, and 46.1 °C (85, 100, and 115 °F). At all three temperatures, the iron contents of these juices remained relatively constant, varying between 0.9 and 2.9 mg/kg of juice. Temperature and length of storage had little effect on the uptake of iron by these canned orange juices. A similar effect on grapefruit juice packed in tinplated cans was reported by Frankenthal et al. (1959). These workers found little iron uptake by grapefruit juice stored for 300 days at 37.8 °C.

Strikingly different profiles were observed for the uptake of tin (Figure 1). Specifically, a continual uptake of tin over the 12-week storage period was shown for all three temperatures. Tin uptake for juices stored at 29.4 °C increased from 14 to 28 mg/kg whereas those juices stored at 37.8 °C increased to 37 mg/kg. Canned SSOJ stored at 46.1 °C showed the most extensive dissolution of the tinplate; tin uptake over the 12-week period increased from

Table II. Effects of Temperatures on the Iron and Tin Contents of Canned Single-Strength Orange Juice Stored for 12 Weeks

season	plant	concn, mg/kg of juice, at											
		21.1 °C ^a		26.7 °C		32.2 °C		37.8 °C		43.3 °C		48.9 °C	
		Fe	Sn	Fe	Sn	Fe	Sn	Fe	Sn	Fe	Sn	Fe	Sn
early	A	2	18 ^b	2	23	2	31	2	31	4	58	3	172
	B	2	21	1	22	3	30	2	35	3	72	4	208
	C	1	37	1	49	2	64	2	70	2	91	3	211
mid	A	2	21	2	25	2	30	3	45	3	68	3	156
	B	2	31	2	30	2	39	3	48	3	85	4	225
	C	2	32	1	37	2	64	3	89	2	93	4	292
early Valencia	A	2	20	2	24	2	27	3	56	2	61	2	145
	B	2	18	2	29	3	31	3	45	3	58	3	156
	C	2	20	1	23	2	30	2	39	2	49	3	141
	D	2	25	2	25	3	37			3	58	3	110
late Valencia	A	2	23	2	26	2	26	3	38			2	115
	B	2	28	1	26	2	40	2	44	2	56	2	138
	C	2	17	2	35	2	36	2	42	2	65	3	168
	D	2	26	1	32	2	37	2	38	2	56	2	125
	mean:	1.9	24	1.6	29	2.2	37	2.5	48	2.5	67	2.9	169
	range:	1-2	17-37	1-2	22-49	2-3	26-64	2-3	31-89	2-4	49-93	2-4	110-292

^a Celsius temperatures when converted to Fahrenheit equal 70, 80, 90, 100, 110, and 120 °F, respectively. ^b Each value is the mean of duplicate determinations.

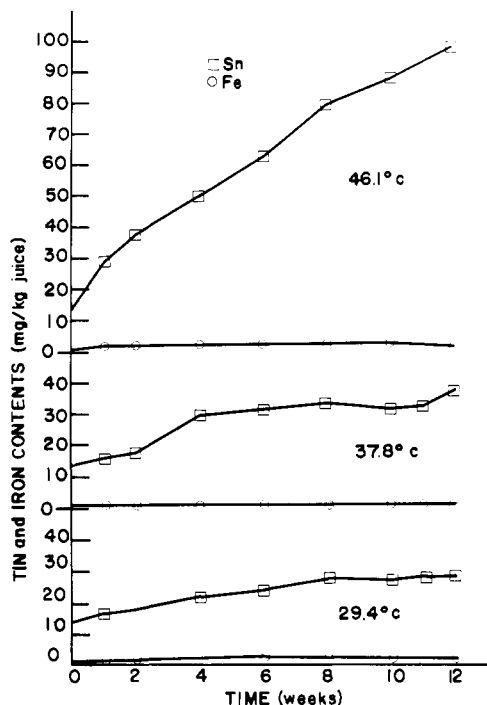


Figure 1. Uptake of tin and iron by canned SSOJ during storage at 29.4, 37.8, and 46.1 °C.

14 to 98 mg/kg. The average weekly rates of tin uptake (mg of Sn/kg of juice-week) for the 12-week period were 1.2 (29.4 °C), 1.9 (37.8 °C), and 7.0 (46.1 °C). Thus, the average weekly rate of tin dissolution increased ~1.6-fold from storage at 29.4 to 37.8 °C and increased ~37.8-fold between 37.8 and 46.1 °C. Those different rates indicated that tin uptake by SSOJ was disproportionately higher at the higher temperature.

