Mineral Concentrations and Variations in Fast-Food Samples Analyzed by X-ray Fluorescence

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Concentrations of P, S, Cl, K, Ca, Mn, Fe, Zn, Br, Rb, and Sr were measured in quadruplicate analyses of 239 fast-food samples representing 40 kinds of breakfast foods, sandwiches, Mexican foods, pizzas, deep-fried foods, salads, desserts, and beverages. Samples were randomly collected from franchised chains in Utah and were analyzed by the CEMAS multielement X-ray fluorescence (XRF) method. Variations among franchise chains (23%) and outlet locations (10.7%) were significant in about half of the determinations when compared to sample and analytical variations. Duplicate sample aliquots exhibited homogeneity variations averaging 6.3%, and duplicate analyses exhibited analytical variations averaging 3.3%. Each element was validated by measurements on 7–13 NIST standard reference materials. Analyses of standards averaged within 7% of reference values, with an average bias of −2.8%. Comparisons with reference atomic absorption determinations of Mn, Fe, and Zn in the fast-food samples indicated a mean bias of +1.3% for the XRF data. Long-term analytical variations monitored from zinc in tomato leaves in 75 batches over a 7-month period averaged 2.1%, and all were within 3σ control chart limits.

INTRODUCTION

This paper presents mineral concentrations and their variations in fast foods from outlets of national and local franchise chains located in the Utah Wasatch Front area. This area previously has been the subject of nutritional epidemiology studies concerning mineral nutrients (Lyon and Sorenson, 1978), but the fast-food segment of dietary consumption was not addressed. The mineral data reported here help fill a particular need, since fast-food analyses generally are not available, yet these foods have increasing consumption rates that comprise up to 40% of total intake in some population segments. The continuing need for improved food composition data and improved analytical methods has been emphasized in reviews of the status of nutrient composition data (Beecher and Vanderslice, 1984; NRC, 1982). The distributions of P, S, Cl, K, Ca, Mn, Fe, Zn, Br, Rb, and Sr reported here include many nutritionally important elements required in public health and epidemiology research and some having regulatory or public-policy interest.

This study of minerals in fast foods is part of a broader research program aimed at characterizing and validating the multielement capabilities of X-ray fluorescence (XRF) analysis for foods. Previous, related mineral studies using the same XRF methods were applied to fruit and vegetable samples (Nielson et al., 1988). The XRF method used in these studies can determine 20–40 elements simultaneously in dried and pelletized food samples without dissolution, ashing, or other destructive preparation techniques or their related dilution and contamination problems. The precisions, accuracies, and detection limits attained by this direct XRF technique were evaluated to demonstrate its potential as a low-cost, large-volume analytical tool. The XRF method utilizes a prior system calibration of element sensitivities and fundamental parameters of X-ray physics for mineral quantitation (Nielson, 1977). This approach eliminates the need for calibration standards of similar composition to the samples and permits use of standard reference materials solely in the role of indicators of accuracy and precision. Since the analyses are nondestructive, samples can be repeatedly reanalyzed, adding flexibility to the experimental designs used here.

The fast-food sampling and analysis protocols were designed to define representative mineral distributions for the geographical area and to define the analytical characteristics of the XRF measurement method. Fast-food samples were collected by using a random sampling frame that emphasized the major distribution chains and the major population centers of Utah. The sampling plan provided replicate sampling of major food items both within and among major franchise chains to separately assess source and location variabilities. The analysis plan included duplicate aliquots and analyses to separately assess sample homogeneity and analytical variability. Accuracy was demonstrated by analyses of 13 standard reference materials and by comparative analyses of Mn, Fe, and Zn by atomic absorption spectrophotometry (AAS).

MATERIALS AND METHODS

Foods and Reference Materials. Fast-food samples were purchased randomly from commercial franchised outlets throughout the Utah Wasatch Front area during February and March of 1988. Lists of candidate food items first were compiled according to frequency and consistency of appearance on the menus of multiple franchise chains. Each item on the resulting list then was matched with one or more different chains for purchase. Major or specialty vendors of selected high-volume items also were selected for replicate sampling from different outlets of the same chain. Specific purchase locations were determined from lists of the outlets in each chain, as compiled from telephone directories of the Logan, Ogden, Salt Lake City, Provo, and Heber City areas. Prioritized purchase locations were selected from the numerical sequence of each list by using a random number generator. The numbers of samples of each type purchased from each franchise chain are listed in Table I.

Fast food sample handling consisted of descriptive documentation, freezing, homogenization, lyophilization, and splitting of aliquots for analysis. Each sample was taken in its original purchase container within 2 h of purchase to the Rogers and

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Table I. Sources, Descriptions, and Moistures of Fast-Food Samples

