

## XXXIV.—CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.

BY ALBERT B. PRESCOTT.

## IV. PROPORTION OF NITROGEN COMPOUNDS IN THE GRAIN AND FLOUR OF DIFFERENT VARIETIES OF WHEAT.

The first six of the analyses numbered below are taken from the record of some analytical work which I did at the request of the Michigan State Millers' Association, in the last ten days of July, 1877. The samples of these six varieties were all furnished me, at that time, by the Secretary of the Association, Mr. W. Hibbard, of Grand Rapids, Michigan. The report of these analyses was received at the meeting of the Michigan Millers' Association, held in Detroit, August 1, 1877, and was published, with the proceedings, in the Detroit daily papers of that date. In that report, the percentages of albuminoids were computed by multiplying the nitrogen percentage by 6.45. Below, to make the results uniform with later-analyses, I use 6.25 as the ratio of albuminoids to nitrogen. Thus, the nitrogen of No. 1 was found to be 2.067 per cent., and the albuminoids of No. 1 were reported to the Millers' Association as 13.33 per cent., while given below as 12.919 per cent.

The analyses given below for Nos. 7, 8 and 9, were made by Mr. Sylvester J. Heimbach, at Ann Arbor, in the spring of 1879, and have not been published before. The samples of grain and flour were furnished to Mr. Heimbach\* as follows :

No. 7, "White Amber," by Wm. Frame, Hamansville, Mich.; No. 8, Red Wheat, "Fulce," by Lantz & Brown, Constantine, Mich.; No. 9, "Clawson," by D. Frazier, Constantine, Mich. Great care was taken to obtain pure and genuine samples of these varieties of the grain; and the flour of each variety was taken after the mill had been running for some time on the same variety.

The work upon No. 10, grain and flour, was done by Mr. F. D. Merritt, at the University, in June, 1880. The grain and both flours of No. 10 were furnished to Mr. Merritt, with due precautions, by a miller whose address I am not able to find. The "patent flour" was understood to have been ground down, from the middlings of No. 10, by a process now well known to millers, for the "patent flour" of the market. Its high percentage of nitrogen corresponds to the exceeding tenacity of its sponge and porosity of bread and crusts baked from it. The middlings are made to give up a part of that rich

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\*The present address of Mr. Heimbach is Oak Bluffs, Mass.

layer of albuminoid cells which lies so close to the woody husk, that it goes most easily to the bran.

The Michigan Millers' Association, in August, 1877, published a resolution unfavorable to the quality of Clawson wheat flour, and expressing a decided opinion that the extensive raising of this variety of wheat in the State, would injure the reputation of Michigan flour wherever it would go. This opinion was based only in part upon the results of the chemical analyses, and in part (as appeared from the report of the meeting) upon other evidences then adduced. The farmers of the State, as far as represented in the papers, generally resisted the conclusions of the millers, and pretty actively attacked the chemical analyses and all other statements adduced by anybody to the disadvantage of Clawson wheat flour. The violence of the discussion in the public prints drew my attention to the matter, and I have since been observant of all evidences as to the import of nitrogen percentage in measuring the bread-making strength of flour. So far as I can ascertain, the proportion of nitrogenous compounds is an unailing, practical measure of the capacity of flour to make light bread, and to make large and heavy loaves from a given weight of flour. Porous bread holds a heavy percentage of moisture, without appearing to be moist, and it is the gluten that sustains porosity. The quantity of gluten is represented—practically, though not absolutely—by the quantity of nitrogen. And, it may be suggested, that the market value of flour depends upon its bread-raising strength, and the whiteness of its bread, rather than upon its nutrient capacity.

PERCENTAGES IN ENTIRE GRAIN.

	Of grain dried at 100° C.		Moisture lost in drying at 100° C.
	NITROGEN.	ALBUMINOIDS.	
No. 1. "Gold Medal" Wheat, Michigan, 1877.....	2.067	12.919	13.55
No. 2. "Crescent Mills" Wheat, Michigan, 1877....	1.713	10.706	10.76
No. 3. "Diehl" Wheat, Michigan, 1877.....	1.789	11.181	12.35
No. 4. "Tapahanoek" Wheat, Michigan, 1877.....	2.516	15.725	11.70
No. 5. "Clawson" Wheat, Michigan, 1877.....	1.680	10.500	11.35
No. 6. "Treadwell" Wheat, Michigan, 1877.....	2.400	15.000	10.74
Mean of the six varieties....	2.027	12.672	11.74

PERCENTAGES IN ENTIRE GRAIN AND IN FLOUR (AIR-DRY).

