	Sirups. cc.	Sugars. cc.
Average	8.5	7.9
Min	6.7	4.7
Max	10.7	13.6

The results on nearly fifty adulterated samples are in each case much lower than the above and correspond closely to the amount of pure maple present in the sample, as indicated by the results of a complete analysis.

BUFFALO LABORATORY.

MALT ANALYSIS; DETERMINATION OF EXTRACT. II.[1]

BY H. AUG. HUNICKE.

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The continuation of a study of the quantitative influence of various disturbing elements in the determinations of the extract of malt has resulted in observations of more or less general interest. The investigation is incomplete and of necessity fragmentary. Little more than the recording of experimental results is contemplated in this paper. Being without immediate hope of completion results are given in their incomplete form because they may even so be of some interest to workers in the same field of research.

The method of extract determination in use in the United States is not explicit in directing the use of the entire filtrate for the density determination as does the German method; it even suggests that only so much of the filtrate need be taken as is sufficient for a density determination. Such a procedure leads to a variation of results which makes the determination one of great uncertainty in the case of coarse grindings.

The difficulties of devising well defined methods of procedure for the extract determination of malt are great both on account of the chemical processes involved and the peculiar physical conditions prevailing. The mashing fluid consisting of carbohydrates, including, besides the crystallizable maltose, a more or less variable amount of viscous dextrins closely related to the original starch, both in their solubility and extreme slowness of diffusion; while the insoluble fibrous cellular pulp remaining in contact with the wort not only retains the more viscous constituents, mechanically preventing a ready diffusion, it also assumes, only very slowly, a state of equilibrium with respect to the solution. The phenomena of absorption and adsorption, both operative, respond to changes of concentration only with great slowness and it is for this reason that the dilution of the unfiltered wort just before filtration formed the subject of a series of experiments. The ordinary procedure of cooling down to the temperature of the room and then adding cold water

[1] Part I, THIS JOURNAL, 26, 1211.

to make up the weight to 450 grams does not by any means insure uniform results even with vigorous stirring after dilution. It is practically impossible to abstract from the fibrous insoluble pulp all of that which it will yield up to the solution before the filtration is complete.

In the following experiments, the malt was mashed in the manner previously described, unless otherwise stated.

SERIES VIII.—MALT II. MOISTURE, 4.45 PER CENT.

Filtrate drawn off in fractions of 75 cc. each and the extract calculated from the density.

75 cc.	Fraction.	1.	2.	3.	4.
1 Mash	Fine	73.67	74.60	74.79	74.83
2 "	"	72.78	74.58	74.69	74.77
3 "	"	73.45	74.47	74.42	74.18
4 "	"	72.81	74.48	74.62	74.37
Average		73.28	74.53	74.63	74.54
1 Mash	(25[1])	67.04	70.84	72.67	74.34
2 "	"	68.19	71.21	72.71	74.34
Average		67.12	71.03	72.69	74.34

From this it appears that the first 75 cc. are far below the average concentration of the remaining fractions. While the second, third and fourth fractions of the finely ground malt are alike within the limits of error, those of a coarsely ground malt continue to increase until the fourth fraction is nearly that of the finely ground series. The usual method of analysis corrects this source of error by returning the first runnings to the filter.

A number of determinations were made in which the amount returned to the filter was varied.

SERIES IX.—MALT II. MOISTURE, 4.45 PER CENT.

First 50 cc. returned.	Fine.	(25).
Took 150 cc.	73.95	...
Average	73.95	...
Took 335 cc.	74.18	71.22
" "	74.14	71.83
" "	74.18	...
" "	74.19	...
" "	74.29	...
" "	74.14	...
Average	74.19	71.53

First 75 cc. returned.	All fine. First 150 cc.	All fine. Second 150 cc.
Took 150 cc.	74.55	74.39
" "	74.43	74.31
" "	74.15	74.26
" "	74.02	74.35
" "	74.63	74.58
Average	74.36	74.38
First and second 50 cc. returned.		
Took 150 cc.	74.03	
" "	74.03	
Average	74.03	

[1] In stating degree of fineness by a number in parenthesis the latter is measured on the scale of the Seck mill as has become the custom quite generally.

SERIES X.—MALT IV. MOISTURE, 4.02 PER CENT.