	sources[a] (number)	description[b]	moisture,[c] %
breakfast items			
cinnamon roll	AL (2); FJ (2); SE (2); SM (2)	[P]	25.1 ± 7.3
danish roll	AL (1); M (1)		25.2 ± 2.5
donuts (raised or cake)	CK (1); RM (1); SE (2); WI (6)	[P]	39.5 ± 15.3
ham, eggs	B (1); CK (1); H (1); M (1)	C, B	27.4 ± 5.1
sausage, eggs, hash-browns	B (1); CK (1); H (1); M (1)	[C], B	38.0 ± 17.9
sandwiches			
beef, roast, regular	AR (3); H (1)	S, B	49.6 ± 3.3
beef, roast, deluxe	AR (3); CK (1); SE (1); SU (1)	S, C, V, B	50.4 ± 3.7
beef, turkey, ham	SU (2)	S, C, V, B	63.2 ± 4.2
chicken	A (1); B (1); DQ (1); H (1); W (1)	F, S, V, B	45.3 ± 5.5
fish	A (1); B (1); H (1); M (1); OJ (1); SK (3)	F, S, [C], V, B	44.6 ± 4.2
frankfurter	A (1); DQ (1); SE (1); WN (6)	S, [C], [V], B	40.9 ± 7.2
ham	BL (3)	S, C, V, B	52.8 ± 11.2
ham, turkey	BL (3); KM (1)	S, [C], V, B	58.4 ± 4.3
ham, pepperoni, bologna	LC (1); SU (3)	S, C, V, B	58.1 ± 2.5
hamburger, regular	A (3); B (3); H (3); M (2); W (3)	S, [V], B	45.1 ± 4.3
hamburger, deluxe	A (3); B (3); H (3); M (3); W (3)	S, [C], V, B	49.3 ± 7.1
Mexican foods			
burrito, bean	NA (2); TB (2)	[S]	50.5 ± 4.4
burrito, beef and bean	CK (1); NA (2); RM (1); TT (4)	S, C, [V]	52.1 ± 4.2
nachos and cheese	KM (1); NA (1); SE (1); TB (1); TT (1)	[S], C, [V]	38.1 ± 13.8
taco, crisp	KM (1); NA (4); TB (4); TT (4)	S, C, V	58.4 ± 5.4
pizza			
cheese	DO (1); GF (2); LC (1); PH (1); PP (3)	S, C	42.0 ± 2.3
combination	DO (3); GF (3); LC (3); PH (4); PP (3)	S, C, V	45.3 ± 4.6
fried foods			
chicken (coated)	B (1); DQ (1); KF (6); M (1); W (1)	F, S, [B]	44.5 ± 15.6
fish (coated)	AW (1); KF (1); OJ (1); SK (3)	F, [S]	46.0 ± 11.1
french fries	A (1); B (1); H (1); M (1); W (1)	F	33.5 ± 9.3
hash-browns	B (1); M (1)	F	34.7 ± 17.5
onion rings (coated)	A (1); B (1); DQ (1); KF (1)	F	35.8 ± 7.3
beans, soups, salads			
beans, chili or BBQ	BL (1); NA (1); KF (1); SM (1)	S	53.9 ± 8.4
chowder, clam	BL (1); SK (1)		59.2 ± 0.5
soup, chicken noodle	SM (1)		91.4
salad, chef (with meat)	AR (1); B (1); H (1); M (1); W (4)	S, V	70.3 ± 12.5
salad, garden	AR (1); B (1); H (1); M (1); W (1)	S, V	74.1 ± 18.1
salad, potato and egg	AL (1); BL (1); KF (1); SM (2)	[V]	65.4 ± 4.1
desserts			
cookies, chocolate chip	AR (1); H (1); M (1); RM (1); SE (1)	[P]	1.4 ± 0.8
ice cream, cone, vanilla	A (1); DQ (1); M (1); NA (1)		63.7 ± 10.4
ice cream, sundae, choc	A (1); DQ (2)		68.5 ± 7.8
pie, apple	AR (1); B (1); H (1); M (1)		46.6 ± 16.3
beverages			
coffee, black	A (1); B (1); H (1); M (1); SE (1)		99.4 ± 0.1
milkshake, strawberry	B (1); DQ (1); H (1); M (1); W (1)		81.3 ± 8.6
orange juice	B (1); M (1); NA (1); OJ (1); W (1)	[P]	82.0 ± 16.3

[a] Sources: A, Arctic Circle; AL, Albertson's; AR, Arby's; AW, A&W; B, Burger King; BL, Blimpie Sandwiches; CK, Circle-K; DO, Domino's; DQ, Dairy Queen; FJ, Farmer Jack's; GF, Godfather's; H, Hardee's; KF, Kentucky Fried Chicken; KM, K-Mart; LC, Little Caesars; M, McDonald's; NA, Naugles; OJ, Orange Julius; PH, Pizza Hut; PP, Peter Piper Pizza; RM, Rainbo Mart; SE, Seven Eleven; SK, Skipper's; SM, Smith's; SU, Subway Sandwiches; TB, Taco Bell; TT, Taco Time; W, Wendy's; WI, Winchell's; WN, Wienerschnitzel. Number of franchise locations sampled is given in parentheses. [b] P, prepackaged; C, cheese; S, sauce (ketchup, mustard, salad dressing, etc.); F, deep-fried; V, added vegetables (lettuce, onions, peppers, pickles, tomatoes, etc.); B, bun, biscuit, croissant, muffin, or roll. Brackets indicate application to only some of the samples. [c] Mean ± standard deviation.

Associates (RAE) laboratory, where it was weighed, examined and described, and cataloged by sample number and point of purchase on sample custody forms. Nonedible portions (bones) were removed, and the samples were immediately transferred to labeled heavy-gauge food-grade Ziploc freezer bags and frozen. The frozen samples were delivered to the Utah State University (USU) laboratories where they were homogenized, lyophilized, and split into aliquots for separate blind analyses by each laboratory. Homogenization utilized a glass blender with a stainless steel cutter. Homogenized samples were weighed, lyophilized, and then reweighed to determine moisture contents. The dry samples were further ground with either a porcelain or agate mortar and pestle and then were stored in a freezer in plastic containers. Moisture in the stored samples was determined at the time of aliquot splitting by oven-drying of a separate aliquot for 2 h in a forced-air oven at 105 °C. Analyzed mineral values then were reported on a dry weight basis, with total moistures (Table I) reported from the combined lyophilization and oven-drying water losses.

Foods were grouped into 40 categories (Table I) for averaging mineral concentrations and analyzing variations. The groups were based on equivalency of food products and similarity of mineral concentrations. Where distinguished, "regular" refers to the least-expensive basic item and "deluxe" refers to the trademark or house-specialty item.

Reference materials were obtained from the National Institute of Standards and Technology (NIST, formerly National Bureau of Standards). They included orchard leaves (SRM-1571), citrus leaves (SRM-1572), tomato leaves (SRM-1573), pine needles (SRM-1575), bovine liver (SRM-1577a), powdered milk (SRM-1549), wheat flour (SRM-1567), rice flour (SRM-1568), oyster tissue (SRM-1566), albacore tuna (RM-50), mixed diet (RM-

Table II. Comparison of XRF Mineral Measurements with NIST and Consensus Concentrations[a]

