THE DETERMINATION BY X-RAY OBSERVATION OF BROMINE AND ZINC LEVELS IN UNTREATED WHEAT FLOUR[1]

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ABSTRACT

The recently developed method of trace element analysis by observation of characteristic X rays with a lithium-drifted silicon detector was used to study levels of heavy elements in wheat flour. The various samples obtained from a pilot mill were each found to contain quantities of zinc at levels of about 2 to 54 p.p.m. and bromine at levels of 2 to 14 p.p.m. An attempt is made to correlate these zinc and bromine concentrations to the standard analyses of ash content and protein level used for flour.

The purpose of this study was to determine if the techniques of trace element analysis by observation of characteristic X rays with a high resolution lithium-drifted silicon [Si (Li)] detector would be a good way to measure bromine levels

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in flour. Since methyl bromide is used as a fumigant during the storage of grains in silos, it is important to determine the amount of bromine present in the processed flour. Untreated (i.e., not exposed to methyl bromide) flour was studied in order to first obtain the levels of bromine that one might expect to be initially present.

In order to obtain information on the location of zinc and bromine concentrations in the wheat, samples from the various stages of a pilot mill were

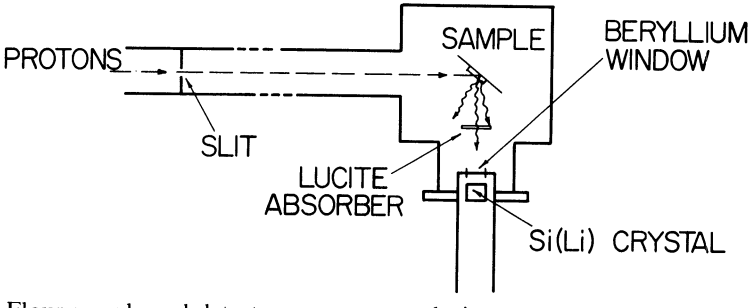

Fig. 1. Flour sample and detector arrangement during proton bombardment.

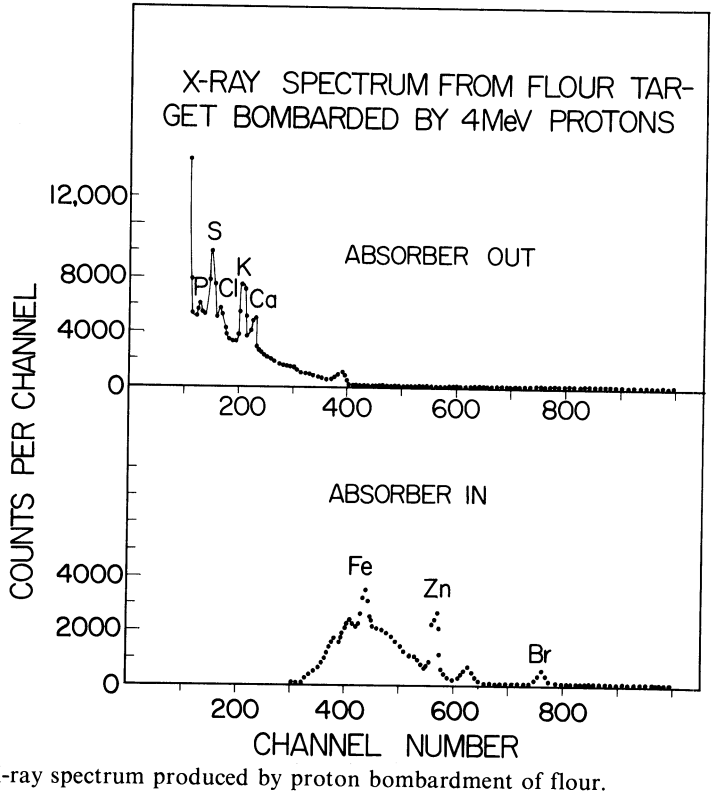

Fig. 2. X-ray spectrum produced by proton bombardment of flour.

analyzed. These samples can be roughly sorted into two categories: 1) bran; and 2) germ and endosperm. Further, since analyses of protein level and ash content were available for each of the samples, linear correlation analysis was applied to the various combinations of zinc, bromine, ash, and protein levels to see if any pattern would be evident.

MATERIALS AND METHODS

Flour samples about 1.3 cm. square and 2 mm. thick were prepared by making a paste of the flour with distilled water (0.5 ml. water in 1 g. of flour) and allowing them to dry in air at room temperature for about 24 hr. The particular variety of wheat used was Scout, grown during 1972 near Hutchinson, Kans. These thin wafers were then cemented with polystyrene to a thin aluminum sheet and placed in a vacuum system. They were bombarded with 4-MeV. protons from the Kansas State University model EN tandem Van de Graaff accelerator to produce X rays (see Fig. 1). Details of this method can be found in the report of Giauque et al. (1). The Si(Li) detector used has a resolution of about 200 eV. for 5.9 keV. X rays. Data were collected in a period of 30 to 60 min. of proton bombardment.

