

ASEAN POST PRODUCTION INFORMATION EXCHANGE (APEX)

SELECTIVE DISSEMINATION OF INFORMATION SERVICE

870516

Tin, iron and aluminium contents of
commercially canned single-strength
grapefruit juice stored at varying
temperatures

Journal of Agricultural and Food
Chemistry
v34 n4, 1986, p 588 (6 pgs)



ASEAN Food Handling Bureau

Level 5, F13 & F14 Damansara Town Centre, 50490 Kuala Lumpur, Malaysia.
Telex: MA 31555 AFHBKL Tel: 2544199 & 2551088

This article is supplied for the purpose of research or private study.

Tin, Iron, and Aluminum Contents of Commercially Canned Single-Strength Grapefruit Juice Stored at Varying Temperatures

Steven Nagy* and Seifollah Nikdel

The extent of corrosion of commercially canned single-strength grapefruit juice was related to storage time and temperature. Storage of juices over a 12-week period at temperatures ranging from 10 to 50 °C resulted in increased levels of tin, iron, and aluminum in the product. The Sn, Fe, and Al uptakes were essentially linear with time, increased with temperature, and were greater for Sn than for Fe or Al. Corrosion of cans was disproportionately higher at temperatures exceeding ca. 37 °C. An Arrhenius plot of $\log K$ (Sn uptake) vs. the reciprocal of absolute storage temperature showed two distinct reaction kinetics. For the region 10–37 °C, an energy of activation, E_a , of 10.1 kcal and a Q_{10} of 1.8 was noted, whereas the region 37–50 °C showed an E_a of 20.2 kcal and a Q_{10} of 2.6. Examination of individual cans for their contents of Sn, Fe, and Al by regression analysis yielded linear correlation coefficients of 0.809 (Sn vs. Fe), 0.791 (Sn vs. Al), and 0.995 (Fe vs. Al).

The corrosiveness of liquid foods packaged in tin plate containers varies considerably, and in canned acidic foods corrosion is influenced by a number of chemical and physical parameters. Studies on canned citrus juices have identified the following corrosion-related factors: pH (Rouseff and Ting, 1985), corrosion accelerators such as sulfites and sulfur dioxide (Saguy et al., 1973), oxygen (Kefford et al., 1959), high storage temperature (Nagy et al., 1980; Rouseff and Ting, 1985), and processing variables such as deaeration, improper cooling, and increased headspace (Bakal and Mannheim, 1966).

During storage of canned citrus juices, an interaction occurs between the components of the juice and compositional material of the can. In plain tin cans (unlacquered), cathodic protection of the steel base is the result of the tin coating functioning as the sacrificial anode. Tin dissolution follows three well-defined stages (Saguy et al., 1973): (1) oil and tin oxide layers are removed from the can surface and the rate of tin dissolution is high; (2) continued dissolution of the tin causes enlargement of existing pores and scratches exposing the steel and the alloy; the corrosion rate is almost constant; (3) large areas

of steel are exposed and there is a high dissolution rate of tin and iron; hydrogen evolves at a fast rate causing loss of vacuum and possible swelling.

An increase in the tin content of canned citrus juices during storage is inevitable. Two advantages of citrus juices packed in cans are that the tin plate minimizes browning development and vitamin C loss (tin functions as an antioxidant). However, disadvantages of canned juices are that elevated tin levels impart a metallic off-flavor (commonly referred to as tinny off-flavor), and if excessive amounts of tin dissolve (>400 ppm) and are ingested, nausea, vomiting, diarrhea, fever, and headache may result (Omori et al., 1955). Additionally, more recent studies with rats have indicated that excessive levels of tin in the diet might cause reduced retention of calcium, copper, and zinc in tissues (Yamaguchi et al., 1980; Greger and Johnson, 1981; Johnson and Greger, 1982). Attempts to reduce the tin content through use of lacquered cans have produced juices with poorer vitamin C retention (Curl, 1949) and significant discoloration (Mannheim and Hoenig, 1971).

Extensive studies on corrosion of canned citrus products by our laboratory (Rouseff and Ting, 1980, 1985; Nagy et al., 1980; Nagy and Rouseff, 1981) prompted us to undertake an extensive study on the effects of storage conditions (time-temperature) on the accumulation of tin,

*Scientific Research Department, Florida Department of Citrus, CREC, Lake Alfred, Florida 33850.

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

plant	pH ^a	% citric acid ^a	deg Brix ^a	mg/kg ± SD		
				Sn	Fe	Al
A	3.60	0.89	9.23	9.3 ± 2.1	1.11 ± 0.10	0.202 ± 0.032
B	3.60	0.90	9.66	18.1 ± 3.1	0.99 ± 0.10	0.157 ± 0.039
C	3.54	1.23	11.72	28.5 ± 4.4	1.03 ± 0.08	0.153 ± 0.028
D	3.56	0.94	9.66	11.9 ± 2.3	1.16 ± 0.19	0.199 ± 0.070
E	3.57	0.94	10.66	19.4 ± 0.6	1.03 ± 0.10	0.158 ± 0.044

^a Coefficient of variation was less than 2%.

iron, and aluminum in unlacquered, canned, single-strength grapefruit juice (SSGJ). This study should provide information as to those conditions that enhance corrosion and the relationships of the corrosion minerals.

