MICRONUTRIENT ADDITIONS TO CEREAL GRAIN PRODUCTS[1]

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ABSTRACT

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In line with the fortification policy for cereal-grain products proposed by the Food and Nutrition Board of the National Academy of Sciences-National Research Council (NAS-NRC), vitamins A, B_6, and folic acid plus zinc, magnesium, and calcium have been added to flour, corn meal, and rice in addition to the normal fortification with thiamine, riboflavin, niacin, and iron. Flour and corn meal have been fortified via powder premixes and rice by means of 1:200 concentrate of rice kernels coated with the nutrients. Stability of the vitamins is good during storage of both concentrates and fortified cereals, as well as in bread baked with commercial equipment using fortified flour. The rice premix is resistant to loss of nutrients when washed with water at room temperature, and the added vitamins in the fortified rice show good stability on cooking.

Fortification of flour and bread with vitamins dates back to the 1920's, when some millers added vitamin D to flour. In the early 30's, efforts were made to achieve higher vitamin B retention in white flour by undermilling. By the late 30's, the possibility of thiamine addition was explored when synthetic thiamine became available commercially. In 1941, the enrichment of flour and bread with thiamine, niacin, riboflavin, and iron was adopted as War Food Order No. 1 (1); the addition of calcium and vitamin D was left as optional. Similar standards for corn meal, grits, macaroni, and rice were promulgated soon after (2–4). During the next quarter century, however, the situation remained static; it was not until the late 1960's that a change was sought in the level of enrichment with iron, the motivating force being the prevalence of iron deficiency. In 1971, the Food and Drug Administration proposed a regulation to increase the level of the three B vitamins in bread and cereal products by at least 50% and the level of iron by a factor of three; an amendment was issued in 1973 to provide for these higher levels (5).

More recently, the Food and Nutrition Board of the National Academy of Sciences reviewed the entire enrichment program and proposed an expanded fortification guide for cereal grain products (6). The board recommended that a proper enrichment formula for cereal grains should provide niacin, thiamine, riboflavin, vitamin A, vitamin B_6, folic acid, calcium, magnesium, iron, and zinc. A significant proportion of the population appears to be at risk of deficiency in one or more of those ten nutrients. Since approximately one-fourth of the daily caloric intake in the U.S. comes from cereal grain products, grain products are logical carriers of fortification for most nutrients; therefore, where technically feasible, they should be used as a means of supplementing the intake of those nutrients. It is a prime object of this paper to show that fortification of flour, rice, and corn meal with those nutrients is, in fact, technologically feasible.

Current fortification levels and the proposed NAS-NRC levels are presented in Table I. The lower figures are minima for bakery products and the higher are

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maxima for either macaroni products or rice. Vitamin E is not on the recommended list, but its importance is recognized. Processors were strongly urged (6) "to refine flour no more than is actually required for consumer acceptance" and to avoid destructive bleaching and maturing agents wherever possible. Significant increases in vitamin E, B_6, pantothenic acid, and many other vitamins occur when the extraction rate is held in the 80% range instead of the 65% range. Losses of alpha-tocopherol during wheat milling have been discussed by Rubin (7), while Bunnell *et al.* (8) showed that the average diet may provide only 7 mg of vitamin E per day instead of the estimated average daily requirement of 14 mg per day (1 mg dl-α-tocopheryl acetate = 1 unit). De Ritter (9), reviewing the stability characteristics of vitamins in processed foods, concluded that, in most cases, the derived vitamin potencies could be maintained if proper technology is applied.

MATERIALS AND METHODS

Materials

The flour used for the flour and bread fortification studies was fairly typical of baker's flour from the 1974 wheat crop, with an ash content of 0.43%, a protein content of 11.50%, and a moisture content of 12.0%.

