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Hepburn, F. N.; Calhoun, W. K.; Bradley, W. B. *Cereal Chem.* **1960**, *37*, 749.
Huschke, G. In "Natural Colours for Food and Other Uses"; Counsell, J. N., Ed.; Applied Science Publishers, Ltd.: London, 1981; pp 153–162.
Kent, L. "Technology of Cereals", 2nd ed.; Pergamon Press: Oxford, New York, Frankfurt, 1978.
Klaui, H. In "Natural Colours for Food and Other Uses"; Counsell, J. N., Ed.; Applied Science Publishers, Ltd.: London, 1981; pp 99–122.
Osborne, D. R.; Voogt, P. "The Analysis of Nutrients in Foods"; Academic Press: London, New York, 1978.
Ratledge, C. "Microbial Production of Oils and Fats in Food from Waste"; Birch, G. G., Worgan, J. T., Eds.; Applied Science Publishers Ltd.: London, 1976; pp 98–113.
Ries, S. K.; Stout, B. A. *Proc. Am. Soc. Hortic. Sci.* **1962**, *81*, 479.
Saguy, I. *J. Food Sci.* **1979**, *44*, 1554.

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Elements in Major Raw Agricultural Crops in the United States. 3. Cadmium, Lead, and Eleven Other Elements in Carrots, Field Corn, Onions, Rice, Spinach, and Tomatoes

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Six raw agricultural crops (carrots, field corn, onions, rice, spinach, and tomatoes) were collected from major U.S. growing areas uncontaminated by human activities other than normal agricultural practices. Handling, preparation, and analysis of the 1215 samples were performed under carefully controlled conditions. Cadmium and lead were determined by differential pulse anodic stripping voltammetry and Ca, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, and Zn by inductively coupled plasma emission spectroscopy. Mean Cd concentrations in carrots, field corn, onions, rice, spinach, and tomatoes were 0.028, 0.012, 0.011, 0.012, 0.065, and 0.017 $\mu g/g$ (wet weight), respectively; mean Pb concentrations in these crops were 0.009, 0.022, 0.005, 0.007, 0.045, and 0.002 $\mu g/g$ wet weight, respectively.

INTRODUCTION

The Food and Drug Administration (FDA) requires detailed information on the levels of elements in agricultural crops in the food chain to assess the toxicological and nutritional significance of human and animal intake of these elements. The normal "background" concentrations of the toxic elements, such as Pb and Cd, must be known to develop limitations on the intake of these elements from foods. Information on background levels provides guidance in evaluating the effect of soil additions, such as phosphatic fertilizers and sewage sludge containing Cd and Pb, as well as the effect of commercial food handling and processing steps, which can result in food contamination.

FDA, the Environmental Protection Agency (EPA), and the U.S. Department of Agriculture (USDA) share a particular interest in the application of sewage sludge to croplands with respect to the benefits of its use and its potential to contaminate the environment and the food supply. In 1979, questions concerning sludge use (Jelinek and Braude, 1978) brought the three agencies together in an agreement to develop data on the background levels of Cd, Pb, and other elements in selected crops and soils collected throughout the United States from major crop production areas uncontaminated by human activities other than normal agricultural practices (*Fed. Regist.*, 1979). Cadmium and lead were of primary concern because of their toxicity and potential for accumulation in food plants. Cadmium was of particular importance to FDA because the estimated Cd burden from food intake in the United States was approaching the joint Food and Agriculture Organization/World Health Organization (FAO/WHO) provisional tolerable weekly intake (Fox, 1976). Levels of other elements were of interest because animal nutrition studies suggest that elemental interactions affect the toxicity of dietary Cd (Fox, 1974). Also, data were unavailable for nutritional elements obtained from an extensive, controlled sampling of raw agricultural products representing major crop production regions of the United States.

Crop types were selected for this study on the basis of market volume, type of usage (human or animal), and potential for accumulation of toxic elements. Results for the six crops collected during the first phase of the study (lettuce, peanuts, potatoes, soybeans, sweet corn, and wheat) were reported previously by Wolnik et al. (1983a, 1983b). Results for carrots, field corn, onions, rice, spinach, and tomatoes are reported here. Correlations between crop element levels and corresponding soil element levels (determined by USDA), crop species, and other factors that may influence mineral uptake are currently being evaluated and will be discussed in future publications.

