directed to be added, which will reduce Sb and Bi as well as As.

To find whether any of the chemicals directed to be tested by the stannous chloride method, could influence the detection of arsenic, specimens were prepared containing the pure chemicals shown to be free from arsenic by other tests, and with these small portions of arsenic were mixed and the tests compared with those in which arsenic was present in equal amount without admixture with the chemicals.

In no case could any difference in the intensity of the test be made out, nor were the differences in the time of the occurrence of the coloration sufficiently great or regular to justify the assumption that the reaction was impeded or accelerated by the presence of other salts.

ST. LOUIS, May 27, 1894.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, SENT BY H. W. WILEY. No. 8.]

THE INFLUENCE OF ALUM, ALUMINUM HYDROXIDE AND ALUMINUM PHOSPHATE, ON THE DIGESTIBILITY OF BREAD.

BY W. D. BIGELOW AND C. C. HAMILTON.

Received June 28, 1894.

THE property which alum possesses of arresting the fermentation of flour, and making it possible to prepare presentable bread from very inferior flour has long been known, and the adulteration of flour by means of alum has been extensively practiced by millers and bakers. Comparatively little attention has been given to this subject in this country, but in Europe, especially in England, the question has been constantly before the minds of the public analysts for at least a quarter of a century. Indeed, as early as 1821 a law was passed prohibiting the addition of alum or any aluminum compound to flour or bread. This law remained in force till 1861 when it was repealed by the passage of a law which made it necessary for the prosecution to prove the injurious quality of the substance added.

It is universally admitted that the presence of alum as such not only impedes digestion but also exercises an injurious effect on the digestive organs. There is one phase of the alum question, however, to which a great deal of attention has been

given, both in this country and abroad; namely, the use of alum as the acid compound of baking powders. Unlike the practice of adding alum to flour or dough, this question has been attended with a long continued and fiercely contested controversy.

Many experienced analysts who have condemned alumed bread in unmeasured terms, have testified that in their opinion, bread baked with alum baking powders exercises no injurious influence on digestion or the digestive organs.

In the famous Norfolk[1] baking powder case, it was contended by the Government that alum united with the soluble phosphates of the flour with the formation of an insoluble compound, and that the flour was thus deprived of one of its most valuable constituents.

The defense, on the other hand, claimed that the aluminum was entirely precipitated as hydroxide. It is a curious fact that shortly after the Norfolk case the manufacturers of alum baking powders began the addition of acid calcium phosphate, and the position taken by prosecution and defense in the Norfolk case were reversed in a recent case[2] before the English courts. In the evidence submitted by the prosecution independent experiments were cited by Dunstan, Hehner, and Claude Thompson, to prove that aluminum hydroxide dried at 100° was soluble in two-tenths per cent. hydrochloric acid. Dunstan found aluminum hydroxide dried at 100° to be soluble in the gastric juice of a dog diluted to two-tenths per cent. of its normal strength, and that this fluid diluted to the same extent dissolved aluminum hydroxide from bread baked with the powder manufactured by the defendant.

Dunstan also found that aluminum hydroxide in bread interfered with the action of diastase (hence, with ptyalin, the digestive ferment of the saliva), and with peptic and pancreatic digestion. Also, that a three-tenths per cent. solution of sodium carbonate (the strength of the alkali in the intestinal juice) would dissolve aluminum hydroxide which had been dried at 100°. He also testified that he had found an aluminum salt in the urine of a man who had eaten one to two grams of aluminum hydroxide which had been dried at 100°.

Morgan testified that he had dissolved aluminum hydroxide

[1] *Analyst*, *1879*, **4**, 231, and *1880*, **5**, 21.

[2] *Analyst*, *1893*, **18**, 152; *Chem. News*, *1893*, **67**, 213.

which had been dried at 100° in his own vomit and in that of his son.

On the other hand, the defence took the ground that aluminum hydroxide was insoluble in the juices of the digestive organs. Sutton repeated Morgan's experiment, using as a dialyzer, however, a fresh sheep's bladder instead of a vegetable parchment as used by Morgan. Unlike Morgan he found no soluble aluminum compound in the dialysate. Luff cites an experiment intended to prove that dried aluminum hydroxide was insoluble in hydrochloric acid of the strength found in the gastric juice.