		P, mg/g	S, mg/g	Cl, mg/g	K, mg/g	Ca, mg/g	Mn, μg/g	Fe, μg/g	Zn, μg/g	Br, μg/g	Rb, μg/g	Sr, μg/g
orchard leaves	XRF	2.16 ± 0.15	2.09 ± 0.13	0.64 ± 0.09	15.0 ± 0.9	19.3 ± 1.1	94 ± 10	309 ± 20	26 ± 3	9.7 ± 0.7	11.6 ± 0.6	36 ± 2
SRM-1571	NIST	2.10 ± 0.10	(1.90)	(0.69)	14.7 ± 0.3	20.9 ± 0.3	91 ± 4	300 ± 20	25 ± 3	(10)	12 ± 1	37 ± 1
	diff	0.06	0.19	−0.05	0.3	−1.6	3	9	1	−0.3	−0.4	−1
citrus leaves	XRF	1.52 ± 0.05	4.17 ± 0.08	0.31 ± 0.13	19.1 ± 0.7	30.0 ± 1.2	24 ± 3	91 ± 4	29.8 ± 1.4	8.0 ± 0.5	4.81 ± 0.38	100 ± 2
SRM-1572	NIST	1.30 ± 0.20	4.07 ± 0.09	(0.41)	18.2 ± 0.6	31.5 ± 1.0	23 ± 2	90 ± 10	29 ± 2	(8.2)	4.84 ± 0.06	100 ± 2
	diff	0.22	0.10	−0.10	0.9	−1.5	1	1	0.8	−0.2	−0.03	0
tomato leaves	XRF	3.33 ± 0.07	6.25 ± 0.09	11.4 ± 0.5	45.7 ± 1.8	29.6 ± 0.5	243 ± 9	658 ± 15	67 ± 7	24.2 ± 0.5	16.6 ± 0.4	44.1 ± 1.9
SRM-1573	NIST	3.40 ± 0.20	[6.20 ± 0.40]	[10.7 ± 0.3]	44.6 ± 0.3	30.0 ± 0.3	238 ± 7	690 ± 25	62 ± 6	(26)	16.5 ± 0.1	44.9 ± 0.3
	diff	−0.07	0.05	0.7	1.1	−0.4	5	−32	5	−1.8	0.1	−0.8
pine needles	XRF	1.39 ± 0.08	1.22 ± 0.07	0.28 ± 0.11	3.61 ± 0.33	3.91 ± 0.21	680 ± 31	195 ± 15	59 ± 3	7.0 ± 0.5	11.7 ± 0.4	3.9 ± 0.5
SRM-1575	NIST	1.20 ± 0.20	[1.32 ± 0.11]	[0.28 ± 0.03]	3.70 ± 0.20	4.10 ± 0.20	675 ± 15	200 ± 10	[67 ± 9]	(9)	11.7 ± 0.1	4.8 ± 0.2
	diff	0.19	−0.10	0.00	−0.09	−0.19	5	−5	−8	−2	0	−0.9
bovine liver	XRF	9.85 ± 0.62	6.42 ± 0.35	2.18 ± 0.14	8.54 ± 0.88	0.09 ± 0.03	8.4 ± 1.2	181 ± 14	115 ± 3	8.8 ± 0.3	12.1 ± 0.3	<0.9
SRM-1577a	NIST	11.1 ± 0.4	7.80 ± 0.10	2.80 ± 0.10	9.96 ± 0.07	0.12 ± 0.01	9.9 ± 0.8	194 ± 20	123 ± 8	(9)	12.5 ± 0.1	0.138 ± 0.003
	diff	−1.25	−1.38	−0.62	−1.42	−0.03	−1.5	−1.3	−8	−0.2	−0.4	
powdered milk	XRF	9.92 ± 0.30	3.37 ± 0.11	10.0 ± 0.5	16.5 ± 0.9	12.2 ± 0.7	<3.3	2.7 ± 1.8	46.0 ± 3.5	11.6 ± 0.5	12.4 ± 0.6	3.0 ± 0.5
SRM-1549	NIST	(10.5)	3.51 ± 0.05	10.9 ± 0.2	16.9 ± 0.3	13.0 ± 0.5	0.26 ± 0.06	(2.1)	46.1 ± 2.2	(12)	(11)	[3.7]
	diff	−0.58	−0.14	−0.9	−0.4	−0.8		0.6	−0.1	−0.4	1.4	−0.7
wheat flour	XRF	1.52 ± 0.10	1.64 ± 0.06	0.60 ± 0.21	1.21 ± 0.03	0.20 ± 0.01	8.2 ± 0.9	16.7 ± 0.5	10.6 ± 1.2	9.7 ± 0.8	<1	<1
SRM-1567	NIST	1.39 ± 0.03	[1.81 ± 0.11]	[0.59 ± 0.02]	1.36 ± 0.04	0.19 ± 0.01	8.5 ± 0.5	18.3 ± 1.0	10.6 ± 1.0	(9)	(1)	[1.0 ± 0.1]
	diff	0.13	−0.17	0.01	−0.15	0.01	−0.3	−1.6	0	0.7		
rice flour	XRF	2.30 ± 0.04	1.21 ± 0.02	0.19 ± 0.21	1.13 ± 0.05	0.15 ± 0.00	19.9 ± 1.6	8.7 ± 1.3	20.0 ± 0.5	1.1 ± 0.3	8.1 ± 0.8	<0.9
SRM-1568	NIST	[1.63 ± 0.04]	[1.35 ± 0.06]	[0.24 ± 0.01]	1.12 ± 0.02	0.14 ± 0.02	20.1 ± 0.4	8.7 ± 0.6	19.4 ± 1.0	(1)	(7)	[0.19]
	diff	0.67	−0.14	−0.05	0.01	0.01	−0.2	0	0.6	0.1	1.1	
oyster tissue	XRF	6.78 ± 0.23	7.32 ± 0.31	8.03 ± 0.66	8.68 ± 0.54	0.95 ± 0.14	15.5 ± 3.1	189 ± 10	824 ± 17	54.2 ± 0.9	3.4 ± 0.3	8.8 ± 0.6
SRM-1566	NIST	(8.10)	(7.60)	(10.0)	9.69 ± 0.05	1.50 ± 0.20	17.5 ± 1.2	195 ± 34	852 ± 14	(55)	4.4 ± 0.1	10.4 ± 0.6
	diff	−1.32	−0.28	−1.97	−1.01	−0.55	−2	−6	−28	−0.8	−1	−1.6
albacore tuna	XRF	7.10 ± 0.45	7.00 ± 0.41	1.16 ± 0.13	10.9 ± 0.9	0.16 ± 0.03	<2.3	50 ± 3	14.3 ± 1.1	10.0 ± 0.4	1.9 ± 0.4	<1.0
RM-50	NIST				(12.2)		1.3		13.6 ± 1			
	diff				−1.3				0.7			
mixed diet	XRF	2.87 ± 0.13	1.94 ± 0.14	4.51 ± 0.24	7.41 ± 0.52	1.70 ± 0.14	8.2 ± 2.4	36 ± 4	15.5 ± 0.9	10.0 ± 0.3	6.5 ± 0.2	2.1 ± 1.0
RM-8431	NIST	3.32 ± 0.31			7.90 ± 4.20	1.94 ± 0.14	8.1 ± 0.3	37.0 ± 2.6	17.0 ± 0.6			
	diff	−0.45			−0.49	−0.24	0.1	−1	−1.5			
corn stalk	XRF	0.78 ± 0.03	0.67 ± 0.04	2.27 ± 0.14	17.3 ± 0.6	2.04 ± 0.09	15.9 ± 3.1	134 ± 6	32.2 ± 0.9	9.4 ± 0.4	4.1 ± 0.2	11.2 ± 0.5
RM-8412	NIST			2.44 ± 0.14	17.3 ± 0.5	2.16 ± 0.08	15 ± 2	139 ± 15	32 ± 3			12 ± 2
	diff			−0.17	−0.0	−0.12	0.9	−5	0.2			−0.8
corn kernel	XRF	2.52 ± 0.09	1.18 ± 0.05	0.37 ± 0.14	3.63 ± 0.12	0.044 ± 0.015	4.0 ± 2.0	22.9 ± 1.5	15.8 ± 0.7	0.9 ± 0.2	1.5 ± 0.3	<0.9
RM-8413	NIST			(0.45 ± 0.12)	3.57 ± 0.37	0.042 ± 0.005	4.0 ± 0.3	23 ± 5	15.7 ± 1.4			
	diff			−0.08	0.06	0.002	0	−0.1	0.1			
rel diff[b]		13.5%	7.3%	10.2%	5.4%	8.6%	4.9%	2.8%	4.2%	6.6%	7.3%	9.2%
rel bias[c]		3.7%	−4.4%	−8.0%	−3.5%	−5.8%	−1.3%	−2.0%	−0.5%	−2.6%	−0.1%	−9.2%