Based on the different dissolutions of the tinplate at different temperatures (Figure 1), we extended our study to cover tin uptake in canned SSOJ processed during four seasons of a processing year (Table II). In this study, SSOJ samples were not monitored regularly but were analyzed for their final iron and tin contents after 12 weeks of storage at 21.1, 26.7, 32.2, 37.8, 43.3, and 48.9 °C (represents 10 °F increments from 70 to 120 °F). After 12

weeks, the iron contents of canned SSOJ showed only minor increases with storage temperature. Tin contents, on the other hand, increased noticeably. Below 43.3 °C tin uptake was minimal, but between 43.3 and 48.9 °C tin uptake was disproportionately greater. The mean weekly rates of tin uptake (mg of Sn/kg of juice-week) by canned SSOJ were 0.4 (21.1 °C), 0.8 (26.7 °C), 1.5 (32.3 °C), 2.4 (37.8 °C), 4.0 (43.3 °C), and 12.5 (48.9 °C).

Corrosion of the tinplate is accelerated by the acidity of the fruit product (Cruess, 1948; Bombara et al., 1970; Willey, 1972). The nature of the acid is probably more significant than the actual pH value (Adams and Blundstone, 1971). If the pH is lowered with citric acid, the citrate ion, which complexes tin, probably has a greater effect than the pH.

In an experiment to test the relationship between corrosion and acidity, Bielig and Treptow (1973) adjusted the pH (2.7, 3.7, and 4.5) of orange juice prior to canning with different concentrations of citric acid. Those investigators found that during storage, detinning of the cans increased as acidity increased (pH decreased). In a similar study, Rouseff and Ting (1980) adjusted the acidity of grapefruit juice (pH 3.0, 3.5, and 4.0) with citric acid and sodium hydroxide prior to canning and found that detinning increased as pH decreased. In our experiment, we found no relationship between the extent of detinning and acid factors (pH; titratable acidity; Brix/acid). Apparently, the acid levels of our juices (Table I) were too similar for any correlation to be made between acidity and detinning.

Ingestion of food products containing excessive amounts of tin (>400 ppm) has been responsible for several physiological disorders, namely, nausea, vomiting, diarrhea, fever, and headache (Omori et al., 1955). Because of potential tin intoxication from ingestion of a canned food, several international studies (Omori et al., 1973; Royo Iranzo and Grima, 1973; Bielig and Treptow, 1973) have been conducted to determine the level of tin in canned citrus juices and to establish maximum values for tin in these juices. The World Food Codex (Codex Alimentarius Commission, 1978) has established a tentative tolerance of 250 ppm for tin in canned orange juice.

CONCLUSION

Our studies show that the uptake of tin by canned SSOJ

was related to storage time and temperature. Storage at temperatures greater than 43.3 °C greatly accelerated detinning of the canned product. Juices stored for 12 weeks at 48.9 °C (120 °F) contained the highest contents of tin; only a sample from midseason, however, exceeded the 250-ppm tolerance limit for tin in canned foods. The possibility of consumption of a juice subjected to these extreme storage conditions is unlikely because this temperature-abused product is unpalatable (aged, rotten flavor) and has an objectionable appearance (dark brown). Whenever possible, high temperatures during the warehousing and transporting of canned SSOJ should be avoided because of the disproportionately higher rates of detinning at these elevated temperatures.