He took this strength of acid to be 0.02 per cent. instead of 0.2 per cent., the strength taken by the prosecution. His aluminum hydroxide also was heated to 150° instead of 100°, which is generally admitted to be the highest temperature attained by the interior of a loaf while baking, and he was not sure but the hydroxide might be changed to oxyhydroxide by heating to this temperature.

The work that has been done upon this subject seems to have been devoted to the influence of the gastric digestion alone, though J. West-Knights[1] and Dunstan,[2] working with diastase, reached the conclusion that the presence of alum, or of insoluble aluminum salts, interferes with the amylolytic action of ptyalin. Dunstan,[2] it is true, states that aluminum hydroxide interferes with pancreatic digestion, but appears to describe no experiment in proof of the statement.

J. West-Knights[1] found that gluten after treatment with alum, or its insoluble compounds, is about one-half less soluble in gastric juice than pure gluten, and pure bread is almost one-third more soluble than alumed bread in the same medium.

Pitkin[3] and Mallet[4] reached the conclusion that the aluminum compounds resulting from the use of alum baking powder were soluble to some extent in the gastric juice, while Patrick[5] found that when the dough was well mixed and bread well baked no aluminum hydroxide, resulting from the use of alum baking powder, was dissolved in the stomach of the cat. Hehner,[6] working

[1] *Analyst*, *1880*, 5, 67.
[2] *Ibid*, *1893*, 18, 152.
[3] *J. Am. Chem. Soc.*, *1887*, 9, 27.
[4] *Chem. News*, *1884*, 58, 276.
[5] *Analyst*, *1879*, 4, 207; from *Sci. Am. Sup.*
[6] *Analyst*, *1892*, 17, 201, and *1893*, 18, 213.

with an artificial pepsin solution, found the detrimental influence of alum baking powder to be equal to that of alum in the digestion of egg and bread.

The suggestion has often been made that the water-soluble salts resulting from the use of an alum baking powder, such as ammonium sulphate and potassium sulphate, would be more likely to retard digestion than the insoluble aluminum compounds. It was to study this question with reference to gastric digestion, but more especially with reference to double digestion with gastric and pancreatic ferments, that we undertook the work which forms the basis of this paper.

For the preparation of samples, flour was obtained which was known to be free from alum and seven two-pound loaves were baked under our direct supervision. The bread was raised in every case by compressed yeast.

As soon as the bread was baked it was cut in thin slices, dried at a temperature of 98°, ground, and bottled.

I. Digestion of Bread Free from Alum and Aluminum Compounds.

Loaf No. 1 was found to contain 12.06 per cent. of albuminoids. Portions of two grams each were subjected to several methods of digestion. The results given are the means of closely agreeing duplicate or triplicate determinations.

1. *Digestion in Pepsin Solution.*—The pepsin solution here employed is that suggested by Wilson in his modification of Stutzer's method.[1] One gram of Merck's granulated pepsin was dissolved in one liter of 0.33 per cent. hydrochloric acid. Two grams of the dried bread, which had been previously extracted with ether, were placed in a flask with 100 cc. of the acid pepsin solution, placed in a water-bath and kept at 40°, with frequent shaking, for twelve hours. The contents of the flasks were then filtered and the residue washed, dried, and kjeldahled. It was found that 93.26 per cent. of the total albuminoids in the bread were digested,

2. *Stutzer's Method.*—Two-gram portions of the bread were then digested according to Stutzer's method, except that an

[1] *J. Soc. Chem. Ind.*, 10, 118. See also Patterson in Report Maryland Experiment Station, *1891*.

artificial pepsin solution, as given above, was employed instead of a solution freshly prepared from the inner membrane of a hog's stomach. The residue from the pepsin digestion, after being thoroughly washed, was digested for six hours in 100 cc. of Stutzer's[1] pancreas solution. The extracted residue was then allowed to dry and the nitrogen determined by the Kjeldahl method. By this method 93.57 per cent. of total albuminoids were digested, only a slight increase over the amount digested by the pepsin solution alone.