Unfortified corn grits, moisture content 11.4%, were supplied by the Quaker Oats Company, Chicago, Ill. For the corn meal experiments, Quaker Yellow Corn Meal, enriched, degerminated, with a moisture content of 6.5%, manufactured by Quaker Oats Co., was used. Since our assay data indicated that thiamine, niacin, and riboflavin were already present at the NAS-NRC proposed

TABLE I
Fortification Comparisons

Nutrient	Presently Used[a] mg/lb	Proposed[b] mg/lb	Proposed[b] mg/100 g
Thiamine	1.1–5.0	2.9	0.64
Riboflavin	0.7	1.8	0.40
Niacin	10–34	24	5.29
Iron	8–26	40	8.81
Calcium	500–1500	900	198.20
Vitamin A[c]	None	2.2 (7300 IU)[d]	0.48 (1600 IU)
Pyridoxine	None	2	0.44
Folic acid	None	0.3	0.07
Magnesium	None	200	44.10
Zinc	None	10	2.20

[a]Minima to maxima, in summary of Code of Federal Regulations, Title 21, enrichment levels baked products, flour, farina, etc.
[b]National Academy of Sciences: Proposed fortification (6).
[c]Retinol equivalent.
[d]The originally proposed level of 2.2 mg/lb (7300 IU) was lowered to 1.3 mg/lb (4300 IU) (22).

levels, only vitamin A, pyridoxine, and folic acid were added to the corn meal, with 14 mg/lb iron to increase the iron content to the required 40 mg/lb.

Vitamin A palmitate Type 250-SD, containing not less than 250,000 IU of vitamin A, USP-FCC per g [1 IU of vitamin A is equivalent to 0.3 μg all trans vitamin A alcohol (retinol)]; thiamine mononitrate (B_1) USP-FCC; niacin USP-FCC; folic acid USP-FCC; pyridoxine HCl (B_6) USP-FCC; and riboflavin-S (B_2) USP-FCC were all supplied by Roche Chemical Division, Hoffmann-La Roche Inc., Nutley, N. J.

The source of iron for the flour, corn grits, and corn meal fortification was Mallinckrodt Reduced Type 4350 from Mallinckrodt Inc., St. Louis, Mo. For the rice fortification, ferric orthophosphate white, food grade, assay 32.3%, obtained from Joseph Turner Co., Ridgefield, N. J., was used.

Zinc and magnesium in the forms of zinc oxide USP powder and magnesium oxide USP heavy powder were Mallinckrodt brands.

The calcium source was reagent grade calcium sulphate ($CaSO_4 \cdot 2H_2O$).

Baking Conditions and Type of Dough System

Bread was baked for 20 min at 415° F. A sponge-dough procedure yielding two 1-lb loaves per dough mix was used.

Analytical Methods

Vitamin A, thiamine, riboflavin, niacin, iron, and magnesium were assayed according to AOAC procedure (10). Pyridoxine was assayed by the microbiological method of Atkin *et* al. (11). Folic acid was extracted according to AOAC procedure (10) and assayed microbiologically using *Streptococcus faecalis* (12,13).

Calculations

Initial nutrient values (added nutrients) were obtained by assaying for the nutrient contents of control (unfortified) samples and deducting these values from the assay values of the fortified samples. Per cent retention was determined as follows:

$$\text{Per Cent Retention} = \frac{\text{Nutrient content of fortified sample} - \text{nutrient content of control sample}}{\text{initial nutrient value}} \times 100$$

Label claim is the level suggested for the fortification of cereal grain products (Table I), unless otherwise indicated. A vitamin overage of 10% and a mineral overage of 5% were included in all fortification studies.

RESULTS AND DISCUSSION

Flour and Bread Fortification

A recent study in our laboratories by Cort *et al.* (13) of enrichment premixes containing the six NAS-NRC recommended vitamins plus iron and vitamin E showed good stability of all components. The study further showed excellent retention of these vitamins in flour, which was additionally fortified with calcium, magnesium, and zinc, and in bread made in small-scale laboratory equipment.

These results were so encouraging that the cooperation of ITT Continental Baking Company Laboratories with commercial baking equipment and experience was sought and obtained. Flour was fortified and bread was baked at ITT Continental Baking Co. Laboratories; vitamin assays were carried out in our laboratories. Initial commercial scale experiments suggested that vitamin A might suffer some losses during baking in the presence of the complete mineral supplement. Therefore, two premixes were compared. Premix A provided all the NRC recommended vitamins and minerals; premix B contained all the proposed nutrients except calcium and magnesium. Results are shown in Table II. The data show very good stability for vitamins B_1, B_2, B_6, and niacin in both experiments. Vitamin A and folic acid show a slight loss in bread fortified with premix A, while almost no loss was observed in samples enriched with premix B, indicating that calcium and magnesium may worsen vitamin A, and, to a lesser extent, folic acid deterioration at the temperatures and moisture levels in the baking process.