EXPERIMENTAL SECTION

Sample and Storage Treatment. Commercially processed, canned SSGJs were obtained in May from five processors identified as A–E. Cans were all 1.36-L (46-oz) capacity, and all were unlacquered tin-plated steel. Cans were from different manufacturers. The cans were taken directly from production lines and placed in a laboratory cold locker at -18°C until storage tests were initiated. For tests, SSGJ cans were thawed and placed in storage lockers of varying temperatures, namely, 10, 20, 30, 40, and 50°C (total of 100 cans) and stored for 3, 6, 9, and 12 weeks.

Preparation and Spectrochemical Analysis. All chemicals for spectrochemical analysis were certified high-purity materials from Spex Industries (Metuchen, NJ). Standard solutions were made by dissolving the high-purity salts of the metals in a matrix to simulate citrus juice mineral constituents. Standardization of the inductively coupled plasma (ICP) atomic emission spectrometer was carried out by using a low and a high standard for the multielement matrix because of the large, linear dynamic range of the plasma (5–6 orders of magnitude). The slope and intercept of the calibration line for each element was calculated by an automated computerized system, and these parameters were used in sample analysis. Both the accuracy and precision of this system for standard solutions was less than 1%. The precision (coefficient of variation) of unknown sample analysis was less than 5%. The matrix contained 2400 $\mu\text{g/mL}$ of K (K_2CO_3), 300 $\mu\text{g/mL}$ of P ($\text{NH}_4\text{H}_2\text{PO}_4$), 150 $\mu\text{g/mL}$ each of Ca (CaCO_3) and Mg (MgCO_3), and 80 $\mu\text{g/mL}$ of Na (Na_2CO_3). Trace elements at levels of parts-per-billion (ng/mL) were dissolved in 0.1 M double-distilled nitric acid solution (GFS Chemicals, Columbus, OH). To prepare samples of SSGJ for spectrochemical analysis, 25 g of SSGJ was weighed in a 150-mL beaker and mixed with 15 mL of acid mixture ($\text{HCl}:\text{HNO}_3$ 3:1). The mixture was poured into a Teflon digestion vessel (Berghof/America, Inc., Raymond, NH), placed inside a desiccator that contained 250 mL of water and, finally, heated to boiling by microwave (Model JET 210, General Electric Co.) for 5 min at medium power and another 5 min at high power. Digestion of samples in an enclosed Teflon vessel by microwave resulted in recoveries of greater than 99% for Sn, Fe, and Al as evidenced by ICP analysis. After cooling to room temperature, the solution is transferred to a 50-mL volumetric flask, rinsed, diluted to 50 mL and then filtered through Whatman 42 ashless paper into a polyethylene bottle. Spectrochemical analysis was carried out with a Jarrel-Ash Atomscan 2000 sequential and computer-controlled spectrometer equipped with an autosampler. Operating conditions: source gas, argon; gas flows, (sample) 0.5 L/min, (auxiliary) 0.8 L/min, (plasma) 12 L/min; power, 1.2 kW; observed height, 15 mm; PM tubes, R427, R300, R889; nebulizer-modified cross-flow;

torch-in-house design with open optical window within the extension tube; sample uptake rate, 1 mL/min; spectral resolution, 0.018 nm for 178–380 nm and 0.036 nm for 380–780 nm. Analytical lines used for this analysis were based on values given in the literature (Winge et al., 1979) and on an experimental investigation of the scanning system of the spectrometer. Lines were 237.34, 238.20, and 235.48 nm for Al, Fe, and Sn, respectively. Line selection was based on minimal spectral interference. For example, the more sensitive line for Al is 396.25 nm; however, experimental scanning showed the Ca line to overlap (line broadening) the Al line. Therefore, we used the less sensitive line (237.34 nm) to eliminate this spectral interference. Degrees Brix, percent citric acid, and pH were determined by official analytical methods (AOAC, 1970).

RESULTS AND DISCUSSION

Freshly canned SSGJ from five processing plants showed the following properties (Table I): pH, 3.54–3.60; percent citric acid, 0.89–1.23; 9.23–11.72° Brix; Sn, 9.3–28.5 mg/kg; Fe, 0.99–1.16 mg/kg; Al 0.153–0.202 mg/kg. Mineral contents of juices prior to canning were not determined because of the continuous flow of juices within a relatively closed system during processing and canning.

The natural Sn levels of citrus juices (noncanned) are found at levels less than 0.5 ppm. For single-strength orange juice, Nikdel and Barros (1984) reported a range of 0.012–0.304 mg/kg (mean 0.097), whereas McHard et al. (1980) reported values of 0.001–0.422 mg/kg. There are no reliable published values on the natural Sn content of noncanned grapefruit juice. Nikdel (1985) found the Sn content of freshly prepared grapefruit juices (grapefruit obtained from groves of the Citrus Research and Education Center) to be less than 0.030 mg/kg. These grapefruit juice Sn values were in a range similar to those reported for orange juices.

