Heavy Metals in Food Products From Corn[1]

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ABSTRACT

Concentrations of seven heavy metals (zinc, manganese, copper, lead, cadmium, chromium, and mercury) were determined for a wide variety of consumer-oriented corn products: milled fractions, prepared breakfast and snack foods, canned and frozen sweet corn items, syrups, oil, and kernel popcorn. Samples were decomposed by wet-oxidation, and six of the elements were determined by flame atomic absorption. Mercury was measured by a nonflame atomic absorption technique. Metal content ranged from a high of more than 200 γ zinc per g. in a defatted corn germ flour to a low of less than 0.001 γ mercury per g. in some products. The possible introduction of heavy metals into finished corn products by industrial processing was studied by comparing concentrations in finished products with previously determined heavy metal concentration in whole kernel corn.

Corn products in the diet provide a significant portion of the minerals and trace elements required by both animals and humans. With the advent of newer analytical techniques such as atomic absorption, concentrations of these trace elements in foodstuffs can now be established. To assess the quantity of trace elements contributed to the human diet by corn products requires the

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examination of a wide variety of foods. In this study the primary objective was to provide information on the content of seven heavy metals (Zn, Mn, Cu, Pb, Cr, Cd, and Hg) in corn-based foods directed primarily for human consumption. Some of the elements serve nutritionally as micronutrients (1); however for lead, cadmium, and mercury no beneficial effects have yet been ascribed. Therefore, it is important to establish the dietary levels of these elements in the different types of corn products commercially available and, in fact, currently being eaten by the consumer.

To provide maximum data that can be used effectively, studies on nutrients in foods should be organized so that analyses will be made on comparable raw and processed foods (2,3). In the case of cereals, food products eaten by humans require some form of processing. A variety of processed and readily available corn products purchased at local grocery stores were analyzed for the same metals analyzed in whole kernel dent corn. Adequate sampling of large numbers of these corn food items in the diet was prohibitive; therefore, a reasonable selection of the more important foods had to be made. Included in this group and representative of dry-milled corn products were: corn grits, corn meal, and a defatted corn germ flour.

Other processed corn foods studied were breakfast and snack foods as well as corn syrups and corn oil. Whole kernel sweet corns processed by both canning and freezing techniques were also examined. This method of foodstuff sampling from local outlets has the advantage that the food analyzed represents the food currently being consumed. However, two disadvantages are that this type of sampling technique confines itself to the eating habits of a certain area and also that the origin of the corn used in the products is unknown.

The inherent metal content of whole kernel corn had to be established to correlate metal concentration values in the corn products. The seven metals studied occur naturally in the corn grain; the mean levels of concentration of these metals in corn (4) were determined for 11 different corn samples. Six of these corn samples were submitted by the American Corn Millers Federation and originated from a geographical area covering six states. Overall mean concentration values for the seven metals in 11 samples ranged from a high of 22.9 γ per g. for zinc to a low of 0.0024 γ per g. for mercury.

After the naturally occurring concentration levels of metals had been determined for whole kernel corn, the next phase of the study had two major objectives: a) to determine where these elements occur in the kernel and how location would affect their presence in different milled product fractions and, eventually, in the corn foods eaten by the consumer; and b) to determine if any concentrating effect of these elements, especially lead, cadmium, or mercury, occurred in the consumer food product during processing.

MATERIALS AND METHODS

The food products were purchased at two different times and 6 months apart. These products were retained in their original containers to avoid contamination problems; frozen items were kept in a freezer until used. Brand name items, in consumer-size quantities, were acquired to ensure that future supplies, if needed, would be available. The defatted dry-milled corn germ flour (5) was prepared in this laboratory from a commercial grade corn germ supplied by Illinois Cereal

Mills, Paris, Ill. This defatted germ flour contained approximately 25% protein and 50% carbohydrates.

Six of the elements (Zn, Mn, Cu, Pb, Cr, and Cd) were determined by flame atomic absorption; the corn products (10 g.) were wet ashed with a nitric-perchloric acid combination as previously described (4). However, corn oil samples (5 g.) were wet ashed with concentrated nitric acid only at a temperature of 70° C. The oil samples were the most difficult to ash, and they required continuous heating for considerably longer heating periods for complete oxidation. Because of the difficulty in ashing oils, sample sizes greater than 5 g. were too time-consuming to be worthwhile. The prolonged heating time also had an unfavorable tendency to elevate metal values for samples and blanks. Finally, the ashed salts were dissolved in a 4% HCl medium. This solution was aspirated in the flame atomic absorption spectrophotometer (Varian AA 120) along with similarly prepared single-element standard solutions; scale expansion techniques were used as needed.

