

CHLORIDE CONTENT OF CAKE FLOURS AND FLOUR FRACTIONS¹

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ABSTRACT

Unbleached cake flours contained 43 to 54 mg. chloride per 100 g. flour. Over 60% of this chloride appeared in the water-solubles. The other fractions were very low in chloride content. However, the prime starch, which often amounted to over 70% of the flour in these low-protein cake flours, contained 20 to 25% of the flour chloride.

Chlorine-bleached cake flours contained 131 to 189 mg. chloride per 100 g. flour. Nearly all this increased chloride was in and rather equally divided between the water-solubles and the gluten. The tailings contained a small part of the increased chloride, and the prime starch had very little of the increase. The chloride of the bleached water-solubles appeared almost entirely in the low-molecular-weight part. More than half of the chloride of the bleached gluten was held in the lipids, but the protein residue retained substantial amounts.

In a cake flour treated with chlorine at five different levels, the increased chloride appeared chiefly in and about equally divided at all levels between the water-solubles and the gluten. The tailings gained chloride slowly. The prime starch did not show any consistent increase.

An improvement in an acetic acid fractionation procedure for flour was made by recovering the soluble protein from the supernatant by dialysis and lyophilization. This made possible 98 to 99% recoveries of dry matter and protein.

Today practically all cake flours are bleached with chlorine or some blend of gases in which chlorine is the principal constituent, but very little is known of the chemistry involved. Earlier work at this laboratory (16) had shown that bleached prime starch was responsible for most of the improvement from bleaching, but that bleached gluten accounted for some.

The determination of the chloride content of bleached prime starch compared to that of unbleached prime starch was the first objective of the present study. After preliminary work showed that bleached prime starch had a very low chloride content, the study was extended to the other fractions. About 150 to 200 mg. of chlorine are required to bleach 100 g. of flour to a pH of 4.8, and the fate of that chlorine after bleaching is the subject of this paper.

Several earlier workers determined the chloride content of flours. Bailey (2) has reviewed the earlier work. Utt (21), in 1914, obtained

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samples of the same flours before and after chlorine bleaching in a Kansas flour mill. He found chloride contents ranging from 0.044 to 0.58% — this is equivalent to 44 to 58 mg. chloride per 100 g. flour — for unbleached flours and from 0.065 to 0.097% for bleached flours. These flours were evidently intended for bread-baking, and the level of chlorine treatment probably was lower than that used today for cake flours, since one authority (9) quoted levels of 1 to 2 oz. per 280 lb. for bread flours and 4 to 5 oz. for cake flours. Sullivan and Howe (19) reported 0.051% for an unbleached patent flour from a hard spring wheat. Pap (12) found that 32 Hungarian flours ranged from 0.060 to 0.074%; it is not clear whether all these flours were unbleached. Damiens and Blaignan (5) obtained 43 to 77 mg. chloride per 100 g. flour.

Materials and Methods

Flours. Both commercial and laboratory-milled cake flours were used in this study. The commercial cake flours were included in each experiment. The first lot of commercial cake flour, from the 1957 crop, became depleted during this study; another lot, from the 1959 crop, was obtained. Both lots were milled from western soft wheats. Each lot contained an unbleached flour and a flour bleached at the mill with chlorine to pH 4.8.

The laboratory flours were prepared by combining the first two break streams and the first two reduction streams from a Buhler mill and passing the composite through a 200-mesh stainless-steel screen. One laboratory flour was milled from Brevor wheat, a soft, white common variety; and the other was from Elmar, a club wheat. Both varieties have good cake-baking quality. These flours were similar in particle size distribution to the commercial cake flour and yielded layer cakes of similar volume and texture.