A typical spectrum is shown in Fig. 2. In the upper portion one can easily see the X ray peaks from P, S, Cl, K, and Ca, indicating the presence of these elements. (Note the gap between Cl and K where Ar would occur.) However, the higher energy X rays from heavier elements are at a much lower level. In order to

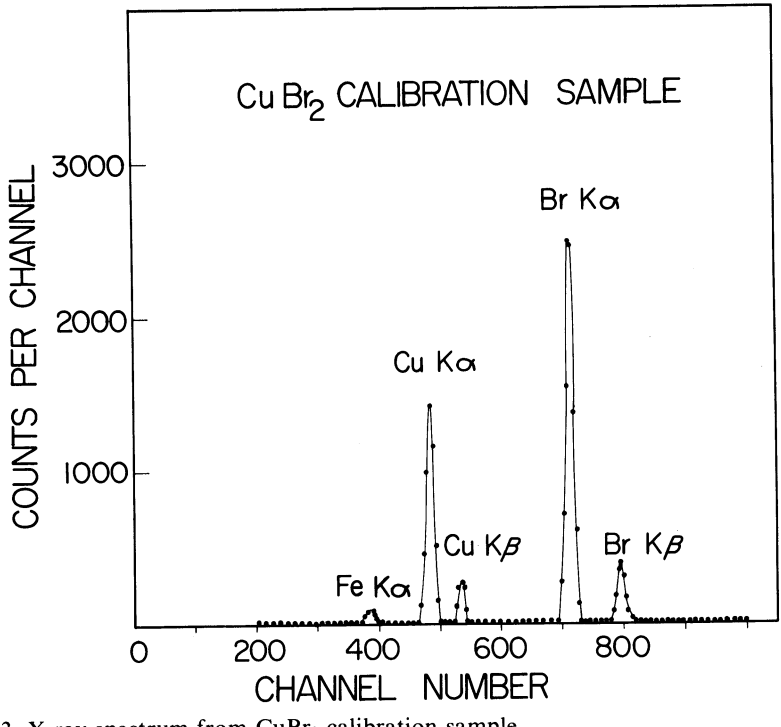

Fig. 3. X-ray spectrum from $CuBr_2$ calibration sample.

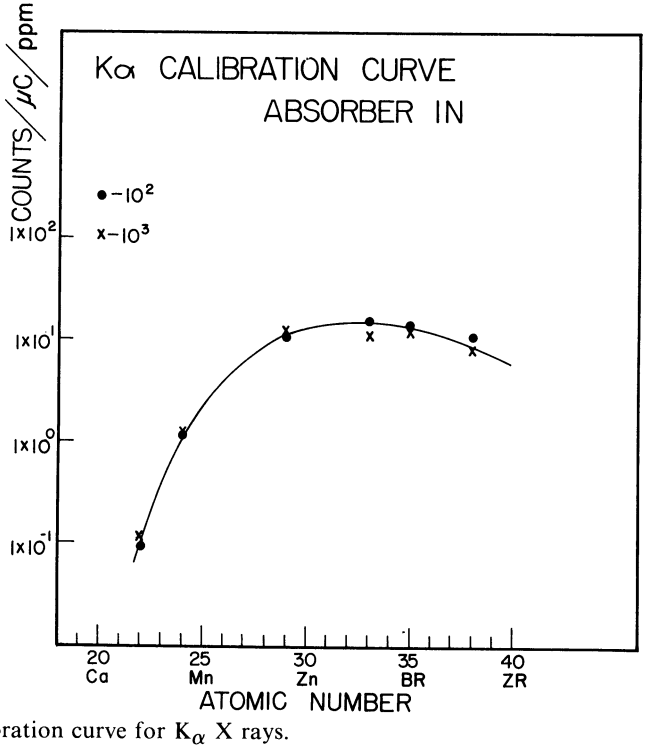

Fig. 4. Calibration curve for K_α X rays.

