of 4-CA applied, the organic matter is available for binding as if no clay were present; but at 500 ppm it is evident that the number of sites has decreased, because of clay interaction with the organic matter, and insufficient sites are available for binding (78% at 5 ppm compared with 53% at 500 ppm). This effect is magnified with the clay-loam soil (5% organic matter-32% clay) where the total amount bound decreased to 46 and 15% at 5 and 500 ppm due to masking of organic matter activity by a greater clay content. Figure 2 shows that as clay concentration increases and OM concentration decreases, total amount of 4-CA bound decreases, thus supporting the above conclusion.

Since the amount of radioactivity released by pyrolysis and extractable into benzene (4-CA) for all soils was very similar (approximately 10%), this observation might be taken to be indicative of a binding mechanism related to organic matter inclusion phenomena; low recoveries of 4-CA indicate thermolysis of "free" 4-CA in the substrate. For geographically different soils of varying organic matter contents, organic matter-4-CA interactions would be expected to vary such that greater differences in release result. From these results it appears that organic matter concentration is not important for release (except below a limiting concentration).

Low recoveries of benzene-extractable radioactivity from the pyrolysate may be due to inclusion phenomena also, whereby application of heat results in thermolysis of 4-CA itself rather than of a 4-CA organic matter covalent bond. It appears that for a reactive compound such as 4chloroaniline tightly complexed to soil or soil humic acids, pyrolysis may be useful if the released residue is stabilized prior to trapping; recoveries are low but reasonably reproducible.

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# Mineral Composition of Small-Grain Cultivars from a Uniform Test Plot in South Dakota

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Seventy-five cultivated varieties (cultivars) of hard red spring wheat (HRS), hard red winter wheat (HRW), durum wheat, oats, and barley were harvested in 1974 from a small-grain trial plot in Harding County, SD, just north of Buffalo. Analysis of the grains reported here includes crude protein for only the wheat cultivars, ash yield, and 17 chemical elements, many of which are not commonly given in the literature (such as B, Cd, Mo, Ni, and Se). Differences in composition between the two classes of hard red wheat indicate that HRS is significantly higher (p < 0.05) than HRW in protein content, ash yield, Ca, K, Mg, Na, P, total S, Sr, and Zn; Cd is significantly higher in the HRW cultivars. For the most part, concentrations were quite uniform within all grain types. Only two cultivars were anomalous: cv. Hi Plains in HRW wheats and cv. Astro in the oat group.

With respect to the mineral composition of wheat grains, probably the most thorough review of the literature prior to 1944 is the monographic compilation by Bailey (1944). We are not aware of any recent report that is comparable, although Czerniejewski et al. (1964) present data on the nutritionally important elements in hard wheat from the United States, and Lorenz and Loewe (1977) have reported the mineral compositions of U.S. and Canadian wheats. Studies of the composition of oats and barley are less

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Figure 1. Small-grain cultivar plots in uniform test plot near Buffalo, SD.

Table I. Estimate of Analytical Precision Based on Duplicate Analyses of 20 Samples of Assorted Small Grains<sup>a</sup>

ash or element	% of total variance	element	% of total variance
ash yield	3.3	Мо	49
В	33	Na	6.2
Ba	5.5	Ni	3.7
Ca	7.2	Р	38
Cd	4.3	S, total	17
Cu	3.6	Se	11
$\mathbf{F}$	no data	Si	<b>2.4</b>
K	5.0	Sr	30
Mg	2.9	Zn	1.8

 $^{a}$  Estimates for the mineral elements, with the exception of S and Se, are based on concentrations in the ash as reported by the analysts.

comprehensive and usually entail only a few elements [see, for example, the paper on Cu, Mo, and S by Todd (1972)] or only a single element, such as Cd (Kjellström et al., 1975).

Relatively few studies have assessed the cultivar effects on the concentration of elements in grain tissue [see, for example, Ashton, (1938), El Gindy et al. (1957), and Schrenk and King (1948)]. A study by Karvanek and Janicek (1969) on oat grains showed that the locality exerted a much greater control on the differences in mineral composition than did the variety. As early as 1941, Beeson (1941) wrote (p 57) the following: "Whether different varieties of the same species differ in mineral content when grown in the same soil is still an unsolved problem". The problem still persists.

