Table III. Treatment Rate and Preharvest Interval for Field-Treated Rice[a]

bensulfuron methyl treatment rate, g ai/ha	preharvest interval, days from last field treatment to harvest
untreated	6 control samples analyzed
25	156
50	156
70	123, 126, 127, 146
75	156
76	110, 110, 120, 120
140	123, 126, 127, 146

[a] All samples of rice straw contained <0.05 ppm bensulfuron methyl.

similarly on rice straw control samples fortified at 1, 2, and 4 times the detection limit. The recovery data are reported in Table I for grain and straw samples analyzed by two analysts working independently on separate equipment. For the 47 rice grain recovery samples, the mean recovery efficiency was 97% with a standard deviation of 17%. For the 11 rice straw recovery samples, the mean recovery efficiency was 88% with standard deviation of 16%.

Bensulfuron methyl residues were determined in 121 rice grain samples from agricultural test plots in the United States, Thailand, Java, Australia, and The Philippines that had been field-treated with Londax rice herbicide at up to 400 g of ai/ha. None of the rice grain samples contained bensulfuron methyl residues in excess of the 0.02 ppm detection limit. These data are summarized in Table II by treatment rate and preharvest interval.

Bensulfuron methyl residues were determined in 21 rice straw samples from test plots in the United States and Australia that had been field-treated with Londax rice herbicide at up to 140 g of ai/ha. None of the rice straw samples contained bensulfuron methyl residues in excess of the 0.05 ppm detection limit. These data are summarized in Table III by treatment rate and preharvest interval.

The absence of detectable residues of bensulfuron methyl in rice grain and straw by these methods is consistent with the results of the metabolism study in which greenhouse-grown rice plants were treated with 14C-labeled bensulfuron methyl at 200 g of ai/ha. Analysis of the mature grain and straw for bensulfuron methyl by measurement of radioactivity 4 months after treatment of the rice plants showed 0.001 ppm in rice straw and 0.002 ppm in rice grain.

The bensulfuron methyl analytical methods have proven adequate for determination of the active ingredient of Londax rice herbicide in rice grain and straw with detection limits of 0.02 and 0.05 ppm, respectively. Residues of bensulfuron methyl were below the limits of detection in all of the grain and straw samples analyzed.

Registry No. Bensulfuron methyl, 104466-83-3.

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X-ray Fluorescence and Atomic Absorption Spectrophotometry Measurements of Manganese, Iron, Copper, and Zinc in Selected Foods

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A simultaneous multielement method for X-ray fluorescence (XRF) analysis was validated for Mn, Fe, Cu, and Zn in biological and food materials. The method uses the CEMAS approach to quantitation without similar standards. Average biases for nine NBS standards ranged from 0.7 ppm (2.2%) for Cu to 3.4 ppm (2.3%) for Mn, and relative standard deviations ranged from 2.5% for Zn to 9.2% for Fe. Detection limits averaged 0.6 ppm for Cu and Zn, 1.2 ppm for Fe, and 1.4 ppm for Mn (dry-weight basis). XRF and atomic absorption spectrophotometry (AAS) measurements were compared for 96 samples from different sources of 21 foods. Average biases between the XRF and AAS data ranged from −2.1 ppm for Cu to +0.4 ppm for Mn. Relative standard deviations ranged from 3.8% for Zn to 8.3% for Fe among sample aliquots and from 21% for Cu to 37% for Fe among different sources of the foods.

The average supermarket has 10000 or more food items (Kinder et al., 1984), and this number is continually increasing. As foods are raised under new agronomic conditions and processed with new procedures, it becomes a major challenge to provide up-to-date data on the mineral composition of the food supply. There is great need for rapid, accurate, multielement analytical methodologies that require minimal sample preparation. Protein, moisture, fiber, and oil are routinely analyzed by nondestructive methods in many foods and animal feeds (Norris, 1984; Hirschfeld and Stark, 1984; Park et al., 1982; Polesello and Giangiacomo, 1983). For mineral determination in foods, atomic absorption spectrophotometry (AAS) is most widely used (Harnly and Wolf, 1984; Ihnat, 1984) and usually requires dissolution of samples. For some elements, chemical interferences or matrix effects are still significant

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and require the use of the reference materials with similar chemical matrices (Harnly and Wolf, 1984).