MATERIALS AND METHODS

Site Selection. As shown in Figure 1, samples of the crops were collected in several of the major production areas of the United States. The limitations imposed on site selection to minimize the effects of contamination caused by human activity are described in part 1 (Wolnik et al., 1983a).

Crop Sampling. All crops were taken directly from the field and were obtained in sufficient quantities to provide a representative sample, such as 40 carrots, 5 ears of field corn, 25 onions, 200 heads of rice, 1000 leaves of spinach,

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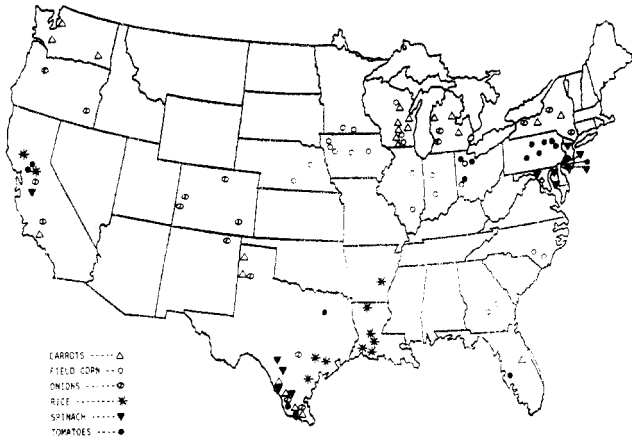

Figure 1. Sampling site locations: (△) carrots; (○) field corn; (⊙) onions; (*) rice; (▼) spinach; (●) tomatoes.

and 15 tomatoes (30, if less than 3 in. in diameter).

All samples were collected with plastic gloves and were packaged in plastic bags for shipment. Carrots, onions, spinach, and tomatoes were shipped refrigerated with Blue Ice to avoid decomposition.

Sample Preparation. Laboratory modifications, special equipment for sample chopping, freeze drying, and compositing, laboratory ware cleaning procedures, and distilled, deionized water (DDW) supply are described in part 1 (Wolnik et al., 1983a). Disposable polyethylene gloves were worn throughout the preparation procedure, and all sample handling after the washing procedure was done in a clean-air environment. The crop units collected from a field were composited for analysis as follows.

Carrots were scrubbed with a plastic vegetable brush (but not peeled), chopped in a chopper, freeze-dried, and blender-ground.

Field corn was dried, if necessary, in a forced air oven at <50 °C to facilitate removal of the kernels from the cob. The kernels were freed from the cob manually, rinsed with DDW, soaked overnight in DDW, freeze-dried, and blender-ground.

Onions were peeled, rinsed, quartered with plastic knives, chopped in a plastic food processor (Cuisinart) with a plastic "kneader" blade, freeze-dried, and blender-ground.

Rice was dried in a forced air oven at <50 °C. Rice grain heads were removed from the stems and whirled in a 7-speed blender at very low speed by coupling a variable rheostat with the lowest blender speed to fracture the hulls while retaining whole rice kernels. Chaff was separated with an air gun, and kernels were rinsed quickly with DDW, dried in a clean-air environment, and blender-ground to produce the equivalent of unpolished brown rice.

Stem tips were removed from the spinach and damaged leaves were discarded. Spinach was cleaned by successive, rapid immersion in four plastic tubs of DDW followed by a final DDW rinse, chopped, freeze-dried, and blender-ground.

Tomatoes with broken skins were discarded. Intact tomatoes were washed with DDW, and peduncle scars were removed with plastic knives; the tomatoes were quartered, chopped in a food processor with a plastic "kneader" blade, freeze-dried, and blender-ground. To prevent melt-back during the freeze-drying process, containers were wrapped with insulating material.

Analysis. Moisture Determination. For rice, the percent moisture was determined by oven drying a portion of the ground composite to constant weight. For other crops, percent moisture was determined by weighing the prepared sample before and after freeze drying. A correction was made for residual moisture, which was determined on a portion of freeze-dried composite, by oven drying to constant weight.

