NOTE

Copper (II) vs. Zinc Inorganic Salts as Oxidizers in Breadmaking

K. F. FINNEY,[1] B. L. BRUINSMA,[1,2] and O. NATSUAKI[3]

Jorgensen (1945) obtained a substantial improvement in the loaf volume of bread by adding 50 ppm copper (II) sulfate (12.73 ppm copper) to the formula, although the addition was reputed to be toxic. De Stefanis et al (1988) compared copper (II) sulfate and potassium bromate at levels of 5, 20, and 40 ppm in a no-time breadmaking method. Specific loaf volumes for 20 and 40 ppm of copper (II) sulfate were greater than those for the corresponding levels of bromate. Neither Jorgensen (1945) nor De Stefanis et al (1988) demonstrated what the minimum level of copper (II) sulfate required for optimum loaf volume was and to what extent loaf volume was stable for levels greater than optimum. The research reported herein answers those questions for four copper (II) and two zinc salts compared to optimum ascorbic acid and presents data by the Subcommittee on the Tenth Edition of the RDAs (1989) concerning levels of copper that are nutritionally adequate and safe.

MATERIALS AND METHODS

A straight grade flour was experimentally milled from a composite of hard winter wheat cultivars harvested at several Kansas locations. The flour contained 12.6% protein (14% mb), had a medium mixing requirement of 3.25 min in the absence of added oxidizer, and had a medium oxidation requirement characterized by a relatively large positive loaf volume response and greatly improved bread crumb grain. Analyses were by AACC (1983) methods.

The $CuCl_2 \cdot 2H_2O$, $CuSO_4 \cdot 5H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $CuCO_3 \cdot Cu(OH)_2$, $ZnCl_2$, and $ZnSO_4 \cdot 7H_2O$ were reagent grade.

The bread-making method (Finney 1984) involved a 90-min fermentation in a straight dough that included 50 ppm of ascorbic acid, an excess in the absence of nonfat dry milk, for comparison with the bread-making data for the copper (II) and zinc salts. A more conventional amount of fermentation (90 min) was employed so that optimum oxidation requirements of doughs would be lower (Finney et al 1976) than those for essentially no-time doughs.

Shogren and Finney (1974) found that adding optimum amounts of ascorbic acid to hard wheat flours that had medium to medium-strong physical dough properties yielded loaf volumes equal to those obtained with optimum amounts of potassium bromate. Also, they found that two flour composites, each representing many hard wheat cultivars, required 20–40 ppm of ascorbic acid for optimum loaf characteristics. Loaf volumes and crumb grains were not over-oxidized with increasing amounts of ascorbic acid to as high as 1,280 ppm. Thus, ascorbic acid is its own buffer against over-oxidation, primarily because it is both an oxidizing and a reducing agent.

The standard deviation of the difference between two treatment means was 13.95 cc for loaf volume and 0.0697 min for mixing time, and the loaf volume difference between any two treatment means ($n = 2$) required for significance was 29 cc for loaf volume and 0.14 min for mixing time ($P = 0.05$).

RESULTS AND DISCUSSION

Adding 7.45–18.64 ppm of copper as the chloride (Table I) increased loaf volumes from 875 cc (no salt or ascorbic acid) to optimum volumes equal to that for 50 ppm of ascorbic acid (984 cc) and improved loaf crumb grains from questionable-

[1]U.S. Grain Marketing Research Laboratory, Agricultural Research Service, U.S. Dept. of Agriculture, Manhattan, KS 66502.

Mention of firm names or trade products does not constitute endorsement by the U.S. Department of Agriculture over others not mentioned.

[2]Present address: Roman Meal Co., Tacoma, WA 98411.
[3]Present address: Pasco Corp. of America, Torrance, CA 90502.

unsatisfactory to satisfactory. Those data corroborate unpublished data for copper chloride obtained by K. Finney and O. Natsuaki early in 1979. Identical improvements in crumb grains and similar increases in loaf volumes were obtained for 7.45–18.64 ppm of copper as the sulfate and nitrate. The loaf volume of the ascorbic acid control for copper nitrate and copper carbonate was 975 cc, instead of 984 cc. As the concentration of copper (II) carbonate increased from 1.86 to 14.91 ppm, loaf volume responses and improvements in crumb grain were less than the corresponding values for the other three salts. Only at the highest copper level did loaf volume (970 cc) approach the optimum volumes of the other three salts. Thus, copper (II) carbonate is not desirable as an oxidizer in breadmaking.