X-ray fluorescence (XRF) can provide simultaneous multielement analyses of foods (Nielson et al., 1986), as can certain atomic absorption and emission spectrometry techniques (Harnly et al., 1984) and neutron activation analysis (Versieck et al., 1974). The XRF approach discussed here is advantageous in that it is rapid compared to the multielement atomic spectrometry techniques and is nondestructive and matrix independent, as is neutron activation analysis. Although sample matrix effects can be significant in XRF, they are relatively constant for foods, due to their predominant contents of carbon, oxygen, nitrogen, and hydrogen. The present CEMAS approach to quantitation (Nielson et al., 1986) is also similar to neutron activation analysis in that it does not require standards of similar physical and chemical form to the samples and that it relies on fundamental parameters of X-ray physics for quantitation of the X-ray intensities (Nielson, 1977, 1986; Nielson and Rogers, 1984). Although XRF analysis of foods has been previously reported (Hall, 1984; Rastegar et al., 1987), its use for accurate multielement analyses without direct comparison to similar standards or destructive preparation has not been previously validated.

This paper is aimed at characterizing and validating the CEMAS XRF method for multielement analysis of foods via determinations of Mn, Fe, Cu, and Zn in eight standard reference materials and in a variety of food materials by comparison with independent determinations by AAS. It is also intended to provide additional food composition data for these elements in the 21 food materials used in the intercomparisons. By analyses of standard reference materials, the precisions, accuracies, and detection limits of the XRF method were determined. The comparisons with AAS analyses were done blind and offer further estimates of accuracy as well as additional estimates of precision and long-term variability.

MATERIALS AND METHODS

Reference Materials and Foods. Nine NBS standard reference materials were used as obtained, including powdered milk (SRM-1549), oyster tissue (SRM-1566), wheat flour (SRM-1567), rice flour (SRM-1568), orchard leaves (SRM-1571), citrus leaves (SRM-1572), tomato leaves (SRM-1573), pine needles (SRM-1575), and bovine liver (SRM-1577a).

Twenty-one selected foods were obtained from each of three to five different sources (fresh, processed, home storage, etc.) for a total of 96 food samples. The foods included beets, broccoli, cake, carrots, corn, enriched white bread, green beans, oatmeal, onions, peas, potato, rice, saltines, shrimp, sour cream, spinach, squash, tomato, waffles, whole wheat bread, and zucchini. Foods were prepared ready for consumption, blended in a glass blender equipped with a stainless steel cutter, weighed, and lyophilized. The lyophilized foods were ground with a porcelain mortar and pestle and stored in plastic 1-lb cottage cheese containers until sampled for analyses. Canned food samples were drained of fluid before blending. Demineralized water was used whenever water was added for cooking using methods, cooking times, and temperatures recommended for vegetables (CFEI, 1975). Onions were peeled and analyzed raw. Potatoes and winter squash were baked. Moisture in the stored, lyophilized food materials was determined whenever an aliquot was sampled for analysis by oven-drying a separate, equivalent aliquot for 2 h in a forced-air oven at 105 °C. Analyzed mineral values were then reported on a dry-weight basis, with total moistures reported from the combined lyophilization and oven-drying losses.

Atomic Absorption Analyses. Aqueous samples were prepared for AAS analyses from a 2–3-g sample, which was weighed into a porcelain crucible and ashed in a muffle furnace at 550 °C for 48 h. To any sample that was incompletely ashed, 5–6 drops of concentrated nitric acid and 5–6 drops of 30% hydrogen peroxide were added and the resulting solution was evaporated on a hot plate and then reashed at 550 °C overnight. This process was repeated if necessary until a white ash was obtained. The ash was then dissolved in 5 mL of 6 N HCl with low heat over a hot plate, quantitatively transferred to a 25-mL, glass-stoppered volumetric flask, and diluted to volume with demineralized water. The contents of the flask were mixed by inverting 25 times. All glassware was boiled in 1 N HCl and thoroughly rinsed with demineralized water.

