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ORIGINAL ARTICLE

Multi-element Analysis of Food by Microwave Digestion and Inductively Coupled Plasma-Atomic Emission Spectrometry

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A microwave digestion procedure for multi-elemental analysis of food was developed using one program to digest a variety of food matrices at the same time. A single program was enabled by an analytical portion mass based on the food's energy content calculated from macronutrient data (fat, protein and carbohydrate). The procedure allows a maximum mass to be analyzed for each food matrix without adjustment of the microwave digestion program to compensate for the variable reactivity of food matrices. Inductively coupled plasma-atomic emission spectrometry with ultrasonic nebulization was used to determine aluminum, arsenic, boron, barium, calcium, cadmium, cobalt, chromium, copper, iron, potassium, magnesium, manganese, molybdenum, sodium, nickel, phosphorus, lead, selenium, strontium, thallium, vanadium, and zinc. Method validation was performed on seven certified reference materials and 20 foods. Element fortification recovery of foods was acceptable (88–113%) and a majority of available comparisons to reference materials indicated agreement except for aluminum, chromium, and selenium. Published by Elsevier Science Ltd.

Key Words: microwave digestion; inductively coupled plasma; atomic emission spectrometry; food; multi-element analysis.

INTRODUCTION

Food and Drug Administration (FDA) regulations (FDA, 2001a) require nutrition labeling for most foods (except meat and poultry) and authorize use of nutrient content claims and FDA approved health claims. The food label clearly displays nutritional information including the content of up to 14 nutrient elements. Reference daily intakes (RDIs) for 12 elements essential to human nutrition, and daily reference values (DRVs) for sodium and potassium have been established (FDA, 2001a): calcium (1000 mg), chloride (3400 mg), chromium (120 μg), copper (2 mg), iron (18 mg), iodine (150 μg), potassium (3500 mg), magnesium (400 mg), manganese (2 mg), molybdenum (75 μg), sodium (2400 mg), phosphorus (1000 mg), selenium (70 μg), and zinc (15 mg). In addition to nutritional concerns, toxic element

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contamination in foods is an important food safety topic. A multi-element analysis method that is applicable to a large variety of foods and easy to use is needed to verify accuracy of element content on food labels and to screen for toxic element contamination.

Currently, FDA conducts routine food analysis using traditional dry ash or acid digestion procedures (FDA, 1993; Capar and Cunningham, 2000). These procedures are reliable but have drawbacks. Dry ashing may take 2–3 days to prepare an analytical solution. Conventional acid digestions are typically faster (normally 3–4 h) than dry ashing but require constant operator attention. Ternary acid digestions (nitric/perchloric/sulfuric acids) offer a more complete digestion, but safety concerns and hazardous waste regulations make use of perchloric acid unattractive.

Microwave digestion offers many advantages over conventional digestion procedures used for food analysis. Microwave digestions are usually performed with nitric acid in a closed high-pressure polytetrafluoroethylene (PTFE) lined vessel at temperatures above the boiling point of nitric acid. These features reduce acid consumption, contamination, and preparation time. Microwave digestion is usually complete within 1 h. The microwave system is controlled by a computer that monitors digestion vessel pressure and temperature and adjusts microwave power to control these variables to user-specified limits. Microwave digestion programs can be operated unattended and are easily transferred to other laboratories. However, the mass of the analytical portion must be carefully selected to prevent excessive pressure during the digestion. The food matrix producing the most pressure is usually used to control the digestion procedure for foods being prepared concurrently. Microwave digestion procedures supplied by manufacturers (CEM, 1991) and published in the literature (Jorhem and Engman, 2000; Rodushkin *et al.*, 1999; Sun *et al.*, 2000; Ziaziaris and Kacprzak, 1995; Sheppard *et al.*, 1994; McCarthy and Ellis, 1991; Sapp and Davidson, 1991; Negretti de Brätter *et al.*, 1995) typically apply to a single food matrix or minimize the analytical portion mass to account for the most reactive food matrix. Thus, each food matrix may require a different microwave program or the analytical portion mass is restricted. This approach is not efficient when analyzing a full range of food matrices on a routine basis. An additional pre-digestion step has also been used to allow various matrices to be digested concurrently (Rhoades *et al.*, 1998). Barnes (1998) was able to prepare various masses of food matrices by using a microwave digestion system that measured pressure in all digestion vessels simultaneously.

The present work uses a food's energy content to determine the appropriate analytical portion mass to enable various food matrices to be prepared concurrently using a single digestion program and measurement of pressure in one digestion vessel. The microwave digestion procedure provides high sample throughput while minimizing contamination, operator intervention, and modifications due to food matrix. These attributes yield a microwave digestion procedure that is easily transferred to other laboratories. The microwave digestion procedure was applied to 20 foods representing various food matrices and seven food related reference materials. Food matrices analyzed include grains, meat, dairy, fish, fruit, nut, vegetable, high-fat foods, and alcoholic beverages. Analytical solutions were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) for aluminum, arsenic, boron, barium, calcium, cadmium, cobalt, chromium, copper, iron, potassium, magnesium, manganese, molybdenum, sodium, nickel, phosphorus, lead, selenium, strontium, thallium, vanadium, and zinc. Precision and accuracy were demonstrated with analysis of replicates and element fortification recovery for each food and reference materials.

MATERIALS AND METHODS

Food Digestion

Laboratory food samples were reserve portions of market basket 94-4 from FDA's Total Diet Study (TDS) (Capar and Cunningham, 2000; FDA, 2001b; Pennington *et al.*, 1996). Each laboratory sample was a composite of food collected from each of these three cities (Albuquerque, NM; San Diego, CA; Seattle, WA) within a geographical region of the United States. Food samples that required washing, trimming, peeling or cooking were sent to an institutional kitchen for preparation according to specified instructions and recipes. The edible portion of table-ready foods from each of the three cities was combined in equal weight portions and homogenized to produce a composite representing each TDS food.

Laboratory food samples were digested using an MDS-2000 microwave system equipped with temperature and pressure control to 200°C and 600 psi, respectively (CEM Corp., Matthews, NC, U.S.A.). The microwave power range was programmable from 0 to 600 W in 1% increments. Microwave digestion vessels were TFM Teflon-lined Heavy Duty Vessels capable of operating up to 200°C and 600 psi (CEM Corp., Matthews, NC, U.S.A.). Digestion vessels were cleaned with laboratory-grade liquid detergent and warm tap water when used for the first time or after an incomplete digestion. Subsequently, digestion vessels were acid cleaned with 10 mL of nitric acid (ACS Reagent grade) using the microwave cleaning program: 600 W power, 0 psi control pressure, 10 min run time, 3 min hold time, and 200°C control temperature. Vessels were rinsed with ASTM Type I grade water (ASTM, 2001) supplied by a Milli-Q UV Laboratory Water System (Millipore, Bedford, MA, U.S.A.) and air-dried. At least one method blank was carried through the procedure with each batch of analytical portions. Batches consisted of 12 analytical portions including method blanks. Laboratory samples were mixed and aliquots transferred to tared vessel liners with Tefzel stir rods (Cole-Parmer, Vernon Hills, IL, U.S.A.). A mixed element fortification standard was prepared from single element standards (High-Purity Standards, Charleston, SC, U.S.A.). The fortification standard was added before digestion.

The pressure buildup from digestion products limits the maximum analytical portion for any food. Maximum analytical portion is determined using food energy content as an indicator of pressure produced during digestion. Maximum energy release permitted for digestion was empirically determined as 3 kcal. This energy limit prevents digestion from reaching maximum operating pressure before the digestion program is complete. The energy of an analytical portion must not exceed these values for safe operation. A food's energy content (usually provided as kcal/100 g) is available from many sources (U.S. Department of Agriculture, USDA, 2002; Souci *et al.*, 1994). In addition, a food's energy content may be estimated from calories and serving size provided on a food's label. For example, a nutrition label on a sports nutrition bar lists a serving size as the entire bar with a mass of 50 g and an energy value of 210 cal (U.S. consumer food label "calories" are kilocalories). Therefore, the kcal/g for this product is 210 kcal/50 g = 4.2 kcal/g. The maximum mass is calculated using the following equation:

$$\text{Maximum analytical portion (g)} = \frac{\text{Vessel max. energy (kcal)}}{\text{Food energy (kcal/g)}}.$$

The maximum analytical portion is 3 kcal/4.2 kcal/g = 0.7 g. Therefore, for a 600 psi microwave digestion vessel, the analytical portion for this sports nutrition bar must be 0.7 g or less.

