The nutritional analysis of corn products

Karen W. Barnes, Ebenezer Debrah, and Zhang Li
PerkinElmer Instruments, 761 Main Avenue, Norwalk, CT 06859 USA

Introduction

The United States Congress enacted the Nutrition Labeling and Education Act of 1990 (NLEA) on November 8, 1990 to help consumers make healthy dietary choices. NLEA mandates significant reform of food labels and requires full nutritional labeling for most packaged food products. The complete regulations were published (1) and a May 8, 1994 compliance deadline was established. The mandatory and voluntary NLEA nutrients are listed in Table 1. Part of the analytical challenge from NLEA results from the large numbers of samples to be tested and widely differing levels of the elements of interest. NLEA methodology should be generic and applicable to many elements and matrices simultaneously to allow effective sample throughput. This report discusses an Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) method for the determination of NLEA metals and minerals in corn products.

Table 1: The Nutrition Labeling Education Act of 1990 Food Labeling Requirements

Mandatory Nutrients	Voluntary Nutrients		
Calories	Calories from Saturated Fat	Vitamin K	Copper
Calories from fat	Calories from Unsaturated Fat	Thiamin	Manganese
Total Fat	Calories from Carbohydrates	Riboflavin	Fluoride
Saturated Fat	Calories from Protein	Niacin	Chromium
Cholesterol	Unsaturated Fat	Vitamin B6	Molybdenum
Sodium	Polyunsaturated Fat	Folate	Chloride
Total Carbohydrates	Monounsaturated Fat	Vitamin B12	
Total Sugars	Sugar Alcohols	Biotin	
Dietary Fiber	Soluble Fiber	Pantothenic Acid	
Protein	Insoluble Fiber	Phosphorus	
Vitamin A	Protein as %	Magnesium	
Vitamin C	Potassium	Zinc	
Calcium	Vitamin D	Iodine	
Iron	Vitamin E	Selenium	

Experimental

Corn Sample Preparation:

One can of whole kernel yellow sweet corn with liquid, and of 50% low salt golden sweet corn with liquid, one pre-homogenized corn sample from a vegetable manufacturer, and one box of white hominy grits were analyzed for this study. Four subsamples of each product were prepared by microwave digestion using a MDS 2100 microwave system (CEM, Matthews, NC). Each corn sample was well homogenized with the packing liquid using a small food processor. The grits were not processed any further. Lined microwave vessels rated to 200 psig (CEM, Matthews, NC) were used for the digestion following the manufacturer's recommendations.

The whole kernel yellow sweet corn with liquid was selected for spiking to monitor recoveries. Samples were spiked at levels that were predicted for the diluted samples and the spikes were digested concurrently with the other samples to monitor any elemental losses in the microwave. Standard Reference Material (SRM) Corn has recently become available from the National Institute of Standards and Technology (NIST, Gaithersburg, MD), but was not available when this work was

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performed, so a sample of NIST SRM 1572 Citrus Leaves was substituted and digested with the corn and grits to provide additional quality assurance. Clear, colored solutions resulted for all samples except the SRM using the following digestion procedure modified from the CEM application note for Feed Grain (2). Since the SRM was not a good substitute for the corn matrix, no further digestion was performed.

Digestion Procedure:

Step 1: Weigh ≤ 2.0 g grits and homogenized corn, or < 0.8 g citrus leaves into the lined digestion vessels.
Step 2: Add 10 mL concentrated, ultrapure HNO_3 to the samples.
Step 3: Cap the vessels.
Step 4: Digest following the procedure Corn Part 1 in Table 2.
Step 5: Cool for 5 minutes, vent, and open the vessels.
Step 6: Add 2 mL of concentrated, ultrapure HCl to the samples.
Step 7: Recap the vessels.
Step 8: Digest following the procedure Corn Part 2 in Table 3.
Step 9: Cool for 5 minutes, vent, and open the vessels.
Step 10: Transfer the samples into clean, acid-washed volumetric flasks and dilute to 100 mL with 18 megohm distilled, deionized water.
Step 11: Transfer the samples to clean, high-density polyethylene bottles.