As an adjunct to establishing base-line data of the mineral composition of selected small grains from the northern Great Plains coal province and assessing the impact of surface mining on agriculture (Erdman and Gough, 1979), we studied the composition of 75 cultivars that were grown in a trial plot north of Buffalo, SD (Figure 1). We were particularly interested in the reported differences between HRS and HRW (Greaves et al., 1940) because the former is cultivated in the northern part of the coal province, whereas the latter occurs in the southwestern part, and it appears that separate base lines should be given for each class of hard red wheat. We were also interested in understanding the variation among cultivars within a specific grain type. Our results are based on samples from a uniform plot and are therefore representative of only one location and environment. They are not intended to serve as base-line data.

## EXPERIMENTAL SECTION

A uniform small-grain test plot was located about 15-km northeast of Buffalo, Harding County (45°40'15" N. 103°29'00" W), where the 75 cultivars were grown in Marmarth fine sandy loam. This soil series determination was based on four probes taken at the experimental test site and described by Warren Johnson (personal communication) of the Soil Conservation Service at Sturgis. The number of cultivars for each type of grain is as follows: 19 for HRS and 19 for HRW (Triticum aestivum); 7 for durum wheat (T. durum); 23 for oats (Avena sativa); 7 for barley (Hordeum vulgare). The winter wheat plot was planted on Sept 6, 1973, and the spring grain plots were planted on April 29, 1974. The HRS, durum wheat, oats, and barley were planted with a conventional double-disk open press drill with 7-in. spacing. The HRW was planted with a hoe drill equipped with a press wheel and 14-in. spacing. Six rows of 300-ft lengths were planted of each cultivar. There were no replications, but the test site was very level. Five samples of 1 square yard each were harvested by hand from each cultivar plot. They were threshed with a head thresher and placed in 1-pt containers.

All grain samples (except oats) were cleaned with a Carter Dockage Tester at the Inspection Division, Federal Grain Inspection Service, U.S. Department of Agriculture, Denver, CO. The oat samples were cleaned by hand, facilitated by the use of a coarse-meshed stainless steel screen to remove the fines. Twenty samples, selected at random, were split and the analytical sequence of the entire suite of 95 samples was randomized. The 20 splits consisted of 5 HRS and 5 HRW samples, 2 durum samples, 6 oat samples, and 2 barley samples. The analysis of blind splits provided a measure of laboratory precision, whereas the analysis of the samples in a randomized sequence circumvented any effects of systematic analytical bias.

The concentrations of antimony, arsenic, fluorine, mercury, selenium, and total sulfur were determined on the dry grains, after they had been ground in a blender, by the following methods: atomic absorption spectrometry, antimony and arsenic; selective-ion electrode, fluorine; flameless atomic absorption, mercury; fluorometry, selenium; turbidimetry, total sulfur. Antimony, arsenic, and mercury are not listed in the tables; the results were below the limits of detection which are 0.05, 0.05, and 0.01 ppm, respectively. All other elements were determined by analysis of the ash obtained from unground material.

A weighed portion of each sample, consisting of whole grains, was burned to ash in a muffle furnace in which the heat was increased 50 °C/h to a temperature of 550 °C and held at this temperature for 14 h. The ash was weighed after cooling to determine the ash yield of the dry grains. The resultant ash had a salt-and-pepper aspect that was unlike all other plant tissues that had been similarly ashed. Sullivan and Near (1927) discussed the problems of obtaining a clean grayish white ash from flour milled from wheats grown in the northern Great Plains. They maintain that a temperature greater than 550 °C is needed to obtain carbon-free ash. Otherwise an ash still containing particles of carbon results.