TABLE II
Stability of the NRC Proposed Vitamins in Bread (38% H_2O)

Supplement	Level Added mg/lb	Premix, % Retention: After baking A[a]	B[b]	5 Days at RT A[a]	B[b]
Vitamin A	992 IU	83	95	83	95
Vitamin B_1	1.8	101	101	101	100
Vitamin B_2	1.1	105	101	108	101
Vitamin B_6	1.2	100	105	100	105
Niacin	15.0	100	102	100	106
Folic acid	0.19	94	105	80	102
Iron	24.8	104	105	NR[c]	NR
Calcium	558.0	NR	...	NR	...
Magnesium	124.0	107	...	NR	...
Zinc	6.2	NR	NR	NR	NR

[a]Fortified with the complete vitamin-mineral supplement.
[b]Vitamin-mineral supplement without calcium and magnesium.
[c]NR = not run.

TABLE III
Scoring Data on Bread

Aspect	Unenriched	Standard Enrichment	Premix A[a]	Premix B[b]
Loaf volume, cc/g	5.9	5.9	5.9	5.9
Crumb color (10)	9.0	8.5	7.5	8.0
Grain (10)	9.0	8.5	7.5	8.0
Proof time, min	57	57	59	56

[a]Complete NRC proposed vitamin-mineral supplement.
[b]NRC proposed vitamin-mineral supplement without calcium and magnesium.

The taste of the breads fortified with either premix A or B was indistinguishable from that of unfortified or normal fortified bread. A panel of 14 experts could not detect any off-flavor in the fortified breads. Taste tests carried out after a week's storage of the bread at room temperature indicated a very slight off-flavor in the bread fortified with premix A, statistically significant at the 5% level. The off-flavor was probably due to magnesium. This mineral is known to cause off taste in bread when used at the proposed level of 200 mg/lb (14). Bread fortified with the vitamins, iron and zinc (premix B) was judged not to have off-flavors.

The fortified breads were slightly darker colored than the unfortified (Table III). The bread containing the full mineral supplement (premix A) gave a slightly lower grain score. The scoring data tabulated at ITT Continental Baking Co. Laboratories also showed no change in the volume of the loaves fortified with the various enrichment premixes. Bread fortified with premix A, containing the full mineral supplement, received the lowest scores, suggesting that addition of large amounts of calcium and magnesium affects color and grain. Also, proof time of 59 min for these loaves was slightly longer than the 56 to 57 min observed for the other samples.

Stability of the vitamins in flour containing approximately 12% moisture is excellent (Table IV). Storage data for 6 months at room temperature of flour fortified with premixes A or B show no loss of vitamin content. All added nutrients retained full potency even when the full mineral supplement was included (premix A). The premixes blended well with the flour, producing a uniform product. The odor and appearance of the fortified flour were the same as those of the unfortified flour. These results agree with those of Cakirer and LaChance (15).

The feasibility of bread fortification with the six recommended vitamins, plus

TABLE IV
Stability of the NRC Proposed Vitamins in Flour (12% H_2O)
(Values given in mg/100 g or IU/100 g)

		% Retention			
		Initial		6 mo. at RT	
Supplement	**Label Claim**	**Premix A[a]**	**Premix B[b]**	**Premix A[a]**	**Premix B[b]**
Vitamin A	1600 IU	1730 IU	1800 IU	101	100
Vitamin B_1	0.64	0.76	0.71	99	101
Vitamin B_2	0.40	0.39	0.40	100	100
Vitamin B_6	0.44	0.48	0.56	100	100
Niacin	5.29	5.60	5.60	100	100
Folic acid	0.07	0.063	0.07	100	96
Iron	8.81	9.34	9.46	97	100
Calcium	198.2	209.0	NR[c]	NR	...
Magnesium	44.1	47.0	NR	NR	...
Zinc	2.2	2.3	NR	NR	NR
Moisture, %		11.6	12.1	11.8	12.5

[a]Fortified with the complete vitamin-mineral supplement.
[b]Vitamin-mineral supplement without calcium and magnesium.
[c]NR = not run.

iron and zinc, has now been demonstrated. The addition of calcium and magnesium at the recommended levels poses problems that require further investigation.