Table 2: Microwave Digestion Program for Corn Analysis Part 1

Parameter	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
Power (%)	10	45	45	45	45
Power (Watts)	51	366	366	366	366
Pressure (psig)	20	40	80	120	160
Run Time (min)	2	10	10	10	20
Time at Parameter (min)	2	5	5	5	10
Temperature (°C)	0	75	85	100	120
Fan Speed (% of maximum)	100	100	100	100	100

All analyses were performed on a PerkinElmer Optima 300™ radial-viewed ICP-OES, equipped with the standard torch assembly, conventional cross-flow nebulizer and AS-90 autosampler. The Optima is a simultaneous ICP-OES with an echelle polychromator and a segmented array charge-coupled detector (SCD). Because measurement of background and analyte emissions were performed simultaneously, multiple wavelengths for each element of interest may be measured with no time penalty. Measuring multiple wavelengths for the elements of interest provides additional quality assurance. The Optima 3000 operating conditions are listed in Table 4 and the wavelength and background correction points are listed in Table 5. No attempt was made to optimize plasma conditions for any particular analyte or to optimize the procedure for best sample throughput.

Table 3: Microwave Digestion Program for Corn Analysis Part 2

Parameter	Stage 1	Stage 2	Stage 3
Power (%)	10	50	0
Power (Watts)	51	411	0
Pressure (psig)	20	90	20
Run Time (min)	2	15	5
Time at Parameter (min)	2	5	5
Temperature (°C)	20	90	0
Fan Speed (% of maximum)	100	100	100

The citrus leaves samples were allowed to stand in the sample tubes for approximately 20 minutes before ICP-OES analysis to allow settling of the particulate material. Sampling was performed above the particulate layer, and no clogging of the sample probe, nebulizer tubing, or nebulizer resulted from the process.

Table 4: Instrument Conditions for the PerkinElmer Optima 3000 ICP-OES

Parameter	Setting
RF Power (Watts)	1100
Nebulizer Flow (L/min)	0.950
Auxiliary Flow (L/min)	1.0
Plasma Flow (L/min)	15
Sample Flow (mL/min)	1.0
Source Equilibration Time (sec)	15
Viewing Height (mm)	15
Background Correction	Manual Selection of Points
Measurement Processing Mode	Area
Auto Integration (sec)	1 min – 50 max
Read Delay (sec)	45
Rinse Delay (sec)	45

Table 5: Wavelength Selections and Background Correction Points for Corn Analysis

Element	Wavelength (nm)	Peak Window (nm)	Lower Bgc Point	Upper Bgc Point
Ca	317.939	0.0098	0.020	0.039
Ca	393.357	0.0120	0.024	0.000
Ca	396.860	0.0240	0.036	0.000
Cr	205.569	0.0126	0.012	0.019
Cr	206.163	0.0063	0.013	0.013
Cu	224.706	0.0069	0.014	0.021
Cu	324.767	0.0099	0.029	0.030
Fe	238.207	0.0072	0.014	0.022
Fe	239.568	0.0073	0.015	0.022
K	766.517	0.0465	0.093	0.000
Mg	279.563	0.0085	0.034	0.000
Mg	280.283	0.0170	0.034	0.000
Mn	257.622	0.0156	0.016	0.000
Mn	260.573	0.0079	0.016	0.024
Mo	202.041	0.0124	0.012	0.019
Mo	203.848	0.0062	0.012	0.019
Mo	204.605	0.0062	0.019	0.012
Na	330.252	0.0202	0.031	0.020
Na	589.596	0.0182	0.000	0.055
P	177.441	0.0054	0.016	0.011
P	213.625	0.0065	0.000	0.020
Pb	217.008	0.0066	0.013	0.013
Pb	220.357	0.0067	0.013	0.020
Se	196.034	0.0060	0.018	0.006
Se	203.971	0.0062	0.012	0.012
Zn	206.207	0.0126	0.013	0.013

Results

According to the supplier of the homogenized corn sample, corn is one of the most popular vegetables in the United States. Pb was included as an analyte because of the interest in monitoring levels in children's diets. Although no Pb was detected in any corn product, it was found in the SRM samples. This suggests that any Pb present in the sample is well below 130 ng/g, which was the concentration present in the diluted SRM samples. No Cr, Mo, or Se was detected in any sample although the spike recoveries were acceptable for these elements. Similar results were reported by Wolnik and coworkers (3) who reported that the ICP-OES detection limits for Pb, Cd, and Se are not sufficient for routine determination of background levels in food crops and that Mo levels are near the detection limit for ICP-OES. The spike recoveries presented in Figure 1 indicate that no gross contamination occurred from grinding the corn using a metal food processor blade. The high recoveries for Ca and Zn may be due to sample inhomo-geneity or to contamination resulting from opening the can. The high Se recoveries are likely due to inherent error of measure-ments made near the limit of detection.