The methods of analysis used for the elements in ash were as follows: atomic absorption spectrometry, calcium, cadmium, copper, magnesium, potassium, sodium, silicon, and zinc; colorimetry, molybdenum and phosphorus. The remaining elements, boron, barium, nickel, and strontium, were determined by emission spectroscopy. Due to analytical problems with Fe determinations by emission spectroscopy, this element is not included. Descriptions

Table II. Protein, Ash Y	ield, and	Minera	l Conten	t (Dry V	Veight Ba	asis) in C	ultivars o	f Hard F	ted Whe	at <sup>a</sup>									
			conc	entratio	n, %							COL	ncentrati	on, ppm	_				
	$protein^b$	$ash^b$	Кb	$^{qd}$	S <sup>b</sup> ,c	$Mg^b$	$Ca^b$	В	Ba	$\mathrm{Cd}^{b}$	Ğ	Ŀ	Mo	$Na^b$	q!N	Se	Si	$Sr^b$	$d^{p}$
							Spring	Cultivar	s (HRS)										
Bonanza	17.4	2.1	0.46	0.38	0.21	0.20	0.046	1.0	6.9	0.042	4.4	1	0.63	13	0.53	0.15	42	1.7	29
Bounty 208	17.0	2.2	0.53	0.40	0.18	0.20	0.044	0.9	6.4	0.044	4.4	1	0.44	11	0.18	0.15	44	1.7	31
BW-25	17.3	2.0	0.46	0.36	0.21	0.18	0.034	0.7	2.3	0.080	4.2		0.40	10	0.21	0.15	40	0.7	36
Chris	18.3	2.1	0.42	0.25	0.21	0.20	0.042	1.3	3.2	0.053	3.4	1	0.42	13	0.21	0.20	42	1.0	34
Ellar	17.7	2.2	0.51	0.26	0.19	0.22	0.029	1.3	4.0	0.055	4.6	1	0.44	11	0.19	0.15	<b>6</b> 6	1.0	33
Era	15.6	1.9	0.47	0.34	0.16	0.16	0.036	1.1	4.4	0.085	4.9	1	0.57	11	0.16	0.20	76	1.3	28
Fortuna	17.6	1.8	0.45	0.32	0.20	0.18	0.034	1.0	2.6	0.081	3.6	-	0.36	6	0.20	0.15	54	1.1	29
Kitt	17.8	2.0	0.48	0.36	0.19	0.19	0.038	0.8	4.5	0.050	5.8	~1 ^	09.0	10	0.19	0.20	60	1.5	32
Nordak	19.6	1.9	0.44	0.34	0.22	0.18	0.038	0.6	2.5	0.057	4.0	<u>~</u> 1	0.38	6	0.22	0.20	57	1.1	30
Nowesta	18.8	1.9	0.40	0.34	0.22	0.13	0.034	0.6	3.5	0.057	3.8		0.38	11	0.22	0.15	38	1.4	27
Olaf	17.5	2.1	0.53	0.38	0.22	0.20	0.034	1.0	4.6	0.053	4.2	<1	0.42	13	0.22	0.15	84	1.2	32
Polk	18.3	2.1	0.46	0.38	0.21	0.17	0.036	1.7	5.5	0.084	2.9	<1	0.42	11	0.21	0.15	42	1.6	32
Prodax	18.1	2.0	0.54	0.24	0.20	0.17	0.040	1.7	3.4	0.070	5.0	1	0.40	10	0.20	0.20	40	1.3	26
Profit 75	16.3	1.9	0.53	0.34	0.19	0.17	0.038	0.9	4.6	0.057	5.1	-	0.57	11	0.19	0.20	19	1.7	28
Protor	17.9	1.9	0.49	0.34	0.20	0.16	0.038	0.5	5.5	0.085	4.6		0.57	6	0.20	0.15	76	1.8	30
Waldron	18.9	2.3	0.58	0.41	0.19	0.21	0.035		2.8	0.092	5.3	•	0.46	12	0.19	0.20	46	0.8	37
World Seeds 3	16.0	1.7	0.43	0.20	0.20	0 1 2	0.029	10	4.3	0.068	46	' \	0.34	14	0.20	0.15	153	1.4	24