3. *Stutzer's Method, Modified by Wilson.*[2]—The pepsin solution here employed was the same as in the preceding experiments. The pancreas solution was made by dissolving one and one-half grams of Merck's "absolute pure" pancreatin, and three grams of sodium carbonate in one liter of water. The well-washed residue from the pepsin digestion was digested for twelve hours in 100 cc. of this solution, with frequent stirring, a temperature of 40° being maintained in the water-bath in which the flasks were immersed. The residue was then filtered, washed, and the nitrogen determined by the Kjeldahl method.

By this method 93.21 per cent. of the total albuminoids were digested.

4. *Niebling's Method.*[3]—Two grams of the sample were washed with ether and introduced into a flask with 100 cc. of two-tenths per cent. hydrochloric acid. The contents of the flask were then heated to boiling and kept at that temperature for fifteen minutes, after which they were allowed to cool and were neutralized, or rendered very slightly alkaline with a solution of sodium carbonate. One hundred cc. of Stutzer's pancreas solution were then added (without previous filtration), and the flasks immersed in the water-bath, which was kept at the temperature of 37°–40° for six hours. The residues were then washed, dried, and kjeldahled.

[1] To prepare this solution take one kilogram of steer's pancreas which has been freed from fat as far as possible, pass through a sausage grinder, rub up in a mortar with sand and allow to stand exposed to the air twenty-four to thirty-six hours. Then add three liters of lime water, one liter of glycerol, sp. gr. 1.23, a little chloroform, and let stand from four to six days. Press through a bag and filter through filter paper. Before using, take 250 cc., add 750 cc. water containing five grams anhydrous sodium carbonate, heat to 37° to 40° for two hours and filter. *Landw. Versuchs-Stat., 1889,* **36,** 321–328. See also U. S. Department of Agriculture, Chem. Div., *Bull.*, **13,** part 8, 1028.

[2] *J. Soc. Chem. Ind.*, 10, 118; through Report Maryland Experiment Station, *1891*, 338.

[3] *Landw. Jahrb., 1890,* **19,** 149–187.

The result showed that 93.28 per cent. of the total albuminoids were digested by this method.

5. *Niebling's Method, Modified.*—This method is the same as the one preceding except that the pancreatin solution given under Wilson's modification of Stutzer's method was used instead of Stutzer's pancreas solution. The sample was digested in the pancreatin solution for twelve hours. By this method, 93.21 per cent. of the albuminoids were digested.

It will thus be seen that closely agreeing results were obtained by the different methods of digestion with bread which was as free as possible from substances which might interfere with its digestion. It was next undertaken to ascertain the effect of alum on the same methods of digestion.

II. Digestion of Alumed Bread.

For this purpose two loaves of "alumed" bread were baked. The alum, in a fine powdered state, was thoroughly mixed with the flour before the dough was made. No. 1 contained eight-tenths gram, and No. 2, 428 grams crystallized alum in the two-pound loaf. As soon as baked the bread was dried, ground, and bottled as before. Loaf No. 1 contained 11.88 per cent., and No. 2, 12.06 per cent. albuminoids in the dried sample.

1. *Digestion in Pepsin Solution.*—

No.	Grams alum.	Per cent. digestible albuminoids.
1	0.8	89.11
2	4.28	80.98

From these figures it is evident that the digestion of albuminoids in a pepsin solution is greatly lessened by the presence of alum. This it is true is universally admitted, and the results of this method are merely given as confirmatory of the work of others.

2. *Stutzer's Method.*—By Stutzer's method, using, however, an artificial pepsin solution instead of the one used by Stutzer, the following results were obtained. Since all the alum would be removed by washing after the pepsin digestion in this method and the next, the amount of alum originally present was dissolved in a little water and added to the sample previous to the pancreatic digestion.

No.	Grams alum.	Per cent. digestible albuminoids.
1	0.8	92.56
2	4.28	92.40

It will be seen that these results would lead us to a conclusion entirely different, and almost contradictory, to the one which we would obtain from the results of the pepsin solution alone. Before making further comment, however, let us examine the results obtained by the other methods of digestion.