[a] Concentrations are on a dry weight basis. XRF values are means ± 95% (2σ) confidence limits, averaged over six measurements (two analyses × three aliquots), except SRM-1567 and SRM-1568, which had two measurements (two analyses × one aliquot). NIST values are certified concentrations and uncertainties (generally stated to be 95% confidence limits). Parentheses denote noncertified values, and brackets denote consensus values from Gladney et al. (1987). [b] Mean of |diff|/NIST, excluding comparisons where uncertainty exceeds 35% of mean. [c] Mean of diff/NIST, excluding comparisons where uncertainty exceeds 35% of mean.

8431), corn stalk (RM-8412), and corn kernel (RM-8413). They were used directly in their dry, powdered form in aliquots of 0.5 g, which corresponded in form and mass to the aliquots used for the fast-food samples.

Atomic Absorption Analyses. Comparative determinations of manganese, iron, and zinc were performed on replicate aliquots of nearly all samples by atomic absorption spectrophotometry (AAS). Dissolved aqueous samples were prepared for AAS analysis from 2–3-g aliquots of the dried fast-food samples. The sample powder was weighed into porcelain crucibles and ashed in a muffle furnace at 550 °C for 48 h. It then was dissolved into an acidic aqueous solution for analysis by AAS (Instrumentation Laboratories Model 457 dual-beam spectrophotometer). Details of the sample dissolution, calibration, blank determination, and interference suppression were reported previously (Nielson et al., 1988). The AAS procedure was verified by repeated analyses of the NIST rice flour and wheat flour standard reference materials throughout the analysis period. The measured means of the mineral concentrations in these standards agreed closely with the certified values.

X-ray Fluorescence Analyses. XRF analyses were performed directly on solid pellets pressed from the powdered samples. Dry 0.5-g aliquots of the fast-food samples and reference materials were weighed into a 3.2 cm diameter hardened steel die and pressed under 2300 kg/cm² to form self-supporting sample pellets. These were mounted in 5-cm square photographic slide frames for introduction into the XRF sample changer. Some pellets of high-fat or low-fiber samples were fragile and required reduced pelletizing pressure and additional support from a 2.5 μm thick Mylar film (No. 105, Chemplex Industries, Tuckahoe, NY) mounted in the slide frame under the pellet. Two pellets were prepared from each of the 239 fast-food samples, and three pellets were prepared from each of 11 of the standard reference materials. Single pellets were prepared from the wheat flour and rice flour standards.

Samples were analyzed in batches based on the 16 positions of the XRF sample changer. Each batch included duplicate pellets from seven fast-food samples plus a single pellet of the tomato leaf standard reference material. The 16th position contained an aluminum–copper alloy that was used to monitor the X-ray intensity each time the excitation source (energy range) was changed. Four excitation sources were used to collect four separate 1024-channel spectra from each sample to optimize the sensitivities of different groups of elements. The 15 spectra from one source were collected and stored on disk before changing to the next source. The four excitation sources utilized Gd, Ag, and Zr secondary targets and 5-kV direct excitation (30, 20, 30, and 10 min, respectively, under vacuum, with a Kevex Model 700 spectrometer). After all 60 spectra were collected and stored on disk for each batch, the batch was analyzed a second time to

Table III. Mineral Concentrations and Variations Measured in Fast-Food Samples[a]

