Elemental Composition of Oat Groats

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Concentrations of P, K, Mg, Fe, Zn, and Mn were determined by emission spectroscopy in groats from six cultivars of oats (*Avena sativa* L.) grown in 1971 and 1972. For 1972, data were also obtained for Ca, Cu, B, and Ba. Protein concentration and groat weight were determined both years. Univariate analyses of variance revealed significant differences among cultivars for each element, protein, and groat weight. Multivariate analysis of variance indicated significant differences among cultivar mean vectors. The close association between multivariate analysis of variance and partitioning of the covariances is pointed out. Positive genotypic correlations were obtained among elemental and protein concentrations, but elemental and protein concentrations were negatively correlated with groat weight. Bran contained higher elemental concentrations than endosperm, and differences among cultivars in per cent bran probably accounted for the positive correlations among elements.

Oats is an important feed grain in temperate regions of the world, and a small but significant portion of the crop is used for human consumption, primarily in the form of rolled oat groats or oat flour. Current interest in nutritional value of our food has caused some oat millers to become highly conscious of the protein concentration of oats which they purchase. While oat cultivars are characterized as to their relative protein concentration, little is known about genetic differences in elemental composition, which may also be of nutritional significance for food and feed.

Differences in elemental concentration among cultivars of corn (Gorsline *et al.*, 1964), barley, wheat, and soybeans (Kleese *et al.*, 1968) have been demonstrated. Morgan (1968) analyzed 171 samples of oats for elemental composition. Mean values and ranges were reported, but the data were not tabulated by cultivar. Our objective was to analyze groats of several oat cultivars adapted to the north-central United States for elemental concentrations to determine whether differences existed. Furthermore, we wished to establish whether there was any relationship among the concentrations of various elements, or between any of the elements and protein concentration or groat weight.

MATERIALS AND METHODS

Plant Culture. Six oat cultivars were grown in randomized complete block experiments at Madison, Wis. One of these, X-1196, is a breeding selection from the oat improvement program of the Wisconsin Agricultural Experiment Station; all others are named varieties. Six replications were planted in 1971 and four in 1972. All plots were fertilized with 11.2 kg of N, 4.9 kg of P, and 9.3 kg of K/ha prior to planting each year.

Sampling and Analysis. At maturity, 4.9 m of row were harvested by hand, threshed, and a representative sample of the oats dehulled with an impact type dehuller. Broken groats were removed, and the remaining intact groats were ground in a Udy Cyclone Sample Mill (Udy Analyzer Co., Boulder, Colo.). Groat samples from a single plot each of Dal and Lodi from the 1972 experiment were milled on a Brabender Quadrumat, Jr., laboratory mill to obtain bran and endosperm fractions. The ground samples were analyzed for elemental concentration by emission spectroscopy at International Minerals & Chemical Corporation, Libertyville, Ill. In 1971, data were obtained on concentrations of P, K, Mg, Fe, Zn, and Mn. In 1972, larger samples were analyzed, so that accurate determinations were also obtained for Ca, Cu, B, and Ba. Groat protein concentration was determined on an "as is" moisture basis by multiplying Kjeldahl N by 6.25. Groat weight was determined on samples of 200–400 groats.

Statistical. The data for P, K, Mg, Fe, Zn, Mn, protein, and groat weight were analyzed separately for each variable by combined analysis of variance over both years (Cochran and Cox, 1957). A model, in which cultivars and years were fixed and blocks were random, was assumed. To test for significant differences between years, the blocks in years mean square was used as the error term. The blocks × cultivars in years mean square was the error term used for testing significance among cultivars. The other four elements, for which valid data were obtained only in 1972, were analyzed separately as a randomized complete block experiment. In these analyses and all others, a probability of 0.05 was chosen as the level of significance. When the differences among cultivar effects were significant, the Student–Newman–Keul's procedure (Steel and Torrie, 1960) was used to judge significant differences among cultivar means.

The data were further analyzed by (1) multivariate analysis of variance and (2) analysis of covariance with correlation coefficients partitioned into genotypic and environmental components. The data for each year's experiment were analyzed separately, because efficient computing techniques were not readily available for multivariate analysis of combined experiments. When measurements are taken on the dependent variables, elemental and protein concentration and groat weight, within each experimental unit (*i.e.*, groat sample), these variables are highly correlated for that sample. In appealing to multivariate techniques, we can use all of the information available from the sample, including the covariances between the dependent measures.