World Seeds 6	18.1	9.4	0.60	0.43	0.18	0 19	0.048	11	2.2	0.048	20.2		0.48	14	0.18	0.20	24	5.0	36
World Seeds 1809	17.1	1.7	0.43	0.20	0.19	0.15	0.037	0.5	2.8	0.068	5.1	' <del>\</del>	0.51	6	0.19	0.15	51	0.7	24
average	17.6	2.0	0.48	0.33	0.20	0.18	0.037	0.96	4.2	0.065	4.5	1.1	0.46	11	0.20	0.17	55	1.3	30
							Winter	Cultiva	wan)	~									
Bronze	191	1 7	0.41	0 97	0 13	0 14	0.030	<b>J</b> 1	0 7	, 0.098	5 0	-	0.45	α	0.13	0 15	60	11	54
Ducket	1.2.1		0.00	17.0	010	0.14 0.14			4.0 0.4	0.000	0.0		0.4.0	0 1	01.0	0.15			# C 7 F
	0.11	7.7	07.0	0.22	21.0	11.0	0.023	~ ~	0.7	0.004 0.004	0.7		0.00	0 נ	21.0	0.15			11
Caprock	14.4		0.43	0.31	0.10	9T'0	0.037	۰. ۱	4.0 0	0.094	0.4 1		10.0	- (	0.10	0.10		- · ·	22
Centurk	11.8	1.5	0.38	0.18	0.12	0.15	0.028	1.1	5.X	0.105	4.5	-	0.45	ı د	0.12	0.15	45	1.2	71
Cloud	13.3	1.8	0.41	0.32	0.14	0.1.0	0.032	1.3	5.2	0.090	4.1	I V	0.54	1	0.14	0.15	54	1.1	1.7
Eagle	12.5	1.7	0.36	0.31	0.15	0.16	0.027	1.0	3.6	0.102	3.6	7	0.51	<b>-</b>	0.15	0.20	17	0.9	26
Froid	13.4	1.8	0.42	0.32	0.15	0.18	0.032	1.3	4.5	0.070	5.4	1	0.53	11	0.15	0.20	88	1.5	30
Gage	13.3	1.4	0.31	0.25	0.16	0.12	0.028	0.9	4.2	0.077	3.2	- <u>1</u> -	0.42	4	0.16	0.15	84	1.1	21
Gent	13.7	1.4	0.32	0.25	0.13	0.14	0.025	0.8	2.9	0.091	4.1	~1	0.56	9	0.13	0.15	42	1.1	22
Hi Plains	16.1	1.5	0.36	0.13	0.16	0.15	0.042	1.3	4.1	0.210	4.6	1	0.45	6	0.16	0.40	75	1.4	$^{24}$
Homestead	13.0	1.6	0.35	0.29	0.16	0.15	0.030	0.7	3.6	0.104	4.0	<1	0.48	ഹ	0.16	0.15	16	0.5	26
Hume	14.7	1.4	0.29	0.25	0.15	0.13	0.031	1.0	4.2	0.063	4.1		0.56	2	0.15	0.15	112	1.3	25
Lancer	12.1	1.6	0.40	0.29	0.12	0.14	0.030	1.0	4.2	0.080	3.5	-	0.48	13	0.12	0.15	16	0.8	22
Minter	14.9	1.8	0.40	0.32	0.16	0.15	0.029	1.1	4.5	0.090	5.8	<u>~</u> 1	0.54	11	0.16	0.20	18	1.4	29
Sage	11.7	1.7	0.39	0.31	0.13	0.16	0.027	1.0	4.0	0.094	3.7	-	0.51	5	0.13	0.15	51	0.9	27
Scout 66	12.3	1.7	0.39	0.31	0.14	0.15	0.029	1.0	3.9	0.102	4.1	<1 1	0.51	27	0.14	0.15	17	1.1	29
Scoutland	13.0	1.4	0.35	0.25	0.15	0.13	0.028	0.8	3.1	0.063	3.6	7	0.28	<b>%</b>	0.15	0.15	84	1.0	24
Sentinel	13.4	1.7	0.36	0.31	0.15	0.16	0.031	1.0	4.8	0.145	4.9	<b>1</b>	0.51	ō	0.15	0.10	68	1.0	31
Winoka	11.1	1.5	0.34	0.27	0.12	0.13	0.022	0.9	3.6	0.098	3.2	~1	0.30	ഹ	0.12	0.15	30	0.7	23
average	13.1	1.6	0.37	0.27	0.14	0.15	0.030	0.99	4.1	0.096	4.1	<1.0	0.47	8.1	0.14	0.17	50	1.0	25
<sup>a</sup> As is moisture basis.	b Average	s signi	ficantly	differen	t at the 9	95% conf	ïdence le	vel. <sup>c</sup> T	otal sul	fur.									