	n[b]	P, mg/g	S, mg/g	Cl, mg/g	K, mg/g	Ca, mg/g	Mn, μg/g	Fe, μg/g	Zn, μg/g	Br, μg/g	Rb, μg/g	Sr, μg/g
breakfast items												
cinnamon roll	8	1.46 ± 0.51	1.14 ± 0.22	8.0 ± 1.5	1.62 ± 0.34	0.51 ± 0.17	5.6 ± 1.5	28 ± 8	7.8 ± 1.5	10.0 ± 3.8	1.6 ± 0.5	1.7 ± 0.9[7]
danish roll	2	1.63 ± 0.39	0.96 ± 0.05	7.5 ± 0.7	1.22 ± 0.30	0.32 ± 0.08	3.6 ± 0.5	23 ± 7	8.8 ± 1.7	4.4 ± 1.1	1.3 ± 0.6	<0.9
donuts (raised or cake)	10	1.90 ± 0.50	0.60 ± 0.28	3.7 ± 1.2	1.94 ± 0.59	0.52 ± 0.08	4.0 ± 0.8	22 ± 7	6.8 ± 1.0	4.8 ± 2.2	2.1 ± 0.9	1.1 ± 0.4
ham, eggs	4	4.12 ± 0.58	2.48 ± 0.54	14.4 ± 1.6	2.66 ± 0.26	2.31 ± 0.79	2.8 ± 0.8	35 ± 7	25 ± 5	15.7 ± 8.7	2.6 ± 0.4	3.6 ± 3.5
sausage, eggs, hash-browns	4	3.97 ± 0.80	2.17 ± 0.69	11.8 ± 1.0	3.56 ± 0.95	1.03 ± 0.37	3.0 ± 1.1	37 ± 4	23 ± 6	10.7 ± 1.0	2.6 ± 0.6	1.2 ± 0.4
sandwiches												
beef, roast, regular	4	3.04 ± 0.55	2.31 ± 0.27	14.8 ± 1.1	3.50 ± 0.51	0.81 ± 0.23	3.6 ± 0.6	48 ± 4	40 ± 10	34.0 ± 4.5	5.3 ± 2.9	2.7 ± 0.3
beef, roast, deluxe	6	3.59 ± 0.69	2.16 ± 0.33	14.9 ± 1.8	3.36 ± 0.55	2.14 ± 0.59	4.3 ± 1.1	44 ± 6	39 ± 8	26.6 ± 3.8	3.2 ± 1.1	3.2 ± 1.1
beef, turkey, ham	2	3.02 ± 0.02	2.48 ± 0.04	18.6 ± 0.4	4.28 ± 0.39	1.19 ± 0.04	4.9[1]	36 ± 0	37 ± 5	26 ± 3	3.7 ± 0.6	4.2 ± 0.5
chicken	5	2.56 ± 0.10	2.29 ± 0.54	13.8 ± 2.6	2.95 ± 0.67	0.98 ± 0.36	4.4 ± 0.6	32 ± 9	9.9 ± 1.0	27 ± 5	4.5 ± 1.6	2.6 ± 0.5
fish	8	2.99 ± 0.43	2.24 ± 0.27	11.4 ± 1.1	2.94 ± 0.32	2.17 ± 1.07	4.4 ± 1.8	25 ± 5	14 ± 6	23 ± 12	0.9 ± 0.3	5.3 ± 1.7
frankfurter	9	2.31 ± 0.37	1.79 ± 0.18	18.9 ± 3.0	2.34 ± 0.38	1.63 ± 0.76	3.9 ± 0.8	40 ± 4	26 ± 7	33 ± 8	2.1 ± 0.7	3.7 ± 0.9
ham	3	2.75 ± 0.53	1.96 ± 0.18	19.0 ± 2.3	3.62 ± 0.44	1.33 ± 0.02	5.5 ± 0.8	43 ± 3	26 ± 5	22 ± 3	3.6 ± 0.8	2.4 ± 0.5
ham, turkey	4	2.89 ± 0.77	2.14 ± 0.42	18.3 ± 3.2	3.98 ± 0.90	1.43 ± 0.18	5.8 ± 1.0	44 ± 8	24 ± 6	24 ± 3	3.3 ± 0.9	3.0 ± 0.9
ham, pepperoni, bologna	4	2.53 ± 0.50	2.08 ± 0.18	21.5 ± 3.3	3.83 ± 0.45	1.32 ± 0.39	4.9 ± 0.6	35 ± 2	29 ± 1	24 ± 9	3.0 ± 0.4	3.7 ± 0.8
hamburger, regular	14	1.72 ± 0.19	2.17 ± 0.19	12.0 ± 1.6	2.81 ± 0.33	1.31 ± 0.47	4.5 ± 0.5	47 ± 7	31 ± 7	35 ± 12	3.6 ± 1.8	5.3 ± 2.3
hamburger, deluxe	15	2.15 ± 0.37	2.05 ± 0.32	11.6 ± 1.6	3.59 ± 0.68	1.67 ± 0.33	4.0 ± 1.0	44 ± 6	36 ± 10	26 ± 9	3.8 ± 2.6	5.5 ± 2.2
Mexican foods												
burrito, bean	4	3.07 ± 0.49	1.66 ± 0.07	18.4 ± 1.4	6.58 ± 0.24	2.44 ± 0.39	7.6 ± 0.6	44 ± 3	22 ± 4	8.7 ± 2.5	2.4 ± 0.9	6.4 ± 2.1
burrito, beef and bean	8	2.91 ± 0.32	2.24 ± 0.29	16.3 ± 2.6	5.90 ± 1.60	2.40 ± 0.45	8.0 ± 1.6	43 ± 6	32 ± 8	7.0 ± 1.6	4.8 ± 2.1	5.2 ± 1.6
nachos and cheese	5	5.20 ± 1.41	1.40 ± 0.41	10.2 ± 2.4	2.18 ± 0.44	3.80 ± 1.40	3.6 ± 0.9	13 ± 3	24 ± 9	3.4 ± 0.4	1.2 ± 0.4	3.2 ± 1.3
taco, crisp	13	3.63 ± 0.41	2.60 ± 0.19	12.9 ± 2.4	6.44 ± 1.11	2.85 ± 0.83	5.3 ± 2.3	37 ± 6	59 ± 8	6.5 ± 2.6	10.4 ± 6.3	4.4 ± 1.0
pizza												
cheese	8	2.33 ± 0.55	1.75 ± 0.23	10.6 ± 1.6	2.68 ± 0.46	2.56 ± 0.71	5.2 ± 1.3	36 ± 6	24 ± 5	12.7 ± 2.9	2.6 ± 0.6	5.2 ± 1.1
combination	16	2.32 ± 0.24	1.85 ± 0.22	13.5 ± 2.7	3.40 ± 0.55	2.40 ± 0.43	5.7 ± 1.0	40 ± 13	30 ± 4	11.9 ± 2.7	3.0 ± 0.6	5.5 ± 1.4
fried foods												
chicken (coated)	10	3.58 ± 0.56	2.82 ± 0.74	13.8 ± 4.8	4.14 ± 0.85	0.49 ± 0.36	2.6 ± 0.6[9]	20 ± 16	17 ± 5	6.0 ± 2.6	8.6 ± 2.3	<0.9[1]
fish (coated)	6	3.59 ± 0.64	3.40 ± 1.10	9.2 ± 6.3	6.30 ± 1.10	0.43 ± 0.15	2.6 ± 1.1	12 ± 3	9.9 ± 0.6	12 ± 4	1.4 ± 0.5	3.4 ± 4.6
french fries	5	2.27 ± 0.14	0.74 ± 0.13	2.8 ± 1.2	10.60 ± 2.70	0.42 ± 0.16	4.2 ± 1.0	16 ± 3	7.8 ± 1.4	2.3 ± 3.2	2.6 ± 0.8	1.5 ± 0.7
hash-browns	2	2.50 ± 1.10	0.75 ± 0.33	15.2 ± 3.2	9.40 ± 5.50	0.33 ± 0.10	3.1 ± 1.2	14 ± 4	8.2 ± 2.1	2.5 ± 1.2	1.4 ± 0.1	<0.9[0]
onion rings (coated)	4	2.62 ± 0.82	0.95 ± 0.17	11.9 ± 4.6	3.90 ± 3.30	0.98 ± 1.07	5.3 ± 1.6	24 ± 23	7.5 ± 0.8	3.3 ± 0.4	1.3 ± 0.9	2.3 ± 2.1
beans, soups, salads												
beans, chili or BBQ	4	2.74 ± 0.16	1.95 ± 0.65	24.0 ± 2.7	8.37 ± 1.06	1.27 ± 0.51	8.0 ± 2.3	57 ± 5	38 ± 21	11 ± 9	6.3 ± 2.6	6.8 ± 0.8
chowder, clam	2	3.10 ± 1.80	2.27 ± 0.22	27.9 ± 0.5	6.00 ± 2.70	2.00 ± 1.90	<2.9[1]	20 ± 12	33 ± 24	11.5 ± 0.7	2.5 ± 2.2	4.4 ± 0.6
soup, chicken noodle	1	3.14	2.84	38.7	2.85	0.78	6.0	33	13	9.0	3.2	3.9
salad, chef (with meat)	8	5.08 ± 0.73	2.95 ± 0.60	30.5 ± 8.0	9.50 ± 3.10	5.00 ± 2.10	11 ± 22	47 ± 62	43 ± 7	8.6 ± 2.2	5.6 ± 1.2	10.8 ± 3.6
salad, garden	5	3.79 ± 0.45	2.48 ± 0.67	37.9 ± 25.0	12.20 ± 7.00	4.10 ± 1.90	6.5 ± 3.9	26 ± 10	32 ± 11	17 ± 15	4.7 ± 2.0	14.0 ± 4.9
salad, potato and egg	5	2.00 ± 0.33	1.06 ± 0.18	20.8 ± 2.3	8.20 ± 1.30	0.55 ± 0.13	3.8 ± 1.6	16 ± 4	9.4 ± 1.2	6.8 ± 1.3	3.2 ± 1.8	3.9 ± 1.6
desserts												
cookies, chocolate chip	5	1.34 ± 0.32	0.55 ± 0.09	3.8 ± 0.6	1.65 ± 0.38	0.37 ± 0.10	5.0 ± 0.6	23 ± 6	6.5 ± 1.4	4.3 ± 2.3	2.5 ± 0.6	1.2 ± 0.8
ice cream, cone, vanilla	4	3.62 ± 0.66	1.45 ± 0.16	4.6 ± 1.3	7.10 ± 2.90	3.84 ± 0.35	<2.5[0]	8.3 ± 8.8	11.9 ± 1.5	9.5 ± 5.3	6.7 ± 3.8	4.0 ± 0.8
ice cream, sundae, choc	3	2.56 ± 0.04	1.04 ± 0.19	3.1 ± 0.2	5.70 ± 0.73	2.57 ± 0.05	<2.5[1]	22 ± 9	10.9 ± 2.0	4.7 ± 0.7	5.5 ± 0.9	2.9 ± 0.2
pie, apple	4	1.04 ± 0.27	0.64 ± 0.17	6.0 ± 1.6	1.04 ± 0.41	0.23 ± 0.11	2.9 ± 0.8	12 ± 11	4.3 ± 1.3	3.0 ± 3.6	0.7 ± 0.2[3]	<0.9[1]
beverages												
coffee, black	5	4.06 ± 0.41	3.70 ± 2.30	13.3 ± 12.9	49.0 ± 27.0	6.70 ± 2.30	27 ± 20	16 ± 9	20 ± 11	28 ± 22	110 ± 62	53 ± 41
milkshake, strawberry	5	3.40 ± 0.45	1.18 ± 0.30	3.4 ± 0.4	5.80 ± 1.20	3.50 ± 0.80	<2.4[0]	8.0 ± 6.2	12.3 ± 2.5	6.6 ± 1.4	5.0 ± 1.3	3.4 ± 0.9
orange juice	5	1.76 ± 0.62	0.52 ± 0.20	0.7 ± 0.3	13.00 ± 4.60	1.18 ± 0.24	<2.8[0]	10 ± 4	3.6 ± 0.5	3.4 ± 1.3	5.1 ± 4.2	12.4 ± 7.1