Varying the quantity returned and taking 300 cc., at the same time varying the degrees of fineness of the malt.

	Fine.	(0)	(25)	(50)
50 cc. returned and took 300 cc.	72.67	71.16	69.96	48.28
75 cc. " " " "	73.05	71.35	69.45	47.95
100 cc. " " " "	73.10	71.44	69.90	48.69
150 cc. " " " "	73.01	71.82	69.33	48.26
Average	72.96	71.44	69.66	48.29

It cannot be said that the variation of the amount returned to the filtrate affects the results sufficiently to be discernible in the presence of errors far in excess of these. The cause of the comparatively large errors of the coarser grades will become more apparent when the results given below are studied more carefully.

The results thus far make it apparent that the wort when thrown on the filter does not contain all the soluble matter it will eventually receive. An attempt was made to leach out the pulp more thoroughly by stirring vigorously after dilution and prior to filtration. As the error from this cause would be most pronounced in the results from the coarse grindings these were taken.

SERIES XI.—MALT V. MOISTURE, 4.23 PER CENT. (ALL "25.")

Stirring varied after completion of mash and dilution and, as the stirring process contemplated would extend the time of the mashing period, in some cases very considerably, some means had to be sought to check the further action of the diastase. It is known that alkalies retard the action of diastase and in sufficient quantities inhibit hydrolysis as completely as for example mercuric chloride. Both these agents were therefore tried with the following result:

First 300 cc. returned and 300 cc. taken.

Stirred ten minutes after dilution.

A. Without addition..... 71.09
B. NaOH added so that diluted mash contained 0.02 per cent..... 71.43
C. $HgCl_2$ added so that diluted mash contained 0.002 per cent..... 70.57

"B" required three hours for filtration which in itself accounts for the higher result.

"C" was satisfactory in all respects and therefore used as the inhibiting agent in all subsequent experiments.

Stirred resulting mash after completion as indicated.

	A.		B.	
	a.	*b.*	*a.*	*b.*
Stirred 10 minutes.....	70.73	70.31	70.03	69.55
" 20 "	70.88	70.43	70.40	70.02
" 30 "	70.48	70.63	70.23	70.51
" 30 "	70.60	70.72	70.50	70.54
" 30 " and gently during mashing.....	70.83	70.27	70.35	70.35
" 30 " " moderately "	70.66	70.16	70.15	70.19
" 30 " " vigorously "	70.75	70.89	70.92	70.45
" well, let stand 24 hours filtered.....	...	71.71	...	71.24

	A.		B.	
	a.	*b.*	*a.*	*b.*
Stirred well, let stand 24 hours filtered	...	71.37	...	71.57
Stirred well, let stand 24 hours, but did not filter, took up with pipette from 80 to 90 cc. of the unfiltered supernatant wort	...	64.52	...	65.68
Stirred well, let stand 24 hours, but did not filter, took up with pipette from 80 to 90 cc. of the unfiltered supernatant wort	...	66.79	...	64.87

A. First 150 cc. returned and 300 cc. taken.
B. First 100 cc. returned and 300 cc. taken.
a. Without addition of inhibiting agent.
b. $HgCl_2$ added so that diluted wort contained 0.002 per cent.[1]

The most striking results are certainly those cases in which the unfiltered mash was allowed to stand twenty-four hours. The results on the filtered mash are, as might be expected, higher than those obtained on mash filtered immediately upon completion while those remaining undisturbed after a vigorous stirring are pronouncedly low, an evidence of a separation of the solute from the solvent in the presence of the fibrous pulp. More evidence of this phenomenon will be offered below.

MALT V. (*Continued*).

Stirring varied during mashing in such a way that each mash was stirred at indicated intervals. Time stated in minutes.

	I. First 75 cc.		II. Second 75 cc.		III. Third 75 cc.		IV. Fourth 75 cc.	
	0.5.	5.	7.5.	10.	15.	30.	60.	90.
I.	70.68	70.00	69.79	68.75	68.32	68.34	68.30	68.58
II.	70.59	69.96	69.73	68.93	69.04	68.87	68.85	68.80
III.	70.87	70.26	70.14	69.49	69.74	69.68	69.79	69.58
IV.	71.21	70.86	70.85	70.74	71.45	...	71.49	71.18
Av.	70.84	70.27	70.13	69.48	69.64	69.46	69.61	69.54

The usual concentration in the higher fractions is again apparent. The vertical columns would seem to indicate that stirring must be done at least every ten minutes to affect the results at all. The averages of the ten-, fifteen-, thirty-, sixty- and ninety-minute intervals are 69.48, 69.64, 69.46, 69.61 and 69.54 respectively, practically identical. The averages of the first three intervals show a well defined increase as the stirring is increased.