Freshly canned single-strength juice (orange or grapefruit) show noticeable levels of tin; the factors responsible for these elevated levels were discussed by Nagy et al. (1980) and by Rouseff and Ting (1985). Commercially canned SSGJ showed Sn contents of 9–28 mg/kg (Table I) while grapefruit juice canned in a pilot plant showed initial Sn contents of 12 mg/kg (Rouseff and Ting, 1985).

The mean tin uptakes (means of five processing plants) by canned SSGJ at 20, 40, and 50°C over a 12-week storage period are typified by Figure 1. Analysis of mean tin corrosion at the three temperatures yielded regression lines of tin corrosion on time with coefficients of correlation of $r = 0.89$ (20°C), $r = 0.99$ (40°C), and $r = 0.97$ (50°C). The standard errors of estimate ($S_{y,x}$) of tin content with time for the regression lines shown in Figure 1 were 2.74, 4.40, and 9.38 mg of Sn/kg of juice for 20, 40, and 50°C storage temperatures, respectively. As noted by Figure 1, juices stored at 20 and 40°C increased from ca. 15 to 24.6 and 46.7 mg/kg, respectively. In contrast, to the 20 and 40°C stored juices, storage of juices at 50°C showed a disproportionate higher rate of detinning. For the 50°C stored juices, tin corrosion increased from ca. 17 to 86.7 mg/kg in 12 weeks. Can-to-can variability was noted

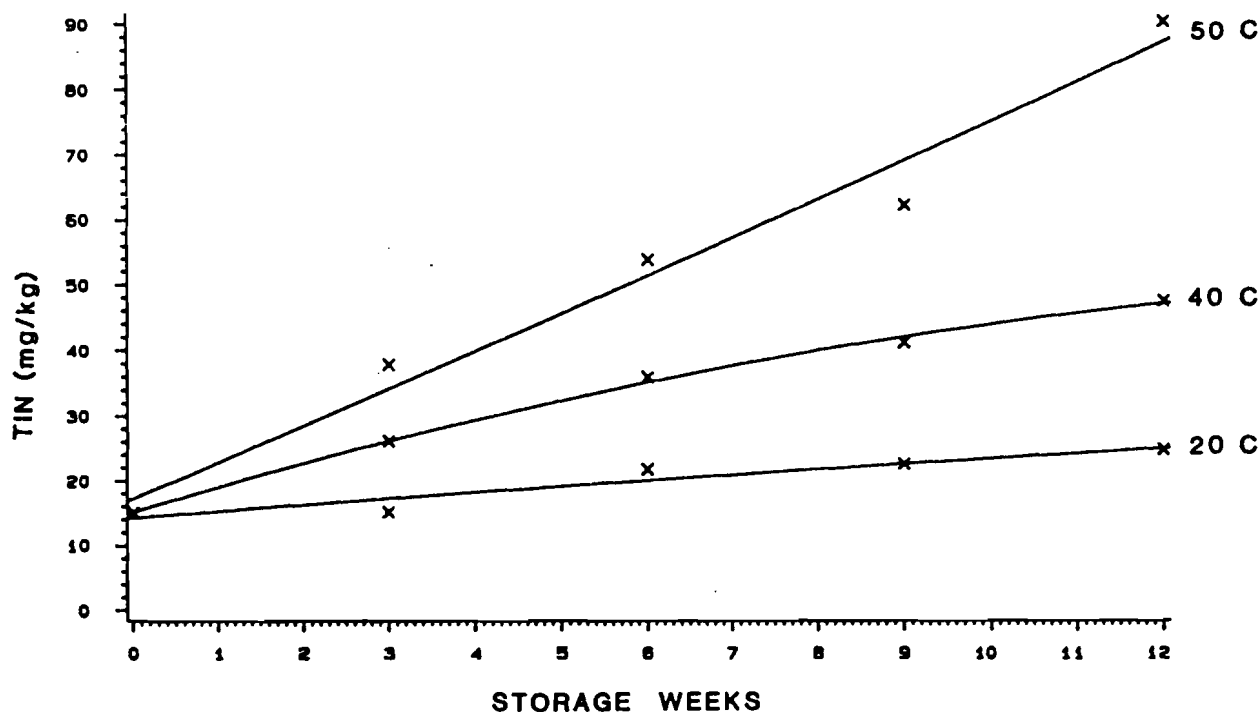


Figure 1. Uptake of tin by canned SSGJ during storage at 20, 40, and 50 °C over a 12-week period.