Flame atomic absorption is not sensitive enough to measure the small quantities of mercury encountered in the corn products; therefore, a sensitive nonflame atomic absorption technique was used. Because mercury can be lost easily by volatilization during decomposition of the sample, a separate decomposition procedure previously described was used (4). At least a 10-g. sample of the corn product was needed to definitely establish the levels of mercury present. In this method, the mercury salts were retained in solution effectively in an aqua regia medium until the mercury was reduced chemically to the elemental form. In a closed system the mercury vapor was swept from the solution into an absorption cell of the mercury analyzer (Coleman MAS-50), where the elemental mercury vapor absorbed light emitted by a mercury vapor lamp. The absorption was recorded as a peak on the recorder. For calibration purposes, mercury standards were carried through the entire procedure.

RESULTS AND DISCUSSION

Major mineral constituents and metals of trace quantities are concentrated in the germ fraction of corn (6). Although the germ itself represents approximately 12% of the whole kernel, it is composed of significant quantities of a) protein of high quality; b) an edible oil; c) carbohydrates that include sugars, starch, and pentosans; and d) mineral constituents principally as phytates. In contrast, the endosperm fraction of corn, which represents the major part of the kernel, is composed largely of carbohydrates with starch being the main constituent.

Whole Kernel Corn Compared to Dry-Milled Cereal Products

In Table I are compared the mean heavy metal concentrations for distinctly different corn products: a) whole kernel corn (where mean metal values for the 11 samples previously described are shown), b) a defatted dry-milled corn germ flour containing about 50% carbohydrates, of which approximately half was starch—mostly of endosperm origin, and c) corn grits and corn meal, common foods essentially of endosperm origin and having starch content of approximately 80% on a dry basis. Included in Table I for comparative purposes are data on a commercially available wheat germ product with a fat content of 11%.

From the data in Table I, it is apparent that six of the metals studied are concentrated in the defatted corn germ flour with an approximate overall factor of almost seven times when compared to the whole kernel corn. For mercury, the seventh metal, the concentration is smaller. Conversely, concentration factors for the same metals for corn grits ranged from only 0.2 to 0.8 times also when compared to whole kernel corn. For the seven metals, no appreciable difference in values was found between white and yellow corn meal. It can be concluded then that the seven elements are associated primarily with the germ fraction; moreover, it follows that corn products which are essentially of endosperm origin will be considerably lower in these elements.

When the diet includes whole kernel corn, the mineral and trace elements are associated with a starch content of about 70%. However during milling, the degerming process separates the mineral-rich germ fraction; consequently many resultant consumer products, although containing the major portion of the original corn kernel, retain only minor quantities of the minerals.

Comparative results show that except for manganese, where the concentration in the wheat germ product is approximately five times greater than for the corn germ flour, counterpart metal concentration values for both types of germ are similar.

Snack and Breakfast Foods

Processed snack and breakfast foods made from corn account for much of the corn consumed by humans. The starting material for most of these processed foods is a degermed corn material similar to corn meal or corn grits and, as such, is principally of endosperm origin. Additionally, in snack foods the finished product frequently contains a quantity of oil used in its preparation.

The metal content of snack and breakfast food items is shown in Table II. In this case, the three processed snack foods contained a quantity of oil. The extruded cheese-flavored snack had a degermed product as a starting material. However, the starting material for corn chips was whole corn. The common breakfast food, corn flakes, as well as the small briquette cereal were both made from a degermed corn product; in both of these finished products the quantity of oil was minor. Included as an unprocessed snack food was whole kernel popcorn. The popcorn represents a corn variety different from the dent corn samples previously studied (4).

The results (Table II) show that for snack and breakfast food items, where the starting material was a degermed corn product, concentrations of metals in these finished products were similar to those previously established for corn grits. However, corn chips, which are more closely related compositionally to the original whole kernel, showed significantly higher values for zinc, manganese, and copper. Further, considering all five processed snack and breakfast foods, concentration values for chromium in this group increased to levels more than double the quantities in whole kernel corn. This increase reflects the apparent introduction of chromium into the product during processing.

In order not to alter the concentration of metals inherently present in the popcorn kernel, unpopped corn was analyzed. Of notable interest is the fact that content of zinc, manganese, and copper in the popcorn was considerably greater than previously established metal values for the 11 varieties of dent corn; however, concentrations of lead, chromium, cadmium, and mercury were very similar to those previously determined (4).