Table I. Elements in Carrots[a]

element	μg/g wet weight mean	median	minimum	maximum	% RSD[b]
Pb	0.009	0.0065	0.001	0.125	127.5
Cd	0.028	0.017	0.002	0.13	92.2
Ca	310	310	210	725	17.6
Cu	0.58	0.54	0.093	1.4	40.8
Fe	3.2	2.9	0.915	12	41.7
K	3400	3400	1600	7000	19.3
Mg	140	130	75	375	27.3
Mn	1.5	1.3	0.29	6.1	62.3
Mo[c]	0.015	0.010	<0.006	0.093	92.8
Na	300	230	35	1300	74.7
Ni[d]	0.071	0.044	<0.02	0.46	102.6
P	370	360	170	850	28.3
Zn	2.6	2.3	0.46	6.7	47.6
wwf[e]	0.114	0.112	0.080	0.250	17.2

[a] n = 207. [b] Relative standard deviation. [c] Eighty-eight results below the detection limit. [d] Sixty-six results below the detection limit. [e] Wet weight factor.

Cadmium and Lead Determination. Composites were dry ashed with a sulfuric acid ashing aid, and Cd and Pb were determined by differential pulse anodic stripping voltammetry (DPASV) according to the procedure described and evaluated for these crops by Satzger et al. (1984).

Multielement Determination. A HNO_3, $HClO_4$, and H_2SO_4 digestion was used for the determination of 11 elements (Ca, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, and Zn) by inductively coupled plasma atomic emission spectroscopy (ICPAES) in composites of carrots, field corn, rice, spinach, and tomatoes (Wolnik et al., 1981). For multielement analysis of onions, HCl pressure dissolution with ICPAES determination (Kuennen et al., 1982) was used.

Quality control procedures and results from this study and previous studies, including the analysis of blanks, duplicate samples, spiked samples, and certified standard reference materials where available, have been described by Wolnik et al. (1982, 1984). In general, relative standard deviations for replicate sample analysis were less than 5%, recoveries for spiked samples ranged from 90 to 110%, and results for NBS Standard Reference Materials agreed with certified levels.

Data Processing. The data were processed by an IBM 370/168 computer as described previously (Wolnik et al., 1983a, 1983b) by using the interactive computer language APL (Falkoff and Iverson, 1973) and special ICP data logging equipment (Capar and Dusold, 1982). Statistical analysis was carried out by using the procedure UNIVARIATE of the Statistical Analysis System (SAS) Release 79.5 (SAS, 1979, 1981).

All elemental results were stored in terms of μg/g dry weight. Wet weight factors (wwf) (i.e., dry weight fraction) were also stored for each sample. Wet weight values were obtained by multiplying the dry weight result by the wwf. The wwf reported can be used to obtain dry weight values (divide reported values for elements by wwf) or percent moisture levels ((1 − wwf) × 100%).

RESULTS AND DISCUSSION

The levels of the elements in the six crops examined are presented in Tables I–VI. Statistical data on the levels of Cd, Pb, and 10 other elements in field corn and rice are presented in Tables II and IV, respectively; statistical data on the levels of Cd, Pb, and 11 other elements in carrots, onions, spinach, and tomatoes are presented in Tables I,

Table II. Elements in Field Corn[a]

element	μg/g wet weight mean	median	minimum	maximum	% RSD[b]
Pb[c]	0.022	0.005	<0.002	2.75	791.5
Cd[d]	0.012	0.0035	<0.001	0.32	266.2
Ca	31	30	14	59	23.3
Cu	1.5	1.4	0.60	3.4	27.1
Fe	18	17	11	28	17.3
K	2900	2900	1900	5200	15.7
Mg	1000	990	620	1700	16.1
Mn	5.1	4.9	2.4	9.2	26.7
Mo[e]	0.22	0.18	<0.06	0.77	68.7
Ni[f]	0.33	0.29	<0.2	1.1	68.6
P	2500	2500	1300	3900	15.8
Zn	18.5	18	10	32	20.1
wwf[g]	0.845	0.852	0.672	0.942	6.0

[a] n = 277; 277 results for Na below the quantitation limit (170 μg/g). [b] Relative standard deviation. [c] Six results below the quantitation limit. [d] Twenty-eight results below the quantitation limit. [e] Thirty-six results below the detection limit. [f] Ninety-one results below the detection limit. [g] Wet weight factor.