All results thus far are characterized by the very gradual yielding up of the extract to the solution. While the first 225 cc. are in most instances in fairly close agreement, the fourth 75 cc. fraction is always considerably higher. The dilution of the mash after cooling is doubt-

[1] Maercker, *Spiritusfabrikation*, 6th Edition, p. 34, states that from one to two parts per two hundred thousand parts of mercuric chloride inhibit the action of diastase completely.

less the main cause of the slow diffusion of some of the extractive matter into the solution. It was decided to modify this feature of the method of operation. Water of 70° centigrade was added under varying conditions.

SERIES X.—MALT V.

The mashing was begun as usual, beginning with a half hour of digestion at 45° and followed by a rise of one degree of temperature for every minute so that after twenty-five minutes the mash had acquired the temperature of 70° where it was allowed to remain, instead of one whole hour, only thirty minutes, when water of 70° was added in portions of 30 cc. at intervals of five minutes, beginning one hour and twenty-five minutes after mashing had been begun, so that the sixth 30 cc. were added one hour and fifty minutes after the beginning, and allowing five more minutes; the entire process was completed as usual, whole was cooled and diluted up to a total weight of 450 grams, filtered after stirring as usual.

	I.	II.	IV.	III.
First 75 cc.	70.11	70.51	70.27	70.35
Second "	70.09	70.44	70.23	70.28
Third "	70.25	70.68	70.43	70.29
Fourth "	70.55	70.99	70.87	70.86
Average	70.25	70.65	70.45	70.47

This series shows far greater concordance than all previous series. As the supply of malt had become exhausted, another sample had to be taken in hand.

SERIES XI.—MALT VI. MOISTURE, 4.84 PER CENT.

Added 50 cc. of water at 70° at one hour twenty-five minutes, thirty minutes thirty-five minutes and forty minutes, making in all 200 cc. hot water added.

First 75 cc.	72.16	71.83	71.59	70.98
Second "	72.16	71.83	71.58	71.01
Third "	72.21	71.86	71.60	71.03
Fourth "	72.37	71.96	71.70	71.12
Average	72.22	71.87	71.62	71.04

While the filtrate fractions show an eminently satisfactory agreement, the four mashes agree only very poorly among themselves. This is at least in part due to the early dilution.

SERIES XII.—MALT VI. MOISTURE, 4.84 PER CENT.

Added 50 cc. of water at 70° at one hour fifty-five, fifty-eight, sixty-one and sixty-five minutes. Stirred vigorously for five minutes, thus prolonging the process fifteen minutes longer than by usual method.

First 75 cc.	71.71	71.93	71.94	72.27
Second "	71.64	71.89	71.94	72.24
Third "	71.65	71.91	71.94	72.25
Fourth "	71.99	71.99	72.04	72.30
Average	71.75	71.93	71.96	72.27

Again the same relations appear, only the four mashes do not differ so much among each other as in the previous series. The separate fractions of each mash show a remarkable agreement.

As above, stirring fifteen minutes while remaining at 70°, cooling and adding the little needed cold water to make up total weight to 450 grams and then filtered.

First 75 cc.	72.40	72.25	72.29	72.24
Second "	72.23	72.20	72.26	72.16
Third "	72.34	72.28	72.34	72.26
Fourth "	72.75	72.38	72.67	72.53
Average	72.43	72.28	72.39	72.30

This series in itself is perhaps as satisfactory as may be expected under the working conditions. The averages represent the results as they would appear from the extract determination on the entire filtrate and show good agreement.

The adding of thirty minutes to the required time of making an extract determination is in itself no recommendation to this method and another effort was made to reduce the time, at the same time using a larger amount of mercuric chloride.

Same as Series XII but adding 0.04 per cent. $HgCl_2$ and adding 200 cc. water in four portions of 50 cc. each, gradually instead of intermittently and stirring whole after completion, five minutes.

