

larger bodies free from the apertures, and allow the smaller ones to pass through without much trouble.

Mr. O. GUTTMANN said that the author had approached an interesting subject from the standpoint of physical chemistry. The peculiar movement of the crystals in Tyndall's experiments on the melting and re-congelation of ice, the crystallisation under movement of Bock, whereby the size of the crystals could be increased, and the very fine grinding of cellulose by means of a beater, resulting in a mass setting as hard as a stone, instead of a spongy-pulp—all these had a chemical as well as a physical aspect. In this case also the author had shown, that, whether due to vortex motion, or to pressure, or to both, different structures of residues could be obtained, from different chemical compounds, which were well worth further investigation.

Dr. J. C. CAIN suggested that it was common knowledge in works that crystalline substances filtered well and gelatinous substances filtered badly. If a substance was found to filter badly, the first thing one tried to do was to make it of a more crystalline nature.

Mr. HATSCHEK, in reply, said he had not been able to go into the question of a comparison between filtration and sifting, but the difference was that in filtration the arrangement of the particles was a stream-like phenomenon, which was determined by the orifices in the septum. The particles did not settle themselves as they would by continual shaking. A cake of calcium sulphate, when taken out of a filter press, would become liquid on agitation. The structure of a filter press cake was radically different from that obtained by continual shaking or sifting. The stoppage of orifices in the septum was really a useful feature, because the particles were never constantly of one size. In the case shown in Fig. 1, the prevailing quantity of spheres would be of one size, but some would be smaller, and these would be set in motion first and would go through. This was a commonly known thing, as evidenced by a small running of turbid filtrate at the beginning of a filtration. Then the large particles entered the orifices and throttled them, and, after that, the small particles would not go through and a clear filtrate resulted.

Take the case of yeast, which was frequently mixed with the bacilli of lactic and butyric acid, which were of much smaller magnitude than the yeast. If a liquid containing only the bacillus of lactic acid were filtered through cloth, it would all go through; but with a liquid containing both yeast and bacillus, after the yeast had deposited itself, the bacilli would be retained.

## Manchester Section.

Meeting held at Manchester on Friday, April 3rd, 1908.

MR. R. H. CLAYTON IN THE CHAIR.

### BEER ANALYSIS.

BY JOSEPH RACE, A.I.C.

#### I.—THE APPLICATION OF THE PULFRICH REFRACTOMETER TO THE ESTIMATION OF ALCOHOL AND EXTRACT.

In the following paper the results are given of a study of the principal processes used in the analysis of beer. Special attention has been paid to the refractometric estimation of alcohol and extract (total solids), and to the determination of sulphates and chlorides, as considerable differences of opinion seem to exist as to the precautions necessary for obtaining accurate results.

*The original gravity.*—The alcohol and extract figures required for the calculation of the original gravity may be obtained by the usual distillation method, or by means of the Zeiss immersion refractometer. The latter method has been fully described in other journals, and although a general criticism of the principles on which the process

is based will, the author hopes, be of interest, he only intends to deal in detail with the adaptation of this method to the ordinary refractometer.

The process is based on the fact that if the specific gravity and refractive index are known, the alcohol and extract percentages may be calculated, for if  $C_1$  be the amount by which the refractive index is raised by each 1 per cent. of alcohol,  $C_2$  the amount by which it is raised by each per cent. of extract,  $C_3$  the amount by which the sp. gr. is lowered by each per cent. of alcohol, and  $C_4$  the amount by which it is raised by each per cent. of extract, and  $X$  and  $Y$  are the percentages of alcohol and extract required,—

then  $r$ , the refractive index of the sample } =  $C_1X + C_2Y$ ,  
- the refractive index of water }

and  $s$ , the sp. gr. of the sample - } =  $-C_3X + C_4Y$ ,  
the sp. gr. of water (1.0) }

from these it follows that,—

$$X = \frac{C_4r - C_2s}{C_2C_3 + C_1C_4} \quad \text{and} \quad Y = \frac{C_3r + C_1s}{C_2C_3 + C_1C_4}$$

Schwarz (Nordd. Brauer. Ztg., 973; Analyst. 12, 200) was the first to determine these constants, but as his figures are incorrect it is unnecessary to discuss them further. Barth (Z. ges. Brauw., 1905, 28, 303—306) this J. 1905, 630, made a number of determinations of the values of  $C_1, C_2, C_3, C_4$ , and the figures so obtained substituted in the above expressions give the following formulæ:—

$$X = [0.007598r - 0.002923s]100,000.$$

and

$$Y = [0.003366r + 0.001303s]100,000.$$

Below I have given the percentages of alcohol and extract as determined by the distillation method, and from the refractive indices of the distillate and residue (at their original volumes) calculated the values of  $C_1$  and  $C_2$ . All specific gravities are taken at 15.5° C. and the refractive indices at the same temperature for the sodium line D.