[a] Means ± standard deviations among samples, dry weight basis, in order of atomic number. Superscript numbers are the number of samples above the detection limit (dl) when one or more was below the dl. If the mean over all samples was below the dl, the result is given as <dl. [b] Number of samples, each of which was analyzed four times (two analyses × two aliquots).

provide the basis for estimating analytical precision. A total of 75 sample batches were involved in the analyses described here. Concentrations of P and S were determined from the 5-kV spectra, concentrations of Cl, K, Ca, Mn, Fe, Zn, Br, and Rb were determined from the Zr spectra, and concentrations of Sr were determined from the Ag spectra. Additional elements also were determined from these spectra and from the Gd spectra. However, data are presented only for minerals for which certified values or consensus values (Gladney et al., 1987) of NIST reference materials were available.

Spectrum analysis and element quantitation also was done in batch mode using the CEMAS program (Nielson, 1986), which automatically computed matrix corrections and individual calibrations for each sample on the basis of its measured constituents and backscattered X-ray intensities. The program also corrected for positional variations (mounting, pellet warping) of each sample (Nielson et al., 1989). Since the CEMAS method uses fundamental parameters of X-ray physics to compute calibrations and matrix corrections (Nielson, 1977), the results were based on prior system calibrations and were independent of the values measured in the tomato leaf standard analyzed in each batch. Concentrations of 25 additional elements besides the 11 reported here also were computed during data reduction, and all were stored on disk for later statistical analysis.

Quality Control and Statistical Analyses. Statistical control over analytical precision was maintained at several levels. Long-term variability was monitored from repeated analyses of the tomato leaf standard with each sample batch. The results of several element concentrations in this standard were plotted on statistical control charts to monitor temporal variations and long-term spectrometer performance over a nominal 7-month period covered by the analyses. Short-term variability was assessed from the duplicate analyses of each batch of samples. Time intervals between duplicate analyses were typically 1–2 days. An additional, independent measure of analytical uncertainty was computed by the CEMAS code from the uncertainty in intensity of each XRF peak on the basis of its counting statistics. This represented a minimum, instantaneous analytical uncertainty associated with each measurement that was increased by any other analytical variables such as instrumental drifts or sampling variations.