First 75 cc.	72.09	72.27	71.94	72.14
Second "	72.08	72.16	71.91	72.11
Third "	72.12	72.31	71.95	72.19
Fourth "	72.38	72.48	72.23	72.33
Average	72.17	72.30	72.01	72.19

These results are not entirely satisfactory and the mashes do not agree to the extent that might be hoped although the results must be considered as very uniform for extract determinations of coarse grindings.

The invariable increase of concentration of the filtrate fractions as each 75 cc. fraction was drawn off made it apparent that the remaining filtrate not included in the extract determination contained a not inconsiderable amount of extract compared with the first three fractions, which always showed the greatest agreement. A set of determinations was therefore made to get an idea as to the quantitative differences resulting from the discarding of the last fraction of filtrates.

Added 0.002 per cent. $HgCl_2$ and diluted to 450 grams in the customary manner. Then let stand forty-eight hours, stirred and filtered.

First 75 cc.	73.17	72.90	73.18	73.02
Second "	73.34	73.07	73.21	73.09
Third "	73.44	73.14	73.33	73.18
Fourth "	73.82	73.43	73.60	73.40
Average	73.44	73.14	73.33	73.17

From this it appears that results obtained are about one per cent. higher than when the process is completed at once. However, in order to investigate the relations further, another series was carried through a similar process.

Adding 0.002 per cent. $HgCl_2$ and 50 cc. water of 70° four times, making nearly 450 grams total weight of beaker content. This required sixteen minutes. Stirred vigorously and let stand twenty-four hours, then filtered.

First 75 cc.	73.63	73.49	73.41	73.20
Second "	73.51	73.39	73.34	73.12
Third "	73.55	73.44	73.37	73.13
Fourth "	73.67	73.57	73.45	73.21
Average	73.59	73.47	73.39	73.17

A good agreement in each set is observed, but a similar disagreement of the sets among each other.

All these results show that it is not so much a matter of less extract resulting from mashing the coarser malt but rather that the slowly converted starch only very slowly diffuses out of the cellular pulp as it is gradually hydrolyzed, the more viscous dextrinous products resulting from the breaking down of the starch molecule being retarded in their diffusion, both by their own physical nature as well as that of the pulp. With the requisite stirring, the viscous and less diffusible products gradually leave the immediate influence of the fibrous pulp and enter the separated solution, which goes to show that mechanical absorption is the more important factor. At the same time any method of extract determination which yields results fully as high for coarse as for fine grindings fails to fulfil its purpose. The method must therefore be so devised that it will not release any too great a portion of the absorbed extract so that it may be a measure of the difference due to the chemical change resulting from the malting process whether due to the latter or to qualities of the grain itself. In other words, the result sought is rather an answer to the technical question than the determination of the amount of extract which can be obtained from a given malt, the fine grindings serving the latter purpose. Only a close comparison with the results of the brewhouse can determine the practical requirements in any given case.

The following method was therefore decided upon as giving results at once in fair agreement with each other and because it withdraws from the pulp that portion of the soluble matter which is directly available.

Weigh off fifty grams malt and grind to finest powder in mill for extract determination of fine grindings or in Seck mill set at (25) mark, observing all precautions to prevent loss in the process of disintegration. Add to malt which is caught in a copper beaker of about 500 to 600 cc. capacity, water (200 cc.) of such temperature that the whole charge may be at 45°. Place beaker in a water bath, stirring charge at regular intervals uniformly. With the apparatus used by the writer, it was found preferable to give the charge a rotary motion by means of a thermometer which served the purpose of a stirring rod. Six rotations were executed every five minutes. After thirty minutes' digestion at 45°, the temperature is made to rise so that every minute the thermometer

will rise one degree until it shall have acquired a temperature of 70°. This requires 25 minutes and then the whole is allowed to remain at 70° for one hour. Ten cubic centimeters of a solution of mercuric chloride of such concentration as to make diluted wort contain 0.002 per cent. are added and 200 grams or an equivalent volume easily measured in practice, of water at 70°. The whole is stirred during the addition of the water, which requires ten minutes, and five minutes longer. Cool to temperature of the room and add enough cold water to make a total weight of 450 grams. The amount can be so regulated that the desired weight is attained with what is needed to rinse the thermometer used as a stirring rod. After vigorously stirring, filter, returning the first 150 cc. to filter, and take 300 cc. for a specific gravity determination.