The experimental values for corn are presented with available authentic data from the USDA (4) and can label claims in Table 6. Variations of

Table 6: ICP-OES Results for the Corn Samples vs. Package Label Claims and USDA Whole Kernel Corn Reference Values in μg/mL

Element	Wavelength	USDA Corn	Processor[b] Sample	Low Salt Corn		Golden Sweet Corn	
				Found	Label	Found	Label
Ca	317.933	40	31.43 ± 11.53	31.47 ± 0.81	162 max	21.28 ± 1.22	176 max
Ca	393.366	40	32.09 ± 11.29	32.19 ± 3.88	162 max	21.62 ± 0.84	176 max
Ca	396.847	40	31.89 ± 11.06	31.94 ± 3.88	162 max	21.60 ± 0.84	176 max
Cu	224.700	0.56	0.27 ± 0.07	0.14 ± 0.02		0.25 ± 0.02	
Cu	324.754	0.56	0.32 ± 0.04	0.194 ± 0.006		0.25 ± 0.01	
Fe	238.204	3.5	4.02 ± 0.15	2.84 ± 0.33	3	3.00 ± 0.18	6
Fe	239.562	3.5	4.03 ± 0.15	2.80 ± 0.33	3	3.00 ± 0.17	6
K	766.491	1530	1666 ± 9	1541 ± 18	1377	1260 ± 7	
Mg	279.553	160	196.0 ± 1.7	167.7 ± 1.7		126.2 ± 1.3	
Mg	280.270	160	196.3 ± 2.2	168.9 ± 1.5		125.7 ± 1.4	
Mn	257.610	0.33	1.04 ± 0.02	0.73 ± 0.02		0.56 ± 0.07	
Mn	260.569	0.33	1.06 ± 0.02	0.74 ± 0.02		0.56 ± 0.07	
Na	330.237	2530	2119 ± 16	1509 ± 11	1458	2394 ± 9	3436
Na	589.592	2530	2184 ± 23	1575 ± 24	1458	2473 ± 37	3436
P	177.428	510	575.5 ± 18.9	479.3 ± 11.8	486	373.4 ± 6.5	
P	213.618	510	563.3 ± 1.5	500.3 ± 3.5	486	397.0 ± 2.4	
Zn	202.548	3.6	5.05 ± 1.86	3.22 ± 0.61		2.27 ± 0.31	
Zn	206.200	3.6	5.12 ± 1.76	3.35 ± 0.62		2.41 ± 0.25	
Zn	213.856	3.6	5.08_ 1.74	3.34 ± 0.61		2.38 ± 0.22	

b Pre-homogenized sample received from vegetable processor.

80-120% of label claim are typical and will be allowed by NLEA. Results for grits are presented in Table 7 and are compared with available authentic data (5) and label claims. The high relative standard deviations (RSD) for the corn and grits samples may be caused by sample inhomogeneity and could be improved by more rigorous processing of the samples. Wolnik (3) reported similar results and found higher %RSD values for corn than for vegetables that were more easily homogenized.

The results for the SRM citrus leaves are presented in Table 8. The poor recoveries for Fe were anticipated based on Lajunen's work (6) and may be attributed to the incomplete digestion. Other elements correlate well with certified values. The values obtained suggest that the microwave digestion procedure used is applicable for many matrices besides corn.