TABLE I. COMPARISON OF HEAVY METAL CONTENT OF WHOLE KERNEL CORN AND DRY-MILLED CEREAL PRODUCTS[1]

(gamma per g., dry basis)

Product [2]	Zinc	Manganese	Copper	Lead	Chromium	Cadmium	Mercury
Whole kernel dent corn[3]	22.9 ± 2.2	6.60 ± 1.10	2.08 ± 0.45	0.271 ± 0.039	0.060 ± 0.035	0.055 ± 0.032	0.0024 ± 0.0017
White corn grits	4.70 ± 0.23	1.20 ± 0.11	0.85 ± 0.07	0.210 ± 0.031	0.034 ± 0.007	0.013 ± 0.005	0.0004 ± 0.0002
White corn meal	9.35 ± 0.53	2.08 ± 0.14	0.57 ± 0.05	0.134 ± 0.023	0.045 ± 0.007	0.022 ± 0.009	0.0010 ± 0.0006
Yellow corn meal	11.0 ± 0.9	2.96 ± 0.18	0.51 ± 0.06	0.194 ± 0.018	0.058 ± 0.008	0.042 ± 0.006	0.0006 ± 0.0007
Defatted dry-milled corn flour	208 ± 4	41.7 ± 1.9	12.4 ± 0.3	2.36 ± 0.11	0.397 ± 0.019	0.254 ± 0.022	0.0043 ± 0.0008
Wheat germ (11% fat content)	204 ± 6	212 ± 6	9.67 ± 0.13	0.791 ± 0.028	0.160 ± 0.014	0.304 ± 0.025	0.0029 ± 0.0006

[1]Mean and standard deviation of four (10 g.) samples.

[2]Products, except whole kernel dent corn and dry-milled corn germ flour, were purchased at local grocery stores.

[3]Mean values previously established for 11 different samples (4).

TABLE II. HEAVY METAL CONTENT OF CORN SNACK AND BREAKFAST FOODS[1]

(gamma per g., wet basis)

Corn Product[2]	Zinc	Manganese	Copper	Lead	Chromium	Cadmium	Mercury
Snack foods							
Processed							
Extruded							
cheese-flavored snack	5.33 ± 0.20	0.50 ± 0.05	0.43 ± 0.02	0.411 ± 0.012	0.147 ± 0.006	0.121 ± 0.019	0.0009 ± 0.0002
Corn chips (brand A)	14.8 ± 0.8	3.25 ± 0.19	1.19 ± 0.02	0.347 ± 0.058	0.185 ± 0.023	0.072 ± 0.042	0.0008 ± 0.0001
Corn chips (brand B)	15.6 ± 0.2	3.17 ± 0.08	1.10 ± 0.04	0.305 ± 0.068	0.164 ± 0.018	0.049 ± 0.005	0.0007 ± 0.0002
Unprocessed							
Popcorn-- whole kernel (unpopped)	42.9 ± 2.9	11.4 ± 0.8	4.26 ± 0.54	0.328 ± 0.018	0.067 ± 0.006	0.048 ± 0.005	0.0006 ± 0.0005
Breakfast foods							
Processed							
Corn flakes	2.49 ± 0.77	0.85 ± 0.31	0.81 ± 0.33	0.195 ± 0.023	0.102 ± 0.022	0.070 ± 0.004	0.0024 ± 0.0020
Small briq-uettes (yellow corn)	3.50 ± 0.52	0.88 ± 0.17	0.75 ± 0.09	0.062 ± 0.016	0.219 ± 0.036	0.060 ± 0.007	0.0013 ± 0.0008

[1]Each value represents the mean and standard deviation of four (10 g.) samples.

[2]All products were brand name items purchased at local grocery stores; two different brands of corn chips are listed.

TABLE III. HEAVY METAL CONTENT OF CORN SYRUPS AND CORN OIL
(gamma per g., dry basis)

Product	Zinc	Manganese	Copper	Lead	Chromium	Cadmium	Mercury
Dark corn syrup[1]	0.28 ± 0.14	1.00 ± 0.19	0.44 ± 0.02	0.022 ± 0.009	0.097 ± 0.003	0.021 ± 0.021	0.0004 ± 0.0004
Light corn syrup[1]	0.15 ± 0.06	1.06 ± 0.15	0.05 ± 0.02	0.019 ± 0.004	0.076 ± 0.003	0.020 ± 0.010	0.0009 ± 0.0013
Corn oil[2]	0.58 ± 0.12	0.01 ± 0.01	0.06 ± 0.06	0.032 ± 0.022	0.054 ± 0.032	0.003 ± 0.006	0.0008 ± 0.0003

[1]Mean and standard deviation of four (10 g.) samples.