Corn Meal and Corn Grits Fortification

Yellow corn meal and corn grits were fortified with the six NRC vitamins and iron premix and stored at room temperature for 6 months (Table V). The data indicate only minor variations in the vitamin levels, showing good stability at room temperature storage and at normal moisture levels. Retention of vitamins after cooking was good in both corn meal and corn grits. Only vitamin A showed losses. Therefore, the stability of this vitamin was further investigated.

Quick grits with a suggested cooking time 2.5 to 5 min and regular grits with a suggested cooking time 30 min were enriched with 5700 IU of vitamin A (250 SD) including 30% excess. Quick grits were stirred into boiling salted water and cooked for 4, 6, and 10 min; regular grits were cooked for 30 min. Vitamin A losses of 20 to 25% were obtained with grits cooked for 4 and 6 min (Table VI). Grits cooked for 10 and 30 min showed 25 to 30% losses, indicating that, with longer cooking time, decreased vitamin A retention is experienced.

Yellow corn meal upon cooking showed only 10 to 15% vitamin A losses. The

TABLE V
Stability of NRC Vitamin-Iron Premix in Yellow Corn Meal (6.5% H_2O) and in Corn Grits (11.4% H_2O) at Room Temperature (Values given in mg/lb or IU/lb)

Nutrient	Corn Meal			Corn Grits		
	Initial	3 mo.	6 mo.	Initial	3 mo.	6 mo.
Vitamin A (250 SD)	6000 IU	5820 IU	5880 IU	6000 IU	5700 IU	4850 IU
Thiamine	3.17	3.25	3.07	3.83	3.81	3.86
Niacin	26.0	25.7	NR[a]	36.0	36.0	NR
Pyridoxine (HCl)	4.5	4.0	4.5	4.4	4.3	4.5
Folic acid	0.6	0.5	0.5	0.49	0.45	0.5
Riboflavin	2.02	1.81	1.96	2.82	2.64	2.58
Iron	41.0	39.0	40.0	55.0	52.1	56.0

[a]NR = not run.

TABLE VI
Per Cent Retention of Vitamin A (250 SD) in Cooked Grits and Cooked Yellow Corn Meal

	Cooking Time (min)				
	4.0	5.0	6.0	10	30
Quick grits	80	...	75	70	...
Regular grits	...	...	...	...	66-75
Yellow corn meal	...	87	...	...	...

significant lower losses are explainable with the difference in the mode of cooking. Corn meal is first wet with cold water, then gradually poured into boiling water and cooked over reduced heat for 5 min. In contrast, corn grits are dropped into boiling water and cooked as described before.

Fortification of Rice

Fortification of rice requires an entirely different concept. Rice is consumed as whole kernels and the problem is compounded by the fact that housewives often wash rice before cooking. Therefore, the enrichment nutrients have to be coated on rice and protected by a rinse-resistant coating. Such premixes have been developed such that one part of rice coated with the premix and then blended with 199 parts of rice will meet the desired specification. Although riboflavin is included in the NRC recommendation for wheat products, the yellow color which surfaces upon cooking rice is considered undesirable by processors and, presumably, housewives; consequently, the requirement for riboflavin was stayed by the Food and Drug Administration (16).

The selection of iron sources for cereal enrichment was reviewed by Harrison *et al.* (17). Although they found great variations in the bioavailability of ferric

TABLE VII
Composition and Stability of the NRC Vitamin-Mineral-Rice Premix[a]
(Made on a Production Scale)

Additive	Label Claim mg/lb	Initial Assay mg/lb	% Retention at RT 6 mo.
Vitamin A	1,460,000 IU	1,850,000 IU	87
Thiamine	580	629	99
Niacin	4,800	5,420	98
Pyridoxine	400	595	100
Folic acid	60	64	100
Iron[b]	8,000	9,380	100
Zinc	2,000	...	...