	In Entire Grain.		In Flour.	
	NITROGEN.	ALBUMINOIDS.	NITROGEN.	ALBUMINOIDS.
No. 7. "White Amber" Wheat, St. Joseph Co., Mich., 1878, on sandy soil (Heimbach) . . . . .	2.013	12.581	1.963	12.269
No. 8. "Fulce" Wheat (red), St. Joseph Co., Mich., 1878, on sandy soil (Heimbach) . . . . .	1.993	12.456	1.900	11.875
No. 9. "Clawson" Wheat, St. Joseph Co., Mich., 1878; very rich soil, half prairie and half "opening" (Heimbach). . . . .	1.794	11.212	1.650	10.312
No. 10. Red Winter Wheat, 1879 (Merritt) . . . . .	2.096	13.104	1.963	12.271
"Patent Flour" from No. 10 (Merritt) . . . . .	.....	.....	2.040	12.750
Mean of Nos. 7, 8, 9 and 10 (not including "Patent Flour" of 10) . . . . .	1.974	12.338	1.869	11.682

All the nitrogen determinations were made by the soda-lime process. Those for Nos. 7 to 10 were made in triplicate operations, with the following results in *percentages of nitrogen*.

	1st.	2nd.	3rd.	Mean.
No. 7. Grain. . . . .	2.02	1.98	2.04	2.013
Flour . . . . .	1.99	1.96	1.94	1.963
No. 8. Grain. . . . .	2.01	1.90	2.08	1.996
Flour. . . . .	1.87	1.92	1.91	1.900
No. 9. Grain. . . . .	1.80	1.76	1.82*	1.794
Flour. . . . .	1.62	1.70	1.63	1.650
No. 10. Grain. . . . .	2.08	2.10	2.11	2.096
Flour. . . . .	1.96	1.95	1.98	1.963
"Patent Flour." . . . .	2.04	2.03	2.05	2.040

V. ANALYSES OF VINEGAR.

The following examinations were made by Mr. John P. Kelly, in May and June, 1879. The *percentage of acetic acid* was found by

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\* For No. 9 grain, a fourth trial gave 1.79, and a fifth gave 1.80. The mean above is that of the five operations.

simple acidimetry, except when sulphuric acid was present. In this case, the total acid was first taken; then the vinegar was evaporated to dryness on the water bath, and several times the evaporation repeated with previous additions of water, when the fixed acid in the residue was determined, and this subtracted from the total acid first found. Examination for *aldehyde* was made in a distillate, obtained at about 20° C., by addition of potassium hydrate solution, leaving several hours for the appearance of the brown "aldehyde resin." The iodoform test was applied for *alcohol*. The estimation by Fehling's solution was made directly for *sugar*, and therefore the results are a little too high, as other reducing agents must slightly increase the reduction of the copper.

Examination for *free sulphuric acid* was made by three qualitative tests:

1. The *ash* was moistened and tested with litmus, when an alkaline reaction should be obtained if no free mineral acid were present.

2. The vinegar was evaporated, the residue extracted with alcohol, the alcohol removed from the extract by evaporation, and test applied by barium salt and free acid, when a precipitate can be determined gravimetrically (J. T. King, Chem. News, 25, 227).

3. The addition of ammonium oxalate solution to two portions of the vinegar, with addition of ammonium hydrate to one portion. A decidedly greater turbidity in the last named portion indicates mineral acid (Thresh, Pharm. Journ. Trans. (3), 6, 1, July 3, 1875; Journ. Chem. Soc., 29, 107).

No mineral acids were found, except a trace of free sulphuric acid in No. 5.

The ash was tested for *poisonous metals*, and none were found except lead in traces in No 2.

No.	Name of vinegar.	Per cent. of acetic acid.	Presence of aldehyde.	Presence of alcohol.	Per cent. of sugar.	Sugar in grains per gal.
1.	White Wine.	3.24	A little.	None.	0.09	55
" 2.	Cider.	4.20	Abundant.	"	0.10	63
" 3.	"	3.26			0.08	52
" 4.	White Wine.	3.79	Traces.	Traces.	0.06	39
" 5.	" "	5.60	A little.	"	0.12	74
" 6.	" "	3.96	"	None.	0.06	39
" 7.	Cider.	3.96	"	"	0.11	66
" 8.	"	3.60	Abundance.	Traces.	0.11	67
" 9.	"	6.60	"	"	0.14	85
" 10.	"	4.40	Traces.	None.	0.06	37
" 11.	White Wine.	4.80	"	"	0.10	59
Mean.....		4.29				

The names of the manufacturers are given in Mr. Kelly's report, preserved at the University.