Analytical accuracy was estimated by comparing measured mineral concentrations with NIST certified concentrations for each standard. Biases were computed as the differences between the XRF and NIST values, and total errors were computed as the absolute values of these differences. Both were averaged on a relative basis (by dividing by the NIST value) for all cases of valid XRF data (uncertainty <35% of mean) and NIST or

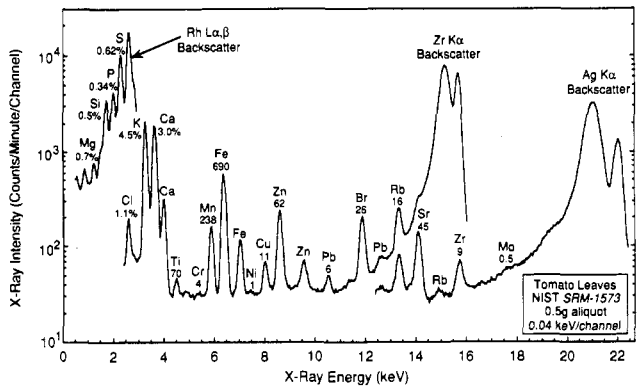

Figure 1. Example of the three X-ray fluorescence spectra used to determine 11 elements in each analysis.

consensus data (Gladney et al., 1987). The means of the six analyses of each of 11 standards and two analyses of the other 2 standards were used for these comparisons. Additional accuracy statistics were summarized from least-squares linear regressions of scatter plots of the AAS and XRF data. These were computed as slopes, intercepts, and correlation coefficients from the scatter plots.

Statistical analyses were used to partition the variations in mineral concentrations into four categories: variations among fast-food franchise chains, variations among different outlets (locations) of franchise chains, variations among replicate aliquots of each sample, and analytical variations among replicate analyses of each aliquot. The variations expected among identical food items from the same outlet were not addressed in the sampling scheme and hence were pooled with the location variations. Total variations first were partitioned into three components by using two-way analyses of variance (Li, 1964), assuming a nested model in which combined location and franchise effects were considered fixed and aliquot and analytical variations each were considered random. From the combined location and franchise variations (V_{lf}), a separate normalized estimate of each was computed as

$$V_{loc} = V_l V_{lf}/(V_f^2 + V_l^2)^{1/2}$$

$$V_{frn} = V_f V_{lf}/(V_f^2 + V_l^2)^{1/2}$$

where V_l and V_f were averaged, respectively, from replicate values from different locations within a chain and from replicate average values from different franchise chains. The variations were computed for each element in each food catetory and were expressed in percentage units as relative standard deviations (RSD = 100 × standard deviation/mean). They were averaged over all foods by element for summary presentation here, and they gave explicit measures of analytical variability, sample homogeneity, product uniformity, and food variations by vendor.

RESULTS AND DISCUSSION

The three XRF spectra from which the 11 elements were determined in each analysis are illustrated for the tomato leaf standard in Figure 1. Mineral measurements in the 13 standard reference materials (Table II) averaged within 7% of the reference values and exhibited a −2.8% overall bias. Average relative differences between the XRF and reference values ranged from 2.8% for iron to 13.5% for phosphorus. Average relative biases ranged from −9.2% for strontium to +3.7% for phosphorus. Seven or more of the standards provided valid comparisons for each of the 11 elements, despite the numerous cases for which no reference value was available, or the XRF means were rejected due to nondetection or high analytical uncertainty. The mineral measurements validated by the comparisons in Table II covered the concentration ranges 1.2–11.1 mg/g P, 1.3–7.8 mg/g S, 0.28–10.9 mg/g Cl, 1.1–45 mg/g K, 0.04–32 mg/g Ca, 8–675 μg/g Mn, 9–690 μg/g Fe, 11–852

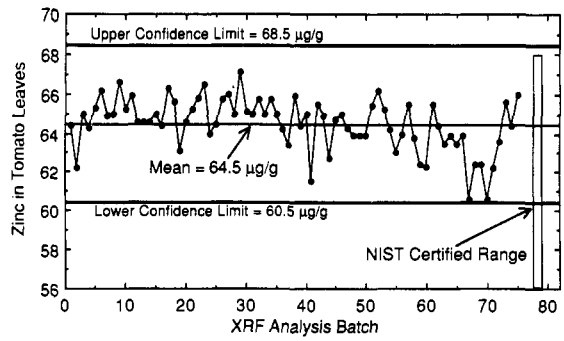

Figure 2. Sample 3σ control chart for zinc concentrations in tomato leaves (NIST SRM-1573) for 75 batches of analyses.

μg/g Zn, 1–55 μg/g Br, 4–17 μg/g Rb, and 4–100 μg/g Sr. All available reference values for elements not detected by XRF were equal to or below the measured XRF detection limits.

Statistical control charts for the tomato leaf standard demonstrated the absence of significant long-term analytical variations, as illustrated for zinc in Figure 2. All of the 75 zinc values are within the NIST certified range and within the 3σ confidence limits, and most were within the 2σ range. The minimal time variation in Figure 2 (1.5%) is comparable to the short-term analytical uncertainties computed from the zinc peak counting statistics. The long-term relative bias of +4% for zinc (Figure 2) is only half of the +8% short-term bias obtained from the duplicate analyses of three tomato leaf pellets (Table II).

Mineral measurements in the 239 fast-food samples are summarized in Table III as means and sample standard deviations averaged by food type. The concentrations of P, S, Cl, K, Ca, Mn, Fe, Zn, Br, Rb, and Sr were measured relative to respective XRF detection limits of about 100, 50, 300, 50, 20, 3, 2, 0.5, 0.5, 0.5, and 0.9 μg/g. General trends in the mineral data include higher concentrations of most minerals in high-protein foods than in high-carbohydrate products. Concentration ranges among the 40 foods in Table III varied from less than a factor of 10 for phosphorus, sulfur, and iron to more than a factor of 100 for rubidium. The coffee sample dominated the high-end range of variation for S, K, Ca, Mn, Rb, and Sr due to its high (dry weight) concentrations of these elements. The concentrations in Table III can be estimated on a fresh, wet weight basis by using the average moistures in Table I.

Comparisons of XRF results with AAS analyses of the fast-food samples indicated generally good agreement, despite somewhat greater differences than were observed in analyses of the standard reference materials. Correlation coefficients from XRF vs AAS plots for manganese, iron, and zinc were 0.94, 0.97, and 0.97, respectively. Corresponding slopes were 0.93, 0.90, and 0.95, with intercepts of 0.4, 2.8, and 1.0 μg/g, respectively. The average biases of XRF measurements relative to the AAS measurements were +1.3% for manganese, +0.4% for iron, and +2.2% for zinc.