Minerals were analyzed by AAS (Instrumentation Laboratories Model 457 dual-beam spectrophotometer) using an air–acetylene flame. Iron, copper, and zinc were analyzed directly from the ash solutions. To determine manganese, 9 mL of the ash solution was diluted with 1 mL of lanthanum oxide solution to give a final concentration of 1000 ppm lanthanum. Iron, copper, and zinc standard curves were obtained in stock solutions containing 1000 ppm of the minerals diluted to volume with 20 mL of 6 N HCl and demineralized water in 100-mL volumetric flasks. Manganese standard curves were obtained similarly, but the reagent blanks and mineral solutions also contained 1000 ppm lanthanum. Lanthanum was used to suppress the effects of interfering anions in the manganese determination. The AAS procedure was verified by repeated analyses of the NBS rice flour and wheat flour standard reference materials with each set of food samples over a 2-year period. The respective means of these determinations in rice and wheat flours were 19.8 and 7.6 ppm Mn (20.1 ± 0.4 and 8.5 ± 0.5 ppm certified); 8.4 and 17.2 ppm Fe (8.7 ± 0.6 and 18.3 ± 1.0 ppm certified); 2.5 and 2.81 ppm Cu (2.2 ± 0.3 and 2.0 ± 0.3 ppm certified); and 19.6 and 10.5 ppm Zn (19.4 ± 1.0 and 10.6 ± 1.0 ppm certified).

X-ray Fluorescence Analyses. The dry powdered standard reference materials and the lyophilized food samples were analyzed directly by weighing 0.5-g aliquots of the dry powders into a 3.2-cm-diameter hardened steel die and pressing self-supporting sample pellets under 2300 kg/cm^2. Four replicate pellets were prepared from each standard reference material, and three replicate pellets were prepared from each food. Four analyses were performed on each of the four NBS standard reference material pellets, and one analysis was performed on each of the food pellets. Each analysis consisted of collection of four separate XRF spectra under vacuum using Gd, Ag, and Ge secondary excitation and 5-kV direct excitation (30, 20, 10, and 10 min, respectively, with a Kevex Model 700 spectrometer system). Only the Ge spectrum was used to obtain the Mn, Fe, Cu, and Zn X-ray intensities. The other three spectra provided data on additional elements, which were all used in the CEMAS calculations.

Spectral analysis, compositing of intensities, and quantitation utilized the CEMAS program (Nielson, 1986), which automatically computed matrix corrections and calibrations for each sample based on its measured constituents and backscattered X-ray intensities. The resulting concentrations of Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, As, Br, Rb, Sr, Mo, Ba, and Pb were all computed for use in the matrix corrections, and the concentrations were stored directly on disk for subsequent

Table I. Aliquot and Analytical Variations for XRF Analyses of NBS Standard Reference Materials

	relative standard deviation,[a] %											
	manganese			iron			copper			zinc		
sample	aliq[b]	anal.[b]	tot.	aliq	anal.	tot.	aliq	anal.	tot.	aliq	anal.	tot.
powdered milk										1.1	1.1	1.6
oyster tissue	0.4	4.2	4.2	0.7	1.2	1.4	0.4	0.8	0.9	0.6	0.7	0.9
wheat flour	1.9	4.6	5.0	10.4	2.5	10.7	2.9	6.9	7.5	1.3	3.3	3.5
rice flour	1.6	3.9	4.2	26.9	40.1	48.3	7.8	6.4	10.1	1.4	2.5	2.8
orchard leaves	2.1	2.1	2.9	1.4	2.2	2.7	2.2	4.5	5.0	2.0	1.8	2.7
citrus leaves	4.1	2.9	5.0	3.0	1.4	3.4	2.6	3.0	4.0	1.4	1.9	2.4
tomato leaves	3.6	2.0	4.1	1.8	1.8	2.5	3.0	4.1	5.1	1.9	2.0	2.8
pine needles	1.2	1.2	1.8	2.8	1.1	3.0	3.9	6.0	7.2	2.3	0.8	2.4
bovine liver	4.3	5.7	7.1	1.7	0.8	1.9	2.9	0.7	3.0	3.0	0.8	3.1
mean	2.4	3.3	4.3	6.1	6.4	9.2	3.2	4.0	5.3	1.7	1.7	2.5

[a] (Standard deviation/mean) × 100. [b] Four analyses were performed on each of four replicate aliquots of each sample.