Moreover, the multivariate analysis of variance table for a randomized complete block design contains all of the information required to perform the partitioning of covariances into environmental and genotypic components (Steel and Torrie, 1960, pp 313, 317; Kramer, 1972, p 151). Thus, the independent univariate analyses along with the usual covariance analysis are essentially performed simultaneously by a multivariate analysis of variance.

In the multivariate analysis of variance, tests of a cultivar main effect, say, relate not to the individual cultivar means separately but to a vector of cultivar means taken as a whole. Here, each cultivar mean for the six elements,

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Table I. Elemental and Protein Concentrations of Groats and Groat Weights of Six Oat Cultivars for 1971 and 1972

		Cultivar							
	Year	Dal	Froker	Lodi	Orbit	X-1196	Goodland	Mean	$s_{\bar{x}}$[a]
P, %	1971	0.62	0.53	0.55	0.51	0.51	0.60	0.55	
	1972	0.59	0.53	0.55	0.48	0.50	0.58	0.54	
	Mean	0.61a[b]	0.53c	0.55b	0.50d	0.50d	0.59a		0.008
K, %	1971	0.42	0.34	0.39	0.32	0.36	0.38	0.37*[c]	
	1972	0.56	0.47	0.53	0.46	0.55	0.49	0.51	
	Mean	0.47a	0.39bc	0.45ab	0.38c	0.43abc	0.42abc		0.016
Mg, %	1971	0.21	0.17	0.19	0.17	0.17	0.20	0.18	
	1972	0.21	0.17	0.20	0.18	0.17	0.19	0.19	
	Mean	0.21a	0.17b	0.19a	0.17b	0.17b	0.20a		0.002
Fe, ppm	1971	43.9	40.8	41.5	40.5	40.3	48.3	42.6*	
	1972	55.2	50.9	55.6	49.2	47.3	52.8	51.8	
	Mean	48.3ab	44.8ab	47.2ab	44.0b	43.1b	50.1a		1.415
Zn, ppm	1971	35.5	32.6	33.1	33.6	31.0	41.4	34.5	
	1972	38.6	38.8	37.6	32.4	33.2	41.9	37.1	
	Mean	36.7b	35.1bc	34.9bc	33.1c	31.9c	41.6a		0.868
Mn, ppm	1971	51.5	44.5	45.5	37.9	38.6	41.1	43.2*	
	1972	57.2	53.1	52.9	38.3	46.7	44.4	48.7	
	Mean	53.7a	48.0b	48.4b	38.1c	41.8c	42.5c		1.221
Protein, %	1971	19.7	17.1	17.3	17.7	16.1	21.2	18.2	
	1972	20.2	17.4	17.2	16.2	15.5	20.6	17.8	
	Mean	19.9b	17.2c	17.2c	17.1c	15.9d	20.9a		0.158
Groat wt, mg	1971	23.8	26.5	28.5	29.8	31.9	24.3	27.5*	
	1972	18.9	22.0	20.7	21.4	23.9	20.6	21.2	
	Mean	21.9d	24.7c	25.4c	26.4b	28.7a	22.8d		0.336

[a] Standard error of the mean, based on blocks × cultivars in years mean square. [b] Mean values followed by the same letter within a variable are not significantly different at the 0.05 probability level. [c] An asterisk indicates significant difference between years at the 0.05 probability level.

Table II. Elemental Concentrations of Groats of Six Oat Cultivars Grown in 1972

	Cultivar						
Element	Dal	Froker	Lodi	Orbit	X-1196	Goodland	$s_{\bar{x}}$
Ca, %	0.065a[a]	0.063a	0.055ab	0.043c	0.050bc	0.050bc	0.003
Cu, ppm	4.30c	4.16c	5.45b	4.15c	4.65c	6.07a	0.188
B, ppm	1.71a	1.07b	1.02b	0.80b	0.91b	1.06b	0.177
Ba, ppm	0.81a	0.43b	0.78a	0.43b	0.74a	0.58ab	0.068

[a] Mean values followed by the same letter are not significantly different at the 0.05 probability level.

protein, and groat weight is a component of an eight-dimensional vector about which inferences are to be drawn.