Table II. Accumulation (mg/kg of Juice) of Sn, Fe, and Al in Canned SSGJ at 12 Weeks of Storage at Varying Temperatures

	storage temp, °C				
	10	20	30	40	50
	Sn				
mean ± SD	18.7 ± 4.9*	24.9 ± 9.7	30.6 ± 10.2	47.0 ± 16.3	98.0 ± 39.0
range	12.9-27.8	13.3-40.8	14.1-43.0	21.2-72.4	56.5-139.0
	Fe				
mean ± SD	1.07 ± 0.12	1.19 ± 0.18	1.42 ± 0.27	1.81 ± 0.56	3.23 ± 0.87
range	0.93-1.22	1.02-1.53	1.12-1.66	1.15-2.68	2.35-4.50
	Al				
mean ± SD	0.20 ± 0.07	0.24 ± 0.06	0.33 ± 0.09	0.50 ± 0.22	1.05 ± 0.36
range	0.14-0.31	0.18-0.34	0.23-0.43	0.25-0.81	0.68-1.57

* Values represent the mean ± SD of five randomly selected samples; samples selected from each of five plants.

during corrosion analysis; therefore, each data point represented the mean of five randomly selected samples. The National Food Processor's Association and FDA recognized this can-to-can variability by establishing a sampling protocol whereby 12 cans of a product were composited to yield a single analysis (Elkins, 1982). Rouseff and Ting (1985) reported that considerable can-to-can variability existed with respect to the tin content of stored single-strength grapefruit juice; even though the cans were from the same manufacturer and from the same lot. Apparently, the preparation of the tin-plated steel and the subsequent preparation of the can were not very uniform processes.

The tin contents of grapefruit juices obtained from five processing plants and stored for 12 weeks at varying temperatures are reported in Table II. The average weekly rates of Sn uptake (mg of Sn/kg of juice per wk) at the various temperatures were 0.41 (10 °C), 0.70 (20 °C), 1.33 (30 °C), 2.67 (40 °C), and 7.00 (50 °C). An Arrhenius plot of $\log K$ (Sn uptake in mg/kg per wk) vs. the reciprocal of absolute storage temperature is shown in Figure 2. Analysis of variance of the reaction slope $[(K_2 - K_1)/(1/T_2 - 1/T_1)]$ between each storage temperature confirmed a statistical change in kinetics around 40 °C. Two distinct reaction kinetics are noted: the first between 10 and 37 °C and the second between 37 and 50 °C (the 37 °C value was determined by solving two simultaneous regression

equations of the form $y = mx + b$). For the region 10-37 °C, regression analysis yielded an energy of activation (E_a) of 10.1 kcal and a Q_{10} (reaction rate increase with 10 °C temperature rise) of 1.8, whereas the region 37-50 °C showed an E_a of 20.2 kcal and a Q_{10} of 2.6.

The commercial grapefruit juice samples used in our study showed a very narrow pH range (3.54-3.60), and therefore, we observed no correlation between pH and the extent of detinning. In a pilot-plant study, Rouseff and Ting (1985) adjusted the grapefruit juice to pH 3.0, 3.5, and 4.0 prior to canning and found that, during storage, detinning of cans increased as acidity increased (pH decreased).

The World Food Codex (Codex Alimentarius Commission, 1978) has established a tentative tolerance of 250 ppm for tin in canned foods (includes canned citrus juices). The 250 ppm value, as the permissible upper limit, is based not on toxicological evidence of safety but rather on the fact that high levels produce a tinny off-taste and are rarely found under normal processing or storage conditions (Mannheim and Passy, 1982). Even when stored for 12 weeks at 50 °C, the tin contents of canned SSGJ were safely below the 250 ppm limit (Table II).

Noncanned SSGJ has been reported to contain Fe in amounts of 0.6-1.9 mg/kg (Nagy, 1977). The range of Fe found in freshly canned SSGJ (Table I) was similar to