Flour Bleaching. A portion (400 g.) of each laboratory-milled flour was treated in a laboratory bleacher at room temperature (72°F.) with chlorine gas of 99.5% purity. The flour was placed in the bleacher, the bleacher was evacuated to about 400 mm. mercury, the chlorine was introduced over a period of 1 minute with agitation, and agitation was continued for 4 minutes. Before the desired flour was treated, several preliminary batches were bleached and discarded; this was to remove air from most of the apparatus. The results obtained were:

Flour	Before Bleaching			Chlorine mg/100 g flour	After Bleaching		
	Moisture	Protein	pH		Immediate pH	Storage Time	pH at Fraction- ation
	%	%				days	
Brevor	12.1	6.9	5.82	200	4.92	28	4.84
Elmar	12.3	7.4	5.84	220	4.83	5	4.81

Portions (500 g.) of the 1959 unbleached commercial cake flour were bleached at five different levels in the laboratory bleacher. This flour had a moisture content of 12.6%, a protein content of 6.87% at 12.6% moisture, and an initial pH of 5.91. The results obtained were:

Chlorine mg/100 g flour	pH Immediately after Bleaching	At Fractionation	
		pH	after Bleaching days
48	5.58	5.50	2
96	5.24	5.22	6
144	5.05	4.90	8
192	4.79	4.41	13
240	4.40	4.22	15

About 190 mg. of chlorine per 100 g. flour would have given a pH of 4.8 at the time of bleaching, and about 154 mg. of chlorine would have resulted in a pH of 4.8 after 1 or more weeks of storage.

Flour Fractionation. All fractionations but one were made by a modification of the acetic acid extraction procedures (14,15). Concentration of the water-extract was omitted, and a dry product was obtained by shelling and lyophilizing the water-extract. The suspension of bleached flour and distilled water was adjusted to pH 6.0 (15). The gluten that precipitated was obtained, and, in addition, the soluble protein remaining in the supernatant, after neutralization and centrifugation, was recovered.

The recovery of soluble protein was made by dialysis followed by lyophilization. The unconcentrated supernatant (pH about 6.0) was dialyzed against distilled water with changes of water at 2-hour intervals four times each day for 2 days. In one experiment, a large volume of supernatant was divided into four equal portions, and portions were dialyzed for two, four, six, and eight changes of water. The soluble protein was recovered and analyzed. The results were:

Times Water Changed	Weight Recovered g	Percent Protein %	Amount Protein Recovered g
2	0.66	34.7	0.23
4	0.52	43.8	0.23
6	0.46	52.3	0.24
8	0.41	62.0	0.25

The two fractions containing most of the chloride were further subdivided. The water-solubles were separated into the alcohol-solubles (low-molecular-weight materials as sugars and amino acids) and the alcohol-insolubles (water-soluble proteins and polysaccharides)

(17). The water-extracts from several flours were prepared, and each was divided into two equal parts. One part was poured into three volumes of ethanol (17). The alcohol-insolubles were removed by centrifuging and redissolved in water. Aliquots of these solutions and of the supernatants (alcohol-soluble material) were analyzed for dry matter and chloride. From these two values the percent chloride was calculated. Aliquots of the original water-extract were likewise analyzed.

The glutens were separated into the lipid portion and the protein residue by extracting with water-saturated normal butanol (11). Aliquots of the entire butanol extract (crude lipids) were taken, and the butanol evaporated on the steam bath. Chloride was determined on the crude lipids. For dry matter, the lipids and the protein residue were dried at 100°C. under vacuum for 4 hours.

One fractionation was made by the doughing procedure developed by Udy (20) so that fractions from a separation in which acid was not used might be compared with the fractions from the acetic acid separations. This was with the unbleached cake flour; all attempts to fractionate bleached cake flour by doughing were unsuccessful.

Analytical Methods. Moisture, protein, and pH were determined by conventional methods (1,10). Particle size measurements were made by a sedimentation method (15).

Determination of total chloride on a macro scale used ashing for digestion. Samples of 5 g. for flours, prime starches, and tailings and 1 g. for water-solubles and glutens were slurried with 25 ml. of 2% potassium carbonate to prevent loss of chloride (8,19,21), dried on the steam bath, and ashed for 2 hours at 550°C. (8). The ashed samples were transferred to beakers with 5 ml. of 1.5N nitric acid and 50 ml. distilled water, and a conventional gravimetric determination was used (13). Final precipitates ranging from 10 to 50 mg. of silver chloride were obtained except with starches, tailings, and unbleached glutens.