Table II. Comparison of XRF Mineral Measurements with NBS-Certified Concentrations

	mineral concentration, ppm											
	manganese			iron			copper			zinc		
sample	XRF[a]	NBS[b]	diff[c]	XRF	NBS	diff	XRF	NBS	diff	XRF	NBS	diff
powdered milk	*d*									45.2	46.1	−0.9
oyster tissue	17.2	17.5	−0.3	198	195	3	62.8	63.0	−0.2	867	852	15
wheat flour	8.5	8.5	0.0	19.3	18.3	1.0	2.0	2.0	0.0	10.1	10.6	−0.5
rice flour	20.6	20.1	0.5	8.2	8.7	−0.5	2.0	2.2	−0.2	19.3	19.4	−0.1
orchard leaves	90.2	91.0	−0.8	291	300	−9	12.6	12.0	0.6	23.9	25.0	−1.1
citrus leaves	23.2	23.0	0.2	94	90	4	16.5	16.5	0.0	29.2	29.0	0.2
tomato leaves	250	238	12	690	690	0	11.8	11.0	0.8	66	62	4
pine needles	691	675	16	208	200	8	2.9	3.0	−0.1	60	*e*	
bovine liver	9.9	9.9	0.0	202	194	8	163	158	5	125	123	2
mean diff			3.4			1.6			0.7			2.3
std dev of mean			2.3			1.7			0.6			1.9
mean rel bias,[f] %			2.3			0.9			2.2			1.6

[a] XRF values are means of 16 determinations. [b] NBS-certified concentrations. [c] Difference between XRF mean and NBS value. [d] Some or all determinations were below XRF detection limits. [e] Zn not certified by NBS. [f] (Mean difference/NBS value) × 100.

Table III. Aliquot and Sample Variations for XRF Analyses of Foods

		relative standard deviation,[a] %							
		manganese		iron		copper		zinc	
food	*N*[b]	aliq	sample	aliq	sample	aliq	sample	aliq	sample
beets	5	3.2	43	3.1	77	3.8	13	1.6	72
broccoli	5	3.1	29	2.9	6	6.3	11	2.7	21
cake	5	15.1	32	15.2	31	*c*		5.8	18
carrots	5	5.6	40	7.7	28	6.0	21	1.9	14
corn	5	11.7	21	14.0	36	7.5	25	5.4	7
enrchd white bread	5	7.8	7	5.8	29	12.2	8	4.7	9
green beans	4	2.1	17	2.7	16	4.9	12	2.8	4
oatmeal	5	4.7	3	5.8	6	6.0	4	3.7	5
onions	4	3.4	30	4.4	21	5.7	10	3.3	8
peas	5	4.6	9	3.1	12	7.0	8	2.3	10
potato	4	7.3	19	19.1	30	3.2	13	4.4	15
rice	4	8.4	48	9.0	34	8.6	14	5.2	38
saltines	5	6.3	12	8.2	14	14.7	19	4.1	12
shrimp	5	12.2	58	15.2	55	5.9	34	2.7	7
sour cream	5	*c*						5.1	69
spinach	4	2.1	55	5.9	107	4.3	44	2.2	70
squash	3	10.6	36	6.3	38	4.8	40	2.3	76
tomato	5	8.8	16	10.2	112	7.3	58	5.6	14
waffles	3	8.3	32	13.0	30	12.3	13	6.4	18
whole wheat bread	5	5.5	44	7.8	42	14.9	24	5.5	22
zucchini	5	6.3	14	6.7	9	4.3	34	2.9	16
mean		6.9	28	8.3	37	7.4	21	3.8	25
std dev		3.6	16	4.7	30	3.6	15	1.5	24

[a] (Standard deviation/mean) × 100, as partitioned by one-way analysis of variance (Li, 1964). [b] Number of samples, each analyzed from three aliquots. [c] Some or all measurements were below detection limits.

statistical analyses. Only the Mn, Fe, Cu, and Zn data were used in this study because AAS data were not available for the other elements. To assess long-term reproducibility of the XRF spectrometer, a thin gallium standard was analyzed at the outset of each of the 21 sets of food sample analyses over a 2-month period. It was intended to be a potential basis for normalizing the X-ray tube brightness for long-term consistency.

Statistical Analyses and Comparisons. Statistical analyses were performed separately for the Mn, Fe, Cu, and Zn in each standard reference material to assess analytical variability and also variability due to sample