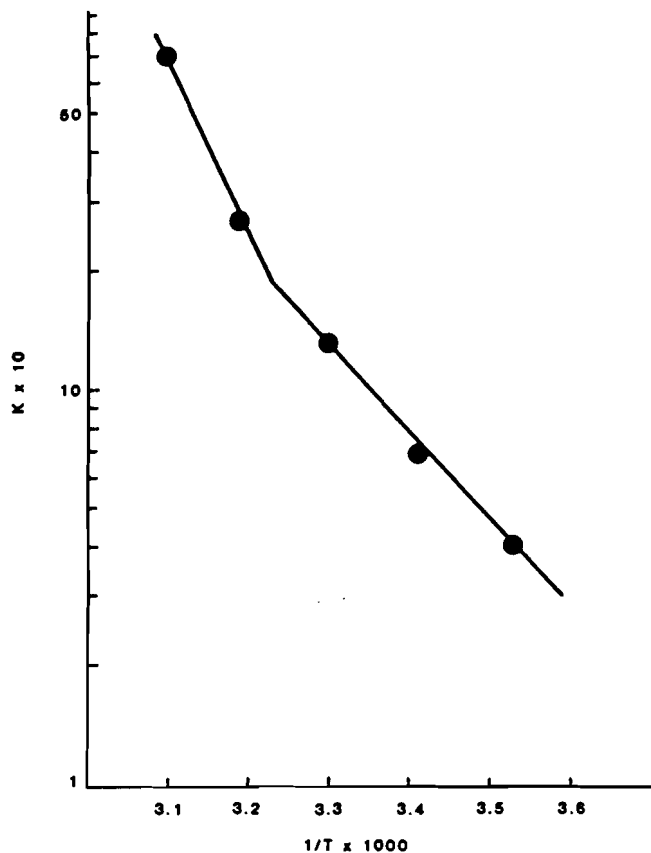


Figure 2. Arrhenius plot of $\log K$ (mg of Sn uptake/kg of juice per wk) vs. reciprocal of absolute storage temperature. The Arrhenius plot indicates a change in kinetics of Sn dissolution at ca. 37 °C.

freshly processed, noncanned SSGJ (Nagy, 1977) and, therefore, indicated that Fe dissolution of the base plate

during initial canning was minimal. However, after canning and during storage, iron dissolves from the base plate and is incorporated in the juice product. The uptake of Fe by these SSGJs is noted in Table II. After 12 weeks of storage the average weekly rates of Fe uptake (mg/kg of juice per wk) were 0.004 (10 °C), 0.01 (20 °C), 0.03 (30 °C), 0.06 (40 °C), and 0.18 (50 °C). Fe uptake increased ca. 2-fold for each 10 °C rise between 10 and 40 °C, whereas from 40 to 50 °C uptake increased ca. 3-fold. As noted with Sn uptake (Figure 1), temperatures in excess of ca. 40 °C cause disproportionately higher uptakes of Fe.

Ting (1977) reported on a survey of commercially canned SSGJ (unknown storage history) that the iron contents ranged from 0.7 to 7.6 mg/L with a mean of 2.3. More recently, Nikdel and Barros (1984) reported the iron contents of Florida-canned SSGJ to range from 0.03 to 6.9 mg/L with a mean of 1.4. The wide range of iron values reported for canned SSGJ, in contrast to the smaller natural range reported by Nagy (1977), is due to iron contribution by the can, the amount of which is dependent on can construction and storage parameters (time, temperature). Large intercan variation has been reported by Thomas et al. (1975) and by Rouseff and Ting (1980). In one experiment (Nikdel and Nagy, 1985), we detected a sample of canned commercial SSGJ to have 11 mg of Fe/kg of juice after 9 weeks of storage at 20 °C. Corrosion was excessive and probably due to bad can construction and/or improper closure during canning. In canned juice, it is not unusual to detect high iron contents. However, high iron values should not be reported as the natural iron level of pure grapefruit juice.

An experiment was conducted on 30 randomly selected cans from various storage temperatures to determine whether any relationships existed among Sn, Fe, and Al within individual cans. A plot of Sn vs. Fe for 30 cans is shown in Figure 3. Regression analysis yielded a correlation coefficient of 0.809 and a linear equation of tin