[a]Premix to be used at 1 lb/199 lb of rice.
[b]Ferric orthophosphate.

TABLE VIII
Average Washing Losses of Rice Premix[a]

Nutrient	Loss, %
Vitamin A	1.1
Thiamine	0.2
Niacin	0.3
Pyridoxine	1.0
Folic acid	No measurable amount
Iron	No measurable amount
Zinc	Not determined

[a]Washing as described in reference (21).

orthophosphate samples, it is the most suitable source for rice fortification due to its white color. Enriched rice kernels must blend well with unenriched kernels; they must be reasonably white so that consumers will not reject them. The whitening of the rice kernels is accomplished by using white ferric orthophosphate and talc. Application of grayish ferric orthophosphate or gray iron compounds will add an undesirable yellowish off color to the kernels.

Historically, there have been two principal procedures for rice premix manufacture, *viz.*, the Hoffmann-La Roche process (18,19) and the Merck process (20). These processes were developed further to accommodate the additional nutrients. Thiamine, niacin, and vitamin B_6 are applied onto the rice as a suspension. Vitamin A, folic acid, zinc, and iron are added as a powder blend in alternate layers with shellac. The coated rice is polished with talc. Calcium and magnesium are not included in the formulation because the suggested amounts would increase the size of rice kernels tremendously, at least two to four times, which constitutes an insurmountable problem.

The composition and stability data of the rice premix are shown in Table VII. The data show excellent retention of all the vitamins added. Rinse resistancy of the vitamins was done by the "federal" rinse test (21). Data in Table VIII show excellent rinse resistance. Losses of the vitamins in rinsings are considered very low—in the range of 0.2 to 1.1%.

Cooking losses of fortified rice were established by using a double boiler to avoid high temperatures at the bottom surface of the pot. One lb of premix was blended with 199 lb of unfortified rice. One-lb samples were boiled with 2 lb of water for about 30 min or until all the water was absorbed. Vitamin assays of the cooked rice showed practically 100% recovery of all added vitamins, bearing out the point that no vitamin loss will occur with proper cooking.

Availability of the added nutrients was studied by cooking the rice in excess water, filtering, and assaying the filtrate for water-soluble vitamins and for vitamin A. The data in Table IX show that 85 to 100% of niacin, thiamine, pyridoxine, and vitamin A were released into the cooking water, attesting to the availability of the added nutrients. Studies in humans are currently underway and will be reported later.

The method worked out for rice enrichment on small scale laboratory equipment was further extended to a 2500-lb production scale batch which was prepared successfully employing commercial equipment (Table VII). The success

TABLE IX
Per Cent of Vitamins Released from Fortified Rice into Excess Cooking Water

Nutrient	Maximum Concentration[a] mg/ml	Found in Filtrate mg/ml	%
Niacin	1.4	1.2	85
Pyridoxine	0.33	0.29	87
Thiamine	0.045	0.045	100
Vitamin A	360 IU	293 IU	81

[a]Maximum concentration calculated from amount of naturally occurring and added nutrient.

of our scale-up trial also was reflected by the fact that manufacturing losses were lower than experienced with the small scale batches.

CONCLUSIONS

The feasibility of flour, bread, and corn meal fortification with NRC recommended vitamins and minerals was established. Data to date indicate no problems in flour fortification and only minor problems in bread or corn meal fortification. Baking bread at high oven temperatures may induce a small loss of the vitamin A and folic acid contents, but this could be counterbalanced by adding 20 to 25% overages of these vitamins to the flour used for baking. Similarly, vitamin A losses are small when corn meal or quick grits are cooked. Regular grits, however, due to their longer cooking time, show increased vitamin A losses, suggesting that, to meet label requirements after blending and cooking, they will have to contain 35 to 40% overages. Enrichment of bread with calcium and magnesium needs to be studied further to titrate levels that may be added without adverse effects on taste and grain. Technology, verified on a full production scale, for enrichment of rice with five vitamins and two minerals, has been developed, with satisfactory data for stability in storage and in cooking, as well as apparent bioavailability. Riboflavin, due to its yellow color, considered undesirable by rice processors, is not included in rice fortification at this time, while the addition of calcium and magnesium needs further consideration because of the bulk they add.

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