Table IV. Summary of Atomic Absorption Spectrophotometry and X-ray Fluorescence Values for Manganese, Iron, Copper, and Zinc in Selected Foods (ppm in Dry Matter)

food (no. of samples)	moisture,[a] %	manganese			iron			copper			zinc		
		AA[b]	XRF[c]	diff[d]	AA	XRF	diff	AA	XRF	diff	AA	XRF	diff
beets (5)	90.5	38.4	47.9	9.5	229	200	−29	15.5	7.2	−8.3	72.9	71.8	−1.1
	1.0	16.9	22.3	2.5	146	166	12	2.9	1.0	1.7	54.0	55.5	1.1
broccoli (5)	91.9	30.6	28.6	−2.0	80.0	78.9	−1.1	6.8	4.8	−2.0	30.1	38.1	7.9
	1.7	12.2	9.1	2.5	6.7	5.0	2.5	2.3	0.6	0.8	13.7	8.6	3.3
cake (5)	35.2	2.9	1.7	−1.2	20.6	12.4	−8.2	3.9			6.7	3.0	−3.6
	4.8	1.1	0.5	0.3	5.5	4.2	2.4	1.7			2.9	0.6	1.2
carrots (5)	89.2	8.6	14.3	5.7	32.5	27.9	−4.6	5.6	5.2	−0.4	22.9	18.4	−4.5
	1.2	3.5	6.1	1.8	9.7	8.5	4.6	1.4	1.2	0.7	4.3	2.8	2.5
corn (5)	76.8	1.7	4.0	2.4	12.1	15.6	3.5	3.1	1.9	−1.2	16.0	15.2	−0.8
	1.3	0.5	0.9	0.3	4.3	6.2	1.1	0.2	0.5	0.2	1.2	1.1	0.3
enr white bread (5)	43.2	6.9	6.4	−0.5	45.1	38.5	−6.6	3.0	1.8	−1.2	19.3	6.8	−12.5
	6.0	1.3	0.5	0.5	6.9	12.0	3.0	1.5	0.2	0.7	22.5	0.6	10.2
green beans (4)	90.7	29.2	33.9	4.7	95.0	79.2	−15.8	8.3	6.3	−2.0	24.1	22.8	−1.3
	1.0	5.6	6.5	0.9	12.4	13.7	2.0	1.8	0.8	0.7	1.9	1.1	0.4
oatmeal (5)	86.5	57.6	44.6	−13.0	50.4	53.2	2.8	6.9	6.1	−0.7	43.7	45.1	1.5
	0.4	19.7	1.4	8.8	7.4	3.2	4.2	0.3	0.3	0.1	2.3	2.2	0.9
onions (4)	90.8	9.9	9.5	−0.4	32.9	25.9	−7.0	9.7	5.8	−3.9	13.7	15.9	2.1
	2.1	7.0	7.1	0.4	3.7	6.0	1.2	1.8	0.6	1.1	2.0	1.4	0.4
peas (5)	78.9	6.5	13.6	7.2	49.2	75.3	26.1	6.4	5.6	−0.8	31.8	33.2	1.4
	1.0	1.1	1.4	0.3	11.7	9.9	5.5	1.2	0.5	0.5	3.1	3.6	0.4
potato (4)	71.5	5.7	8.0	2.4	49.3	52.6	3.3	7.1	4.8	−2.3	18.9	11.1	−7.8
	4.0	1.2	1.7	0.3	13.4	17.4	3.1	1.3	0.7	0.4	4.5	1.8	1.6
rice (4)	70.1	11.2	9.3	−1.9	40.1	29.3	−10.8	2.1	2.3	0.1	14.0	12.7	−1.3
	1.2	4.9	4.9	0.2	17.2	11.0	5.2	0.5	0.4	0.2	4.8	5.4	0.5
saltines (5)	7.0	7.7	7.6	−0.1	44.6	32.6	−12.0	1.9	1.7	−0.2	8.0	6.3	−1.8
	2.4	3.6	1.0	1.4	3.3	5.0	2.0	1.0	0.4	0.4	1.3	0.8	0.7
shrimp (5)	80.5	5.4	3.5	−1.9	57.7	52.4	−5.4	9.1	7.9	−1.2	63.9	65.3	1.4
	6.5	2.3	2.2	0.6	22.9	30.9	10.3	3.7	2.9	0.7	17.3	5.2	7.5
sour cream (5)	74.8	2.0			15.7			2.4			5.5	6.4	0.9
	3.9	0.6			5.5			1.9			4.4	4.8	0.4
spinach (4)	91.8	68.3	70.0	1.7	580	629	49	15.1	13.0	−2.1	69.1	84.7	15.6
	0.9	45.7	47.5	5.2	665	743	42	6.2	6.3	0.5	44.4	65.3	11.0
squash (3)	92.2	2.0	3.0	1.0	34.8	21.6	−13.2	7.3	6.3	−1.0	19.4	14.8	−4.6
	0.9	0.4	1.5	0.8	12.4	3.8	9.1	2.7	3.3	0.3	14.3	13.1	4.0
tomato (5)	93.9	11.9	11.5	−0.4	151	149	−2	28.0	19.2	−8.8	28.1	23.6	−4.6
	1.3	1.5	2.0	1.3	137	180	20	14.1	12.0	1.4	4.6	3.5	0.9
waffles (3)	7.4	6.7	5.8	−0.9	36.2	34.3	−1.9	3.2	1.5	−1.6	8.5	5.5	−3.1
	1.1	1.0	1.5	0.5	8.9	12.8	2.8	0.5	0.1	0.2	3.4	0.6	1.6
wh wheat bread (5)	39.6	18.9	17.8	−1.1	50.8	41.6	−9.2	3.3	2.8	−0.5	16.2	13.7	−2.6
	5.7	9.3	8.5	0.8	20.5	18.9	1.6	1.1	0.7	0.4	4.6	3.2	1.0
zucchini (5)	94.8	24.7	22.4	−2.3	81.5	85.9	4.4	10.5	9.6	−0.9	41.2	43.7	2.4
	1.0	3.8	3.4	2.3	13.7	8.1	2.7	2.5	3.6	0.6	7.8	7.6	2.7
mean	71.3	17.7	18.2	0.4	88.7	86.8	−1.9	8.0	6.0	−2.1	27.3	26.6	−0.8
std dev	27.9	18.7	18.2	4.6	125.8	135.7	16.1	6.2	4.4	2.5	20.2	23.5	5.6