Two tests, the likelihood ratio test and the union intersection test (Kramer, 1972), were performed to determine whether significant differences existed among cultivar mean vectors. Significant differences among cultivar mean vectors will arise because of differences among cultivars for some or all components of those vectors. Simultaneous confidence intervals were then calculated for the means of the individual variables for pairs of cultivars (Kramer, 1972) to determine which cultivars and which variables were responsible for the significant results obtained by these two multivariate tests.

RESULTS

The concentrations of six elements in groats of six oat cultivars for two seasons are presented in Table I. Cultivar mean values over both seasons differed significantly for each element, as determined by separate univariate analyses of variance. Elemental concentrations, averaged over all cultivars, were significantly higher in 1972 than in 1971 for K, Fe, and Mn. The cultivar × year interaction was significant only for P. For this element, Froker and Lodi had equal concentrations both years, while the other four cultivars were higher in 1971.

Data for Ca, Cu, B, and Ba are presented in Table II.

Table III. Elemental Concentrations of Bran and Endosperm Fractions of Two Oat Cultivars

	Cultivar			
	Dal		Lodi	
Element	Bran	Endosperm	Bran	Endosperm
P, %	1.02	0.26	0.86	0.28
K, %	1.00	0.16	0.97	0.21
Mg, %	0.38	0.07	0.33	0.08
Ca, %	0.11	0.02	0.10	0.03
Fe, ppm	89.8	18.2	92.1	22.5
Zn, ppm	58.5	24.3	50.2	27.8
Mn, ppm	87.8	30.8	75.5	32.4
Cu, ppm	4.93	2.82	6.41	3.17
B, ppm	2.82	0.00	2.62	0.00
Ba, ppm	2.50	0.10	2.30	0.59

Again, there were significant differences among cultivar means for each of the elements.

Goodland was highest in protein concentration, and Dal was also higher than the other four cultivars. The protein concentration of X-1196 was significantly lower than that of the other cultivars (Table I). These results are consistent with past observations over several seasons (Shands,

Table IV. Phenotypic (r_p), Genotypic (r_g), and Environmental (r_e) Correlations among Elemental and Protein Concentrations and Weights of Oat Groats[a]

1971

Character	Corr. coeff.	P	K	Mg	Fe	Zn	Mn	Protein
K	r_p	0.78*						
	r_g	0.86						
	r_e	0.75						
Mg	r_p	0.96*	0.83*					
	r_g	0.94	0.90					
	r_e	0.91	0.73					
Fe	r_p	0.80*	0.74*	0.80*				
	r_g	0.82	0.53	0.76				
	r_e	0.90	0.82	0.86				
Zn	r_p	0.73*	0.54*	0.69*	0.81*			
	r_g	0.74	0.38	0.68	0.97			
	r_e	0.82	0.70	0.72	0.83			
Mn	r_p	0.67*	0.75*	0.71*	0.57*	0.38*		
	r_g	0.70	0.77	0.72	0.20	0.09		
	r_e	0.70	0.76	0.73	0.82	0.71		
Protein	r_p	0.65*	0.30	0.54*	0.51*	0.78*	0.25	
	r_g	0.86	0.51	0.80	0.94	0.96	0.31	
	r_e	0.12	−0.57	−0.64	0.08	0.24	−0.21	
Groat wt.	r_p	−0.61*	−0.27	−0.47*	−0.26	−0.42*	−0.36*	−0.68*
	r_g	−0.88	−0.59	−0.80	−0.75	−0.73	−0.69	−0.84
	r_e	0.22	0.15	0.20	0.27	0.21	0.29	0.28