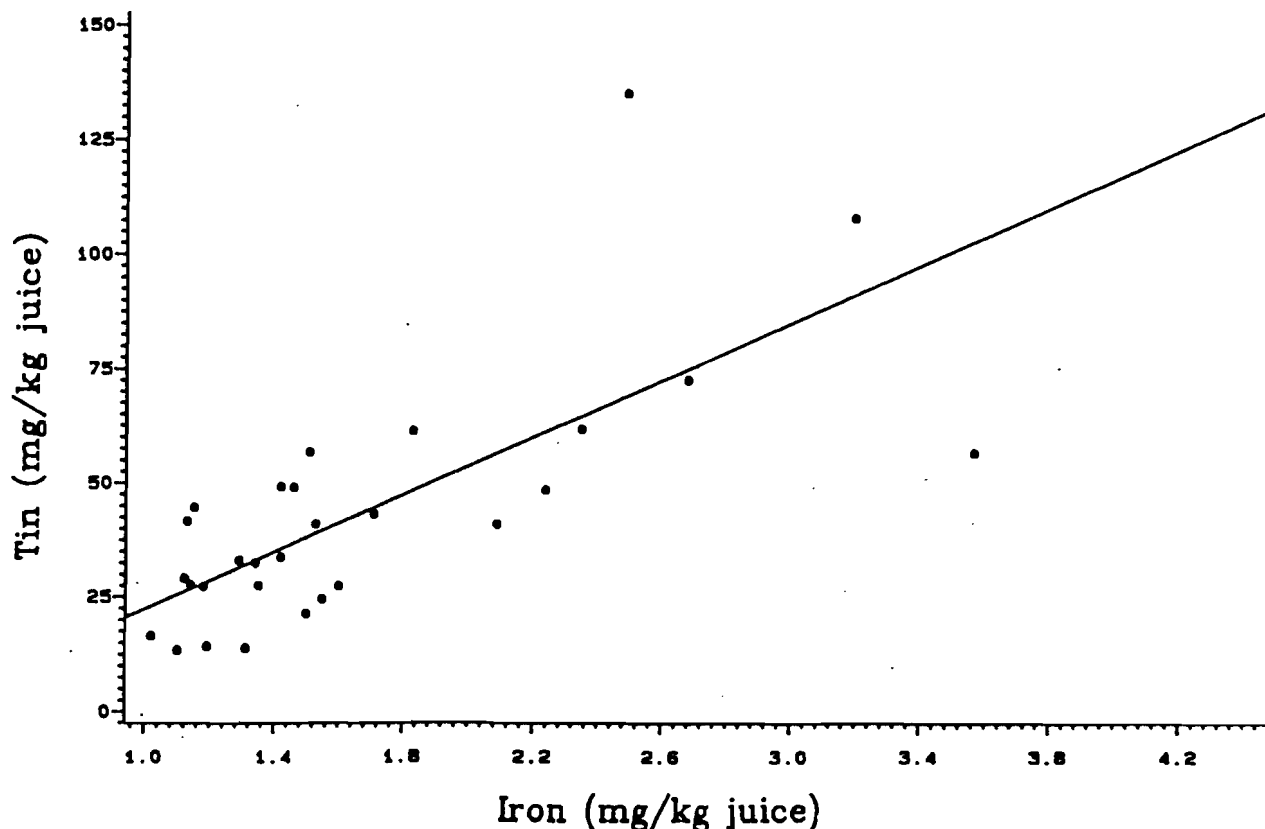


Figure 3. Linear regression plot of Sn vs. Fe from 30 cans stored at temperatures ranging from 20 to 50 °C.

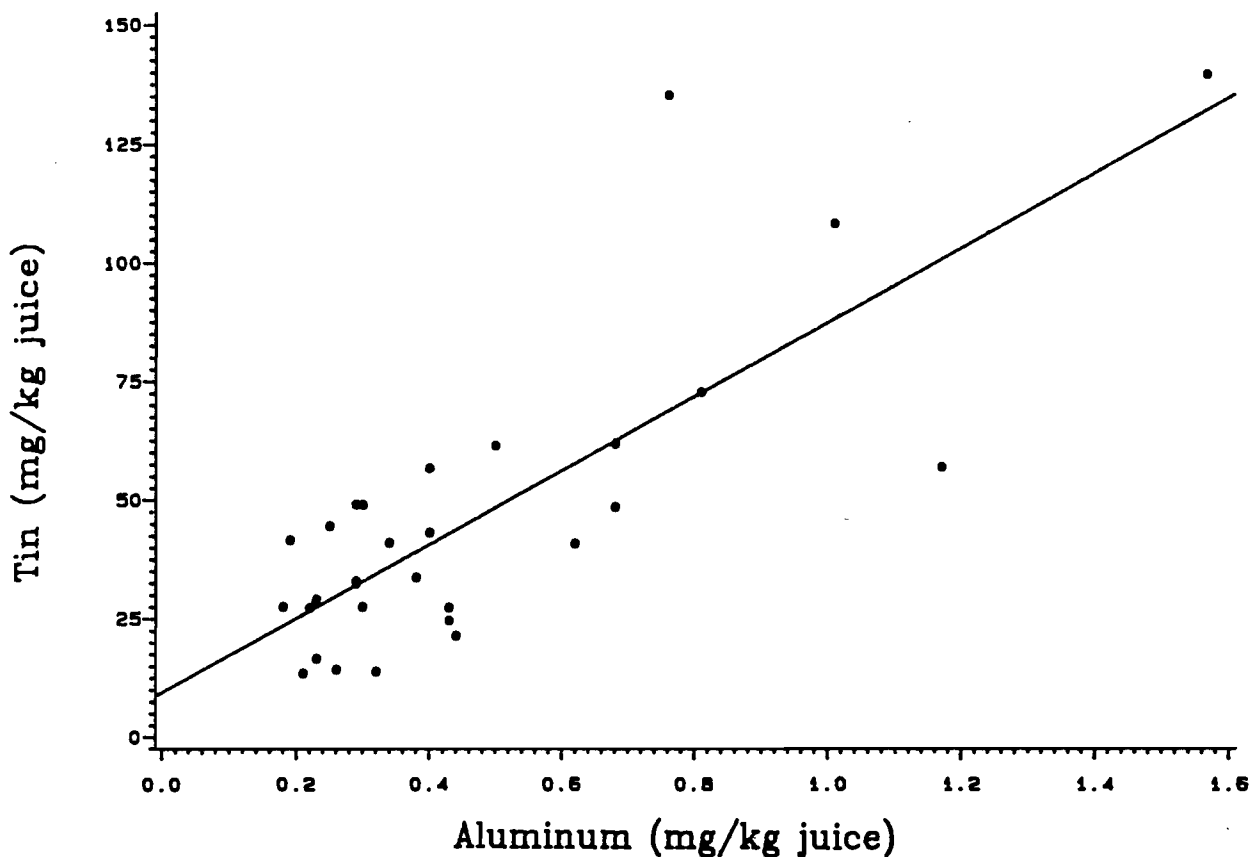


Figure 4. Linear regression plot of Sn vs. Al from 30 cans stored at temperatures ranging from 20 to 50 °C.