TABLE 1

Microwave digestion program

Stage[1]	1	2	3	4
Power (W)	300	400	600	600
Run time (min)	10	10	10	10
Control pressure (psi)	85	200	450	600
Control temperature (°C)	130	150	180	200
Hold time (min)	3	3	3	3

[1]For each stage, power is applied for the run time minutes or until control pressure or control temperature is met. If control pressure or control temperature is met before the end of run time then program proceeds to hold time prior to proceeding to next stage. If run time is met then program proceeds to next stage.

A maximum analytical portion of 0.5 g (dry matter) should be taken for samples of unknown composition. Larger analytical portions for unknowns may be taken after digestion behavior has been characterized. Once proper analytical portion mass was taken, 9 mL of trace metals grade nitric acid (Fisher Scientific, Springfield, NJ, U.S.A.) was added to each analytical portion. Vessels were sealed, placed in the microwave oven and digestion was performed under microwave conditions listed in Table 1. Digestions were judged complete if digestion temperature reached 200°C and clear to light yellow analytical solutions were produced. Analytical portions that were incompletely digested were discarded and a lower mass portion was digested. The microwave digestion program typically took 30–35 min to complete with another 20–30 min to allow vessels to cool for safe handling. Microwave digestions were performed unattended allowing the next batch of analytical portions to be prepared for microwave digestion. After a complete digestion, analytical solutions were quantitatively transferred to 50 mL graduated polypropylene tubes (Falcon brand, Fisher Scientific, Springfield, NJ, U.S.A.) and diluted to volume with Type I grade water (ASTM, 2001).

Multi-element Analysis

Element concentrations were measured with an Applied Research Laboratories Model 3580 ICP-AES (Valencia, CA, U.S.A.) in simultaneous mode using an extended tangential flow torch with side arm, and a 3.5 turn, shielded load coil. The spectrometer, described in detail by Dolan *et al.* (1991), was equipped with a 2.5 kW, 27 MHz crystal-controlled radio frequency generator (Henry Electronics, Los Angeles, CA, U.S.A.) and an automatic matching network (Montaser *et al.*, 1989). Analytical solutions were introduced by an ultrasonic nebulizer (Model U5000AT, CETAC Technologies Inc., Omaha, NE, U.S.A.). A peristaltic pump (Model Minipulse 2, Gilson Medical Electronics, Middleton, WI, U.S.A.) was used to deliver analytical solution to the nebulizer at 1.0 mL/min. A mass flow controller (Model 8200, Matheson Gas Products, East Rutherford, NJ, U.S.A.) was used to control injector gas flow at 0.85 L/min.

Plasma operating parameters were 1150 W forward power, <10 W reflected power, 15 mm (above load coil) observation height, and argon flows of 0.8 and 12 L/min for intermediate and outer gases, respectively. The ultrasonic nebulizer's heating chamber and condenser were operated at 140 and 1°C, respectively. Multi-element calibration solutions were prepared from single-element standard solutions (High-Purity Standards, Charleston, SC, U.S.A.). Dual, symmetrical, off-peak measurements for background correction were performed at ± 0.070 nm by moving the primary slit via stepper motor control. Integrated peak data were taken from the spectrometer data system and concentrations were calculated with Microsoft Excel spreadsheet program using a linear calibration fit.

RESULTS AND DISCUSSION

Microwave Digestion

Analytical portions (Table 2) ranged from 0.41 g for mayonnaise to 9.5 g for broccoli. Larger analytical portions may produce a complete digestion for some foods but maximum vessel energy of 3 kcal allows for inaccuracy of energy estimates, variability in analytical portion composition, and digestion behavior of different food matrices in the same batch. A 10 g maximum analytical portion is recommended to limit the dilution of acid strength by sample water content (i.e., fruits, vegetables and beverages). Incomplete digestion occurred when analytical portions were greater than 10 g despite reaching the temperature control limit (200°C). Completeness of digestion was judged by clarity after dissolution and a slowdown in pressure buildup during the final digestion stage. Incomplete digestions are usually dark-colored solutions (yellow to brown), have a bad odor and might contain partially digested sample. When analyzed by ICP-AES, analytical solutions produced by incomplete digestion caused severe matrix effects and plasma instability. Digestion program time was approximately 35 minutes plus 30 min for cooling. An analyst can prepare 24 analytical solutions from food analytical portions each day with one microwave system.

Analytical Limits

Instrumental detection limits (IDL) were estimated using three times the standard deviation of the element concentration of 11 calibration blanks. Limits of detection (LOD) were estimated as the lowest concentration that can be detected in an analytical portion according to the statistics of hypothesis testing, with a 95% confidence by using two times the one-sided Student's t at 95% times the standard deviation of 18 method blanks (Currie, 1999). Limits of quantification (LOQ) were estimated as the element concentration in an analytical portion that would have a

TABLE 2

Typical food analytical portion

Food	Analytical portion (g)	Food	Analytical portion (g)
Beef, strained	2.2	Mayonnaise	0.41
Beer	6.7	Pancakes	1.4
Broccoli	9.5	Peanut butter	0.59
Cheddar cheese	0.88	Pears, canned	5.0
Corn	2.7	Pork bacon	0.58
Eggs, boiled	1.7	Prune juice	4.4
Evaporated milk	2.3	Spaghetti and meatballs	2.8
Fruit-flavored cereal	0.84	Sweet potato	2.2
Haddock	1.7	Tuna, canned in oil	1.0
Lemonade	7.7	White bread	1.2

TABLE 3

Instrumental detection limits (IDL) and limits of quantification (LOQ)

Element	Wavelength (nm) × order[1]	IDL[2] (μg/L)	LOQ[3] (mg/kg)
Aluminum	308.22 × 2	3	0.6
Arsenic	189.04 × 3	2	0.2
Barium	493.41 × 1	0.09	0.8[4]
Boron	249.68 × 3	2	0.3
Cadmium	226.50 × 3	0.5	0.03
Calcium	317.93 × 2[5]	0.6	80[4]
Chromium	267.72 × 3	2	0.4
Cobalt	228.62 × 3	0.6	0.03
Copper	324.75 × 2	0.3	0.05
Iron	259.94 × 2	0.3	0.3[4]
Lead	220.35 × 3	3	0.3
Magnesium	383.83 × 1[5]	7	40[4]
Manganese	257.61 × 3	0.07	0.006
Molybdenum	202.03 × 3	0.7	0.06
Nickel	231.60 × 3	2	0.2
Phosphorus	178.29 × 3[5]	4	0.4
Potassium	766.49 × 1[5]	8	4
Selenium	203.99 × 3	6	0.7
Sodium	589.59 × 1[5]	2	70[4]
Strontium	407.77 × 1[5]	0.03	2[4]
Thallium	190.86 × 3	5	0.3
Vanadium	292.40 × 2	0.4	0.04
Zinc	213.86 × 2	0.2	0.09

[1]Background correction performed at ±0.070 nm except as noted.
[2]Instrumental detection limit (IDL) based on 11 measurements of calibration blank.
[3]Limit of quantification (LOQ) based on 18 measurements of method blank, 2 g analytical portion and 50 mL analytical solution.
[4]LOQ elevated due to element concentration found above IDL in method blank.
[5]No background correction performed.

relative standard deviation of 10% using 10 times the standard deviation (Currie, 1999) of element concentration of 18 method blanks. "Trace" concentrations are defined as those greater than or equal to LOD and less than LOQ. Table 3 lists IDLs and LOQs calculated using an analytical portion of 2 g and an analytical solution of 50 mL. Comparison of IDLs (based on calibration blank) and analytical solution LOQs (based on method blanks) revealed a discernible environmental contamination component present in the method blanks for barium, calcium, iron, magnesium, sodium, and strontium.