			cont	centration	1, %							Ŭ	oncentra	tion, pp	E				
cultivar	protein	ash	К	Р	$\mathbf{S}^{b}$	Mg	Ca	В	Ba	Cd	Cu	ίΞ.	Мо	Na	ï	Se	Si	Sr	Zn
Botno	16.3	1.8	0.41	0.32	0.20	0.16	0.029	1.0	4.1	0.23	5.4	-	0.54	13	0.25	0.15	36	1.2	29
Crosby	17.2	1.8	0.45	0.32	0.19	0.15	0.029	1.1	3.6	0.23	5.6	$\stackrel{<}{\sim}$	0.36	11	0.17	0.15	54	1.1	32
Hercules	16.6	1.9	0.46	0.34	0.20	0.17	0.030	1.1	4.0	0.13	5.5	$\sim 1$	0.57	6	0.16	0.15	57	1.2	30
Leeds	17.4	1.9	0.46	0.34	0.19	0.16	0.036	1.0	3.8	0.23	5.3	Ţ	0.57	6	0.24	0.15	57	1.7	34
Rolette	17.4	1.9	0.46	0.34	0.21	0.15	0.028	1.5	4.4	0.23	4.7	$\stackrel{<}{\sim}$	0.38	6	0.27	0.15	38	1.4	30
Rugby	16.6	1.7	0.44	0.31	0.20	0.16	0.031	1.4	3.8	0.21	5.1	$\stackrel{<}{\sim}$	0.45	12	0.22	0.20	17	1.2	29
Ward	16.9	1.9	0.44	0.34	0.19	0.16	0.034	1.3	4.2	0.25	5.3	$\sim$ 1	0.57	11	0.25	0.20	152	1.3	30
average	16.9	1.8	0.45	0.33	0.20	0.16	0.030	1.2	3.9	0.22	5.2	$^{\vee}$	0.49	11	0.22	0.16	58	1.3	30
<sup>a</sup> As is moist	ure basis.	<sup>b</sup> Total	sulfur.																

Wheat <sup>a</sup>	
Durum	
Cultivars of	
sis) in (	
Veight Bas	
(Dry V	
Content	
Mineral	
l, and	
Vielo	
λ, Ash	
Proteir	
Table III.	

Table IV. As h Yield and Mineral Content (Dry Weight Basis) in Cultivars of  $\operatorname{Barley}^a$ 