TABLE I
Zn and Br Concentrations in Pilot Mill Samples

Sample	Zn p.p.m.	Br p.p.m.
1 MB	4.2	5.0
1 MT	8.6	4.4
2 MT	21.1	4.2
2 MB	8.9	2.0
FST	17.1	3.2
CSB	9.3	5.0
FSB	13.8	10.6
3 M	2.6	3.2
CST	27.8	6.6
123 BK Red	7.4	8.5
2 BK	26.6	6.5
3 BK	13.4	2.3
4 M	17.8	10.2
2 Q	17.7	5.4
4 BK	9.4	4.7
P BK	11.6	4.6
1 T	9.5	5.0
SUC	48.6	13.8
5 M	26.1	12.1
5 BK	16.1	4.2
6 M	14.9	7.1
B & SO	53.5	6.4
St. Grade	15.2	6.8

enhance the relative amount of these higher X rays in the spectrum, a 1/16-in. Lucite® sheet was placed over the detector to absorb all of the X rays from elements up to Ca. In the lower spectrum, labeled "Absorber in," there are peaks from Fe, Zn, and Br. The Fe peak is partially due to some stainless steel in the vacuum chamber, and the small peak to the right of the Zn peak is the Zn K_β X ray.

Calibration of the system for absolute yields was performed by preparing flour mixed with concentrations of one part in 10^2 or one part in 10^3, by weight, for various chemicals. A typical calibration spectrum is shown in Fig. 3 for $CuBr_2$. At these levels of 1 and 0.1% for the calibration samples, any Br that occurs naturally in the target is negligible by comparison. Also, at these levels problems of accurate weighing and mixing are much reduced. A further check on the reliability of the procedure is obtained by the use of the two calibration samples at both 1 and 0.1%. The calibration curve obtained from these techniques is shown in Fig. 4. Since the X ray production cross sections depend smoothly upon atomic number (2), a smooth curve can be drawn from element to element. This is one of the primary advantages of this technique over other analysis procedures where adjacent elements require different analysis. Data analysis consists then of comparing the number of X ray counts obtained in a flour sample to the number of counts expected for 1 p.p.m. after correcting for the relative amount of proton charge collected.

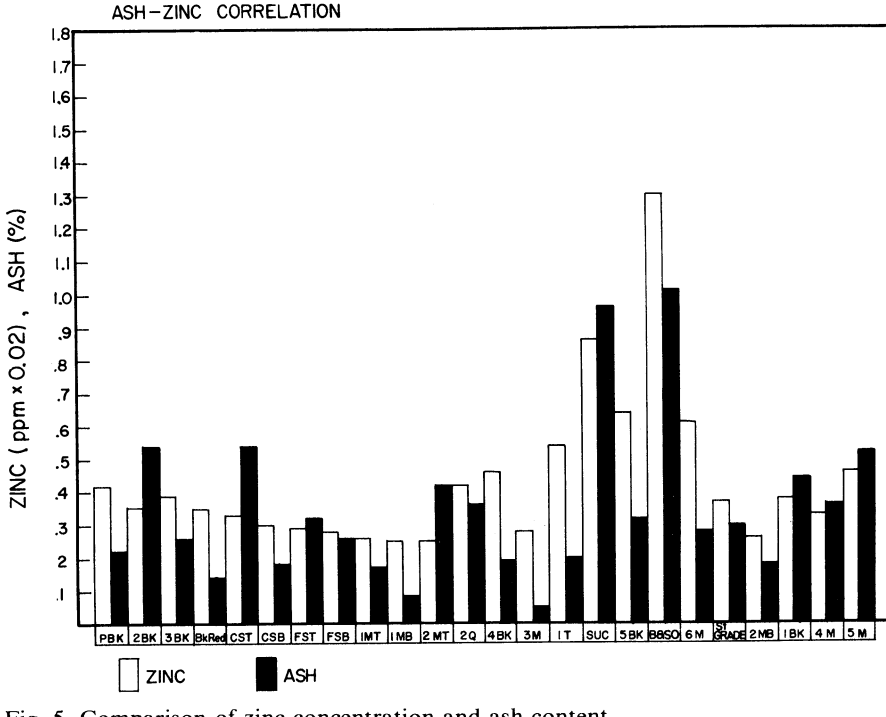

Fig. 5. Comparison of zinc concentration and ash content.

RESULTS AND DISCUSSION

The data obtained are presented in Table I. The concentrations of bromine varied from 2.0 to 13.8 p.p.m. in the various samples, with a value of 6.8 p.p.m. in the straight-grade flour. These levels are consistent with those reported in other work (3).

The flour samples from a pilot mill come from various stages of grinding and sifting, but are not directly categorizable as the bran, endosperm, and germ