Determination of total chloride on a micro scale required 1 to 100 γ of chloride. These quantities were obtained through either ashing, Carius digestions, or Schöniger combustions. For ashing, samples of 100 mg. were slurried with 6 ml. of 2% potassium carbonate, dried, and ashed for 2 hours at 550°C. (8). The residues were transferred with 5 ml. 1.5N nitric acid and distilled water to either beakers or 50-ml. volumetric flasks. Carius digestions were made by a conventional method (18). Samples of 50 mg. plus 0.5 ml. fuming nitric acid were sealed in glass tubes and heated inside water-pipe bombs for 2 hours at 250°C. The residues were transferred with distilled water to

beakers or volumetric flasks. Schöniger combustions were carried out in a commercial apparatus³. Samples of 50 mg. were burned in oxygen and transferred to beakers or volumetric flasks.

Some of the methods available for determination of chloride on a micro scale have been reviewed by Gunther and Blinn (6). Potentiometric determination followed closely the method of Helmkamp *et al.* (6,7). Best results were obtained when the silver electrode was cleaned and recoated each day with silver chloride. Measurements of mv. were made with a student potentiometer⁴ and a sensitive galvanometer. The colorimetric determination was that of Bergmann and Sanik (3) adapted to a final volume of 59 ml.

Results

Flour Fractionation. The earlier acetic acid extraction procedures for flour fractionation (14,15) gave 97 to 99% recoveries of dry materials but only 83 to 87% recoveries of flour protein for cookie flours and as low as 79% protein recovery for a bleached cake flour. In the present study, the recovery of the protein remaining soluble after neutralization substantially increased the recovery of flour protein, as shown in Table I; 98 to 99% of the protein can be recovered by careful work. Table I also shows the yields and protein contents of the fractions and the protein contents of the original flours.

TABLE I
YIELDS AND PROTEIN CONTENTS OF CAKE FLOURS AND FRACTIONS

MATERIAL	1959 COMMERCIAL UNBLEACHED FLOUR		1959 COMMERCIAL BLEACHED FLOUR		1959 COMMERCIAL UNBLEACHED FLOUR: DOUGHING PROCEDURE	
	Yield ^a	Protein ^b	Yield	Protein	Yield	Protein
	g	%	g	%	g	%
Flour	100.0	6.76	100.0	6.59	100.0	6.76
Fractions						
Water-solubles	4.1	17.7	3.9	15.4	4.5	18.5
Gluten	6.7	69.2	6.4	65.2	5.6	64.6
Soluble protein	1.3	55.9	1.8	56.4
Tailings starch	13.2	3.01	15.0	3.08	21.8	9.15
Prime starch	74.3	0.30	72.6	0.32	67.4	0.28
Dry matter recovery, %	99.6	99.7	99.3
Protein recovery, %	99.5	98.6	99.1

^a Grams at 14% moisture from 100.0 g. flour at 14% moisture.

^b At 14% moisture.

³ Arthur H. Thomas Co., Philadelphia, Pa. Mention of firm names or trade products does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

⁴No. 83411, Central Scientific Co., Chicago, Ill.

TABLE II
CHLORIDE CONTENTS OBTAINED BY DIFFERENT ANALYTICAL METHODS
FOR A BLEACHED CAKE FLOUR AND ITS FRACTIONS

MATERIAL	ASHING PLUS GRAVIMETRIC		ASHING PLUS POTENTIOMETRIC		COMBUSTION PLUS COLORIMETRIC		COMBUSTION PLUS POTENTIOMETRIC	
	Chloride Content ^a	Std. Error	Chloride Content	Std. Error	Chloride Content	Std. Error	Chloride Content	Std. Error
	mg	mg	mg	mg	mg	mg	mg	mg
Flour ^b	125	2	137	1	149	9	89	6
Fractions								
Water-solubles	1,490	14	1,480	35	1,350	36	1,090	14
Gluten	499	3	533	13	520	24	407	7
Soluble protein	272	14	297	9	297	21	194	7
Tailings starch	35	4	39	2	43	6	36	4
Prime starch	7	2	18	4	10	4	6	1
Chloride recovery, %	84	..	85	..	71	..	91	..

^a Chloride in mg. per 100 g. of the fraction or flour indicated; all results are on a 14% moisture basis.
^b A 1957 commercial bleached cake flour.