concentration, ppm	B Ba Cd Cu F Mo Na Ni Se Si Sr Zn	0.9 $2.8$ $0.15$ $5.0$ $1$ $0.40$ $74$ $0.26$ $0.10$ $1800$ $1.1$ $28$	1.4 $3.1$ $0.08$ $4.8$ $1$ $0.48$ $115$ $0.22$ $0.10$ $2160$ $1.8$ $26$	1.2 $2.5$ $0.11$ $4.3$ $1$ $0.48$ $96$ $0.17$ $0.10$ $2160$ $1.1$ $34$	1.3 $3.0$ $0.08$ $3.8$ $1$ $0.40$ $116$ $0.16$ $0.10$ $1800$ $1.6$ $26$	1.6 $2.6$ $0.06$ $4.4$ $1$ $0.44$ $106$ $0.24$ $0.10$ $3960$ $1.2$ $29$	1.4  3.4  0.12  4.1  1  0.23  115  0.21  0.10  2300  1.2  25	1.3 $3.8$ $0.11$ $4.2$ $1$ $0.20$ $100$ $0.21$ $0.08$ $1600$ $2.0$ $24$	
oncentration, pp	Mo Na	0.40 74	0.48 115	0.48 96	0.40 116	0.44 106	0.23 115	0.20 100	100
ö	Бц	1	1	1	-	1	-	1	- -
	ਹੌ	5.0	4.8	4.3	3.8	4.4	4.1	4.2	VV
	Cd	0.15	0.08	0.11	0.08	0.06	0.12	0.11	010
	Ba	2.8	3.1	2.5	3.0	2.6	3.4	3.8	¢ c
	B	0.9	1.4	1.2	1.3	1.6	1.4	1.3	ۍ ۲
	Ca	0.034	0.041	0.034	0.032	0.033	0.044	0.044	0.037
	Mg	0.14	0.14	0.15	0.12	0.16	0.14	0.12	0.1.1
tration, %	$S^b$	0.17	0.17	0.17	0.16	0.17	0.15	0.15	0.16
concen	е,	0.24	0.29	0.29	0.18	0.20	0.28	0.18	10 0
	R	0.40	0.50	0.50	0.42	0.44	0.48	0.44	0.46
	ash	2.0	2.4	2.4	2.0	2.2	2.3	2.0	00
	cultivar	Beacon	Cree	Dickson	Larker	Nordic	Prilar	Primus II	ODGAGGO

<sup>a</sup> As is moisture basis. <sup>b</sup> Total sulfur.

Table V. Ash Yield and Mineral Content (Dry Weight Basis) in Cultivars of Oats<sup>a</sup>

			concer	itration	1, %						con	centra	tion,	ppm				
cultivar	ash	K	Р	$\mathbf{S}^{b}$	Mg	Ca	В	Ba	Cd	Cu	F	Мо	Na	Ni	Se	$\mathbf{S}_{i}$	Sr	Zn
Astro	4.2	0.55	0.25	0.14	0.18	0.118	4.0	5.2	0.025	3.4	1	0.42	21	7.1	0.10	12600	3.5	25
Burnett	3.1	0.40	0.28	0.18	0.15	0.074	<b>2.1</b>	3.8	0.124	5.0	1	0.93	37	5.2	0.15	6820	1.6	22
Cayuse	2.8	0.50	0.25	0.16	0.13	0.053	1.8	3.6	0.042	3.6	1	0.56	<b>25</b>	3.6	0.10	5600	1.4	20
Chief	3.4	0.48	0.31	0.23	0.16	0.082	2.3	4.5	0.034	6.8	1	0.68	<b>27</b>	5.6	0.15	7480	2.8	<b>24</b>
Dal	3.5	0.67	0.32	0.23	0.18	0.084	<b>2.4</b>	4.8	0.011	4.2	<1	1.05	32	6.7	0.20	5600	1.6	25
Diana	3.4	0.44	0.31	0.21	0.18	0.068	<b>2.1</b>	3.7	0.034	4.4	1	1.02	20	5.7	0.15	6800	2.3	20
Dupree	3.2	0.48	0.29	0.23	0.16	0.070	2.1	3.8	0.032	6.4	<1	0.64	19	6.4	0.10	6400	1.9	<b>22</b>
E-74	3.6	0.43	0.32	0.21	0.18	0.079	<b>2.4</b>	3.9	0.072	5.4	<1	1.08	<b>22</b>	5.4	0.15	8640	<b>2.4</b>	32
Froker	3.4	0.48	0.31	0.21	0.16	0.075	<b>2.4</b>	4.5	0.020	4.1	<1	0.68	<b>27</b>	5.8	0.15	6800	1.5	<b>27</b>
Grundy	3.5	0.42	0.32	0.19	0.16	0.070	2.2	4.2	0.021	4.9	<1	0.70	<b>21</b>	5.6	0.15	7700	1.8	25
Harmon	2.9	0.55	0.26	0.21	0.14	0.058	1.7	3.0	0.017	3.5	1	0.87	26	5.3	0.20	4060	1.8	20
Holden	3.4	0.44	0.31	0.22	0.18	0.075	2.5	4.4	0.020	5.8	1	1.02	<b>27</b>	6.8	0.15	6800	<b>2.4</b>	<b>27</b>
Kelsey	2.9	0.49	0.26	0.18	0.15	0.058	1.7	3.2	0.017	3.5	1	0.58	23	4.9	0.15	5220	1.5	17
Lodi	3.1	0.53	0.28	0.21	0.16	0.074	2.1	4.0	0.062	4.0	<1	0.62	<b>25</b>	5.1	0.15	4960	2.2	19
M-73	3.3	0.46	0.30	0.22	0.16	0.079	2.1	4.4	0.066	5.6	1	0.99	26	6.6	0.15	7260	2.6	20
Noble	3.3	0.49	0.30	0.22	0.18	0.079	1.9	4.3	0.049	6.6	1	0.99	33	5.9	0.15	6600	2.4	20
Nodaway 70	2.6	0.39	0.23	0.19	0.12	0.062	1.3	2.4	0.052	4.4	1	0.78	26	4.1	0.15	4680	1.1	20
Otee	3.6	0.47	0.32	0.21	0.18	0.072	2.6	4.0	0.022	4.7	<1	1.08	40	7.2	0.15	6480	1.8	25
Portal	3.1	0.46	0.28	0.21	0.16	0.068	2.3	3.5	0.019	5.9	1	0.93	<b>22</b>	8.2	0.15	6200	2.0	<b>25</b>
Random	3.2	0.58	0.29	0.19	0.14	0.064	2.3	<b>3.4</b>	0.032	4.5	1	0.64	<b>32</b>	7.1	0.15	2880	<b>2.4</b>	19
Russell	3.1	0.56	0.28	0.20	0.14	0.062	1.9	4.1	0.031	4.6	1	0.62	31	6.7	0.15	5580	1.9	22
Spear	3.2	0.42	0.29	0.19	0.16	0.064	2.0	3.8	0.048	6.1	1	0.96	26	6.7	0.15	7040	1.9	26
Trio	3.6	0.40	0.32	0.22	0.21	0.086	2.2	3.8	0.036	4.0	1	1.08	29	6.1	0.15	8640	1.5	29
average	3.3	0.48	0.29	0.20	0.16	0.073	2.2	3.9	0.039	4.8	1.0	0.82	27	6.0	0.15	6600	2.0	23