1972

Character	Corr. coeff.	P	K	Mg	Fe	Zn	Mn	Ca	Cu	B	Ba	Protein
K	r_p	0.49*										
	r_g	0.36										
	r_e	0.66										
Mg	r_p	0.88*	0.56*									
	r_g	0.83	0.43									
	r_e	0.95	0.70									
Fe	r_p	0.79*	0.45*	0.77*								
	r_g	0.85	0.27	0.92								
	r_e	0.76	0.61	0.63								
Zn	r_p	0.87*	0.17	0.63*	0.68*							
	r_g	0.86	−0.03	0.51	0.66							
	r_e	0.88	0.40	0.83	0.70							
Mn	r_p	0.71*	0.57*	0.60*	0.65*	0.57*						
	r_g	0.65	0.57	0.51	0.63	0.47						
	r_e	0.89	0.71	0.87	0.77	0.84						
Ca	r_p	0.66*	0.48*	0.49*	0.63*	0.58*	0.91*					
	r_g	0.66	0.39	0.42	0.56	0.54	0.97					
	r_e	0.64	0.67	0.65	0.66	0.55	0.79					
Cu	r_p	0.09	0.17	0.00	0.21	0.14	−0.05	−0.10				
	r_g	0.28	0.27	0.08	−0.01	0.38	−0.19	−0.27				
	r_e	0.01	0.08	−0.05	0.20	0.04	−0.04	−0.17				
B	r_p	0.61*	0.70*	0.56*	0.58*	0.35	0.62*	0.61*	0.21			
	r_g	0.80	0.54	0.72	0.64	0.48	0.76	0.81	−0.10			
	r_e	0.42	0.85	−0.43	0.61	0.24	0.51	0.56	0.26			
Ba	r_p	0.31	0.57*	0.36	0.39	0.02	0.44*	0.27	0.18	0.43*		
	r_g	0.47	0.96	0.62	0.48	0.08	0.56	0.34	0.31	0.52		
	r_e	0.05	0.17	−0.05	0.26	−0.09	0.18	0.15	0.06	0.29		
Protein	r_p	0.67*	0.06	0.48*	0.48*	0.66*	0.29	0.37	0.16	0.50*	0.18	
	r_g	0.92	0.09	0.70	0.68	0.86	0.36	0.45	0.35	0.70	0.19	
	r_e	−0.30	0.03	−0.28	−0.02	−0.26	−0.27	0.03	0.28	0.19	0.24	
Groat Weight	r_p	−0.50*	0.02	−0.52*	−0.44*	−0.31	−0.26	−0.23	0.04	−0.45*	−0.23	−0.65*
	r_g	−0.79	−0.08	−0.90	−0.86	−0.56	−0.39	−0.42	0.14	−0.72	−0.25	−0.79
	r_e	0.04	0.13	−0.15	0.01	0.13	0.09	−0.03	−0.09	−0.02	−0.34	−0.11

[a] An asterisk indicates $P < 0.05$. Degrees of freedom are: 1971, $r_p = 34$, $r_g = 4$, $r_e = 24$; 1972, $r_p = 22$, $r_g = 4$, $r_e = 14$.

Table V. Cultivar Pairs for Which Simultaneous Confidence Intervals as Determined by the Union Intersection Test Indicated Significant Differences[a]

Protein	Groat wt
Dal–Froker	Orbit–Dal
Dal–Lodi	Orbit–Goodland
Dal–X-1196	X-1196–Dal
Goodland–Froker	X-1196–Froker
Goodland–Lodi	X-1196–Goodland
Goodland–Orbit	
Goodland–X-1196	

[a] For each pair, the cultivar with the greater mean is listed first. $P < 0.05$.

1974). All cultivars had heavier groats in 1971 than in 1972, and differences among cultivar means were significant (Table I). Cultivar × year interactions were significant for both protein concentration and groat weight. Dal and Froker had higher protein concentrations in 1972 than in 1971; all other cultivars had higher concentrations in 1971. All cultivars had higher groat weights in 1971 than in 1972, but differences between years were greater for some cultivars than for others.

Elemental concentrations of bran and endosperm for Dal and Lodi are shown in Table III. As expected, concentrations in the bran were considerably higher than those in the endosperm for all elements. Statistical analysis was not possible with this unreplicated data.

Positive, significant phenotypic correlations were obtained among all elemental concentrations in 1971, and among most in 1972, the notable exception being Cu (Table IV). Among the six elements in common, results were generally similar both years except for K with Mg and Zn. The positive significant correlations of P, Mg, Fe, Zn, and B with protein concentration were accounted for by the genotypic component. All elements except Cu were negatively correlated with groat weight, both phenotypically and genotypically.