Chloride Analysis. Table II lists the chloride values obtained by the useful combinations of digestions and determinations for a commercial bleached cake flour and fractions. Three combinations not included in Table II gave high and erratic values for blanks, standards, and samples: ashing followed by colorimetric determination, and Carius digestions with either colorimetric or potentiometric determinations. The gravimetric determination was not used with the digests from the Carius digestion and the Schöniger combustions because of the small sample size. Bethge and Troëng (4) have reported successful combustions of 500 mg. and more by using repeated ignitions with the same absorption liquid.

Ashing plus gravimetric determination gave good recoveries of standards and reproducible values for samples but was tedious and time-consuming. Schöniger combustions followed by colorimetric or potentiometric determinations gave low results, as shown in Table II, although Bethge and Troëng (4) reported higher recoveries for chloride in wood pulp by combustion than by ashing.

Ashing combined with potentiometric determinations gave reproducible values for standards and values for samples that were equal to or slightly higher than results by ashing plus gravimetric determination. Ashing plus potentiometric determination was reliable, was adaptable to large numbers of samples, was tolerant to a large range in sample size, and was rapid. It was adopted for all further analyses in this study.

Recovery of Chloride in Fractions. Recoveries of chloride in the

fractions ranged from 80 to 100% and averaged 89% for the 14 fractionations in which the chloride content of all the fractions was determined by ashing combined with the potentiometric method.

The recoveries of chloride in the fractions were rather low. Possibilities considered in trying to account for the low recoveries were:

1. Recovery of dry matter averaged 99%; an adjustment for this 1% loss would raise chloride recovery about 1% and more if part of a fraction high in chloride were lost. One known loss was that of water-solubles which were lyophilized in large glass bottles. A small amount was always left in the bottle. In several instances this residue was dissolved in water, and aliquots were analyzed. Amounts of chloride were found that would raise the recovery about 1% from this source alone.

2. Gluten samples were more difficult to determine than the other fractions, therefore:

- a. Gluten chloride values may be somewhat low.
- b. Losses of chloride may have occurred during dialysis of the soluble protein.

Chloride Content of Flours and Fractions. The chloride values for three pairs of unbleached and bleached cake flours and their fractions are shown in Table III.

Unbleached flour had an appreciable chloride content. During growth the wheat plant evidently deposits chloride from the soil in the endosperm. The three flours listed ranged from 43 to 54 mg. per 100 g. flour. This is in good agreement with Utt (21) and Sullivan and Howe (19) and is somewhat lower than Pap (12) and Damiens and Blaignan (5). Of the fractions from unbleached flours, the water-solubles were high in chloride content, ranging from 630 to 852 mg.

TABLE III
CHLORIDE CONTENTS OF UNBLEACHED AND BLEACHED CAKE FLOURS AND FRACTIONS

MATERIAL	CHLORIDE CONTENT ^a					
	1959 Commercial Flour		Brevor Flour		Elmar Flour	
	Unbleached	Bleached	Unbleached	Bleached	Unbleached	Bleached
	mg	mg	mg	mg	mg	mg
Flour	54	131	43	145	46	189
Fractions						
Water-solubles	852	1,690	630	1,300	751	1,840
Gluten	17	463	19	666	10	937
Soluble protein	63	271	27	538	62	426
Tailings starch	16	49	18	42	13	52
Prime starch	13	15	17	20	13	18

^a Chloride in mg. per 100 g. of the fraction or flour indicated; all results are on a 14% moisture basis.

TABLE IV
DISTRIBUTION AMONG FRACTIONS OF THE CHLORIDE FROM ONE HUNDRED GRAMS OF
CAKE FLOUR

MATERIAL	AMOUNT OF CHLORIDE ^a					
	1959 Commercial Flour		Brevor Flour		Elmar Flour	
	Unbleached	Bleached	Unbleached	Bleached	Unbleached	Bleached
	mg	mg	mg	mg	mg	mg
Flour	54	131	43	145	46	189
Fractions						
Water-solubles	34.9	65.9	26.1	59.9	29.6	76.7
Gluten	1.1	29.6	1.4	42.6	0.7	65.4
Soluble protein	0.8	5.0	0.3	7.5	0.7	5.1
Tailings starch	2.1	7.4	3.7	7.2	1.9	11.3
Prime starch	9.7	11.6	11.2	13.5	9.4	11.8
Total	48.6	119.5	42.7	130.7	42.3	170.3
Chloride recovery, %	90	91	99	90	92	90

^a Amount of the flour chloride found in the fraction indicated (yield of fraction from 100 g. flour times chloride content of the fraction).

per 100 g. water-solubles, while the other fractions were all very low in chloride content.