This method gives very satisfactory results so long as it is possible to conduct the mashing process in exactly the same way, especially during the period of rise of temperature. The writer firmly believes that with a properly designed mechanical stirring apparatus and means to insure a thorough and uniform transfer of heat by the use of water baths heated electrically and made to circulate so that the temperature may be uniform in the bath and regulated to a nicety, the process is the best available.

The method applied to the fine grindings of Malt VI gave the following results:

	I.	II.	Average.
75 cc.	74.53	74.67	74.60
75 cc.	74.32	74.51	74.42
75 cc.	74.41	74.52	74.47
75 cc.	74.46	74.66	74.56
Average	74.43	74.59	74.51

On coarsely ground (25) malt of the same lot the following results were obtained:

Mashed according to directions, then added 0.04% mercuric chloride then 200 cc. water of 70° in four portions, which required ten minutes, stirred five minutes, cooled and filtered.

First 75 cc.	72.31
Second "	72.21
Third "	72.39
Fourth "	72.44
Average	72.34

Repeated last test returning first 100 cc. to filter and taking 300 cc. for density determination, result 72.25; when first 150 cc. were returned and 300 cc. taken result was 72.27; while in a duplicate of the latter after letting stand twenty four hours before filtering the result was 72.98.

These results (72.34, 72.25, and 72.27) show very satisfactory agreement.

For comparison the German method of returning 100 cc. to the filter and taking the entire filtrate, which amounts to anything from about 320 cc. to perhaps 335 cc. at most, gave the following results:

Fine	73.78	73.55
Coarse (25)	71.22	....

The lower values of the German method are due essentially to the diluting of the mash after cooling while in the writer's method, dilution is effected at 70°.[1]

When the filtrate fractions of one mash are compared with each other, it will be found that there is a prevailing tendency for the first seventy-five cc. to be slightly higher than the second 75 cc., the subsequent ones increasing, as remarked before. By averaging thirty-two results from among those obtained on the coarse grindings representing the most uniform results, we find the following values:

First 75 cc.	72.14
Second "	72.12
Third "	72.15
Fourth "	72.23

The first fraction is so persistently higher that four worts, which had already been filtered and consequently left no residue upon refiltering, were filtered through four different ten-inch filters and 75 cc. fractions taken for density determinations.

Fraction.	1st.	2nd.	3rd.	4th.	5th.
French gray paper	74.44	74.43	74.34	74.29	74.30
S and S 797	74.26	74.15	74.15	74.14	74.13
Henry Heil cut	73.87	73.78	73.91	73.80	73.86
S and S 798	73.08	72.84	72.82	72.85	72.87
Average	73.91	73.80	73.78	73.77	73.79

From these results there can be no doubt as to the first 75 cc. being more highly concentrated than the remaining fractions. In seeking an explanation for the apparent concentration in the first fraction it should be noted that in the case of the previously filtered wort, the fractions run through the filter so rapidly that it requires all the dexterity at the command of the operator to make a change of receptacle for the various fractions, perhaps more particularly the first fraction. Doubtless the first fraction represents the solution in the unchanged condition while the later fractions have been impoverished, by a small amount, of the more colloidal constituents through the adsorptive properties of the fiber of the filter paper. This explanation accounts for the difference appearing only on the first fraction in the case of the homogeneous wort free from any insoluble matter, while the remaining fractions are almost identical. In the filtration of a mash, the retention of soluble constit-

[1] The method recently adopted by the brewing research stations at Berlin, Hohenheim, Munich, Nuremberg, Weihenstephan, Vienna and Zurich is a modification of the old method consisting in adding the first 100 cc. of water at 70° when the charge attains that temperature, the remaining 100 cc. of water being added as before at the completion of the mashing process. Accordingly, while results by this new method will be higher than those obtained by the old method they will not be quite so high as those obtained by the writer's method nor will they be as uniform.

uents by the fibrous pulp complicates matters so that the later fractions show an increasing amount of soluble constituents, which only very slowly drain out from the pulp.