[a] Moisture means and standard deviations. [b] Atomic absorption means and standard deviations. [c] X-ray fluorescence means and standard deviations. [d] Mean difference (XRF − AA) and standard deviation of the mean difference.

inhomogeneity. They consisted of one-way analyses of variance (Li, 1964) to provide partitioned estimates of the interaliquot variations separate from the variations among replicate analyses of a given aliquot. The agreement between the XRF data and NBS-certified concentrations was characterized by the mean bias in the XRF data and its standard deviation. Variations among food sources and among replicate analyses of different sample aliquots were estimated for the 96 other food samples by one-way analyses of variance. The differences between the XRF and AAS concentrations were characterized by the means of the differences between analyses of samples of each food and their standard deviations. Variations were expressed as relative standard deviations (RSD = 100SD/mean) for simplicity of interpretation.

RESULTS AND DISCUSSION

The results of each XRF analysis consisted of four X-ray spectra, similar to those illustrated for NBS tomato leaves in Figure 1. The concentrations of Mn, Fe, Cu, and Zn resulting from the replicate analyses of the NBS standard reference materials were analyzed for variations among replicate analyses and replicate aliquots, and the results are presented in Table I. Average relative standard deviations among replicate XRF determinations ranged from 2.5% for Zn to 9.2% for Cu, with generally similar variations resulting from analytical precision and from sample inhomogeneity. Variation among aliquots exceeded 10% only for Fe in wheat flour and rice flour, suggesting minor inhomogeneity in these cases. The high analytical uncertainty for Fe in rice flour occurred because the concentration was near the detection limit.

The comparison of XRF results with NBS certified concentrations (Table II) indicates agreement that is consistently within the quoted NBS uncertainties. The maximum relative error was 9% (0.2 ppm) for copper in rice flour, and the maximum absolute error was 16 ppm (2.4% relative) for manganese in pine needles. The mean of the differences in the analyses ranged from 0.7 ppm for copper to 3.4 ppm for manganese, or on a relative basis, it ranged from 0.9% for iron to 2.3% for manganese. These agreements are the main basis for validating the XRF method.

XRF detection limits were computed as 2σ detection limits for each analysis, based on background intensities. The intensity detection limits were defined as 2SQRT