Reference Materials

The results of replicate analyses of reference materials (0.5–1 g analytical portions) were used to assess accuracy and precision. Data quality for quantifiable results was examined by using a "*z*-score" (Thompson and Wood, 1993), recovery of the reference value based on available certified values or consensus values derived from three or more results (Roelandts and Gladney, 1998), and precision based on relative standard deviation (RSD). For this study, the *z*-score is defined as

$$z = \frac{x_{\mathrm{m}} - x_{\mathrm{c}}}{\sigma},$$

where x_m is the measured analyte mass fraction, x_c is the accepted mass fraction ("reference value"), and

$$\sigma = \sqrt{\sigma_m^2 + \sigma_c^2},$$

where σ_m is the combined uncertainty assigned a target value of 5% of the measured mass fraction and σ_c is the combined uncertainty of the accepted mass fraction. *z*-Scores were based either on certified values with σ_c taken to be one-half of the uncertainty stated on the certificate (given at the 95% confidence level) or, for non-certified analytes, on consensus values with σ_c taken to be the uncertainty given in the references (1 standard deviation). Absolute values of *z*-scores of ≤ 2, between 2 and 3, and $\geqslant 3$ were used as indications of agreement, questionable agreement, or disagreement between measured values and certified or consensus values.

Recovery and z-Score. Results for seven reference materials are listed in Table 4. At least one *z*-score and recovery were attainable for each element except thallium. All *z*-scores indicated agreement for arsenic, barium, calcium, cobalt, copper, iron, lead, manganese, molybdenum, sodium, strontium, and vanadium. All recoveries were acceptable (80–120%) for arsenic, barium, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, phosphorus, potassium, sodium, strontium, vanadium and zinc. Aluminum *z*-scores for two of four reference materials indicated disagreement and recovery was poor for these two reference materials. The aluminum recovery for oyster tissue was low (65%) probably due to the presence of silicon which is present at about 0.11% (Nadkarni, 1984). Low recovery of aluminum has been reported to be associated with incomplete dissolution of samples containing silica which would require the use of hydrofluoric acid to obtain complete recovery (Hoenig *et al*., 1998; Schelenz and Zeiller, 1993; Sun *et al*., 2000). The aluminum recovery for bovine liver was very high (344%) probably due to a contamination problem or the concentration being near the LOQ (2 mg/kg). All three boron recoveries were acceptable but one *z*-score (for total diet) indicated questionable agreement. All four cadmium recoveries were acceptable but one *z*-score (for dogfish muscle) indicated questionable agreement. The single chromium recovery (for dogfish muscle) was acceptable but the *z*-score indicated questionable agreement. All seven magnesium recoveries were acceptable but *z*-scores for three of seven reference materials indicated less than agreement. The magnesium *z*-scores for rice flour and total diet indicated questionable agreement and for mussel indicated disagreement. A low (68%) nickel recovery was obtained for one (dogfish muscle) of three reference materials and this material's *z*-score indicated questionable agreement. The reason for this low result is unknown. All five phosphorus recoveries were acceptable but the *z*-score for rice flour indicated questionable agreement. All seven potassium recoveries were acceptable but *z*-scores for two of seven reference materials indicated less than agreement. The potassium *z*-score for dogfish muscle indicated questionable agreement and the *z*-score for bovine liver indicated disagreement. Selenium recoveries for all three reference materials were high (mean 157%) and all three *z*-scores indicated either questionable agreement or disagreement. The selenium LOQ for all these reference materials was 2 mg/kg, which is near the reference values (2–3 mg/kg). Therefore, the high results may indicate that the estimated LOQ is too low or there was insufficient correction of spectral background emission. All seven zinc recoveries were acceptable but the *z*-score of one dogfish muscle indicated disagreement. The trace vanadium result for total diet reference material is a factor of 10 lower than a consensus value ($n = 1$). A more recent publication by one of the same authors whose work provided the consensus value reported a vanadium concentration for the total

TABLE 4

Reference material results[1]

Element	Rice flour (NIST 1568a)					Total diet (NIST 1548)				
	Mean (mg/kg)	RSD (%)	Ref. value (mg/kg)	*z*-Score	Rec. (%)	Mean (mg/kg)	RSD (%)	Ref. value (mg/kg)	*z*-Score	Rec. (%)
Aluminum	5.3 ± 0.3	6	4.4 ± 1.0	1.6	120	39 ± 1	2	33[2]	—	—
Arsenic	(0.36 ± 0.07)	21	0.29 ± 0.03	—	—	< 0.2	—	0.104[3]	—	—
Barium	< 0.7	—	nv	—	—	(1.3 ± 0.02)	1	nv	—	—
Boron	(0.44 ± 0.05)	11	0.54 ± 0.12[4]	—	—	2.23 ± 0.15	7	2.61 ± 0.12[4]	−2.3	86
Cadmium	(0.044 ± 0.019)	44	0.022 ± 0.002	—	—	(0.041 ± 0.013)	32	0.028 ± 0.004	—	—
Calcium	(151 ± 21)	14	118 ± 6	—	—	1680 ± 30	2	1740 ± 70	−0.7	97
Chromium	< 0.3[5]	—	nv	—	—	< 0.4	—	0.5[3]	—	—
Cobalt	< 0.03[5]	—	0.018[2]	—	—	(0.043 ± 0.005)	12	nv	—	—
Copper	2.5 ± 0.03	1	2.4 ± 0.3	0.6	105	2.68 ± 0.05	2	2.6 ± 0.3	0.4	103
Iron	7.6 ± 0.1	1	7.4 ± 0.9	0.3	103	30.6 ± 0.9	3	32.6 ± 3.6	−0.9	94
Lead	< 0.2	—	< 0.010[2]	—	—	< 0.3	—	0.05[2]	—	—
Magnesium	483 ± 5	1	560 ± 20	−2.9	86	494 ± 10	2	556 ± 27	−2.2	89
Manganese	20.3 ± 0.4	2	20.0 ± 1.6	0.3	102	4.88 ± 0.08	2	5.2 ± 0.4	−1.0	94
Molybdenum	1.62 ± 0.01	1	1.46 ± 0.08	1.7	111	0.30 ± 0.02	8	0.27[2]	—	—
Nickel	(0.31 ± 0.07)	24	nv	—	—	(0.27 ± 0.09)	32	0.43 ± 0.03[3]	—	—
Phosphorus	1750 ± 50	3	1530 ± 80	2.3	114	3590 ± 70	2	3240 ± 40	1.9	111
Potassium	1220 ± 30	2	1280 ± 8	−1.0	95	5950 ± 110	2	6060 ± 280	−0.3	98
Selenium	< 0.6	—	0.38 ± 0.04	—	—	< 0.7	—	0.245 ± 0.005	—	—
Sodium	< 60	—	6.6 ± 0.8	—	—	6560 ± 140	2	6250 ± 260	0.9	105
Strontium	< 2	—	nv	—	—	(3.8 ± 0.2)	5	nv	—	—
Thallium	< 0.2	—	nv	—	—	< 0.3	—	nv	—	—
Vanadium	< 0.03	—	0.007[2]	—	—	(0.048 ± 0.008)	17	0.49[3]	—	—
Zinc	19.3 ± 0.8	4	19.4 ± 0.5	−0.1	99	29.9 ± 0.9	3	30.8 ± 1.1	−0.6	97