Table III. Elements in Onions[a]

element	μg/g wet weight mean	median	minimum	maximum	% RSD[b]
Pb[c]	0.005	0.004	<0.0002	0.054	106.8
Cd	0.011	0.009	0.001	0.054	79.4
Ca	270	260	140	530	29.2
Cu	0.37	0.34	0.078	0.99	43.6
Fe	1.45	1.3	0.50	3.65	43.9
K	1400	1300	820	2850	28.9
Mg	91	88	56	180	21.4
Mn	1.2	0.94	0.35	5.6	64.6
Mo[d]	0.016	0.014	<0.006	0.10	84.6
Na[e]	23	16.5	<15	110	71.0
Ni[f]	0.036	0.030	<0.02	0.16	77.1
P	280	255	155	770	39.3
Zn	1.7	1.6	0.51	3.9	44.0
wwf[g]	0.102	0.0995	0.062	0.182	21.6

[a] n = 230. [b] Relative standard deviation. [c] One result below the quantitation limit. [d] Seventy-two results below the detection limit. [e] One hundred nineteen results below the quantitation limit. [f] Ninety results below the detection limit. [g] Wet weight factor.

Table IV. Elements in Rice[a]

element	μg/g wet weight mean	median	minimum	maximum	% RSD[b]
Pb[c]	0.007	0.005	<0.002	0.070	114.4
Cd[d]	0.012	0.0045	<0.001	0.23	249.1
Ca	47	47	26	79	21.2
Cu	1.9	1.9	0.53	5.1	39.1
Fe	3.6	2.7	1.4	10	59.2
K	650	490	125	1950	66.3
Mg	235	160	39.5	920	82.9
Mn	12	9.9	4.15	39	53.3
Mo	0.66	0.59	0.18	3.05	53.5
Ni[e]	0.285	0.225	<0.2	1.2	81.1
P	930	750	480	2300	45.9
Zn	13.5	14	7.2	21	19.6
wwf[f]	0.896	0.898	0.739	0.945	3.5

[a] n = 166; 166 results for Na below the quantitation limit (180 μg/g). [b] Relative standard deviation. [c] Fifteen results below the quantitation limit. [d] Twenty-four results below the quantitation limit. [e] Seventy-eight results below the detection limit. [f] Wet weight factor.

III, V, and VI, respectively. The number of samples analyzed per crop ranged from 104 for spinach to 277 for field corn. Complete data and more extensive statistical analyses are available in the supplementary material (see paragraph at end of paper regarding supplementary material).

Table V. Elements in Spinach[a]

element	μg/g wet weight mean	median	minimum	maximum	% RSD[b]
Pb	0.045	0.039	0.016	0.17	52.2
Cd	0.065	0.0605	0.012	0.195	54.1
Ca	820	740	225	1900	44.6
Cu	0.66	0.62	0.145	2.0	40.3
Fe	17	15	4.6	50	47.7
K	4600	4300	1500	11000	36.7
Mg	740	690	290	1400	32.0
Mn	7.1	5.9	1.25	25	64.2
Mo[c]	0.024	0.015	<0.006	0.15	100.3
Na[d]	580	360	<16	2500	105.5
Ni[e]	0.098	0.085	<0.02	0.30	72.1
P	410	410	140	710	27.8
Zn	4.5	3.2	0.85	25	81.8
wwf[f]	0.077	0.077	0.028	0.139	26.1

[a] n = 104. [b] Relative standard deviation. [c] Fifty results below the detection limit. [d] Thirteen results below the quantitation limit. [e] Twenty-nine results below the detection limit. [f] Wet weight factor.