Variations in the mineral concentrations are summarized by their components as average relative standard deviations for each element (Table IV). Variations among different franchise chains were greatest, followed by variations among different locations within a chain, by variations among replicate sample aliquots, and finally by analytical variations. The partitioned variations in Table IV are combined quadratically to obtain the total variations presented in the last column. The range of analytical variations exceeded a factor of 5 (2% for P to 11% for Mn), while aliquot, location, and franchise variations all

Table IV. Partitioned Mineral Variations Averaged by Element over All Food Samples

	rel SD,[a] %				
element	analysis	aliquot	location	franchise	total
P	2.0	6.1	9.6	16	19
S	2.2	5.8	7.4	17	20
Cl	2.5	4.6	8.4	19	22
K	2.3	5.0	8.8	21	24
Ca	2.6	7.0	13.7	27	31
Mn	11.0	8.2	8.5	20	26
Fe	3.9	7.8	10.3	27	30
Zn	2.3	6.7	11.4	19	23
Br	2.4	3.9	8.8	31	33
Rb	4.7	6.5	17.6	32	38
Sr	6.9	9.4	12.4	25	30
av	3.9	6.5	10.6	23	27

[a] Standard deviations divided by means, partitioned from analyses of variance.

varied by a factor of 2–3. Variations were greatest for Rb, Br, and Ca and least for P, S, and Cl. Similar analyses of variations by food type showed the range of analytical variations to be less than a factor of 3 among different foods, while aliquot, analytical, and franchise variations each covered a range of a factor of 5–6. Coffee, onion rings, and apple pie exhibited the greatest franchise variations, despite their low to moderate analytical and aliquot variations.

Many of the analyses of variance summarized in Table IV indicated significant ($p < 0.01$) differences among franchise chains, outlet locations, or sample aliquots, for certain elements. These included franchise and location variations in donuts, frankfurters, hamburgers, Mexican foods, fried meats, lettuce salads, desserts, and beverages for most of the 11 elements. The analyses indicated that location and franchise variations were significant compared to aliquot and analysis variations in about half of the determinations or for an average of 6 of the 11 elements in the 40 food types. These analyses were highly variable, however, and ranged from no significant location or franchise variations (ham and turkey sandwiches) to significant variations in all 11 elements (donuts, coffee).

Plots of the mineral means in cases of significant franchise or location variations helped identify the trends that accounted for the variations. For example, the minerals in regular hamburgers exhibited lower iron and bromine and higher strontium for the McDonald's chain than for the other chains (Figure 3). Deluxe hamburgers showed the same trend for bromine and strontium, but was less significant for iron. Calcium means exhibited higher values in all deluxe hamburgers than in regular hamburgers, while zinc showed this trend only for the Hardee's and McDonald's chains.

Numerous aliquot variations also were significant at the $p < 0.01$ level. Although this suggests significant sample inhomogeneities, the significance of the aliquot tests was influenced more by the smallness of the analytical

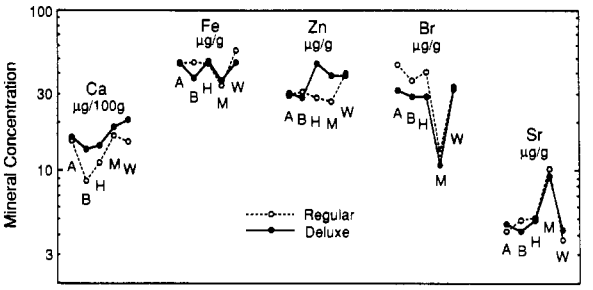

Figure 3. Comparison of mean mineral concentrations in hamburgers from Arctic Circle (A), Burger King (B), Hardee's (H), McDonald's (M), and Wendy's (W).

variations than by excessive aliquot variations. The mean aliquot variations presented in Table IV were less than 10% in all cases. The overall mean variations when averaged by both food type and element were similar to the element means in Table IV, averaging 3.3% for analytical variations, 6.3% for aliquot variations, 10.7% for location variations, and 23% for franchise variations.

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LITERATURE CITED

Beecher, G. R.; Vanderslice, J. T. Determination of Nutrients in Foods: Factors that Must be Considered. In *Modern Methods of Food Analysis*; Stewart, K. K., Whitaker, J. R., Eds.; AVI Publishing: Westport, CT, 1984.

Gladney, E. S.; O'Malley, B. T.; Roelandts, I.; Gills, T. E. *Compilation of Elemental Concentration Data for NBS Clinical, Biological, Geological, and Environmental Standard Reference Materials*; NBS Special Publication 260-111; U.S. National Bureau of Standards: Washington, DC, 1987.

Li, J. C. R. *Statistical Inference*; Edwards: Ann Arbor, MI, 1964.

Lyon, J. L.; Sorenson, A. W. Colon Cancer in a Low-Risk Population. *Am. J. Clin. Nutr.* **1978**, *31*, S227–S230.

National Research Council. *Diet, Nutrition and Cancer*; National Academy Press: Washington, DC, 1982.

Nielson, K. K. Matrix Corrections for Energy Dispersive X-ray Fluorescence Analysis of Environmental Samples with Coherent/Incoherent Scattered X-rays. *Anal. Chem.* **1977**, *49*, 641–648.

Nielson, K. K. CEMAS: An Advanced Approach for Quantitative XRF Analysis without Standards. *Kevex Anal.* **1986**, *11*, 9–11.

Nielson, K. K.; Mahoney, A. W.; Rogers, V. C. X-Ray Fluorescence and Atomic Absorption Spectrophotometry Measurements of Manganese, Iron, Copper and Zinc in Selected Foods. *J. Agric. Food Chem.* **1988**, *36*, 1211–1216.

Nielson, K. K.; Rogers, V. C.; Shuman, R. Determination of X-ray Fluorescence Sample Geometry from Compton Backscatter Energy. *X-Ray Spectrom.* **1989**, *18*, 67–72.

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Registry No. P, 7723-14-0; S, 7704-34-9; Cl, 7782-50-5; K, 7440-09-7; Ca, 7440-70-2; Mn, 7439-96-5; Fe, 7439-89-6; Zn, 7440-66-6; Br, 7726-95-6; Rb, 7440-17-7; Sr, 7440-24-6.