Element	Whole egg power (NIST 8415)					Dogfish muscle (NRCC DORM-1)				
	Mean (mg/kg)	RSD (%)	Ref. value (mg/kg)	*z*-Score	Rec. (%)	Mean (mg/kg)	RSD (%)	Ref. value (mg/kg)	*z*-Score	Rec. (%)
Aluminum	604 ± 38	6	540 ± 86	1.2	112	11.4 ± 0.8	7	nv	—	—
Arsenic	< 0.2	—	0.01[2]	—	—	18.6 ± 0.5	3	17.7 ± 2.1	0.7	105
Barium	3.6 ± 0.2	5	3[2]	—	—	< 0.7	—	nv	—	—
Boron	< 0.4	—	0.41 ± 0.26	—	—	0.87 ± 0.04	5	nv	—	—
Cadmium	< 0.04	—	0.005[2]	—	—	0.103 ± 0.006	5	0.086 ± 0.012	2.2	120
Calcium	2580 ± 110	4	2480 ± 190	0.6	104	1390 ± 40	3	nv	—	—
Chromium	(0.78 ± 0.26)	34	0.37 ± 0.18	—	—	4.3 ± 0.4[5]	10	3.60 ± 0.40	2.3	119
Cobalt	(0.044 ± 0.042)[5]	96	0.012 ± 0.005	—	—	< 0.03[5]	—	0.049 ± 0.014	—	—
Copper	2.86 ± 0.14	5	2.70 ± 0.35	0.7	106	5.21 ± 0.55	11	5.22 ± 0.33	0.0	100
Iron	104 ± 3	3	112 ± 16	−0.8	93	59.0 ± 0.7	1	63.6 ± 5.3	−1.2	93
Lead	< 0.3	—	0.061 ± 0.012	—	—	(0.43 ± 0.07)	17	0.40 ± 0.12	—	—
Magnesium	295 ± 12	4	305 ± 27	−0.5	97	1070 ± 40	4	1210 ± 130	−1.7	88
Manganese	1.75 ± 0.07	4	1.78 ± 0.38	−0.1	99	1.17 ± 0.04	3	1.32 ± 0.26	−1.1	88
Molybdenum	0.26 ± 0.02	9	0.247 ± 0.023	1.0	105	(0.180 ± 0.003)	2	nv	—	—
Nickel	< 0.2	—	nv	—	—	0.81 ± 0.11	13	1.20 ± 0.30	−2.5	68
Phosphorus	10 600 ± 380	4	10 010 ± 320	1.1	106	11.0 ± 0.3	3	nv	—	—
Potassium	3140 ± 430	14	3190 ± 370	−0.2	98	13 700 ± 300	2	15 900 ± 1000	−2.6	86
Selenium	2.2 ± 0.5	22	1.39 ± 0.17	6.1	162	2.84 ± 0.25	9	1.62 ± 0.12	7.9	175
Sodium	3900 ± 300	8	3770 ± 340	0.5	103	7930 ± 150	2	8000 ± 600	−0.1	99
Strontium	(6.8 ± 0.4)	6	5.63 ± 0.46	—	—	9.1 ± 0.1	1	nv	—	—
Thallium	< 0.3	—	nv	—	—	< 0.2	—	nv	—	—
Vanadium	0.536 ± 0.065	12	0.459 ± 0.081	1.6	117	(0.044 ± 0.007)	17	nv	—	—
Zinc	66.6 ± 3.5	5	67.5 ± 7.6	−0.2	99	18.0 ± 0.9	5	21.3 ± 1.0	−3.3	84

(*continued on next page*)

TABLE 4 (*continued*)

Element	Oyster tissue (NIST 1566)					Mussel (NIES No. 6)				
	Mean (mg/kg)	RSD (%)	Ref. value (mg/kg)	*z*-Score	Rec. (%)	Mean (mg/kg)	RSD (%)	Ref. value (mg/kg)	*z*-Score	Rec. (%)
Aluminum	166±9	5	255±19[3]	−4.3	65	218±11	5	220[2]	—	—
Arsenic	14.0±0.2	2	13.4±1.9	0.5	105	9.6±0.1	1	9.2±0.5	0.8	105
Barium	3.9±0.04	1	4.9±0.7[3]	−1.4	80	< 0.8	—	nv	—	—
Boron	7.20±0.43	6	8.0±0.9[3]	−0.8	90	12.2±0.2	1	12.9±0.7[4]	−0.7	95
Cadmium	3.65±0.10	3	3.5±0.4	0.6	104	0.849±0.012	1	0.82±0.03	0.6	104
Calcium	1430±30	2	1500±200	−0.6	95	1260±30	2	1300±100	−0.5	97
Chromium	< 0.4[5]	—	0.69±0.27	—	—	(0.88±0.75)[5]	85	0.63±0.07	—	—
Cobalt	0.317±0.015	5	0.35±0.04[3]	−0.8	91	0.307±0.018	6	0.37[2]	—	—
Copper	63.0±1.4	2	63.0±3.5	0.0	100	5.31±0.66	12	4.9±0.3	1.4	108
Iron	184±5	3	195±34	−0.6	94	147±6	4	158±8	−1.3	93
Lead	(0.54±0.05)	—	0.48±0.04	—	—	0.83±0.09	11	0.91±0.04	−1.7	91
Magnesium	1150±30	3	1280±90	−1.8	90	1750±40	2	2100±100	−3.5	83
Manganese	16.8±0.5	3	17.5±1.2	−0.6	96	15.0±0.4	3	16.3±1.2	−1.4	92
Molybdenum	(0.163±0.004)	2	0.20±0.07[3]	—	—	0.84±0.03	3	nv	—	—
Nickel	0.91±0.05	5	1.03±0.19	−1.1	88	0.87±0.11	13	0.93±0.06	−1.1	94
Phosphorus	8170±250	3	7600±400[3]	1.0	108	8220±160	2	7700[2]	—	—
Potassium	8830±240	3	9690±50	−1.9	91	5270±170	3	5400±200	−0.5	98
Selenium	2.8±0.2	7	2.1±0.5	2.5	134	2.3±0.21	9	1.5[2]	—	—
Sodium	5140±120	2	5100±300	0.1	101	9640±280	3	10 000±300	−0.7	96
Strontium	10.7±0.2	2	10.36±0.56	0.6	103	18.5±0.5	3	17[2]	—	—
Thallium	< 0.2	—	≤0.005[2]	—	—	< 0.2	—	nv	—	—
Vanadium	2.44±0.07	3	2.6±0.3[3]	−0.5	94	0.562±0.018	3	nv	—	—
Zinc	788±33	4	852±14	−1.6	92	100±2	2	106±6	−1.0	95

Element	Bovine liver (NIST 1577a)					Mean Rec. (%)	n
	Mean (mg/g)	RSD (%)	Ref. value (mg/kg)	z-Score	Rec. (%)		
Aluminum	5.8 ± 0.9	15	1.7 ± 0.6[3]	6.2	344	160	4
Arsenic	< 0.2	—	0.047 ± 0.006	—	—	105	3
Barium	< 0.9	—	0.08 ± 0.04[3]	—	—	80	1
Boron	< 0.4	—	0.84 ± 0.20[3]	—	—	90	3
Cadmium	0.454 ± 0.028	6	0.44 ± 0.06	0.4	103	108	4
Calcium	(153 ± 7)	5	120 ± 7	—	—	98	4
Chromium	(0.79 ± 0.16)	21	0.2 ± 0.1[3]	—	—	119	1
Cobalt	0.205 ± 0.015	7	0.21 ± 0.05	−0.2	98	94	2
Copper	149 ± 4	3	158 ± 7	−1.1	94	102	7
Iron	175 ± 5	3	194 ± 20	−1.5	90	94	7
Lead	< 0.3[5]	–	0.135 ± 0.015	–	–	91	1
Magnesium	554 ± 17	3	600 ± 15	−1.6	92	89	7
Manganese	9.45 ± 0.33	4	9.9 ± 0.8	−0.7	95	95	7
Molybdenum	3.69 ± 0.12	3	3.5 ± 0.5	0.6	105	107	3
Nickel	(0.30 ± 0.06)[5]	21	0.71 ± 0.08[3]	—	—	83	3
Phosphorus	11 600 ± 400	3	11 100 ± 400	0.8	105	109	5
Potassium	8590 ± 230	3	9960 ± 70	−3.2	86	93	7
Selenium	(0.99 ± 0.44)	44	0.71 ± 0.07	—	—	157	3
Sodium	2370 ± 60	3	2430 ± 130	−0.4	98	100	6
Strontium	< 3	—	0.138 ± 0.003	—	—	103	1
Thallium	< 0.3	—	0.003[2]	—	—	—	0
Vanadium	(0.068 ± 0.017)	25	0.099 ± 0.008	—	—	105	2
Zinc	115 ± 5	4	123 ± 8	−1.1	93	94	7

[1] $n = 3$ except $n = 4$ for rice flour, whole egg powder, and mussel. Ref. value is certified value unless noted. NIST = National Institute of Standards and Technology, NRCC = National Research Council of Canada, NIES = National Institute for Environmental Studies of Japan, nv = no value available. Mean results in () are "trace" levels and mean results below LOD listed as <LOD.