The tenacity with which the pulp retains a part of the soluble matter is shown in the following results: Four mashes were made by the method described. When complete and diluted to 450 grams, two of these were poured into a liter measuring cylinder, and after thorough mixing, allowed to stand two days so that the pulp settled to the bottom. From the supernatant solution were taken 500 cc. in 100 cc. portions (approximately) and extract determinations made of each; the remaining fluid was filtered, yielding 130 cc. and containing 75.90 per cent. extract. The five fractions gave respectively 74.42, 74.47, 74.45, 74.40, and 74.45. As might be expected, the latter results are all alike, showing that the solution which separated from the pulp is homogeneous where it is out of contact of the latter. The third mash was poured into a liter flask and shaken repeatedly at intervals during two days, then filtered. This gave 75.19 per cent. extract. The fourth mash was poured into a liter cylinder and allowed to stand two days. It was then shaken thoroughly. On the third day it was again shaken and allowed to stand two more days, having thus had five days' allowance for thorough diffusion. The supernatant fluid, after filtration, gave 75.17 per cent. extract while the fluid entrapped in the pulp gave 75.47 per cent. Comparing the results from these four mashes, it appears, taking mash one and two, which had been combined, and yielded 480 cc. of a solution containing 74.44 per cent. extract and 320 cc. containing 75.90 per cent. extract, which for the entire 800 cc. makes 75.02 per cent. Mash 3 gave 75.19 per cent as stated. Mash 4 yielded 330 cc. with 75.17 per cent. extract and 70 cc. with 75.47 per cent. which for the entire 400 cc. makes 75.22 per cent. Thus the three results, 75.02, 75.19, and 75.24, agree very well.[1]

In commenting upon some earlier results of the writer, O. Mohr[2] expresses doubt as to the results, which showed that the smaller the malt charge taken for analysis, the lower was the percentage of extract found. This could, perhaps, not be expected *a priori* because the operations are designed to insure a complete conversion by the diastase. It will be shown, however, that the dilution resulting in the case of the smaller charges does affect the rate of conversion sufficiently to make itself felt in all determinations, especially so in the case of the smallest charges, where in addition the extreme dilution affects the hydrolyzing effect

[1] The inhibiting power of the mercuric chloride should be verified as all mashes yielded higher extract values after standing over night or longer. The writer believes that this result is essentially due to the slow release of the extractive matter.

[2] *Z. angew. Chem.*, **15**, 572 (1902).

of the diastase, which ceases to act appreciably on soluble starch when less than 0.75 per cent. is present.[1]

To verify the earlier results, mashes were made in the manner described above with varying charges. It must be noted, however, that the method of mashing differs from that previously used. The following results were obtained:

	50 grams.	40 grams.	30 grams.	20 grams.
I	74.47	74.15	73.92	73.45
II	74.95	74.29	74.19	73.19
III	74.29	74.58	73.22	73.49
Average	74.57	74.34	73.78	73.49

While this preliminary series corroborates previous results, it was deemed sufficiently important to investigate these relations still farther so that the quantitative influence might become better known. A similar set of determinations was made with charges of malt as indicated.

Weight of charge in grams.	Specific gravity found.	Per cent. extract in wort.	Per cent. extract in malt.	Calc. to dry.
50	1.03193	7.933	69.44	73.85
40	1.02514	6.278	69.06	73.44
30	1.01847	4.618	68.07	72.39
25	1.01537	3.843	68.18	72.51
20	1.01220	3.050	67.88	72.19
15	1.00904	2.260	67.19	71.39
10	1.00602	1.505	67.34	71.61
5	1.00294	0.735	65.94	70.13

Another series was made, operating in all respects as in the previous case save that the maximum temperature was not reached as promptly and was not maintained as accurately, so that the entire results fall short of these of the last series.