3. *Stutzer's Method, Modified by Wilson.*—

No.	Grams alum.	Per cent. digestible albuminoids.
1	0.8	92.21
2	4.28	92.44

4. *Niebling's Method.*—

No.	Grams alum.	Per cent. digestible albuminoids.
1	0.8	92.54

5. *Niebling's Method, Modified.*—

No.	Grams alum.	Per cent. digestible albuminoids.
1	0.8	92.74
2	4.28	92.02

It is evident from these results that the custom of judging the influence of alum on the digestion by its effect on the digestion in the pepsin solution alone has led to grave errors. It is evident that the presence of alum interferes materially with the gastric digestion, but the aluminum seems to be precipitated by the alkali of the pancreatic fluid, so that a portion of the digestion which should be effected by the former ferment is effected by the latter. Of course, this paper does not take into consideration the toxic properties of alum, but we are led to believe that its influence on the digestion has been greatly overestimated.

III. Digestion of Bread Containing Aluminum Hydroxide.

It was next desired to ascertain the digestibility of bread which contained aluminum hydroxide but was free from the soluble salts which result from the use of baking powders. For this purpose two two-pound loaves of bread were baked, ground, and dried as before. Loaf No. 1 contained 0.54 gram of aluminum hydroxide, corresponding to about 3.24 grams of crystallized

alum. This amount might readily be obtained by the use of an alum baking powder. Loaf No. 2 contained two and one-half grams of aluminum hydroxide, a larger amount than should ever be found in bread.

This aluminum hydroxide was prepared by precipitation from an alum solution by means of ammonium hydroxide and washing with hot water till all soluble salts were removed. It was then heated to 100° till perfectly dry, and finely powdered in a mortar. The dried and powdered aluminum hydroxide was thoroughly mixed with the flour before the dough was made.

1. *Digestion in Pepsin Solution.*—As before stated, the evidence concerning the solubility of aluminum hydroxide which has been heated to 100° in the gastric juice is of the most contradictory description. Portions of two grams each of these samples were treated with 100 cc. of the acid pepsin solution with the following results:

No.	Grams aluminum hydroxide.	Per cent. digestible albuminoids.
1	0.54	87.03
2	2.50	86.78

According to these results the presence of aluminum hydroxide interferes materially with the digestion of albuminoids in a pepsin solution. We notice, however, that this retarding influence is not by any means proportional to the amount of hydroxide present. Indeed, although widely differing quantities of hydroxide were taken, their effect seems to be approximately the same. It seems probable, therefore, that even a much smaller amount of aluminum hydroxide might have given approximately the same results as the amounts employed. Concerning this point Hehner[1] found that when only a small amount of aluminum hydroxide was present its detrimental influence on the pepsin digestion was equal to that of an equivalent amount of alum, but when a larger amount was taken its effect was relatively less.

2. *Stutzer's Method.*—As before, a solution of Merck's granulated pepsin was used in this method in place of Stutzer's pepsin solution. The following results were obtained:

No.	Grams aluminum hydroxide.	Per cent. digestible albuminoids.
1	0.54	92.18
2	2.50	90.43

[1] *Analyst, 1893*, 18, 213.

3. *Stutzer's Method, Modified by Wilson.*—

No.	Grams aluminum hydroxide.	Per cent. digestible albuminoids.
1	0.54	92.00
2	2.50	90.21

4. *Niebling's Method.*—

No.	Grams aluminum hydroxide.	Per cent. digestible albuminoids.
1	0.54	91.77
2	2.50	89.13

5. *Niebling's Method, Modified.*—

No.	Grams aluminum hydroxide.	Per cent. digestible albuminoids.
1	0.54	91.90
2	2.50	88.96

Methods 4 and 5 give results which are noticeably lower than were obtained by the other methods. Their lack of agreement with each other also is such as to cause a serious error if these methods were adopted for this work.

These results make it evident that with aluminum hydroxide, as with alum, the results by the pepsin digestion alone cannot be taken as a guide to the influence of the aluminum hydroxide resulting from the use of an alum baking powder on the digestion. Here, as with alum, the albuminoids whose digestion is prevented in the pepsin solution by dissolved aluminum compounds, seem to be almost all digested by the alkaline pancreas solution. It is true that the digestion is not quite as complete in the presence of alum or aluminum hydroxide as in their absence. It is possible that this is due to the presence of sodium aluminate in the pancreas solution.[1] Although it appears that the influence exerted on the digestion of albuminoids by aluminum hydroxide is very slight, the possible toxic effects of even the slight amount of aluminum chloride produced in the gastric juice should not be overlooked.