[2]Mean and standard deviation of four (5 g.) samples;
except for mercury determination where result represents the mean of four (10 g.) samples.

TABLE IV. SUMMARY OF HEAVY METAL CONTENT OF CANNED AND FROZEN SWEET CORN
(gamma per g., "as-is" basis)

Product	Zinc	Manganese	Copper	Lead	Chromium	Cadmium	Mercury
Whole kernel corn[1]							
Frozen yellow sweet (brand A)	4.76 ± 0.11	1.26 ± 0.10	0.49 ± 0.04	0.059 ± 0.040	0.038 ± 0.003	0.005 ± 0.004	0.0027 ± 0.0041
Canned yellow sweet (brand B)	4.37 ± 0.24	0.96 ± 0.19	0.45 ± 0.08	1.16 ± 0.85	0.019 ± 0.023	0.014 ± 0.002	0.0007 ± 0.0002
Canned white sweet (brand C)	6.85 ± 0.080	0.62 ± 0.02	0.33 ± 0.05	0.100 ± 0.197	0.013 ± 0.003	0.031 ± 0.001	0.0007 ± 0.0001

[1]Each value represents the mean and standard deviation of four (10 g.) samples.

Corn Syrups and Corn Oil

Expressed on an "as-is" basis in Table III are results for the metal content of two corn syrups and one corn oil sample.

Corn syrups are used extensively in a wide variety of food products. Syrups are consumed as table syrups or as ingredients in other prepared foods. The syrups are produced from starch which has its origin in the endosperm fraction of the corn. Starch, a major product of the corn refining industry, is converted to sugars by treatments with acid, enzymes, or both. We determined the concentration of the seven metals in dark and light table syrups prepared by conversion by acid treatment.

The metal content in both types of syrup was similar and considerably lower than in other corn products. Of the seven metals, manganese showed the highest content at about 1 γ per g. Apparently, corn syrups contain only minor concentrations of the seven metals determined.

Corn oil is a product extracted from the germ fraction of the corn. The consumer product studied was a refined oil purchased in a glass bottle. Although corn oil originates from the mineral-rich germ fraction, metal concentration values for this refined oil were very low when compared to other corn products. The prolonged heating period in the ashing process, slightly higher blank values, lower concentrations of the metals in the oil, and smaller quantity of original sample analyzed were all factors that contributed to higher deviation of values between the oil samples analyzed.

Canned and Frozen Sweet Corn

Canned and frozen sweet corn are widely accepted food products and are an important part of the human diet. In canned or frozen corn where the whole kernel is eaten, the drained edible product had a moisture content of approximately 76%, which was in agreement with other published data (7). The major differences between canned and frozen corn are storage temperature and storage container. All items designated "canned" in this study were purchased in metal cans, whereas all frozen items were purchased in 10-oz. cardboard boxes. After these samples had reached ambient temperature conditions, the liquid was drained off completely before weighing the drained sample for analysis.

Results are summarized in Table IV (on a wet basis) of the metal content of canned and frozen whole kernel corn. Except for the higher value for lead (1.16 γ per g.)in the canned yellow corn (brand B), metal values for canned and frozen corns were similar. This mean value (1.16 γ per g.) was derived from four values that ranged from 0.24 to 2.0 γ per g., indicating considerable variation in lead content.

SUMMARY AND CONCLUSIONS

The seven metals measured in processed and prepared corn food products are inherent in raw corn in a parts per million (γ per g.) concentration range. These naturally occurring trace elements are concentrated mainly in the germ fraction of corn. As might be expected, in the variety of unprocessed or processed corn-based foods analyzed, metal content depended primarily on whether the germ was present in the finished product. Concentrations of these metals, excluding mercury, were approximately seven times greater in a dry-milled corn germ flour than in whole kernel corn. In contrast, degermed milled products showed levels of metal considerably lower than in whole kernel corn. Products with the lowest metal content were corn syrups and corn oil. For all corn products, metal content ranged from a high of more than 200 γ per g. zinc in the deffated germ flour to a low of less than 0.001 γ per g. mercury in some products.

By relating metal concentration values for the corn foods selected to values established for whole kernel corn, it was possible to indicate that minor additional quantities of these same metals may have been introduced into the products as a result of processing.

In conclusion, corn products studied here contribute only minor quantities of lead, cadmium, and mercury to the diet when the total amount of food eaten daily is considered. Of special significance is the extremely low quantities of mercury in all corn products.

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