Table VI. Elements in Tomatoes[a]

element	μg/g wet weight mean	median	minimum	maximum	% RSD[b]
Pb[c]	0.002	0.002	<0.0001	0.025	121.2
Cd	0.017	0.014	0.002	0.048	58.8
Ca	83	77	20	210	41.1
Cu	0.645	0.65	0.19	1.1	27.1
Fe	3.0	3.0	1.0	5.2	25.5
K	2400	2300	1500	3850	17.9
Mg	110	110	69	165	14.3
Mn	1.1	0.96	0.52	7.8	63.4
Mo[d]	0.024	0.017	<0.005	0.12	95.0
Na[e]	27.5	18	<13	120	91.1
Ni[f]	0.070	0.052	<0.02	0.255	75.1
P	250	250	140	530	23.7
Zn	1.4	1.4	0.78	2.2	21.7
wwf[g]	0.063	0.062	0.044	0.095	13.5

[a] n = 231. [b] Relative standard deviation. [c] Three results below the quantitation limit. [d] Fifty-six results below the detection limit. [e] One hundred three results below the quantitation limit. [f] Twenty-four results below the detection limit. [g] Wet weight factor.

Quantitation limits for Cd and Pb were defined as 1 ng/g on a dry weight basis. Quantitation limits on a wet weight basis vary, depending on sample moisture content. Matrix effects due to differences in ashing characteristics of some samples resulted in higher quantitation limits for these samples. In instances in which the analytical result was less than the quantitation limit, half of the quantitation limit was used in the statistical calculations.

Carrots and spinach are considered likely to accumulate Cd at higher levels compared to other crops, onions, at moderate levels, and corn and tomatoes, at low levels. However, the mean Cd levels for all crops sampled in this study were relatively low. Small differences in Cd levels in carrot crops from different states were evident. Mean Pb levels were also relatively low, with only one field corn sample exceeding 1 μg/g on a wet weight basis. Overall state differences in Pb levels were not significant.

Table VII compares the data for Cd and Pb from this study with two other major surveys conducted by the FDA in 1976 and 1977. Levels of Pb found in this study are lower than those previously reported. A variety of factors may be responsible for this decrease: selection of relatively uncontaminated fields; sampling, handling, and shipping procedures that are more careful than those used by commercial harvesters and shippers; and practices that reduce the potential for contamination of samples during preparation and analysis.

Table VII. Comparison of Mean Cadmium and Lead Levels[a] in Three Crops

reference	carrots			onions			tomatoes		
	n	Cd	Pb	*n*	Cd	Pb	*n*	Cd	Pb
this study	207	0.028	0.009	203	0.011	0.005	231	0.017	0.002
FDA[b]	48	0.01	0.07	48	0.01	0.02	46	0.02	0.08
FDA[c]				36	0.02	0.014	60	0.02	0.090

[a] μg/g (wet weight). [b] Compliance Program Evaluation (1980); samples collected during fiscal year 1976. [c] Compliance Program Evaluation (1981); samples collected during fiscal year 1977.

Table VIII. Comparison of Mean Values:[a] USGS Report[b] and This Study

element	carrots		onions		tomatoes	
	USGS[c]	this study[d]	USGS[e]	this study[f]	USGS[g]	this study[h]
Ca	310	310	460	270	74	83
Cd	0.018	0.028	0.005	0.011	0.0059 (48)	0.017
Cu	0.55	0.58	0.46	0.37	0.46	0.645
Fe	1.9	3.2	3.3	1.45	3.0	3.0
K	3300	3400	1300	1400	2100	2400
Mg	110	140	120	91	110	110
Mn	1.0	1.5	1.6	1.2	0.62	1.1
Mo	(0)	0.015 (119)	0.024 (5)	0.016 (158)	0.042 (30)	0.024 (175)
Na	410	300	110	23 (111)	21	27.5 (128)
Ni	0.031 (3)	0.071 (141)	0.059	0.036 (140)	0.022 (10)	0.070 (207)
P	200	370	190	280	150	250
Pb	(0)	0.009	(0)	0.005 (229)	(0)	0.002 (228)
Zn	2.5	2.6	2.2	1.7	1.4	1.4

[a] μg/g (wet weight); values in parentheses are numbers of results above the quantitation limit. [b] Shacklette (1980); geometric mean. [c] Collected in two areas of commercial production; $n = 20$. [d] $n = 207$. [e] Collected in one area of commercial production; $n = 10$. [f] $n = 230$. [g] Collected in five areas of commercial production; $n = 50$. [h] $n = 231$.