The bleached flours studied ranged from 131 to 189 mg. chloride per 100 g. flour. This was two and one-half to four times as high as the unbleached flours. The water-solubles from bleached flours had about twice the chloride content of those from unbleached flours, whereas the bleached glutes had much greater chloride contents than the unbleached glutes. Bleached tailings were three to four times as high in chloride as those from unbleached flours, but the prime starches increased only very slightly in chloride after bleaching.

Distribution of Flour Chloride among Fractions. The water-solubles and the gluten plus the soluble protein were rather small parts by weight of the flour — about 4 and 8 g., respectively, from 100 g. of the cake flours studied. In contrast, the prime starch usually amounted to over 70 g. from 100 g. of cake flour. The distribution of the flour chloride among the fractions was calculated and is shown in Table IV.

Most of the chloride of the unbleached flours was in the water-solubles, although the relatively large weight of prime starch caused it to contain 20 to 25% of the chloride. The combined gluten plus soluble protein and the tailings starches contained very little chloride.

The increased chloride in the bleached flours was divided chiefly between the water-solubles and the combined gluten plus soluble protein. In the commercial flour, each of these fractions gained about 30 mg. or about 40% of the 77 mg. increase over the unbleached flour. In the laboratory-bleached flours, the water-solubles gained

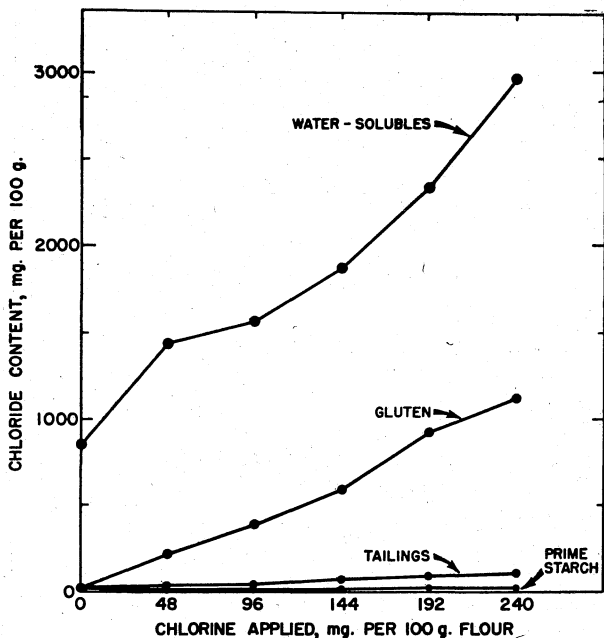


Fig. 1. Chloride contents of flour fractions at several levels of chlorine bleaching. The soluble protein is omitted to improve the legibility.

about 33% and the combined gluten plus soluble protein had about 40 to 45% of the increased chloride. The tailings accounted for 4 to 7% of the increase, and the prime starches held 2 to 3%.

Results with Fractions Obtained by Doughing. Table V compares the results of similar analyses of the fractions from a doughing procedure (20) with those of the fractions from an acetic acid separation. The results were about the same.

Fractions from Flours Bleached with Varying Amounts of Chlorine. Part of each of the flours bleached at five different levels in the laboratory was fractionated. The chloride content of the flours and their fractions was determined. The results are shown in Figs. 1 and 2. The soluble protein results were omitted from Fig. 1 for greater clarity; they did not differ greatly from the gluten results.