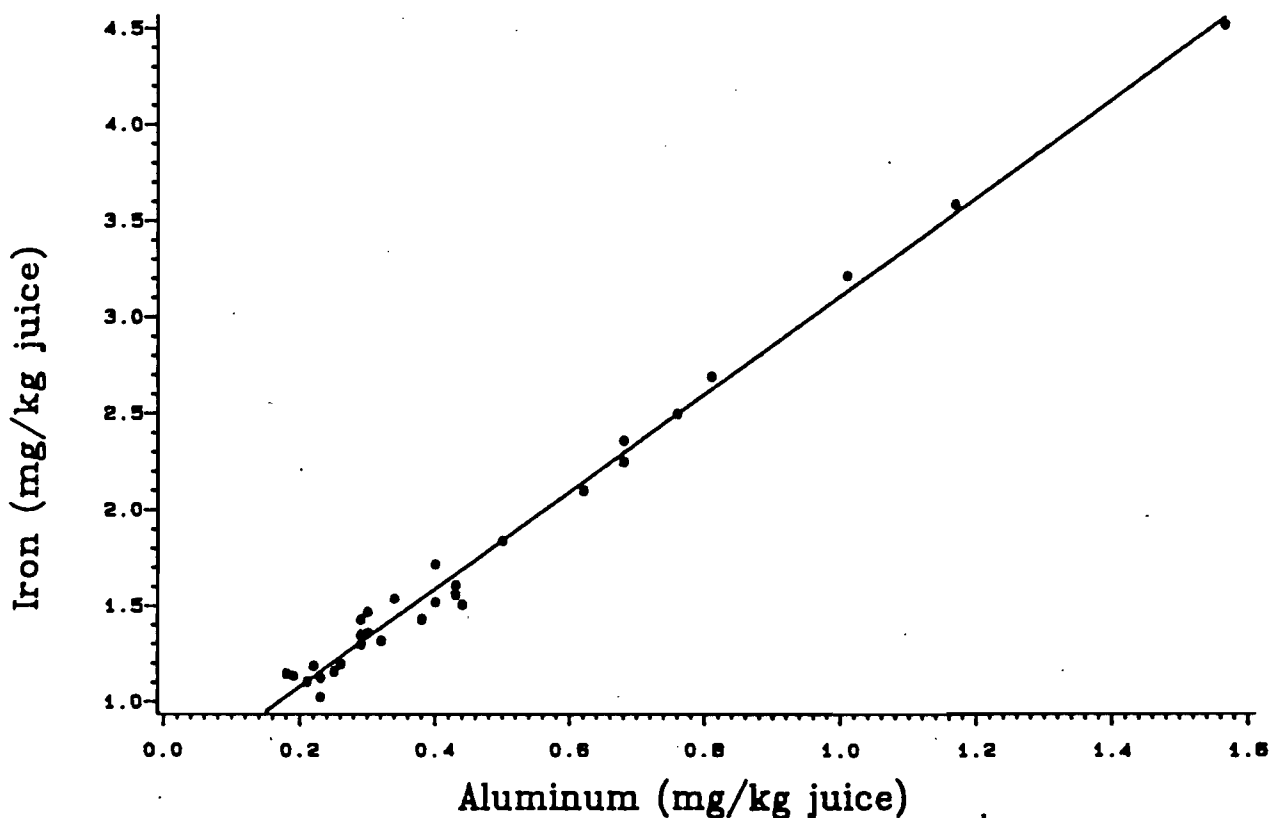


Figure 5. Linear regression plot of Fe vs. Al from 30 cans stored at temperatures ranging from 20 to 50 °C.

content = $-9.1386 + 31.3358$ (iron content) [or $y = -9.1368 + 31.3358x$]. Figure 4 depicts the linear relationship between Sn and Al. Regression analysis resulted in the equation $y = 9.3938 + 77.8482x$ where y is the tin content and x is the aluminum content. The correlation coefficient

for this equation was 0.791. A plot of Fe vs. Al (Figure 5) resulted in a very high correlation coefficient of 0.995. This linear relationship was noted by the following regression equation: $y = 0.5711 + 2.5272x$ where y is the iron content and x is the aluminum content. Iron and aluminum are

components of the alloy steel plate, and, apparently, the juice dissolves them in a very uniform manner.

Limited information exists on the Al contents of citrus juices. McHard et al. (1980) reported a range of 0.041-0.155 mg Al/kg juice for noncanned single-strength orange juice, whereas Nikdel and Barros (1984) reported a range of 0.054-0.415 mg of Al/kg of juice for single-strength orange juice. No information is available on the Al content of noncanned SSGJ, but Nikdel (1985) determined a range of 0.079-0.094 mg of Al/kg of juice for freshly prepared single-strength grapefruit juice.