Molybdenum and nickel were present at levels below the detection limits in some of the crop samples. Sample detection limits were defined as the concentration of these elements in the sample equivalent to two times the standard deviation of 10 consecutive blank determinations. In these instances, half of the detection limit was used in the statistical calculations for Tables I–VI.

ICPAES parameters for Na were selected to provide accuracy at high concentration levels. Consequently, all Na results for field corn and rice were below the quantitation limit and are not reported. For statistical calculations, half of the quantitation limit was used for individual results that were lower than the quantitation limit (defined as 600 μg of Na/g on a dry weight basis for spinach and 200 μg of Na/g on a dry weight basis for the other crops).

The statistical data shown in Tables I–VI, such as the means, medians, and relative standard deviations, show differences not only in absolute levels but also in variability. Most major elements, such as Ca, K, Mg, and P, fall within a fairly narrow range, whereas greater differences exist between minimum and maximum values for trace elements. Although Na was found in carrots, onions, spinach, and tomatoes at levels similar to those of Ca, K, Mg, and P, Na shows a greater range and variability than the other major elements. The levels of Mg in rice exhibit greater variability than those observed for Mg in the other crops.

For the six crops sampled in the first phase of this study (Wolnik, 1983b), normal probability distributions were observed for some elements, especially the major nutrients, and this is also true for the present study. Generally, those elements which have a low % RSD and nearly identical mean and median values show normal or near normal distribution plots. (Examples are provided in the supplementary material; see paragraph at end of paper regarding supplementary material.)

In 1980 the U.S. Geological Survey (USGS) published a report (Shacklette, 1980) on the determination of numerous elements in various vegetables, fruits, and soils from areas of commercial production within the United States. A limited number of samples of each crop type were collected from a few selected production areas. The mean results for those elements determined in three crops in both the USGS and this study are compared in Table VIII. Although in the USGS study there are fewer samples, the collection sites are not widespread, and the date of collection differs by nearly a decade (1972–1973 vs. 1981–1982); the mean values for many elements are remarkably close to those in the present study, particularly those values for Ca, K, Mg, and Zn in carrots and tomatoes. This comparison provides additional evidence that with respect to several elements crop genetic factors are more important than fertility, soil, and environment.

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Registry No. Pb, 7439-92-1; Cd, 7440-43-9; Ca, 7440-70-2; Cu, 7440-50-8; Fe, 7439-89-6; K, 7440-09-7; Mg, 7439-95-4; Mn, 7439-96-5; Mo, 7439-98-7; Na, 7440-23-5; Ni, 7440-02-0; P, 7723-14-0; Zn, 7440-66-6.

Supplementary Material Available: Computer printouts containing data tabulations on elements, including Cd and Pb in six crops, and statistical calculations, histograms, and normality plots (109 pages). Ordering information is given on any current masthead page.

LITERATURE CITED

Capar, S. G.; Dusold, L. R. *J. Assoc. Off. Anal. Chem.* **1982**, *65*, 1259.