Figure 1 shows that the chloride content of the water-solubles, which was high in the beginning compared to the other fractions, increased as the amount of the chlorine applied to the flour increased and was consistently the highest of any of the fractions. The chloride content of the gluten increased with increasing amounts of applied

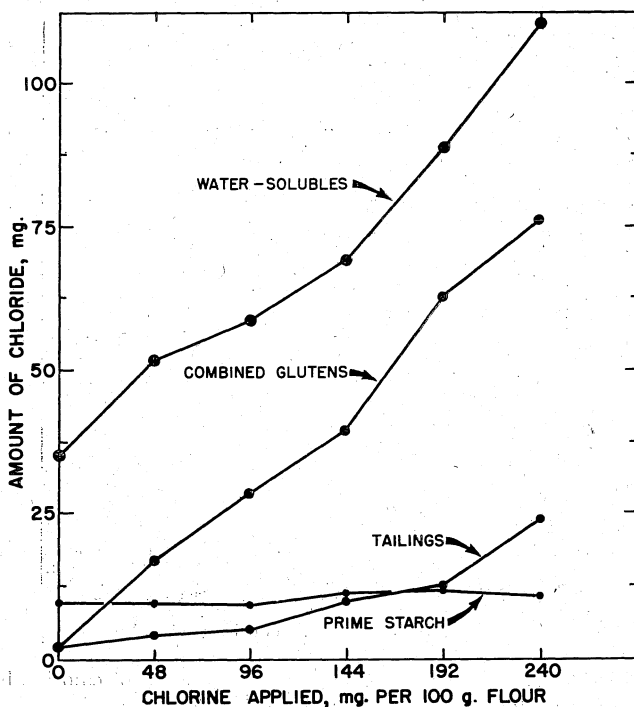


Fig. 2. Total amount of chloride in each fraction at several different levels of bleaching.

TABLE V

COMPARISON OF CHLORIDE CONTENTS OF, AND DISTRIBUTION OF, THE FLOUR CHLORIDE AMONG THE FRACTIONS OBTAINED FROM AN UNBLEACHED COMMERCIAL CAKE FLOUR BY AN ACETIC ACID EXTRACTION PROCEDURE AND BY A DOUGHING PROCEDURE

MATERIAL	TYPE OF FRACTIONATION			
	Acetic Acid Fractionation		Doughing Procedure	
	Chloride Content ^a	Amount of Chloride ^b	Chloride Content	Amount of Chloride
	<i>mg</i>	<i>mg</i>	<i>mg</i>	<i>mg</i>
Flour	54	54	54	54
Fractions				
Water-solubles	852	34.9	851	38.3
Gluten	17	1.1	12	0.7
Soluble protein	63	0.8
Tailings starch	16	2.1	9	2.0
Prime starch	13	9.7	9	6.1
Total	...	48.6	...	47.1
Chloride recovery, %	...	90	...	87

^a Chloride in mg. per 100 g. of the fraction or flour indicated; all results are on a 14% moisture basis.

^b Amount of flour chloride found in the fraction indicated (yield of fraction from 100 g. flour times chloride content of fraction).

TABLE VI
AMOUNT OF CHLORINE APPLIED, AMOUNT TAKEN UP BY THE FLOUR, AND PERCENT OF
CHLORINE UTILIZED IN LABORATORY BLEACHING OF FLOURS

FLOUR	CHLORINE APPLIED ^a	INCREASE IN FLOUR CHLORIDE ^a	CHLORINE UTILIZED
	mg	mg	%
Brevor	200	102	51
Elmar	220	143	65
Commercial	48	41	86
	96	69	72
	144	88	61
	192	142	74
	240	190	79

^a In mg. per 100 g. flour.

chlorine and reached high levels compared to the unbleached gluten. The tailings fraction showed slight increases in chloride, and the prime starch did not show any consistent increase in chloride.

Again, the difference in yield of the fractions must be considered to determine the total amount of chloride taken up by each fraction. This is done in Fig. 2, which shows that after the higher yield of gluten is considered, the two fractions, the water-solubles and the combined gluten plus soluble protein, each took up about the same amount of chlorine at any stage of bleaching.

Figure 2 also shows that there was no over-all increase in the amount of chlorine taken up by the prime starch. This differs somewhat from the data given in Tables III and IV which indicated slight increases in chloride for bleached prime starches.

Chlorine Utilization by Flour in Laboratory Bleaching. The differences between the amount of chlorine used in treating flour and the amount retained by the flour are illustrated in Table VI. At normal levels of bleaching, only one-half to two-thirds of the chlorine appeared in the flour.