<sup>a</sup> As is moisture basis. <sup>b</sup> Total sulfur.

of these methods of analysis are given by Harms and Papp (1975) and Sutton (1976). For those elements analyzed in ash, the dry weight equivalent concentrations were calculated by using the formula  $C_d = C_a A/100$  where  $C_d$  is the concentration in the dry material,  $C_a$  is the concentration in the ash, and A is the percent ash yield.

In Table I analytical variance (a measure of precision) is expressed as a percentage of the total variance, not in terms of absolute precision. Estimates of the analytical error for both Mo and P, expressed as 49% and 38% of the total variance, respectively, appear to be fairly high. But they are due to a low total variance for both elements and the semiquantitative nature of the colorimetric method.

The accuracy of most elements not analyzed by emission spectroscopy was evaluated by analyzing a sample of the NBS Standard Reference Material 1567, Wheat Flour (Alvarez and Rook, 1978). The flour standard (milled from a blend of HRS and HRW grown mainly in South Dakota) has only recently been available, but since our analytical methods have remained the same for several years, the comparisons are still valid. The results are as follows:

USGS	NBS (certified)
0.034	$0.032 \pm 0.007$
0.95	$1.1 \pm 0.2$
0.020	$0.019 \pm 0.001$
10.6	$8.0 \pm 1.5$
0.16	$0.136 \pm 0.004$
1.8	$2.0 \pm 0.3$
12.5	$10.6 \pm 1.0$
0.6	$(0.4)^{a}$
	USGS 0.034 0.95 0.020 10.6 0.16 1.8 12.5 0.6

<sup>a</sup> Noncertified value

Accuracy of the other elements was judged by comparing our results with those previously published.

