Rapid Direct Analysis of Zinc in Sugar Products and Molasses

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Citric acid added at 10 grams per 100 ml. makes possible the direct analysis of zinc in sugar-containing solutions by atomic absorption spectrophotometry. All but 2 to 3% of the zinc in sugar-factory juices is precipitated by the practice of treating the hot juice with $Ca(OH)_2$ to a pH of 7.5 to 8.0.

Plant tissue and soil is analyzed for zinc by atomic absorption spectrophotometry which requires ashing to remove interfering organic substances (AOAC, 1965). Slavin (1968) has reviewed techniques for, and interferences with, zinc determination in plants and vegetables, fertilizers, animal tissues and fluids, wine and other beverages, and water. However, the authors wished to develop a direct analysis method using diluted aqueous solutions, because ashing is time-consuming and because molasses tends to foam during both dry and wet ashing. A corollary study ascertained whether or not all of the zinc present in sugarcane juice was concentrated into the molasses fraction during sugar processing. Initial attempts to apply atomic absorption spectrometry directly to the diluted samples were disappointing; nonreproducible zinc values were obtained at pH levels between 1 and 12 adjusted with mineral acid or base, at different temperatures, and with various porosities of sintered glass used in filtration.

When an aqueous solution of citric acid was used as the solvent, greater accuracy and precision were obtained. The recovery of zinc from molasses averaged 99%, with a minimum sensitivity of about 0.1 μg. of zinc per gram of molasses.

EXPERIMENTAL

Standard Curve. A 1000-μg.-per-ml. zinc stock solution was prepared by dissolving reagent-grade zinc metal in 0.6*N* HCl and diluting to volume with double glass-distilled water. A 10-μg.-per-ml. solution was prepared by diluting 10 ml. of the stock solution to 1 liter with aqueous citric acid (pH 1.7) that contained 10 grams of reagent-grade acid per 100 ml. of solution in double-distilled water. Serial dilutions with up to 2 μg. zinc per ml. were prepared with the citric acid reagent. Absorbance was measured at 213.8 mμ with a Beckman Atomic Absorption Spectrophotometer 1300 equipped with a Techtron type AB-41 burner. A lamp current of 10 mA. was used for the zinc lamp. An air-acetylene flame, at pressures of 20 p.s.i. for the air and 3 p.s.i. for the fuel, was used. The slit width was 0.15 mm. There was a linear relationship between absorbance and zinc concentrations from zero to 2 μg. of zinc per ml. Addition of carbohydrates (D-glucose, D-fructose, or sucrose) up to 20 grams per 100 ml. did not interfere with the analysis.

Raw and Refined Sugars. Samples of 5 and 10 grams of raw or refined sugar were dissolved in the aqueous citric acid solution to a volume of 100 ml. and analyzed directly in the spectrophotometer.

Sugarcane Juice. Aliquots of 5 to 10 ml. were diluted with the aqueous citric acid to about 75 ml., heated to boiling, and cooled to room temperature. The volume was adjusted to 100 ml. with citric acid solution before spectrophotometer analysis.

Molasses. Well-mixed molasses (1 gram) was dissolved in 25 ml. of aqueous citric acid solution in a 50-ml. beaker. The mixture was transferred quantitatively to a 100-ml. flask and diluted to volume with citric acid solution. Before being burned in the flame, the solution stood for 30 minutes to ensure complete equilibration.

RESULTS AND DISCUSSION

Citric acid in aqueous solutions containing at least 10 grams per 100 ml. appears to chelate zinc in sugar solutions in such a way that sugar and other contaminants do not interfere with the determination. Raw sugarcane juice is exceptional, as will be shown below, in that the citric acid solution must be heated to boiling to release zinc from interfering substances in the juice.