As little as 7.45 ppm of copper as the chloride, sulfate, and nitrate oxidized bread dough as effectively as 50 ppm of ascorbic acid. Loaf volumes and crumb grains for higher concentrations of those three copper salts essentially remained on plateaus and were not over-oxidized, as has been found for comparably high levels of potassium bromate (Finney 1946).

Zinc chloride and zinc sulfate (2.40–23.98 ppm zinc) did not improve crumb grains or loaf volumes relative to the values for no added salt and no ascorbic acid (data not given).

As the parts per million of the metal in all salts increased, time of dough mixing to the point of minimum mobility gradually increased from 3¹/₄ to 3⁷/₈ min for copper chloride and copper sulfate and to 3⁵/₈ min for copper nitrate, copper carbonate, zinc chloride, and zinc sulfate.

TABLE I
Effect on Functional (Breadmaking) Properties of Adding Varying Amounts of Copper (II) Salts at the Mixing Stage[a]

Metal in Salt[b] (ppm)	Ascorbic Acid (ppm)	Dough Mix Time (min)	Loaf	
			Crumb Grain[c]	Volume (cc)
Copper chloride				
0	0	3 1/4	Q–U	875
1.86		3 3/8	Q	905
7.45		3 1/2	S	975
11.18		3 3/4	S	990
14.91		3 5/8	S	975
18.64		3 7/8	S	965
	50	3 1/2	S	984
Copper nitrate				
0	0	3 1/4	Q–U	865
1.86		3 3/8	Q	900
7.45		3 3/8	S	970
11.18		3 1/2	S	980
14.91		3 5/8	S	968
18.64		3 5/8	S	953
	50	3 1/2	S	975
Copper sulfate				
0	0	3 1/4	Q–U	875
1.86		3 3/8	Q	915
7.45		3 1/2	S	970
11.18		3 1/2	S	975
14.91		3 3/4	S	960
18.64		3 7/8	S	950
	50	3 1/2	S	984
Copper carbonate				
0	0	3 1/4	Q–U	865
1.86		3 3/8	Q–U	888
7.45		3 3/8	Q	938
11.18		3 1/2	Q–S	950
14.91		3 5/8	S	955
18.64		3 5/8	S	970
	50	3 1/2	S	975

[a] Data are on a 14% moisture basis.
[b] The 1.86, 7.45, 11.18, 14.91, and 18.64 ppm of copper are equivalent to 5, 20, 30, 40, and 50 ppm of copper chloride, respectively. The parts per million of the other three copper (II) salts varied with their molecular weights relative to that of copper chloride.
[c] S, Q, and U indicate satisfactory, questionable, and unsatisfactory, respectively.

The data in Table I show that 7.45 ppm of copper gave close to maximum loaf volume when added as the chloride, sulfate, or nitrate. The 7.45 ppm of copper is only 58.5% of Jorgensen's (1945) 12.73 ppm of copper in 50 ppm of copper sulfate.

The Subcommittee on the Tenth Edition of the RDAs (1989) stated that

> an FAO/WHO Expert Committee concluded that no deleterious effects can be expected in humans whose copper intake is 0.5 mg/kg body weight per day (FAO/WHO 1971). Usual diets in the United States rarely supply more than 5 mg/day.

The subcommittee also gave estimated safe and adequate daily dietary intakes of up to 1.5 mg for ages 4–6, 2.0 mg for ages 7–10, 2.5 mg for over 11 years, and up to 3.0 mg for adults.

Assuming 300 g of flour in a 1-lb loaf of bread containing 20 slices, there would be 2.235 (0.745 × 3) mg of copper per loaf and 0.112 mg per slice for the 7.45-ppm (0.745-mg) level of copper in Table I. There would be 3.354 (1.118 × 3) mg per loaf and 0.168 mg per slice for the 11.18-ppm (1.118-mg) level of copper. According to Betschart (1988), flour contains 0.62–0.63 mg of copper per kilogram (0.186 mg/300 g). The native copper in flour would increase that in each slice of bread by 0.0093 mg (0.186 ÷ 20), so the above values per slice would increase to 0.121 and 0.177 mg of copper, respectively, and four slices would contain 0.484 and 0.708 mg, respectively. Both values apparently are nutritionally safe and adequate, but using the lower level of 7.45 ppm in Table I, up to no more than 9.31 ppm, would be preferable. Even 13 slices of bread containing 7.45 ppm copper would be nutritionally safe and adequate.

The mechanism of the oxidation and improved loaf volume (gas retention) of wheat flour doughs containing copper (II) salts is unknown. At the end of fermentation, the added copper (II) of the salt may be associated with one or more dough components, thereby affording a research tool for studying the mechanism of dough improvement and possible oxidation.

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