Crude protein was determined on 10-g samples at the Denver Grain Exchange as total nitrogen  $\times 5.7$  by using the American Association of Cereal Chemist's method (improved Kjeldahl method). The error was  $\pm 0.1\%$ .

#### RESULTS AND DISCUSSION

The concentrations of 17 mineral elements, the protein content, and ash yield given in Tables II–V are generally similar to those reported by others (Czerniejewski et al., 1964; Mathews and Douglass, 1978; Schrenk and King, 1948; Toepfer et al., 1972). The only notable exception is Na whose levels are consistently low when compared with amounts given in the literature. Sullivan and Near (1927) reported that Na may be partially lost during high-temperature ashing, and Czerniejewski et al. (1964) discussed the problems of Na determinations when large amounts of Ca and phosphate are present. Yet the accuracy of the Na data reported here seems to be acceptable as judged by the results on the NBS Standard Reference Material sample (see Experimental Section).

Comparison of means of constituents in HRS and HRW wheats (Table II) was made by analysis of variance and showed statistically significant differences (p < 0.05) for protein, ash yield, and the mineral elements Ca, Cd, K, Mg, Na, P, total S, Sr, and Zn. With the exception of Cd, the HRW wheat cultivars contained the lower amounts. This is consistent, so far as comparisons can be made, with the results given by Greaves et al. (1940), the only published report that, to our knowledge, compares cultivars of these two classes of wheat grown under uniform conditions. An earlier report (Sullivan and Near, 1927) stated that cultivars of HRS contain more total ash than do cultivars of HRW, and the mineral composition of different wheats varies considerably. The differences in protein content between the two classes clearly seem to be genetically controlled, but apparently there are equally strong environmental influences involved in the grain protein content of wheat (Miezan et al., 1977). Of course, the only obvious environmental factor with a uniform garden plot would be the planting season—autumn vs. spring.

When looking at cultivars within grain types, we are impressed with the general uniformity in concentrations. With the exception of Cd in oats, Si in oats, durum, and hard red wheats, and Na in HRW, the differences between

the maximum and minimum concentrations vary by factors of 2 or 3 at the most and generally are less. In their study of the composition of several cultivars of Kansasgrown wheat, Schrenk and King (1948) concluded that the variety was not nearly so great an influence as the location in which the wheat was grown. Ashton (1938) came to the same conclusion for cultivars of oats grown under similar conditions in Wales. In this present study the HRW wheat cultivar Hi Plains (Table II) is clearly an unusual variety in that it is more similar to HRS wheat in its protein and Ca content but unlike both HRS and HRW wheat in Cd and Se levels. In Table III, the durum wheat cultivars are quite similar compositionally, with the exception of Si. Among the oat cultivars (Table V), cv. Astro is notably high in its ash yield and in the concentrations of B. Ba. Ca, Si, and Sr. Conversely, it shows the lowest concentrations of Cu, Mo, and S. The barley cultivars (Table IV) are all similar compositionally; Se and total S levels are especially uniform.

A comparison across grain type in Tables II-V shows K, P, total S, Mg, and Ca, in decreasing order, to be the main mineral elements. This is consistent with a summary report on wheat by Toepfer et al. (1972). Although durum is genetically different from the hard red wheats (HRS and HRW), its protein, K, and total S contents are nearly the same as those of HRS. The HRS and HRW classes of wheat, although genetically similar, are significantly different in the levels of these constituents. Elements that show considerable uniformity, on average, among grain types are the major constituents K, Mg, P, and S and the minor constituents Ba, Sr, Cu, Se, and Zn. In contrast, notably high concentrations of Cd are found in durum, Ca, Mo, and particularly Ni in oats, and Na in barley.

In conclusion, this study indicates that hard red and durum wheats, oats, and barley grains are generally quite similar in their mineral element composition and for the main elements show the following pattern: K > P > S >Mg > Ca. Moreover, with a few exceptions, cultivars within a particular grain type have fairly uniform concentrations. The results suggest that environment must exert a strong influence on differences in mineral composition observed in grains collected from various localities throughout the United States.

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