With regard to the multivariate analysis, the likelihood ratio test statistic, U, obtained for the 1971 experiment was 0.00016. This statistic was smaller than the critical value, $U_{(8,5,25)}(0.05) = 0.8520$, indicating that cultivar mean vectors were significantly different. The union intersection test statistic, θ, was 0.988, larger than the critical value of $\theta_{(5,1,8)}(0.05) = 0.7125$. This result also supported the conclusion that significant differences existed among cultivar mean vectors. Analysis of the 1972 data by these tests also indicated significant differences, although these tests were weak because of the greater number of variables (12) and fewer degrees of freedom for error (15).

Table V indicates the variables and cultivar pairs whose means were significantly different, *i.e.*, for which simultaneous confidence intervals did not encompass zero, for the 1971 experiment. The multivariate analysis did not indicate any significant differences among cultivars for elemental concentrations, but there were differences in protein concentration and groat weight.

DISCUSSION

The separate univariate analyses of variance indicated significant differences among cultivars for each element, protein, and groat weight (Table I), and when all dependent variables were considered together by multivariate analyses, significant differences among cultivar mean vectors were found for each year. However, when simultaneous confidence intervals were computed to compare pairs of cultivars for each variable, significant differences were found only for protein concentration and groat weight. This is not surprising, for the length of simultaneous confidence intervals in a multivariate analysis is much greater that that in a univariate analysis. Moreover, this discrepancy becomes greater as the number of variables is increased. With eight dependent variables, the simultaneous confidence intervals were sufficiently broad that cultivar differences for the elemental concentrations did not appear significant. That protein concentrations and groat weights showed significant differences among cultivars is due, in part, to the smaller variability in these measurements.

The failure of multivariate analysis to support entirely the results of the univariate analyses should not be viewed with alarm. The comments above regarding lengths of simultaneous confidence intervals indicate that the multivariate procedure for this problem is a statistically conservative one. However, its results should not be ignored. Kramer (1972) has cited some cogent examples to illustrate that, by disregarding this covariance structure and performing only independent univariate analyses, one can be led to erroneous conclusions. Then, too, there is a certain amount of efficiency gained by performing the multivariate analysis straight away rather than performing separate univariate analyses followed by a partitioning of covariance.

The many significant positive correlations between pairs of elements indicate that kernel morphology may have a predominant influence upon their concentrations. All elements were more concentrated in the bran than in the endosperm (Table III). Although we did not determine the percentage of bran and endosperm in these experiments, Youngs (1972) previously reported such data for some of these cultivars. In fact, those cultivars containing higher concentrations of elements (Dal, Goodland) had a higher percentage of bran (Youngs, 1972; Dal and Goodland were identified as X-1289 and X-1656, respectively).

Likewise, the negative correlations between elemental or protein concentrations and groat weight are probably caused by the higher bran percentage found in smaller groats (Youngs, 1972).

The negative associations between groat weight and elemental concentrations were accounted for by genotypic effects, as the environmental components of the covariances were of opposite sign. However, a comparison of data from 1971 with 1972 indicates than Mn, Fe, and K concentrations increased as groat size decreased. Thus, environmental effects on concentration of these elements need further investigation before valid conclusions may be drawn. For protein, P, and Mg, the decrease in groat size from 1971 to 1972 within cultivars was not associated with increased concentration in our experiment (Table I).

The data indicate the possibility of breeding for nutritional improvement in elemental concentration of oat groats, as Rasmusson *et al.* (1971) previously showed for barley. Requirements for elemental nutrients in the rations of various domestic animals have been tabulated (National Academy of Sciences, 1971, and other sources), and for several elements an increase in content would be beneficial to the diet of animals whose ration consisted predominantly of oats.

The many positive genotypic correlations obtained between pairs of elements indicate that possibly a breeding objective could be overall increase in concentration of all elements, rather than striving separately for increased amounts of individual elements. In fact, the positive relationship of most elements with protein concentration indicates that increased elemental concentration may be an unintentional result of breeding for increased protein.