#### VI. TEST LIMITS IN THE EXAMINATION OF SUGAR FOR INJURIOUS METALS.

Mr. A. L. Walker made a series of trials to ascertain the least proportion of tin salts that could be detected in white sugars. The sugar was dissolved in distilled water, to make a thin syrup; this was acidulated with hydrochloric acid, and then washed hydrosulphuric acid gas was passed through, for half an hour. No coloration or precipitate appearing, solutions of tin salts of known strength were added, and the treatment repeated. The precipitate was filtered out and washed, and the tin estimated as dioxide. First was tried the addition of one part of stannous chloride to 14,000 parts of sugar; 0.004 grm of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  to 56 grms sugar; the proportion of one grain of tin salt to two pounds sugar. In the first operation,  $\frac{1}{4}$  of the tin was recovered; in a second,  $\frac{2}{5}$  of the tin was recovered. Two experiments were made with stannic chloride, with about the same results. Then, for qualitative purposes, one part of tin salt was added to 56,000 parts of sugar (one grain to eight pounds), and a distinct light-brown precipitate obtained. With one part tin salt to 112,000 parts of sugar (one grain to sixteen pounds), a distinct coloration, but no precipitate, was obtained. Parallel trials with stannous and stannic salts gave the same result. And this was accepted as the qualitative limit, to establish negative results, as to presence of tin in white sugars.

Some time ago I reported similar determinations of limits of delicacy of tests of sugar for lead by hydrogen sulphide, and for arsenic by sodium amalgam, to obtain arsenious hydride in reaction with silver nitrate\* (*Am. Journ. Pharm.*, 49, 487, Oct., 1877; analyses by Messrs. Johnson and Parkill). Placing all the results together, we have the following comparison of tests of sugar, *by methods without destruction of the organic matter.*

#### QUALITATIVE LIMITS FOR NEGATIVE RESULTS.

Arsenic,	one grain of the element in	476 pounds sugar.
Lead,	“ “ “ “ metal “	10 “ “
Tin,	“ “ “ “ salt “	16 “ “

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\*The thin syrup, made slightly alkaline with fixed alkali hydrate, is placed in a half-liter flask, with addition of sodium amalgam, to cause a slow evolution of hydrogen, and left several hours, while the mouth of the flask is covered by a disk of filter paper wet with silver nitrate solution, and held down by a watch glass.

A positive result, at these limits, would, of course, be ambiguous; and a larger proportion of either metal would be required to enable the operator to identify it positively by these methods.

Methods by destruction of the organic matter—besides requiring great labor, and involving much danger of contamination from the chemicals and the exposure—can hardly reach the limit of delicacy attained with these simple methods.

Twenty-six samples of sugar, taken from the market, were subjected to examination, by the method above described, and no indication of the presence of tin (or lead) was obtained.

#### VII. ESTIMATION OF NICOTIA IN TOBACCO.

Some work was done by Mr. E. T. Pease, in the estimation of alkaloid in leaf and manufactured tobacco, by the volumetric method with potassium mercuric iodide, as directed in detail by Dragendorff (*Werthbestimmung einiger starkwirkenden Drogen*, 1874, 52).

The tobacco was first dried, the portion weighed, then macerated for at least twenty-four hours with water acidulated with sulphuric acid, and the expressed liquid concentrated and filtered. The solution from 2 to 3 grms of tobacco, was brought to 50 c.c., and of this 10 c.c. were taken for titration. The end of the reaction was found by filtering a few drops through a very small filter, trying the filtrate on a watch glass with a drop of the volumetric reagent, and rinsing the filter into the whole solution. The potassium mercuric iodide was twentieth normal, or old decinormal, Mayer's standard ( $\text{HgCl}_2 + 6\text{KI}$ ).

The precipitate first obtained appears milky when formed, but soon turns black and waxy, and settles to the bottom in a coherent mass. Several of the operations were duplicated, with but very slight differences in results. The end of the precipitation is sharply defined.