IV. Digestion of Bread Containing Aluminum Phosphate.

It seems to have been quite generally assumed that aluminum phosphate was much less soluble in the gastric juice than aluminum hydroxide, and that it would exert a correspondingly less influence on digestion. Indeed, some have gone so far as to

[1] See Dunstan, *Analyst*, *1893*, **18**, 152.

state that the only influence which could be exerted by the compounds resulting from an aluminum phosphate baking powder must be due to the soluble salts. In order to determine the effect of aluminum phosphate in the absence of the soluble salts, the preceding set of digestions was repeated with bread containing aluminum phosphate. Two two-pound loaves of bread were baked with the addition of aluminum phosphate and prepared for analysis as before. Loaf No. 1 contained 0.64 gram of aluminum phosphate, which is equivalent to 2.56 grams of crystallized alum. This amount has frequently been found in bread prepared by alum baking powder. Loaf No. 2 contained 3.20 grams of aluminum phosphate, an amount largely in excess of that usually found in bread.

For the preparation of this compound, alum was dissolved in water, an excess of hydrogen disodium phosphate added, and the resulting precipitate washed with water until the filtrate ceased to be acid. It was then dried at 100° and reduced to a fine powder in a mortar. The dried and powdered aluminum phosphate was thoroughly mixed with the flour before the dough was made.

1. *Digestion of Pepsin Solution.*—Portions of the samples were digested in the acid pepsin solution, as before, after washing with ether to remove the fat. The following results were obtained:

No.	Grams aluminum phosphate.	Per cent. digestible albuminoids.
1	0.64	80.87
2	3.20	71.21

Comparing the result obtained in sample 1 with that obtained by the peptic digestion of alumed bread, we find that even when a relatively large amount of aluminum phosphate is present, its effect on the pepsin digestion is equal to that of an equivalent amount of alum. It is also apparent that its effect is much greater than that of an equivalent amount of hydroxide.

2. *Stutzer's Method.*—As in the previous digestions, this method was modified by substituting a solution of Merck's granulated pepsin for Stutzer's pepsin solution. The following results were obtained:

No.	Grams aluminum phosphate.	Per cent. digestible albuminoids.
1	0.64	83.11
2	3.20	78.26

3. *Stutzer's Method, Modified by Wilson.*—

No.	Grams aluminum phosphate.	Per cent. digestible albuminoids.
1	0.64	82.56
2	3.20	81.32

4. *Niebling's Method.*—

No.	Grams aluminum phosphate.	Per cent. digestible albuminoids.
1	0.64	86.35
2	3.20	82.18

These results differ materially from those obtained by the other methods of digestion.

5. *Niebling's Method, Modified.*—

No.	Grams aluminum phosphate.	Per cent. digestible albuminoids.
1	0.64	86.46
2	3.20	81.74

These results agree fairly closely with those obtained by method 4, but are materially lower than those obtained by methods 2 and 3.

From these results it appears that the influence of aluminum hydroxide on the digestibility of bread is about the same as that of an equivalent amount of alum, when present in about the quantity which is usually found as a result of the use of alum baking powder which contains no phosphate.

The action of aluminum phosphate is quite different, however, for notwithstanding the supposed insolubility of this compound, ten to twelve per cent. of the albuminoids which are digestible in the presence of alum or aluminum hydroxide appear to be insoluble in the presence of an equivalent amount of the phosphate.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, SENT BY H. W. WILEY.—No. 9.]

SOME CHARACTERISTICS OF CALIFORNIA WINES.

BY W. H. KRUG.

AMONG the exhibits of American products at the World's Columbian Exposition, at Chicago, in the year 1893, one of the most interesting and varied was that of the California wine producers at the California State Building. The wines shown there, represented all the important districts in the state and the various types grown. At the suggestion of Dr. H. W. Wiley, Chief Chemist of the U. S. Department of Agriculture, the Cali-