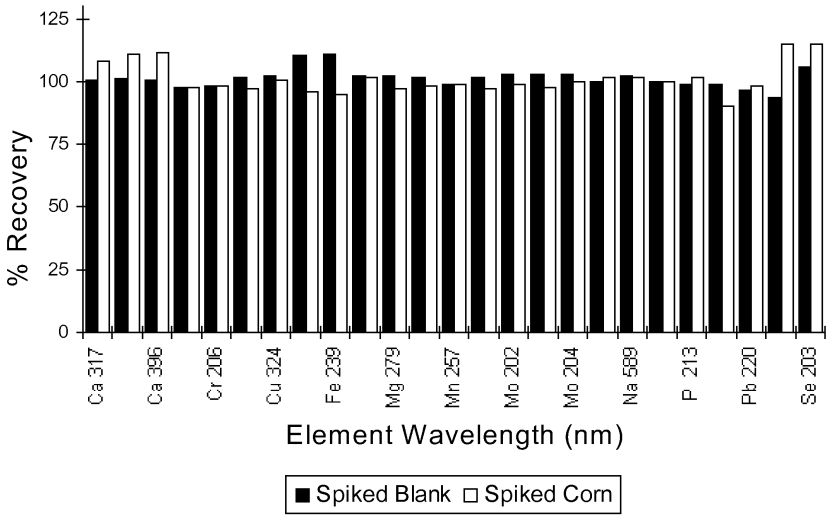

Figure 1. Spike recoveries for corn

Table 7: ICP-OES Results for Enriched White Hominy Grits Compared With Package Label Claims and USDA Reference Values in μg/mL

Element	Wavelength	USDA White Hominy Grits	Enriched White Hominy Grits Found	Enriched White Hominy Grits Label
Ca	317.933	20	16.54 ± 1.98	714 max
Ca	393.366	20	17.49 ± 2.05	714 ma
Ca	396.847	20	17.41 ± 2.09	714 max
Cu	224.700	0.75	0.41 ± 0.04	
Cu	324.754	0.75	0.45 ± 0.01	
Fe	238.204	39.1	14.77 ± 1.72	2
Fe	239.562	39.1	16.46 ± 1.23	26
K	766.491	1370	1679 ± 57	1071
Mg	279.553	270	366.9 ± 45.4	
Mg	280.270	270	369.7 ± 46.5	
Mn	257.610	1.06	1.29 ± 0.11	
Mn	260.569	1.06	1.32 ± 0.11	
Na	589.592	10	0.5 ± 0.1	179 max
P	177.428	730	1002 ± 61	
P	213.618	730	955.4 ± 77.5	
Zn	202.548	4.1	5.1 ± 0	
Zn	206.200	4.1	5.3 ± 0.5	

Table 8: ICP-OES Results for NIST SRM 1572 Citrus Leaves in μg/ml

Element	Wavelength	NIST SRM 1572 Citrus Leaves Certified	Found
Ca	317.933	31500 ± 1000	30220 ± 774
Cu	224.700	16.5 ± 1.0	13.9 ± 0.5
Cu	324.754	16.5 ± 1.0	15.2 ± 0.6
Fe	238.204	90 ± 10	58.2 ± 2.6
Fe	239.562	90 ± 10	58.6 ± 2.7
K	766.491	18200 ± 600	18000 ± 806
Mg	279.553	5800 ± 300	5109 ± 308
Mg	280.270	5800 ± 300	5479 ± 176
Mn	257.610	23 ± 2	19.9 ± 0.7
Mn	260.569	23 ± 2	19.7 ± 0.6
Na	330.237	160 ± 20	140.1 ± 12.8
Na	589.592	160 ± 20	156.7 ± 5.9
P	177.428	1300 ± 200	1333 ± 72
P	213.618	1300 ± 200	1277 ± 33
Pb	216.999	13.3 ± 2.4	11.6 ± 0.9
Pb	220.353	13.3 ± 2.4	11.2 ± 0.3
Zn	206.200	29 ± 2	26.5 ± 0.6

Conclusion

This work demonstrates that the analysis of metals and minerals stipulated by NLEA may be performed in corn products using ICP-OES. ICP-OES will be an effective tool for the analyst attempting to meet the challenges imposed by NLEA. Microwave digestion has been shown to be a useful sample preparation tool allowing acceptable precision, spike recoveries, and agreement with authentic and certified values. Trace levels of elements were determined simultaneously with macro levels of nutrient metals and minerals. Sample preparation time, which was the primary limitation to sample throughput, was minimized due to the wide linear dynamic range and useful analytical range of the ICP-OES. All nutrients were determined simultaneously in all samples without multiple dilution/analysis steps. Although no attempts were made to optimize sample throughput, actual instrumental sample throughput was impressive relative to current validated methods.

References

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PerkinElmer
761 Main Avenue
Norwalk, CT 06859-0010 USA
Tel: 800-762-4000 or
(+1) 203-762-4000
Fax: (+1) 203-762-4228

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