The evidence from the commercial flour bleached at five different levels indicated that: 1) at low levels of chlorine treatment, nearly all the chlorine was taken up by the flour; 2) at normal levels of bleaching, a low point in the amount of chlorine taken up was reached; and 3) at higher than normal levels of bleaching, the utilization of chlorine improved markedly. The upswing in chloride contents and amounts shown for the water-solubles and glutes in Figs. 1 and 2 is explained by the higher utilization at these levels, since in these figures the contents and amounts were plotted against the amount of chlorine applied. If the chloride contents and amounts of the fractions were plotted against the amounts of chlorine retained

TABLE VII
CHLORIDE DISTRIBUTION AMONG THE SUBFRACTIONS OF THE WATER-SOLUBLE FRACTIONS
OF SOME CAKE FLOURS

FLOUR, TREATMENT, AND FRACTION	YIELD ^a	TOTAL CHLORIDE	CHLORIDE CONTENT ^b
	g	mg	mg
1959 Commercial unbleached:			
Total water-solubles:	4.27	34.8	815
Subfractions:			
Alcohol-soluble	3.08	31.5	1020
Alcohol-insoluble	1.03	0.8	78
Total	4.11	32.3
Recovery, %	96	93
1959 Commercial bleached:			
Total water-solubles	4.01	61.1	1520
Subfractions:			
Alcohol-soluble	3.04	59.6	1960
Alcohol-insoluble	0.96	1.0	104
Total	4.00	60.6
Recovery, %	100	99
Brevor bleached:			
Total water-solubles	4.44	60.2	1360
Subfractions:			
Alcohol-soluble	3.48	58.2	1670
Alcohol-insoluble	0.97	0.8	83
Total	4.45	59.0
Recovery, %	100	98
Elmar bleached:			
Total water-solubles	4.06	70.7	1740
Subfractions:			
Alcohol-soluble	2.99	66.5	2220
Alcohol-insoluble	0.96	1.2	125
Total	3.95	67.7
Recovery, %	97	96

^a Grams at 14% moisture obtained from 100.0 g. of flour at 14% moisture.

^b Chloride in mg. per 100 g. of the fraction or flour indicated; all results are on a 14% moisture basis.

by the flour, approximately linear relations were found for any one fraction.

This evidence may also indicate that either the reaction occurred in two different phases or that there were two different reactions occurring, depending on the concentration of the chlorine.

Chloride Distribution among Subfractions of the Water-Solubles. Table VII shows that practically all the chloride of the water-solubles was in the low-molecular-weight material. Presumably this was free inorganic chloride ion. The water-soluble proteins and polysaccharides from unbleached flours had low levels of chloride and increased very little in chloride from bleaching. The chloride content of the original water-solubles as found in this manner agreed closely with those values reported in Table III.

Chloride Distribution among Gluten Subfractions. The crude

TABLE VIII
CHLORIDE DISTRIBUTION AMONG THE SUBFRACTIONS OF
THE GLUTENS OF SOME CAKE FLOURS

FLOUR, TREATMENT, AND FRACTION	YIELD	TOTAL CHLORIDE	CHLORIDE CONTENT ^a
	g	mg	mg
1959 Commercial unbleached:			
Original gluten	1.00	0.2	17
Subfractions:			
Butanol extract	0.09	0.2	220
Residue	0.89	0.1	11
Total	0.98	0.3
Recovery, %	98	"150"
1959 Commercial bleached:			
Original gluten	1.00	4.6	463
Subfractions:			
Butanol extract	0.07	2.9	4100
Residue	0.90	0.9	100
Total	0.97	3.8
Recovery, %	97	83
Brevor bleached:			
Original gluten	1.00	6.7	666
Subfractions:			
Butanol extract	0.10	3.2	3200
Residue	0.87	2.7	310
Total	0.97	5.9
Recovery, %	97	88
Elmar bleached:			
Original gluten	1.00	9.4	937
Subfractions:			
Butanol extract	0.05	4.3	8600
Residue	0.94	2.6	280
Total	0.99	6.9
Recovery, %	99	72

^a Chloride in mg. per 100 g. of the fraction or flour indicated.

lipid portion (butanol extract) contained the major part of the gluten chloride as shown in Table VIII. The crude lipids from the bleached glutes reached 3 to 9% chloride contents (3,000 to 9,000 mg. chloride). However, the protein residues retained a substantial part of the gluten chloride.