[2] Not certified; informational value provided by certifying organization.

[3] Consensus value (Roelandts and Gladney, 1998).

[4] Not certified (Anderson and Cunningham, 2000; Anderson *et al.*, 1999)

[5] One highly divergent result excluded due to spectral interference or environmental contamination.

diet reference material of 0.037 mg/kg (mean of two analyses) (Baker *et al.*, 1999) which more closely agrees with the trace result.

Precision. Replicate analysis precision (measured as RSD) was 15% or less for all element concentration measurements above LOQ except for chromium in mussel (85%) and selenium in whole egg powder (22%). Extremely high variability was observed for chromium and many divergent results were excluded from performance assessment. The cause of this variability was not thoroughly investigated but environmental contamination or spectral interference is suspected. Chromium reference values for all reference materials except dogfish muscle were below LOQ. The somewhat high selenium variability for whole egg powder is probably due to a low estimate of the LOQ.

Foods

The results of replicate analyses of element fortified foods were used to assess analyte recovery and matrix-induced interference. Results of the FDA TDS (FDA, 2001b) enable comparison of results for some elements.

Fortification Recovery. Fortified and unfortified analytical portions were prepared and analyzed for all elements except calcium, magnesium, phosphorus, potassium, and sodium. Results for the 20 foods studied are listed in Table 5. Fortification recoveries for all foods were acceptable (80–120%) for arsenic, barium, cadmium, chromium, copper, iron, manganese, molybdenum, nickel, strontium, thallium, and vanadium. Aluminum fortification recovery was low for three foods: peanut butter (44%), pancakes (62%), and broccoli (73%). Low aluminum recoveries for pancakes and broccoli may be attributed to fortification at less than one times the native level. Low aluminum recovery for peanut butter cannot be explained with confidence but appears to be contamination or an instrument anomaly that caused the result of the unfortified analytical portion to be high (12.0 mg/kg). An aluminum concentration of 6.61 mg/kg for this peanut butter was determined by instrumental neutron activation analysis. Using this result for the unfortified analytical portion produces a 95% fortification recovery for the ICP-AES aluminum fortification result. This acceptable fortification recovery suggests that the unfortified aluminum results for peanut butter are erroneously high. Boron fortification recovery was high for prune juice (123%). This high recovery may be attributed to fortification at less than one times the native level. One low cobalt recovery for corn (67%) could not be explained. Lead fortification recovery was slightly low for two foods: pork bacon (74%) and broccoli (79%). These low recoveries cannot be readily explained. The high sodium concentration of the pork bacon may have hindered the ultrasonic nebulization but the other analyte fortification recoveries for this food are acceptable. For broccoli, other analyte fortification recoveries are on the low end of the acceptable range (except selenium) which may indicate an inaccurate fortification. Selenium fortification recoveries are slightly high for two foods: spaghetti (122%) and haddock (121%). These high recoveries cannot be readily explained. A high bias on reference material results was also observed as mentioned above. In addition, most selenium fortification recoveries were on the high end of the acceptable range (average of acceptable recoveries was 112%). These results indicate that insufficient correction of spectral background emission may be the cause of the slightly high bias on selenium results. One low zinc recovery for fruit-flavored cereal (69%) may be attributed to fortification at less than the native level.

Precision. The precision of replicate analysis of unfortified portions (measured as RSD; Table 5) was 15% or less for all element concentration measurements above LOQ except for cadmium in spaghetti (19%), calcium in haddock (30%), copper in

TABLE 5

Food results[1]

Element	Evaporated milk					Cheddar cheese					Pork bacon				
	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)
Aluminum	<0.2	—	2.6	88	—	(0.6)	28	7.3	95	—	(1.3)[5]	5	11	92	—
Arsenic	<0.05	—	5.3	97	<0.01	<0.2	—	15	93	<0.02	<0.2	—	23	87	<0.02
Barium	<0.3	—	1.1	103	—	(1.0)	18	2.9	93	—	<1	—	4.5	101	—
Boron	0.71	8	5.3	90	—	(0.47)	20	15	96	—	(0.69)	42	23	95	—
Cadmium	<0.009	—	0.53	98	<0.002	<0.03	—	1.5	94	<0.003	<0.04	—	2.3	91	(0.004)
Calcium	1770	5	—	—	2040	6220	5	—	—	7480	(120)	13	—	—	84
Chromium	<0.2	—	2.6	91	—	<0.3	—	7.3	97	—	<0.5[5]	—	11	92[5]	—
Cobalt	<0.009	—	1.1	88	—	<0.03	—	2.9	90	—	<0.04	—	4.5	88	—
Copper	<0.02	—	2.6	89	<0.25	0.35	16	7.3	92	(0.401)	0.96	1	11	93	(0.886)
Iron	0.45	6	26	85	(0.713)	1.51	19	73	87	(2.53)	8.03	0.3	113	86	8.74
Lead	<0.07	—	5.3	95	<0.007	<0.2	—	15	85	<0.014	<0.3[5]	—	23	74	(0.014)
Magnesium	157	8	—	—	194	238	7	—	—	283	(182)	10	—	—	181
Manganese	0.024	12	5.3	86	<0.3	0.182	8	15	89	<0.4	0.122	6	23	87	<0.4
Molybdenum	<0.02	—	1.1	92	—	(0.13)	23	2.9	92	—	<0.07	—	4.5	92	—
Nickel	<0.04	—	2.6	90	<0.025	<0.09	—	7.3	91	<0.05	<0.2	—	11	87	<0.05
Phosphorus	1900	6	—	—	1700	4890	3	—	—	4840	3420	3	—	—	3390
Potassium	2440	5	—	—	2860	733	9	—	—	736	3260	6	—	—	2940
Selenium	<0.2	—	11	114	0.040	<0.5	—	29	113	0.217	<0.8	—	45	102	0.295
Sodium	702	10	—	—	786	5340	7	—	—	6240	17 400	6	—	—	17 500
Strontium	(1.6)	20	2.6	95	—	6.2	11	7.3	98	—	<3	—	11	100	—
Thallium	<0.07	—	11	87	—	<0.2	—	29	88	—	<0.3	—	45	85	—
Vanadium	<0.01	—	0.53	85	—	<0.03	—	1.5	93	—	<0.04	—	2.3	92	—
Zinc	6.34	1	11	91	6.90	32.3	9	29	86	36.0	19.8	6	45	83	22.3

(*continued on next page*)

TABLE 5 (*continued*)