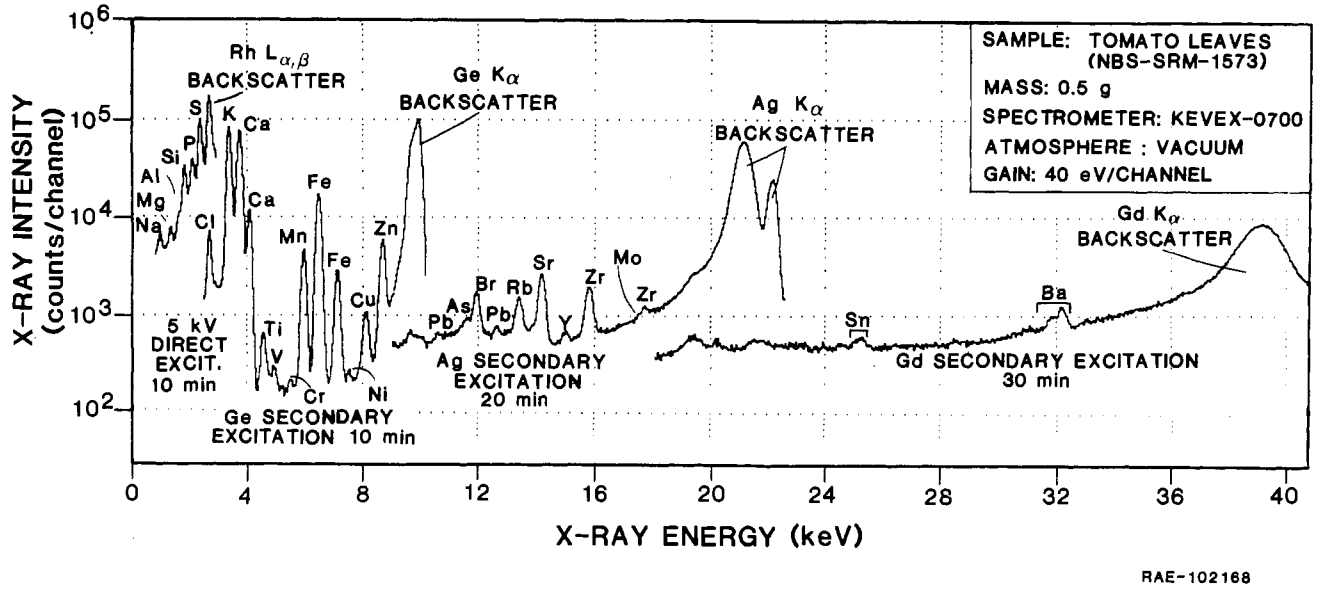

Figure 1. X-ray fluorescence spectra from analysis of NBS tomato leaves.

(2Bkg), where Bkg is the number of spectral background counts in the peak integration region. The detection limits were averaged over all analyses for each of the nine NBS standards, and found to average 1.4 ± 0.5 ppm for Mn, 1.2 ± 0.4 ppm for Fe, 0.6 ± 0.2 ppm for Cu, and 0.6 ± 0.1 ppm for Zn. The detection limits varied most for Mn, due to the variations in matrix composition of the standards. The detection limits are based on the 10-min analyses with the Ge secondary source and can be scaled as the square-root of the analysis time. For example, 20-min analyses would yield detection limits about 1.41 times lower than the limits quoted here.

The analyses of the gallium standard with each set of analyses for the 21 food samples yielded a mean and standard deviation of 38.6 ± 0.2 $\mu g/cm^2$. The 0.5% relative standard deviation of these analyses was considered to constitute adequate precision, and no intensity normalization of individual sets of data was attempted.

The variations in the XRF analyses of the 96 food samples (Table III) were dominated by the typically larger variations among food samples than those among aliquots of a given sample. The aliquot variations in Table III included both analytical uncertainties and sample inhomogeneity. Overall relative standard deviations among different food samples ranged from an average of 21% for copper to 37% for iron. Corresponding overall relative standard deviations among replicate sample aliquots ranged from 3.8% for zinc to 8.3% for iron.

The comparisons of the XRF and AAS results via scatter plots yielded slopes that were within 10% of unity for Mn, Fe, and Zn, with a lower (0.7) slope for copper, suggesting a bias in the copper data. Intercepts were less than 3 ppm except for Fe whose −11 ppm intercept still amounts to a relatively small error considering the higher iron concentrations. Correlation coefficients ranged from 0.94 for manganese and copper to 1.00 for iron. The comparisons were linear for all four elements over the entire ranges of data (1–100 ppm Mn, 3–1600 ppm Fe, 0.5–50 ppm Cu, 2–140 ppm Zn). One data point, for manganese in oatmeal, is considered an outlier out of the 362 analytical comparisons. A detailed quantitative comparison of the XRF and AAS data is presented in Table IV, with the mean mineral concentrations in each of the 21 foods. Average overall biases were 0.4 ppm for Mn, −1.9 ppm for Fe, −2.1 ppm for Cu, and −0.8 ppm for Zn. The largest variation in biases was 16.1 ppm for iron, again due to the much higher iron concentrations in some of the foods.