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Phytic Acid and Other Phosphorus Compounds of Beans (*Phaseolus vulgaris* L.)

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Fifty cultivated varieties and lines of mature dry beans (*Phaseolus vulgaris* L.) were analyzed for phytic acid, total P, inorganic P, and other than phytate organic P. The respective concentrations on a dry weight basis were: 0.54–1.58, 0.259–0.556, 0.021–0.044, and 0.050–0.135%. A correlation coefficient of 0.9847 was found between total P content and phytic acid content. A protein–phytate complex was also isolated. The observation was made that 99.6% of the total phytic acid was in a water-soluble form.

Beans, as other seeds, are rich sources of phosphorus (P). According to Earle and Milner (1938), P compounds found in seeds may be classified into four groups: phytates, phosphatides, nucleic compounds, and inorganic P compounds.

Phytins, the mixed Ca and Mg salts of *myo*-inositol 1,2,3,4,5,6-hexakis(dihydrogen phosphate), also known as phytic acid, are widespread in nature. They are the principal form of P in many seeds; 60–90% of all the P in these seeds is present as phytic acid (Barré, 1956).

Several physiological roles have been suggested for phytic acid in plants. It may be used as P store (Hall and Hodges, 1966), as energy store (Biswas and Biswas, 1965), or as an initiator of dormancy (Sobolev and Radionova, 1966). Recently, Williams (1970) presented evidence that phytic acid serves only as a source of P and cations for the germinating seed. Asada *et al.* (1968) found that phytate contains over 80% of the total P of mature rice grain and the turnover of phytate P is practically nil in the resting grain. From that they concluded that phytate can be considered a final product of P metabolism in the ripening process.

The animal nutritional importance of phytic acid lies in its ability to chelate several mineral elements, especially Ca, Mg, Fe, Zn, and Mo, and thereby reduce their availability in the intestinal tract (Rackis, 1974; Oberleas, 1973). Bruce and Callow (1934) found that phytic acid reduces the absorption of Ca and is responsible for the rachitogenic properties of certain cereals. Roberts and Yudkin (1960) caused Mg deficiency in rats fed purified diets containing sodium phytate. Evidence was furnished that phytate decreased zinc availability in chicks (O'Dell and Savage, 1960). Earlier, it had been demonstrated that phytic acid interferes with iron absorption in boys (Sharpe *et al.*, 1950).

Phytic acid reacts with proteins to form complex products of varying composition and it has been shown to have an inhibitory effect on the peptic digestion of ovalbumin and elastin (Barré, 1956). This effect is believed to be related to its property to form insoluble combinations with proteins in an acid medium and in a range of pH which corresponds precisely to the optimum for the action of pepsin. It has also been found that elimination of phytic acid from soybean meal extracts is an essential preliminary step to the study of the individual soybean proteins (Smith and Rackis, 1957).

In this work, 50 varieties and lines of mature dry beans (*Phaseolus vulgaris* L.) were analyzed for phytic acid, total P, inorganic, P, and organic P, other than phytic acid. Special attention was directed to a possible relation between total P and phytic acid, and a relation between phytic acid and nitrogen content. A protein–phytate complex in the Sanilac beans (Navy beans) was also isolated and analyzed.

MATERIALS AND METHODS

All the beans analyzed were grown in Michigan and obtained from the Crop and Soil Science Department of Michigan State University.

Total P was determined colorimetrically after digestion of the sample with perchloric acid according to Allen's (1940) method. The determination of inorganic P was based on the colorimetric method of Pons and Guthrie (1946). For the determination of phytic acid a combination of two methods was used. The extraction and precipitation of phytic acid were performed according to the method of Wheeler and Ferrel (1971), while the iron of the precipitate was measured by Makower's (1970) method. A 4:6 Fe/P atomic ratio was used to calculate phytic acid content. Residual P representing nonphytic acid organic P was calculated by subtracting inorganic P and phytic acid P from total P. The protein–phytate complex was isolated from bean flour according to the method of Rackis *et al.* (1961), dried by lyophilization, and analyzed for nitrogen, total P, and inorganic P. The AOAC (1970) Kjeldahl method was followed for the determination of the nitrogen content of beans.

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