Element	Tuna (canned in oil)					Eggs (boiled)					Peanut butter				
	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)
Aluminum	(0.9)	2	5.6	91	—	(0.38)	23	3.0	95	—	12.0	8	11	44	6.61
Arsenic	0.86	8	11	101	0.966	<0.07	—	6.0	98	<0.01	<0.2	—	21	102	(0.021)
Barium	<0.6	—	2.2	100	—	(0.64)	4	1.2	100	—	3.6	2	4.2	95	—
Boron	(0.60)	16	11	90	—	(0.20)	51	6.0	95	—	16.2	0.1	21	93	—
Cadmium	(0.028)	20	1.1	105	0.022	<0.02	—	0.60	105	<0.002	(0.099)	4	2.1	105	0.067
Calcium	(100)	15	—	—	78	523	2	—	—	506	592	4	—	—	499
Chromium	<0.3	—	5.6	118[6]	—	(0.25)	29	3.0	102	—	<0.5	—	11	97	—
Cobalt	<0.02	—	2.2	97	—	<0.02	—	1.2	97	—	<0.04	—	4.2	81	0.031
Copper	0.45	1	5.6	90	(0.403)	0.58	1	3.0	95	(0.550)	4.66	1	11	92	4.48
Iron	7.93	3	56	92	8.38	16.6	1	30	94	16.9	19.9	1	106	95	19.5
Lead	<0.2[5]	—	11	86	(0.011)	<0.1	—	6.0	95	<0.007	<0.3	—	21	106	<0.014
Magnesium	242	3	—	—	251	114	2	—	—	109	1650	1	—	—	1580
Manganese	0.265	4	11	94	<0.3	0.272	1	6.0	95	<0.3	13.9	1	21	94	13.0
Molybdenum	<0.05	—	2.2	99	—	0.084	6	6.0	95	—	1.30	2	4.2	98	—
Nickel	(0.08)	23	5.6	96	(0.041)	<0.05	—	3.0	98	<0.025	1.24	7	11	98	0.931
Phosphorus	1610	4	—	—	1490	2080	2	—	—	1870	3980	5	—	—	3230
Potassium	1930	2	—	—	2070	1180	2	—	—	1170	5490	2	—	—	5500
Selenium	(0.88)	2	22	114	0.613	(0.48)	9	12	110	0.375	<0.8	—	42	116	0.118
Sodium	3200	3	—	—	3530	1200	2	—	—	1180	4260	3	—	—	4160
Strontium	<2	—	5.6	111	—	(0.86)	6	3.0	103	—	(5.5)	3	11	101	—
Thallium	<0.2	—	22	94	—	<0.1	—	12	95	—	<0.3	—	42	96	—
Vanadium	<0.03	—	1.1	97	—	<0.02	—	0.60	100	—	<0.04	—	2.1	98	<0.12
Zinc	4.45	9	22	94	4.40	12.2	2	12	91	12.0	26.0	1	42	87	25.2

Element	Corn					White bread					Pancakes				
	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)
Aluminum	(0.21)	6	1.8	91	<0.052	2.3	2	4.2	101	2.32	61.3	4	3.7	62	—
Arsenic	<0.04	—	3.7	95	<0.01	<0.1	—	8.5	100	<0.02	<0.09	—	7.3	100	<0.01
Barium	<0.2	—	0.73	101	—	(1.2)	2	1.7	103	—	(0.65)	5	1.5	99	—
Boron	0.61	3	3.7	93	—	(0.47)	12	8.5	99	—	1.4	4	7.3	98	—
Cadmium	(0.009)	24	0.37	102	(0.004)	(0.041)	6	0.85	103	0.021	<0.02	—	0.73	102	0.011
Calcium	(32)	8	—	—	23	577	2	—	—	578	1380	2	—	—	1330
Chromium	<0.1	—	1.8	93	—	<0.3	—	4.2	107	—	<0.2	—	3.7	103	—
Cobalt	<0.007	—	0.73	67	0.0011	<0.02	—	1.7	110	0.0073	<0.02	—	1.5	92	—
Copper	0.28	0.4	1.8	91	<0.25	1.07	3	4.2	96	(1.07)	0.90	3	3.7	95	(0.746)
Iron	2.4	6	18	90	(2.93)	29.5	2	42	91	31.5	14.2	2	37	90	14.1
Lead	<0.06[5]	—	3.7	90	<0.007	<0.2	—	8.5	93	<0.01	<0.2	—	7.3	85	(0.012)
Magnesium	189	2	—	—	183	212	2	—	—	206	316	2	—	—	292
Manganese	0.884	2	3.7	92	(0.855)	4.36	2	8.5	94	4.46	3.06	1	7.3	90	2.80
Molybdenum	(0.031)	2	0.73	95	—	0.16	3	1.7	98	—	0.30	3	1.5	94	—
Nickel	(0.044)	33	1.8	93	<0.025	(0.17)	7	4.2	95	0.124	0.29	5	3.7	91	0.191
Phosphorus	683	2	—	—	613	1170	1	—	—	1040	4140	2	—	—	3540
Potassium	1600	1	—	—	1730	1150	1	—	—	1160	2340	1	—	—	2150
Selenium	<0.2	—	7.3	110	<0.01	<0.4	—	17	115	0.146	<0.4	—	15	116	0.123
Sodium	<20	—	—	—	<7	4900	1	—	—	5180	4620	1	—	—	4470
Strontium	<0.5	—	1.8	110	—	(2.5)	8	4.2	104	—	(1.3)	6	3.7	102	—
Thallium	<0.06	—	7.3	91	—	<0.2	—	17	94	—	<0.2	—	15	90	—
Vanadium	<0.008	—	0.37	96	<0.0047	<0.02	—	0.85	101	<0.12	(0.021)	28	0.73	96	—
Zinc	3.50	1	7.3	87	3.92	5.56	2	17	93	5.83	6.99	4	15	86	6.79

(*continued on next page*)

TABLE 5 (*continued*)

Element	Fruit flavored cereal					Prune juice					Lemonade				
	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)
Aluminum	2.0	5	7.2	102	—	0.44	10	1.3	97	—	(0.09)	11	0.76	100	—
Arsenic	<0.2	—	14	101	<0.01	<0.03	—	2.6	103	<0.01	<0.02	—	1.5	100	<0.01
Barium	<0.7	—	2.9	101	—	(0.28)	12	0.52	99	—	<0.08	—	0.30	110	—
Boron	<0.3	—	14	97	—	4.8	8	2.6	123	—	0.32	8	1.5	97	—
Cadmium	(0.057)	7	1.4	107	0.018	<0.005	—	0.26	109	<0.001	<0.003	—	0.15	105	<0.001
Calcium	703	4	—	—	645	83	11	—	—	98	32	1	—	—	28.8
Chromium	(0.38)	68	7.2	107	—	(0.17)	123	1.3	93	—	<0.04	—	0.76	109	—
Cobalt	(0.068)	9	2.9	99	—	<0.005	—	0.52	100	—	<0.003	—	0.30	100	—
Copper	1.01	5	7.2	98	0.96	0.17	8	1.3	96	(0.213)	0.06	1	0.76	97	<0.2
Iron	214	5	72	81	201	2.31	9	13	98	3.2	0.27	2	7.6	96	<0.5
Lead	<0.2	—	14	102	(0.010)	<0.04	—	2.6	96	<0.005	<0.03	—	1.5	97	<0.004
Magnesium	273	5	—	—	249	94	11	—	—	126	17	4	—	—	17.2
Manganese	6.91	3	14	95	6.56	0.660	9	2.6	100	(0.862)	0.041	1	1.5	97	<0.2
Molybdenum	0.23	3	2.9	100	—	(0.010)	24	0.52	99	—	<0.006	—	0.30	101	—
Nickel	0.55	4	7.2	98	0.441	0.10	16	1.3	101	0.113	<0.01	—	0.76	100	<0.014
Phosphorus	1370	3	—	—	1160	188	13	—	—	192	26	3	—	—	(22.5)
Potassium	1160	3	—	—	1090	1760	9	—	—	2350	229	4	—	—	262
Selenium	<0.6	—	29	110	0.055	<0.1	—	5.2	115	<0.01	<0.06	—	3.0	103	<0.01
Sodium	5140	3	—	—	5300	(16)	11	—	—	(16.9)	(14)	0.1	—	—	(12.9)
Strontium	<2	—	7.2	119	—	(0.70)	11	1.3	104	—	(0.25)	3	0.76	104	—
Thallium	<0.2	—	29	98	—	<0.04	—	5.2	97	—	<0.02	—	3.0	98	—
Vanadium	0.093	6	1.4	101	—	(0.008)	84	0.26	99	—	<0.003	—	0.15	104	—
Zinc	159	5	29	69	157	0.94	9	5.2	99	1.30	0.11	13	3.0	93	<0.2