Discussion

Prime starch isolated from bleached flour had approximately the same chloride content as prime starch isolated from unbleached flour. Increased chloride contents were observed in the water-soluble and gluten fractions isolated from bleached flour. The large increase in water-soluble chloride may indicate that a reaction occurs with some flour component in which chlorine serves as an oxidizing agent and is reduced to the chloride ion. No preferential uptake of chlorine by gluten or water-solubles was evident.

The possibility exists that chlorine may be oxidizing the prime starch, thus creating new reactive sites within the starch polymer. Further work to investigate possible oxidation of starch is being undertaken.

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Literature Cited

1. AMERICAN ASSOCIATION OF CEREAL CHEMISTS. Cereal laboratory methods (6th ed.). The Association: St. Paul, Minnesota (1957).
2. BAILEY, C. H. Constituents of wheat and wheat products, pp. 240-242. Reinhold Pub. Corp.: New York (1944).
3. BERGMANN, J. G., and SANIK, J., JR. Determination of trace amounts of chlorine in naphtha. *Anal. Chem.* **29**: 241-243 (1957).
4. BETHGE, P. O., and TROENG, T. Determination of chlorine in wood pulp, and paper. *Svensk Papperstidning* **62**: 17, 598 (1959).
5. DAMIENS, A., and BLAIGNAN, S. Sur le brome normal (regne vegetal): graines comestibles, blé, pain. *Compt. rend.* **193**: 1460-1462 (1931).
6. GUNTHER, F. A., and BLINN, R. C. Analysis of insecticides and acaricides, pp. 366-368. Interscience: New York (1955).
7. HELMKAMP, G. K., GUNTHER, F. A., WOLF, J. P. III, and LEONARD, J. E. Residue analysis. Direct potentiometric method for chloride ion applied to residues of chlorinated insecticides. *J. Agr. Food Chem.* **2**: 836-839 (1954).
8. JOHNSON, C. M., HUSTON, R. P., and OZANNE, P. G. Measurement of microgram amounts of chlorine in plant materials. *J. Agr. Food Chem.* **6**: 114-119 (1958).
9. KENT-JONES, D. W., and AMOS, A. J. Modern cereal chemistry (5th ed.), pp. 308-309. Northern Pub. Co., Ltd.: Liverpool (1957).
10. KEYS, A. A rapid micro-Kjeldahl method. *J. Biol. Chem.* **132**: 181-187 (1940).
11. MECHAM, D. K., and MOHAMMAD, A. Extraction of lipids from wheat products. *Cereal Chem.* **32**: 405-415 (1955).
12. PAP, L. Natural chlorine content of wheat flours. *Kiserlet. Kozlemenyek* **31**: 480-486 (1928). [*Chem. Abstr.* **25**: 2773 (1931).] (Original not seen.)
13. PIERCE, W. C., HAENISCH, E. L., and SAWYER, D. T. Quantitative analysis (4th ed.), pp. 358-360. Wiley: New York (1958).
14. SOLLARS, W. F. A new method of fractionating wheat flour. *Cereal Chem.* **33**: 111-120 (1956).
15. SOLLARS, W. F. Fractionation and reconstitution procedures for cake flours. *Cereal Chem.* **35**: 85-99 (1958).
16. SOLLARS, W. F. Cake and cookie flour fractions affected by chlorine bleaching. *Cereal Chem.* **35**: 100-110 (1958).
17. SOLLARS, W. F. Effects of the water-soluble constituents of wheat flour on cookie diameter. *Cereal Chem.* **36**: 498-513 (1959).
18. STEYERMARK, A. Quantitative organic microanalysis, pp. 157-164 and 178-184. Blakiston: New York (1951).
19. SULLIVAN, BETTY, and HOWE, MARJORIE. Minerals of wheat. Part I. Sulfur and chlorine. *Cereal Chem.* **6**: 396-400 (1929).
20. UDY, D. C. Some viscoelastic properties of wheat gluten. *Cereal Chem.* **30**: 353-366 (1953).
21. UTT, C. A. A. Some characteristics of chlorine-bleached flours. *Ind. Eng. Chem.* **6**: 908-909 (1914).