Table I reports the Al contents of freshly canned SSGJ, and Table II reports the Al contents of juices subject to a 12-week storage at varying temperatures. After 12 weeks, the average weekly rates of Al uptake (mg/kg of juice per wk) were 0.003 (10 °C), 0.005 (20 °C), 0.013 (30 °C), 0.027 (40 °C), and 0.073 (50 °C). A 2-fold uptake of Al occurred for every 10 °C rise between 10 and 40 °C, whereas from 40 to 50 °C uptake increased ca. 2.7-fold.

CONCLUSION

Internal corrosion of canned SSGJ is characterized by dissolution of the container metal into the juice. The uptake of tin, iron, and aluminum by canned SSGJ was related to storage time and temperature. The rates of uptake for the metals were Sn > Fe > Al. Storage of juices at temperatures below 40 °C showed a relatively uniform Q_{10} of ca. 2, whereas storage above 40 °C showed Q_{10} values of 2.6 (Sn), 3 (Fe), and 2.7 (Al). Iron and aluminum are found in canned SSGJ at relatively minor levels.

Examination of the Sn, Fe, and Al contents of 30 individual cans by linear regression analysis revealed definitive relationships. The correlation coefficients for Sn vs. Fe (0.809) and Sn vs. Al (0.791) were statistically significant, whereas the Fe vs. Al (0.995) value was highly significant. The data indicate that the tin coating material of the base plate dissolves inconsistently (considerable intercan tin variability, even with cans stored at the same temperature), whereas when the steel base corrodes, the Fe and Al of the alloy dissolve into the juice in a more uniform manner.

Registry No. Al, 7429-90-5; Fe, 7439-89-6; Sn, 7440-31-5.

LITERATURE CITED

- Association of Official Analytical Chemists *Official Methods of Analysis*, 11th ed.; AOAC: Washington, DC, 1970.
- Bakal, A.; Mannheim, H. C. *Isr. J. Technol.* 1966, 4, 262.
- Codex Alimentarius Commission *Report of the 12th Session*; FAO/WHO: Rome, 1978; p 45.
- Curl, A. L. *Food Res.* 1949, 14, 9.
- Kefford, J. F.; McKenzie, H. A.; Thompson, P. C. O. *J. Sci. Food Agric.* 1959, 10, 51.
- Elkins, E. R. *J. Assoc. Off. Anal. Chem.* 1982, 65, 965.
- Greger, J. L.; Johnson, M. A. *Food Cosmet. Toxicol.* 1981, 19, 163.
- Johnson, M. A.; Greger, J. L. *Am. J. Clin. Nutr.* 1982, 35, 655.
- Mannheim, C. H.; Hoenig, R. *Confructa* 1971, 16, 165.
- Mannheim, C.; Passy, N. *CRC Crit. Rev. Food Sci. Nutr.* 1982, 17(4), 371.
- McHard, J. A.; Foulk, S. J.; Jorgensen, J. L.; Bayer, S.; Winefordner, J. D. In *Citrus Nutrition and Quality*; Nagy, S., Attaway, J. A., Eds.; ACS Symposium Series 143; American Chemical Society: Washington DC, 1980; Chapter 16.
- Nagy, S. In *Citrus Science and Technology*; Nagy, S., Shaw, P. E., Veldhuis, M. K., Eds.; AVI Publishing Westport, CT, 1977; Vol. 1, Chapter 13.
- Nagy, S.; Rouseff, R. L. *J. Agric. Food Chem.* 1981, 29, 889.
- Nagy, S.; Rouseff, R. L.; Ting, S. V. *J. Agric. Food Chem.* 1980, 28, 1166.
- Nikdel, S. Florida Department of Citrus, unpublished results, 1985.
- Nikdel, S.; Barros, S. M. *Proc. Fla. State Hortic. Soc.* 1984, 97, 79.
- Nikdel, S.; Nagy, S. Florida Department of Citrus, unpublished data, 1985.
- Omori, Y.; Takanaka, A.; Ikeda, Y.; Furuya, T. *Nippon Yakurigaku Zasshi* 1955, 61, 77.
- Rouseff, R. L.; Ting, S. V. *J. Food Sci.* 1980, 45, 965.
- Rouseff, R. L.; Ting, S. V. *J. Food Sci.* 1985, 50, 333.
- Saguy, I.; Mannheim, C. H.; Passy, N. *J. Food Technol.* 1973, 8, 147.
- Thomas, B.; Edmunds, J. W.; Curry, S. J. *J. Sci. Food Agric.* 1975, 26, 1.
- Ting, S. V. *Proc. Fla. State Hortic. Soc.* 1977, 90, 178.
- Winge, R. K.; Peterson, V. J.; Fassel, V. A. *Appl. Spectrosc.* 1979, 33, 206.
- Yamaguchi, M.; Saito, R.; Okada, S. *Toxicology* 1980, 16, 267.

Received for review October 21, 1985. Revised manuscript received April 4, 1986. Accepted May 8, 1986. Florida Agricultural Experiment Stations Journal Series No. 6852.