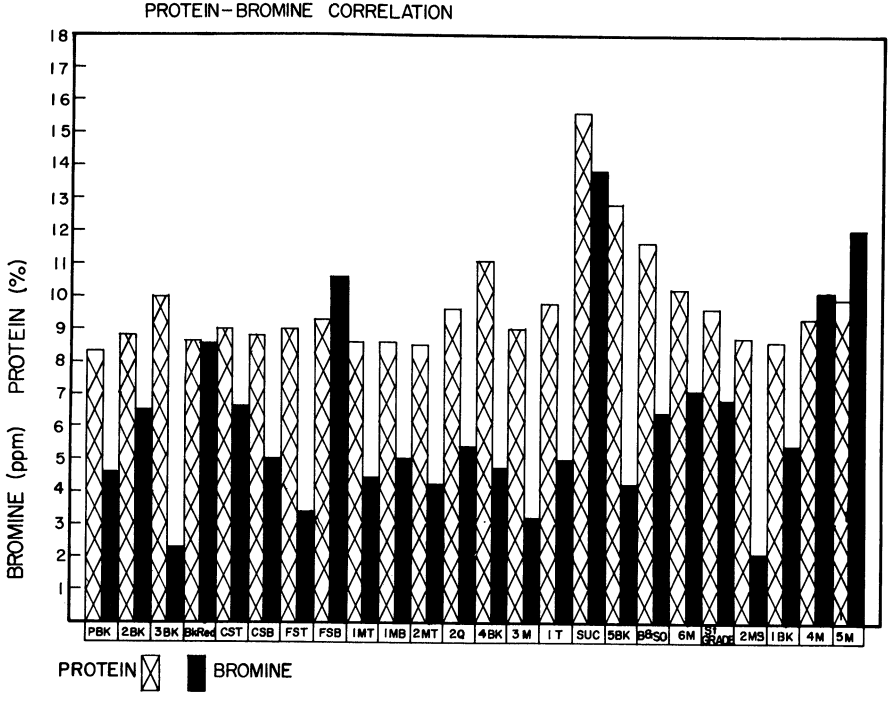

Fig. 6. Comparison of bromine concentration and protein content.

TABLE II
Linear Correlation Coefficients r

Comparison	r	P(r) from Random Samples %
Zn-ash	0.76	<0.1
Br-protein	0.40	5.3
Zn-protein	0.56	0.4
Br-ash	0.29	17.5
Zn-Br	0.52	0.9
Protein-ash	0.67	<0.1

portions of the wheat kernel. The 1 BK, 2 BK, 3 BK, and 4 BK portions are sifted after grinding, with the coarser parts becoming the 5 BK sample. After further grinding, the coarse component of 5 BK is the bran. However, the germ and endosperm are the result of further grinding of the finer components of the BK series, and are the bulk of the flour output. (For a more complete discussion of the pilot mill, consult reference 4.)

Wheat flour is normally tested for its ash content; the amount of ash left after heating at 550° C. for 12 to 14 hr.; and the amount of protein, based on nitrogen content (5). One would expect that the ash content would be correlated with the amount of metal salts present, and, as shown in Fig. 5, this appears to be qualitatively true, for the zinc. Note that the BK series samples are relatively high in zinc and ash content, as expected for the bran, while the fine component after several grindings and siftings, such as 1 MT, 2 MT, and 3 M are relatively low. A similar apparent correlation between bromine level and protein is shown in Fig. 6, although it is not so striking.

Linear correlation coefficients r (6) have been calculated for the different combinations of ash, zinc, bromine, and protein, and are presented in Table II. Column 3 gives the probability for obtaining the value r for a random set of data, based on 24 samples. Since the coefficient r would be unity for perfect correlation, the value of 0.76 for the Zn-ash correlation is high. The bromine, at only 0.29, is relatively uncorrelated with ash. All other combinations show some correlation, so further arguments as to relative association of bromine, protein, etc., cannot be strongly made.

In conclusion, the method of using high-resolution X ray detectors to determine levels of heavy elements in biological samples, such as flour, appears to be useful for obtaining concentrations down to a few p.p.m. The chief advantages of the technique are that a large number of elements can be analyzed at the same time, and that absolute calibrations can be carried out in a straightforward manner. These studies will be extended to flour samples from wheat that has been fumigated with methyl bromide.

Acknowledgment

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Literature Cited

1. GIAUQUE, R. D., GOULDING, F. S., JAKLEVIC, J. M., and PEHL, R. H. Trace element determination with semiconductor detector X-ray spectrometers. Anal. Chem. 45: 671 (1973).
2. MERZBACHER, E., and LEWIS, H. W. X-ray production by heavy charged particles. Handbuch der Physik, Vol. 34, p. 166. Springer-Verlag: Berlin (1958).
3. UNDERWOOD, E. J. Trace elements in human and animal nutrition; 3rd ed., p. 434. Academic Press: New York (1971).
4. Annual report of the 1972 Hard Winter Wheat Quality Council. Kans. State Agr. Exp. Sta., Bull. 572; Kans. State Univ. (1972).
5. AMERICAN ASSOCIATION OF CEREAL CHEMISTS. Approved methods of the AACC (7th ed.). The Association: St. Paul, Minn. (1962).
6. BEVINGTON, P. R. Data reduction and error analysis for the physical sciences; pp. 172ff. McGraw-Hill: New York (1969).

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