LITERATURE CITED

- Adams, J. B.; Blundstone, H. A. W. In "The Biochemistry of Fruits and their Products"; Hulme, A. C., Ed.; Academic Press: New York, 1971; Vol. 2, Chapter 15.
- American Can Company "The Sanitary Can"; American Can Co.: Barrington, IL, 1973.
- Bielig, H. J.; Treptow, H. *Chem., Mikrobiol., Technol. Lebensm.* 1973, 2, 129.
- Birdsall, J. J.; Derse, P. H.; Teply, L. J. *J. Am. Diet. Assoc.* 1961, 38, 555.
- Bombara, G.; Azzetti, N.; Baudo, G. *Corros. Sci.* 1970, 10, 847.
- Codex Alimentarius Commission "Report of the Twelfth Session", FAO/WHO, Rome, 1978, p 45.
- Cruess, W. V. "Commercial Fruit and Vegetable Products", 3rd ed.; McGraw Hill: New York, 1948; Chapter 14.
- Curl, A. L. *Food Res.* 1949, 14, 9.
- Frankenthal, R. P.; Carter, P. R.; Laubscher, A. N. *J. Agric. Food Chem.* 1959, 7, 441.
- Kefford, J. F.; McKenzie, H. A.; Thompson, P. C. O. *J. Sci. Food Agric.* 1959, 10, 51.
- Koehler, E. L. *Corrosion (Houston)* 1961, 17, 93t.
- Koehler, E. L.; Canonico, C. M. *Corrosion (Houston)* 1957, 13, 227.
- Kohman, E. F.; Sanborn, N. H. *Ind. Eng. Chem.* 1928, 20, 76.
- Lambeth, V. N.; Fields, M. L.; Brown, J. R. *Food Technol. (Chicago)* 1967, 21, 1516.
- Lueck, R. H.; Blair, H. T. *Trans. Am. Electrochem. Soc.* 1928, 54, 257.
- Mahadeviah, M.; Eipeson, W. E.; Balakrishnan, K.; Sastry, L. V. *J. Food Sci. Technol.* 1975, 12, 234.
- McHard, J.; Foulk, S. J.; Jorgensen, J. L.; Bayer, S.; Winefordner, J. D. *ACS Symp. Ser.* 1980, No. 143, Chapter 16.
- McHard, J.; Foulk, S. J.; Winefordner, J. D. *J. Agric. Food Chem.* 1979, 27, 1326.
- McHard, J.; Winefordner, J. D.; Ting, S. V. *J. Agric. Food Chem.* 1976, 24, 950.
- Moore, E. L.; Atkins, C. D.; Huggart, R. L.; MacDowell, L. G. *Citrus Ind.* 1951, 32, 8, 11, 14.
- Nagy, S. In "Citrus Science and Technology"; Nagy, S.; Shaw, P. E.; Veldhuis, M. K., Eds.; Avi Publishing Co.: Westport, CT, 1977; Vol. 1, Chapter 13.
- Omori, Y.; Takanaka, A.; Ikeda, Y.; Furuya, T. *Nippon Yakurigaku Zasshi* 1955, 61, 77.
- Omori, Y.; Takanaka, A.; Tanaka, S.; Iketa, Y.; Furuya, T. *Shokuhin Eiseigaku Zasshi* 1973, 14, 69.
- Riester, D. W.; Braun, O. G.; Pearce, W. E. *Food Ind.* 1945, 17, 742.
- Rouseff, R.; Ting, S. V., submitted for publication in *J. Food Sci.*
- Royo, Iranzo, J.; Grima, R. *Rev. Agroquim. Tecnol. Aliment.* 1973, 13, 326.
- Saguy, I.; Mannheim, C. H.; Passy, N. *J. Food Technol.* 1973, 8, 147.
- Ting, S. V. *Proc. Fla. State Hort. Soc.* 1977, 90, 178.
- Vaurio, V. W. *Corrosion (Houston)* 1950, 6, 260.
- Veldhuis, M. K. In "Fruit and Vegetable Juice Processing Technology", 2nd ed.; Tressler, D. K.; Joslyn, M. A., Eds.; Avi Publishing Co.: Westport, CT, 1971; Chapter 2.
- Willey, A. R. *Br. Corros. J.* 1972, 7, 29.

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Extraction and Isolation of Soluble and Insoluble Fiber Fractions from the Pinto Bean (*Phaseolus vulgaris*)

Woodrow C. Monte* and Joseph A. Maga

A method was tested to separate the fiber portion of the pinto bean into 13 fractions. The method overcame many problems which make extraction of fiber from high-starch and/or high-protein products difficult. The lipid, fatty acid, and protein content associated with each fraction was investigated in both raw and cooked beans. Cooked beans contained more than twice the amount of soluble fiber than the raw pinto beans, while the cooking process reduced by one-third the extractable hemicellulose A and completely depleted the hemicellulose B. Extraction by this technique revealed a 50% decrease in the levels of lignocellulose and crude cellulose after the cooking process. Some protein contamination was found in all fiber fractions except the bound pectin. Lipids, as phospholipids, monoglycerides, diglycerides, triglycerides, and free fatty acids were found in all fiber fractions tested except at the lignocellulose level of the cooked beans.

Although there are techniques available for the detailed analysis of the structural macromolecular components of the plant cell wall, they are very time consuming, require elaborate, expensive equipment, and often are destructive of the molecules they seek to elucidate (Talmadge et al.,

1973). To date, it is generally agreed that no single procedure is entirely satisfactory if one considers the complexity of dietary fiber in a normal mixed diet (Southgate, 1976).

Furda (1977) proposed a fiber extraction technique which for the most part was based on methodology long accepted by the scientific community. It included extraction techniques to isolate water-soluble fiber fractions.

During this study, several major changes were incorporated into Furda's original outline. Typical of the changes was the use of both amyolytic and proteolytic enzymatic

*Department of Home Economics, Arizona State University, Tempe, Arizona 85281 (W.C.M.), and Department of Food Science and Nutrition, Colorado State University, Fort Collins, Colorado 80523 (J.A.M.).