For reasons that are not known, neither dilute hydrochloric

Table I. Zinc Content of Raw and Refined Sugars as Measured by Direct Method

Sugar Source	Zinc, μg./g.
Raw	
Plantation A	4.5
Plantation B	3.0
Plantation C	1.3
Plantation D	8.8
Plantation E	7.5
Plantation F	1.7
Refined	
Hawaiian sugarcane, granulated composites	
1966–1967	1.25
1968	1.30
Confectioners FF	0.62
Puerto Rico sugarcane	1.25
New Zealand sugarbeet	1.12
U. S. sugarbeet	1.12

Table II. Zinc Content of Molasses as Measured by Direct Method

Molasses Source	Zinc, μg./g.[a]
Island of Hawaii	
Composite A	9
Plantation 1	21
Plantation 2	24
Plantation 3	40
Island of Kauai	
Plantation 4	10
Composite B	22
Composite C	10
Island of Maui	
Plantation 5	24
Island of Oahu	
Plantation 6	50
Fiji	20

[a] Values were identical at dilutions of 0.5, 1.0, and 2.0% in citric acid reagent.

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Table III. Recovery of Zinc Added to Molasses

Zinc, µg./g.				
Initial content	Added	Total Calculated	Total Measured	Recovery, %
0.6	2.5	3.1	3.1	100
0.4	5.0	5.4	5.2	96
0.6	5.0	5.6	5.8	103
0.2	7.5	7.7	7.8	102
0.4	7.5	7.9	8.0	101
0.2	10.0	10.2	10.0	98
0.4	10.0	10.4	10.2	98
			Average	99 ± 2%

Table IV. Zinc Content of Molasses as Measured by Direct Method and by Ashing

	Absorbance Readings at 213.8 mµ		
	Direct Method		Dry Ashing
Sample	25° C.	100° C.	Method
Composite 1	0.020	0.020	0.020
Composite 2	0.021	0.020	0.021

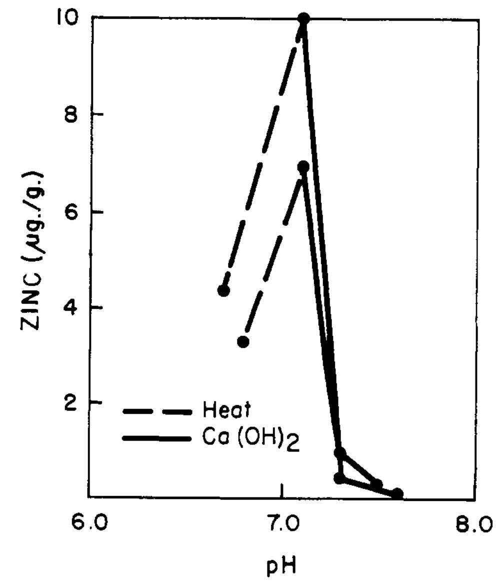

Figure 1. Effects of heat and $Ca(OH)_2$ on pH and zinc content of two sugarcane juices

acid (0.6*N*) nor disodium EDTA (1 to 10 grams per 100 ml.) gave reproducible readings with sugar and molasses solutions. Both reagents contained traces of zinc.

The zinc content of various sugar and molasses samples (Tables I and II) was determined from the linear standard curve. Table III shows the recoveries of zinc added to molasses. Ashed molasses in HCl and direct measurements in citric acid solution gave nearly identical zinc values (Table IV). Compared to the amounts of zinc normally present in sugarcane, the zinc content of molasses appeared to be surprisingly low. Zinc in sugarcane varies from 1 to 10 µg. per gram (fresh weight basis) depending on the amounts of available zinc in soil and water. Should the zinc in sugarcane be concentrated into the molasses, the expected amounts would range from 30 to 300 µg. per gram. The analysis of molasses samples showed that zinc content ranged from 9 to 50 µg. per gram (Table II)—about 15 to 30% of the expected amounts.

The low recovery of zinc in molasses may be accounted for by the practice of treating hot sugarcane juice with $Ca(OH)_2$ to adjust the pH to values between 7.0 and 8.0. This would precipitate much of the soluble zinc in the form of the oxide or hydroxide. As shown in Figure 1, heat alone increased the soluble zinc concentration and slightly increased the pH, while addition of $Ca(OH)_2$ drastically reduced the zinc remaining in solution. The precipitated calcium and zinc salts are removed by filtration. The remaining 2 to 3% of the zinc would be contained in the molasses.

LITERATURE CITED

Association of Official Agricultural Chemists, "Official Methods of Analysis," 10th ed., Washington, D. C., p. 24, 1965.
Slavin, W., "Atomic Absorption Spectroscopy," pp. 213–216, Interscience Publishers, New York, 1968.

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