Weight of charge in grams.	Specific gravity found.	Per cent. extract in wort.	Per cent. extract in malt.	Calc. to dry.
50	1.03093	7.689	67.13	71.39
40	1.02434	6.083	66.78	71.02
30	1.01799	4.499	66.23	70.43
25	1.01483	3.706	65.66	69.83
20	1.01177	2.941	65.34	69.49
15	1.00875	2.189	65.00	69.13
10	1.00576	1.439	64.33	68.41
5	1.00278	0.694	62.27	66.22

In order to determine the bearing of the phenomena of adsorption and absorption on the results obtained on varying charges, an attempt was made to eliminate the factor of concentration of the wort by adding such amounts of a carbohydrate to each mash as would make the concentration about the same in all cases. As the wort is a solution of great complexity, a study of various additions was planned, including glucose,

[1] *Die Fermente und ihre Beziehungen*, p. 209, C. Oppenheim.

maltose, sucrose, dextrin and a wort of proper concentration to bring about the desired effect. With glucose additions, results as follows were obtained:

Weight of charge in grams.		Specific gravity found.	Per cent. extract in wort.
Malt.	Glucose.		
50	0.00	1.03189	7.923
40	7.50	1.03141	7.806
30	15.00	1.03102	7.711
25	18.75	1.03100	7.706
20	22.50	1.03079	7.655
15	26.25	1.03065	7.621
10	30.00	1.03048	7.580
5	33.75	1.03021	7.514

For purposes of comparison, the differences of the percentage of extract in the first and third series are added, together with the ratio of the resulting differences and the amount of glucose taken.

Differences of two series.	Ratio of differences to amount of glucose taken.	Corrected ratio.
0.00	0.000	0.000
1.528	0.204	0.204
3.099	0.207	0.204
3.863	0.206	0.208
4.605	0.205	0.206
5.361	0.204	0.204
6.075	0.203	0.208
6.779	0.201	0.206

It appears that the ratio is practically constant, especially when a correction is applied which allows for the slight difference in mashing temperature which evidently prevailed in the two mashes, calculated on the basis of the results of the second series. Of course, this so-called corrected ratio is distorted by the summation of the errors of all three series, but the suspicion which the uncorrected ratio might provoke, is thus removed, the uncorrected ratio showing a perceptible decrease as the dextrose charges increase. The series made with the addition of dextrose thus agrees very closely with that made without such addition.

While it does not appear from these results that the phenomenon of adsorption materially affects the results on varying the charges, it is quite clear that the decreased yield of extract is primarily due to the retarding effect of dilution.

The complexity of the solution does not justify the application of the formula representing the relation of concentration of solutes between the liquid and solid solvents and, if applied, the formula leads to contradictory results.

Similar determinations with other carbohydrates could not be made, as the investigation had to be discontinued. This is the more to be re-

gretted as especially the dextrin and wort would have introduced colloidal constituents which would in all probability have brought out more strongly the effect of adsorption which phenomenon must of necessity be associated with the changes of the relation of the solution and the pulp.

This investigation was undertaken solely for the purpose of finding conditions which would make it possible to obtain definite and uniform results for the extract in malt, more particularly for the coarse grindings. Although the result may not stand for a completed reaction but rather the attainment of an equilibrium between the solution and the insoluble pulp the method suggested gives results far more uniform than any method heretofore proposed.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE, SUGAR LABORATORY.]

THE ESTIMATION OF DRY SUBSTANCE BY THE REFRACTOMETER IN LIQUID SACCHARINE FOOD PRODUCTS.[1]

BY A HUGH BRYAN

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The Abbé heatable prism refractometer has come into use in England and on the continent for determining the dry substance content of sugar house products. On account of its ease of manipulation, and the accuracy of the readings as compared with actual dry substance, it has grown into favor. In 1906, Tolman and Smith[2] found that for practical purposes all sugars have the same index of refraction for the same concentration. They prepared a table for whole percentages of sucrose, giving the index of refraction taken at 20°. From their work, they came to the conclusion that the refractometer is a satisfactory instrument for determining the soluble carbohydrates in solution under the same conditions as those under which specific gravity can be used. In the same year Hugh Main, chemist of the Tate Refinery, London, England, called the attention of Drs. Wiechmann, Geerligs and Herzfeld, to the employment of the refractometer in estimating dry substance in refinery products. He had prepared a table from which the per cent. of water could be obtained from the refractive index. This table and his work were not published until 1907.[3] He found the readings accurate to 0.1 per cent. as compared with the usual methods of estimating water in sirups by drying on sand. Prinsen Geerligs,[4] at the suggestion of the above author,

[1] Published by permission of the Secretary of Agriculture.

[2] THIS JOURNAL, **28**, 1476 (1906).

[3] *Intern. Sugar Journal*, **9**, 481 (1907).

[4] *Ibid.*, **10**, 68 (1908).