No. 1. Cigars . . . . .	2.00 per cent. nicotia.
No. 2. Kentucky leaf tobacco . . . . .	4.05 " " "
No. 3. Sweet peach chewing, manufactured, with much steaming, from same grade as No. 2.	3.24 " " "
No. 4. Filler from real Havana tobacco cigar.	4.21 " " "
No. 5. "Havana-seed" leaf tobacco (grown in this country from imported seed) . . . . .	3.94 " " "
No. 6. Gem cigarette tobacco, Richmond, Va.	3.93 " " "

A short clay pipe, some time in use and partly colored, though not darker than pipes seen on the street daily, was pulverized, macer-

ated in acidulated water, and the solution treated as from tobacco. The result of titration, if due to nicotia, indicated 0.4779 grm of that alkaloid. The pipe weighed 23.619 grms; therefore 2.02 per cent. of alkaloid were indicated.

Mr. Pease also made an experiment in determination of tobacco smoke. The presence of nicotia in the smoke has been made the subject of discrepant reports. I report the following result, also the one with the old pipe, above stated, with some reservation. At present I am not assured but that some of the empyrenmatic products of nicotia (or of tobacco) may react with Mayer's solution. Until research or experiment settles the question, I could not interpret the results as positive evidences of unchanged nicotia. A quantity of the dried Havana-seed leaf tobacco (No. 5), weighing 3.6685 grms, was burned in a brier-wood pipe (one long in use). The pipe bowl was tightly connected to glass tubing reaching to the bottom of a four ounce flask, containing acidulated water, and this flask was suitably connected with another holding acidulated water. All the smoke was drawn through the flasks. The filtered solutions were concentrated, and titrated. A total of 0.081 grm of nicotia was indicated, this being 2.48 per cent. of the dried tobacco burned.

#### VIII. ESTIMATIONS OF ARSENIC IN WALL PAPER, GREEN TARLETAN, AND GREEN CAMBRIC.

Mr. Arthur S. Parker found the following proportions of arsenic in wall papers of green and drab colors:

IN ONE SQUARE YARD.		IN EQUIVALENT OF ARSENIC ANHYDRIDE.
No. 1	contained	0.520
" 2	"	1.296
" 3	"	0.216
" 4	"	0.900
" 5	"	0.792
" 6	"	2.260
" 7	"	4.840
" 8	"	0.324
" 9	"	4.312

Of nine samples of tarletan, only two were found to contain arsenic, and these in proportions too small for determination.

Two samples of green cambric were found to contain arsenic, the one giving 4.000 grms, and the other 3.879 grms, per square yard.

The arsenic was dissolved from the fabrics by treatment with hydrochloric acid. From the filtered solution, the copper was precipitated by excess of potassium hydrate. The filtered liquid,

acidulated, was now treated with hydrogen sulphide, and the precipitate oxidized with nitric acid, and heated on the sand bath, to vaporize sulphuric acid and dispel organic matter, the residue being weighed as arsenic anhydride (Vaughan's method, *Am. Chemist*, 7, 348, March, 1877).

#### IX. EXAMINATION OF PICKLES FOR COPPER.

Mr. Edwin Hawley subjected fifteen samples of grocers' pickles to an analysis for copper and other poisonous metals. They were obtained in Michigan, except two samples which were furnished by Chicago dealers. Only one sample was found to contain copper, and this was in an enormous amount. From 5.909 grms of pickle (drained, but not dried), the weight of cuprous sulphide was 0.0755 grm. This gives over four per cent. (4.58 per cent.) of crystallized copper sulphate in the pickle. The pickles of this sample left a decided copper deposit upon a bright knife, upon a few minutes contact. In the examination, the pickle was dried, and ignited in a porcelain crucible, with additions of sulphuric acid. The residue was treated with dilute nitric acid and water, and the resulting solution charged with hydrosulphuric acid gas. Negative results showed absence of lead, etc., as well as copper.

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#### XXXV.—NOTE ON THE DETERMINATION OF ALCOHOL WITH COBALT SULPHOCYANIDE.

BY T. T. MORRELL.

In the *American Chemist*, 6, 370, I published a process for the determination of alcohol, based upon the use of cobalt sulphocyanide. A. Vogel has lately experimented in the same direction, and observes that approximate results may be reached. As I think the principle capable of giving very exact results, I trust that I may be permitted a few words of explanation.

The method as published, directed to place a measured quantity of the dark blue alcoholic solution of sulphocyanide, of standard strength, in the testing tube, and pour the sample to be examined upon it, until just the faintest blue color remained, matching a strip of pale blue glass. This method had the advantage that the temperature was not much altered by the treatment, but had the disadvantage that the red tint of the aqueous sulphocyanide, which decidedly tones the last traces of the blue, was differently diluted in treating samples of different richness. This I overcame, at first, by