The XRF and AAS means in Table IV represent best estimates for the four elements in each of the 21 foods. The sample standard deviations, also in Table IV, give an estimate of intersample variability. As indicated by Table III, variations between samples (from different food sources) were much greater than analytical variations or variations due to inhomogeneity, which typically were in the 3–7% range.

Registry No. Mn, 7439-96-5; Fe, 7439-89-6; Cu, 7440-50-8; Zn, 7440-66-6.

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New Method for Microdetermination of Triforine and Its Metabolite Using Thermal Reaction with Alcohol

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A new method for microdetermination of triforine [TF, 1,4-bis(2,2,2-trichloro-1-formamidoethyl)-piperazine] and its major metabolite [TF/2, 1-(2,2,2-trichloro-1-formamidoethyl)piperazine] is described. Thermal reaction of triforine or TF/2·HCl [1-(2,2,2-trichloro-1-formamidoethyl)piperazinium 4-hydrochloride] with several alcohols in a closed glass tube resulted in formation of highly sensitive compounds to electron capture detector (ECD) on gas chromatography (GC). The compounds were identified as *N*-(1-alkoxy-2,2,2-trichloroethyl)formamides. The reaction was applied to the residue analysis of triforine and TF/2 in several crops. The analytical method involves extraction with acetone, separation to triforine and TF/2 portions by liquid–liquid partition, thermal reaction with methanol, and analysis by GC. Minimum limits of detections were 0.005 ppm for triforine and 0.01 ppm for TF/2·HCl. Recoveries of added triforine and TF/2·HCl from peach, green pepper, and strawberry averaged 99% and 70%, respectively.

Triforine [1,4-bis(2,2,2-trichloro-1-formamidoethyl)-piperazine, Saprol] is a systemic fungicide used for controlling powdery mildew, scab, rust, monilia, and leaf spot disease on a wide range of crops (Schicke and Veen, 1969). Piperazine and 1-(2,2,2-trichloro-1-formamidoethyl)-piperazine (TF/2) have been shown to be metabolites in barley plants (Rouchaud et al., 1978).

The most widely used approach to the analysis of triforine and TF/2 metabolite has been that of acidic hydrolysis and gas chromatographic measurement of the liberated chloral hydrate (Eichler, 1972; Bourke et al., 1977; Rouchaud, 1977). Methods for the determination of piperazine by gas–liquid chromatography (Rouchaud, 1977; Newsome, 1982) are also available for the analysis of triforine and its metabolites. While triforine can be detected when it is directly introduced into gas chromatograph (GC) (Ishii, 1980; Nagayoshi et al., 1981), accurate measurements cannot be obtained because the method is based upon the determination of triforine's thermal product formed in the injection port of GC.

We developed a new method for the determination of triforine and its metabolite (TF/2) using thermal reaction of these compounds with methanol in a closed glass tube, followed by the measurement of thermal product with GC. The availability of the method for residue analysis in several crops was demonstrated by the analysis of triforine and TF/2·HCl [1-(2,2,2-trichloro-1-formamidoethyl)-piperazinium 4-hydrochloride] added to peach, green pepper, and strawberry.

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MATERIALS AND METHODS

Apparatus. A Hewlett-Packard Model 5890 gas chromatograph equipped with electron capture detector was used for all measurements. A 2.4 m × 2 mm (i.d.) glass column was packed with Ultra-Bond 20M (100–120 mesh). Column temperature was held at 160–170 °C; inlet and detector temperatures were 280 and 300 °C, respectively. Carrier flow (N_2) was 40 mL/min. Quantitation was achieved by measurement of peak heights.

Identification of the products obtained by the thermal reaction of triforine or TF/2 with several alcohols was achieved through gas chromatography–mass spectrometric analysis performed on a JEOL JMS DX-300 gas chromatograph–mass spectrometer [equipped with a dual electron impact (EI)/chemical ionization (CI) source] interfaced to a JEOL JMA DA-5000 data system. Ion source operating temperature was maintained at 200 °C with an ionizing voltage of 70 eV. All CI spectra were measured with use of isobutane. Samples were introduced through a gas chromatographic column fitted to a JEOL MS-DC05 gas chromatograph and interfaced via a glass jet separator. The GC analyses were accomplished on a 1.5 m × 3 mm

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