Element	Broccoli					Sweet potato					Spaghetti and meatballs				
	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)
Aluminum	1.3	4	0.60	73	—	(0.40)	10	2.4	100	—	6.46	2	2.0	88	—
Arsenic	<0.02	—	1.2	90	<0.01	<0.06	—	4.8	94	(0.011)	<0.04	—	3.9	95	<0.01
Barium	0.34	4	0.24	83	—	2.2	3	0.97	97	—	(0.44)	2	0.78	96	—
Boron	1.7	3	1.2	91	—	1.5	2	4.8	93	—	0.84	4	3.9	97	—
Cadmium	0.013	10	0.12	88	0.014	(0.013)	39	0.48	100	0.010	0.024	19	0.39	97	0.019
Calcium	280	4	—	—	331	264	1	—	—	275	307	5	—	—	332
Chromium	<0.03	—	0.60	91	—	<0.2	—	2.4	106	—	<0.09	—	2.0	102	—
Cobalt	0.017	2	0.24	83	—	(0.025)	10	0.97	94	—	<0.007	—	0.78	91	—
Copper	0.28	1	0.60	86	(0.295)	1.26	2	2.4	95	1.27	1.01	0.3	2.0	90	0.961
Iron	3.67	4	6.0	81	4.69	3.55	3	24	91	3.93	10.6	0.5	20	86	11.2
Lead	<0.02	—	1.2	79	<0.007	<0.08	—	4.8	91	<0.007	<0.06	—	3.9	88	<0.007
Magnesium	92	2	—	—	107	179	2	—	—	199	146	5	—	—	168
Manganese	1.34	5	1.2	86	1.60	8.40	2	4.8	92	8.85	1.65	5	3.9	87	1.80
Molybdenum	0.023	1	0.24	85	—	(0.046)	8	0.97	96	—	0.098	7	0.78	93	—
Nickel	0.17	2	0.60	84	0.167	0.19	6	2.4	94	0.127	0.11	9	2.0	91	(0.078)
Phosphorus	439	1	—	—	441	599	1	—	—	558	779	4	—	—	724
Potassium	858	3	—	—	1170	3470	4	—	—	4450	1600	4	—	—	2090
Selenium	<0.05	—	2.4	117	<0.01	<0.2	—	9.7	109	<0.01	<0.2	—	7.8	122	0.094
Sodium	124	2	—	—	116	235	0.1	—	—	237	2020	3	—	—	2190
Strontium	2.4	1	0.60	85	—	2.8	4	2.4	100	—	(1.6)	2	2.0	98	—
Thallium	<0.02	—	2.4	81	—	<0.08	—	9.7	92	—	<0.06	—	7.8	87	—
Vanadium	(0.004)	34	0.12	89	—	<0.01	—	0.48	99	—	<0.008	—	0.39	97	—
Zinc	1.52	5	2.4	80	1.79	2.52	3	9.7	90	2.73	8.38	4	7.8	84	9.01

(*continued on next page*)

TABLE 5 (*continued*)

Element	Mayonnaise					Beer					Beef (baby food)				
	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)
Aluminum	(1.3)	8	12	96	—	(0.17)	2	0.76	84	—	(0.41)[5]	4	2.4	93	—
Arsenic	<0.3	—	24	100	<0.02	<0.02	—	1.5	94	<0.01	<0.05	—	4.8	93	<0.01
Barium	<2	—	4.8	106	—	<0.09	—	0.31	103	—	<0.3	—	0.96	101	—
Boron	(1.1)	9	24	96	—	0.33	4	1.5	93	—	(0.28)	33	4.8	93	—
Cadmium	<0.05	—	2.4	107	<0.007	<0.003	—	0.15	101	<0.001	<0.009	—	0.48	104	<0.002
Calcium	<200	—	—	—	83.7	45	2	—	—	52.8	(52)	9	—	—	40.6
Chromium	<0.7	—	12	110	—	<0.04	—	0.76	108	—	<0.2	—	2.4	106	—
Cobalt	<0.05	—	4.8	100	—	<0.003	—	0.31	92	—	<0.009	—	0.96	96	—
Copper	(0.10)	19	12	97	<0.34	(0.018)	5	0.76	88	<0.17	0.42	2	2.4	92	(0.428)
Iron	2.26	17	121	96	(2.61)	(0.06)	13	7.6	88	<0.5	14.4	1	24	91	15.0
Lead	<0.4	—	24	97	<0.035	<0.03	—	1.5	87	<0.004	<0.08	—	4.8	94	<0.007
Magnesium	<70	—	—	—	(13.3)	50	1	—	—	62.9	124	1	—	—	141
Manganese	0.072	4	24	98	<0.4	0.088	1	1.5	90	<0.2	0.052	2	4.8	93	<0.3
Molybdenum	<0.1	—	4.8	103	—	0.024	7	0.31	93	—	<0.02	—	0.96	97	—
Nickel	<0.2	—	12	100	—	<0.02	—	0.76	94	<0.014	<0.04	—	2.4	97	(0.060)
Phosphorus	261	2	—	—	276	159	1	—	—	159	1230	0.05	—	—	1170
Potassium	183	17	—	—	98.3	205	1	—	—	281	1670	1	—	—	2200
Selenium	<1	—	48	115	(0.029)	<0.07	—	3.1	115	<0.01	<0.2	—	9.6	115	(0.030)
Sodium	5190	2	—	—	4930	35	1	—	—	41.6	393	1	—	—	427
Strontium	<4	—	12	110	—	(0.20)	3	0.76	95	—	<0.7	—	2.4	104	—
Thallium	<0.4	—	48	98	—	<0.03	—	3.1	90	—	<0.07	—	9.6	94	—
Vanadium	<0.06	—	2.4	103	—	0.030	2	0.15	95	—	<0.01	—	0.48	98	—
Zinc	1.49	1	48	93	(1.98)	<0.01	—	3.1	84	<0.2	32.4	2	9.6	83	32.2

Element	Haddock					Pears (canned)					Mean fort. rec. (%) ($n=20$)
	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)	Unfort. result[2] (mg/kg)	RSD (%)	Fort. level (mg/kg)	Fort. rec.[3] (%)	TDS result[4] (mg/kg)	
Aluminum	0.85[5]	7	3.3	87	—	(0.19)	5	1.1	97	—	89
Arsenic	5.91	2	6.7	95	6.59	<0.03	—	2.2	94	<0.01	97
Barium	<0.4	—	1.3	102	—	0.34	4	0.44	101	—	100
Boron	0.79	8	6.7	96	—	1.9	2	2.2	91	—	96
Cadmium	<0.02	—	0.67	101	<0.002	<0.004	—	0.22	103	<0.002	101
Calcium	204	30	—	—	269	46	3	—	—	45.2	—
Chromium	<0.2	—	3.3	105	—	(0.06)	59	1.1	105	—	102
Cobalt	<0.02	—	1.3	95	—	<0.004	—	0.44	98	—	93
Copper	0.25	9	3.3	94	<0.29	0.38	2	1.1	96	(0.413)	93
Iron	1.54	2	33	91	(1.64)	6.52	2	11	92	6.39	90
Lead	<0.1	—	6.7	90	<0.01	(0.041)	12	2.2	92	0.032	91
Magnesium	345	6	—	—	400	38	2	—	—	40.0	—
Manganese	0.340	10	6.7	92	(0.410)	0.979	2	2.2	94	1.03	92
Molybdenum	<0.03	—	1.3	97	—	<0.008	—	0.44	98	—	96
Nickel	(0.06)	28	3.3	93	<0.036	(0.044)	11	1.1	96	(0.042)	94
Phosphorus	2500	2	—	—	2300	67	3	—	—	68.4	—
Potassium	3060	6	—	—	3860	533	1	—	—	650	—
Selenium	(0.82)	20	13	121	0.503	<0.09	—	4.4	107	<0.01	113
Sodium	1440	1	—	—	1460	45	2	—	—	41.3	—
Strontium	(1.7)	40	3.3	102	—	(0.36)	9	1.1	103	—	102
Thallium	<0.09	—	13	93	—	<0.04	—	4.4	96	—	92
Vanadium	(0.034)	62	0.67	97	—	<0.005	—	0.22	101	—	97
Zinc	4.24	2	13	86	4.58	0.40	3	4.4	92	(0.447)	88

[1]Foods portions from FDA Total Diet Study market basket 94-4. Results in () are "trace" levels and results below LOD are listed as <LOD.