Compliance Program Evaluation "Compliance Program Report of Findings, FY-75 Pesticide Program (7320.07) and FY-76 Pesticides and Metals Program (7320.55)"; U.S. Food and Drug Administration: Washington, DC, 1980.
Compliance Program Evaluation "Compliance Program Report of Findings, FY-77 Pesticides and Metals Program (7320.79)"; U.S. Food and Drug Administration: Washington, DC, 1981.
Falkoff, A. D.; Iverson, K. E. *IBM J. Res. Dev.* **1973**, *17*, 324.
Fed. Regist. **1979**, *44* (148), 44940.
Fox, M. R. S. *J. Food Sci.* **1974**, *39*, 32.
Fox, M. R. S. In "Trace Elements in Human Health and Disease, Vol. II, Essential and Toxic Elements"; Prasad, A. S., Ed.; Academic Press: New York, 1976; p 401.
Jelinek, C. F.; Braude, G. L. *J. Food Prot.* **1978**, *41*, 476.
Kuennen, R. W.; Wolnik, K. A.; Fricke, F. L.; Caruso, J. A. *Anal. Chem.* **1982**, *54*, 2146.
SAS "SAS User's Guide"; SAS Institute: Cary, NC, 1979.
SAS "SAS Technical Report P-115"; SAS Institute: Cary, NC, 1981.
Satzger, R. D.; Bonnin, E.; Fricke, F. L. *J. Assoc. Off. Anal. Chem.* **1984**, *67*, 1138.
Schacklette, H. T. "U.S. Geological Survey, Professional Paper 1178"; U.S. Government Printing Office: Washington, DC, 1980.
Wolnik, K. A.; Fricke, F. L.; Capar, S. G.; Braude, G. L.; Meyer, M. W.; Satzger, R. D.; Bonnin, E. *J. Agric. Food Chem.* **1983a**, *31*, 1240.
Wolnik, K. A.; Fricke, F. L.; Capar, S. G.; Braude, G. L.; Meyer, M. W.; Satzger, R. D.; Kuennen, R. W. *J. Agric. Food Chem.* **1983b**, *31*, 1244.
Wolnik, K. A.; Fricke, F. L.; Gaston, C. M. *Spectrochim. Acta* **1984**, *39B*, 649.
Wolnik, K. A.; Fricke, F. L.; Kuennen, R. W. In "Developments in Atomic Plasma Spectrochemical Analysis"; Barnes, R. M., Ed.; Heyden: London, 1981; pp 685–696.
Wolnik, K. A.; Fricke, F. L.; Kuennen, R. W. *ICP Inf. Newsl.* **1982**, *8*, 4.

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Determination of Methionine in Peas by Near-Infrared Reflectance Spectroscopy (NIRS)

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Methionine and protein were determined in field peas (*Pisum sativum*) by standard chemical methods. Three different near-infrared reflectance techniques were employed to measure both constituents directly in ground peas without hydrolysis or any chemical treatment. Accuracy of prediction of methionine was ±0.011% and of protein ±0.76% of the whole peas with a commercially available near-infrared reflectance instrument. Time for testing each sample for both methionine and protein was 45 s.

Methionine, isoleucine, lysine, threonine, and tryptophan are the most frequently limiting amino acids in the plant materials used as human food. Of these, methionine and tryptophan are the most difficult to determine with accuracy, since both tend to become degraded during hydrolysis, which normally precedes the determination of amino acids by standard ion-exchange chromatography. Recently Finlayson and Mackenzie (1976) and Mackenzie (1977) announced improved techniques for the determination of methionine, both of which were faster and less destructive of methionine than the ion-exchange chromatography method. Their procedure involves gas/liquid chromatography following selective extraction of methionine and does not call for hydrolysis.

One of the most important applications of methionine determination is associated with the identification of genotypes of food legumes with higher methionine content. Although food legumes offer valuable sources of protein and lysine for the diets of peoples of developing countries they are often deficient in methionine (Ackroyd and Doughty, 1964; Kelly, 1972; Hulse, 1975). Table I compares the methionine content of several food legumes with the cereal staples and illustrates the generally lower methionine content of the legumes. The breeding of cultivars with enriched methionine content has been inhibited by the lack of a practicable method for the rapid, accurate determination of methionine. Since its first description as a spectroscopic method for the determination of moisture in soybeans (Ben-Gera and Norris, 1968) near-infrared reflectance spectroscopy (NIRS) has become a

Table I. Comparison of Methionine Content of Some Food Legumes with Cereal Staples

source	species	mg of methionine/g of total N	ref[a]
chickpea	*Cicer arietinum*	80	1
cowpea	*Vigna unguiculata*	120	1
broad bean	*Vicia faba*	30	1
lentil	*Lens esculenta*	50	1
pea	*Pisum sativum*	70	1
phaseolus bean	*Phaseolus vulgaris*	60	1
pigeon pea	*Cajanus cajans*	80	1
millet	*Panicum miliaceum*	117	2
rice (milled)	*Oryza sativa*	145	3
sorghum	*Sorghum vulgare*	100	2
wheat	*Triticum aestivum*	106	4

[a] 1. Ackroyd, W. R., and Doughty, J., 1964. 2. Hulse, J. H., et al., 1981. 3. Juliano, B. O., 1972. 4. Ksarda, D. D., et al., 1971.

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