[2]$n=3$ for all elements except $n=6$ for calcium, magnesium, phosphorus, potassium, and sodium. For evaporated milk $n=2$ for all elements except $n=5$ for calcium, magnesium, phosphorus, potassium, and sodium or as indicated.

[3]$n=3$ except $n=4$ for haddock or as indicated. Calcium, magnesium, phosphorus, potassium and sodium not fortified.

[4]FDA Total Diet Study market basket 94-4 results ($n=1$; FDA, 2001b). Nickel results by graphite furnace atomic absorption spectrometry (FDA, 1996) and aluminum, cobalt, and vanadium results by neutron activation analysis (FDA, 1998).

[5]$n=2$.

[6]$n=1$.

cheddar cheese (16%), iron in cheddar cheese (19%) and mayonnaise (17%), nickel in prune juice (16%), potassium in mayonnaise (17%), and selenium in haddock (20%). Imprecision due to concentration measurements being near the LOQ and sample non-homogeneity may explain the results for cadmium in spaghetti (LOQ 0.02 mg/kg), copper in cheddar cheese (LOQ 0.2 mg/kg), iron in mayonnaise (LOQ 2 mg/kg), and selenium in haddock (LOQ 0.8 mg/kg). Imprecision of calcium in haddock may be explained by non-homogeneity caused by haddock bone fragments and the relatively low level of calcium (LOQ 90 mg/kg). Imprecision due to levels being near the LOQ could not explain the slightly poor precision of iron in cheddar cheese (LOQ 0.7 mg/kg), nickel in prune juice (LOQ 0.05 mg/kg) or potassium in mayonnaise (LOQ 20 mg/kg). Non-homogeneity may be the cause of the imprecision for iron in cheddar cheese. An extremely divergent aluminum result was obtained for one of the three replicates of unfortified pork bacon, beef, and haddock. These results ranged from a factor of about 2–5 higher than the other replicates and were excluded from the calculations. The cause of this variability was not thoroughly investigated but environmental contamination is suspected. Extremely divergent chromium results were obtained for one of the three replicates of unfortified pork bacon, one of the three replicates of fortified pork bacon, and two of the three replicates of fortified tuna. Most of these results were negative values indicating spectral interference that may have affected background correction. An extremely divergent lead result was obtained for one of the three replicates of unfortified pork bacon, tuna, and corn. These results ranged from a factor of about 70–300 higher than the other replicates and were excluded from the calculations. The cause of this variability was not thoroughly investigated but environmental contamination is suspected.

Comparison to Total Diet Study Results. TDS results ($n = 1$) were available for comparison for all elements except barium, boron, chromium, molybdenum, strontium, and thallium (FDA, 2001b). TDS results were obtained using a nitric/perchloric/sulfuric acid digestion followed by hydride generation atomic absorption spectrometry for determination of arsenic and selenium and ICP-AES for determination of calcium, copper, iron, magnesium, manganese, phosphorus, potassium, sodium, and zinc. A dry ash mineralization followed by graphite furnace atomic absorption spectrometry was used for determination of cadmium, lead, and nickel. Aluminum, cobalt, and vanadium results were obtained for three foods by instrumental neutron activation analysis (FDA, 1998) and nickel was not available for one food. The majority of the results for each element were in agreement with TDS results (Table 5). Direct comparisons were made when both results were above LOQ and results were considered in agreement if within $\pm 20\%$ of the TDS result. Comparisons were not available for cobalt, lead, selenium or vanadium. Two of the three sets of aluminum results agree and the high result for peanut butter (as discussed above) is probably due to environmental contamination. The two arsenic comparisons and one cadmium comparison agreed. Fourteen of the 15 calcium comparisons agreed. The slightly low and imprecise calcium result for haddock is probably due to non-homogeneity and the relatively low concentration (LOQ 90 mg/kg). All four copper comparisons agreed. Eleven of 13 iron comparisons agreed. The iron results for prune juice and broccoli were about 25% lower than the TDS result. Both TDS results for these foods are near the LOQ (2 and 3 mg/kg, respectively) which may account for the discrepancy. Iron fortification recoveries for these foods were good. Seventeen of 18 magnesium comparisons agreed. The magnesium result for prune juice was about 25% lower than the TDS result. No reasonable explanation for this discrepancy was found. All eight manganese comparisons agreed. Only three of the six sets of nickel comparisons agreed. Nickel results for peanut butter, pancakes, and fruit-flavored cereal were 25–50% higher than TDS results. No reasonable explanation for this discrepancy was found but environmental contamination is suspected. Nickel fortification recoveries for these foods were good. Eighteen of 19 phosphorus comparisons agreed. The phosphorus result for peanut butter was about 25% higher than the TDS result. No reasonable explanation for this discrepancy was found. Twelve of 20 potassium comparisons agreed. Potassium results for prune juice, broccoli, sweet potato, spaghetti, beer, beef and haddock were 21–27% lower than TDS results. No reasonable explanation for this discrepancy was found. The potassium result for mayonnaise was about 85% higher than the TDS result. The potassium level in mayonnaise was relatively low compared to the other foods and the precision was moderately high which may indicate an underestimate of the potassium LOQ for mayonnaise (20 mg/kg). In addition, the TDS result for potassium was near the estimated LOQ (40 mg/kg). All 19 sodium comparisons agreed. Fifteen of 16 zinc comparisons agreed. The zinc result for prune juice was about 30% lower than the TDS result. The TDS zinc result for prune juice was near the LOQ (1 mg/kg) which may explain the disagreement.

CONCLUSIONS

A single microwave digestion program has been shown applicable to various food matrices by choosing an analytical portion mass based on the energy content of the food. Application of the microwave digestion program to multi-element analysis by ICP-AES of foods indicates the following elements can be reliably measured: arsenic, barium, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, phosphorus, potassium, sodium, strontium, vanadium, and zinc. Thallium appears to be reliably measured but accuracy assessment is hindered by the lack of appropriate reference materials. The following elements appear to be prone to laboratory environmental contamination and therefore require extensive assessment of quality control results to judge the reliability of measurement: aluminum, chromium, and lead. Results for aluminum do not account for aluminum bound to silicates. Selenium concentrations appear to have been biased high in this study. Use of ICP-AES for determination of selenium in foods requires a thorough assessment of background correction effectiveness.

The use of the single microwave digestion program with ICP-AES and ultrasonic nebulization is capable of determining percent RDIs or DRVs for calcium, chromium, potassium, magnesium, molybdenum, sodium, phosphorus, copper, iron, manganese, and zinc of foods with a serving size of 100 g or less. Application of the method to monitoring other elements in foods depends on the applicability of the element's LOQ. Many elements had insufficient LOQs to measure background concentrations in foods but screening foods for overt contamination is feasible. Use of a more sensitive multi-element technique, such as ICP mass spectrometry, would improve the measurement of background concentrations.

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