	Alcohol per cent. by wt.	$C_1 \times 100,000$	Extract per cent.	$C_2 \times 100,000$
1....	3.55	57.0	2.46	160
2....	3.26	56.0	3.23	157
3....	3.78	57.8	3.38	162
4....	4.50	58.0	3.40	158
5....	4.03	58.5	4.12	159
6....	5.10	59.0	4.10	157
7....	5.37	59.8	5.04	157
8....	5.70	60.1	5.30	158

It will be seen that as the alcohol percentage increases,  $C_1$  also increases, whilst  $C_2$  seems to be practically constant for all percentages at which well attenuated English beers usually fall.

$C_3$ , as the following table shows, decreases continually with increasing alcohol percentage, and as the solution curve for sugar is practically a straight line within the limits for the sugar content of beer,  $C_4$ , like  $C_2$ , is constant.

Alcohol per cent.	1000 - Sp. gr.	$C_3 \times 1000$
2.0	3.80	1.90
3.0	5.46	1.82
4.0	7.13	1.79
5.0	8.78	1.75
6.0	10.38	1.73
7.0	11.88	1.69
8.0	13.22	1.63

An examination of the above figures shows that  $C_1$  increases at practically the same rate that  $C_3$  decreases, and thus, for the purpose of calculation, the constants determined for any particular sample should be applicable to all other samples in which  $X$  and  $Y$  are within reasonable limits. For samples under about 4.5 per cent. of alcohol

the formulæ of Barth give very satisfactory results, but over that figure the tendency is to give rather low results for both X and Y. For such samples I prefer the formulæ,

$$X = [0.00778r - 0.0029s]100,000.$$

$$Y = [0.0035r + 0.00130s]100,000.$$

A comparison of the results (expressed as grms. per 100 c.c.) given by the formulæ after correction for temperature is shown below:—

Alcohol per cent. by distillation.	Alcohol by Barth's formulæ.	Alcohol by modified formulæ.	Extract by drying.	Extract by Barth's formulæ.	Extract by modified formulæ.
5.76	5.48	5.78	4.00	3.93	3.95
5.21	5.13	5.22	3.65	3.61	3.63
5.43	5.37	5.47	3.83	3.75	3.77
6.10	6.00	6.10	4.21	4.13	4.17
4.89	4.84	4.94	3.27	3.24	3.27

The modified formulæ give on the average 0.5 to 0.7% higher original gravity. The original gravity is calculated in the usual way from the alcohol and extract figures by the use of spirit indication tables. There is no doubt that the refractometer method gives results which are quite as accurate as those obtained by distillation, and as much less time is required, the process would be a great boon to those having many determinations to make.

**Chlorides.**—50 c.c. of the sample is evaporated with 0.5 gm. of barium carbonate and subsequently ignited to a black ash. The ash is well extracted with hot water, filtered, and titrated with silver nitrate in the usual manner.

Ratcliff (Analyst, 32, 86) states that it is unnecessary to make alkaline in order to fix the chlorine, but from the results of a large number of experiments the author is of opinion that unless previous to evaporation and ignition the solution is made distinctly alkaline, a considerable loss of chlorine will result. Barium carbonate gave the most satisfactory results, as it obviates the tendency of the ash to fusion, and, being insoluble does not interfere with the subsequent titration. The method of Loubion (Rep. Pharm., 1898, 3, 10, 493) is rapid, but as the author was unable to obtain a satisfactory end reaction he found it of very little value.

**Sulphates.**—The estimation of sulphate is sometimes important in tracing the origin of a beer, although the modern tendency to use artificial hardening mixtures has to a great extent impaired its utility. The ordinary process of evaporation, ignition, washing, and treating with barium chlorides is now generally acknowledged to give low results. Windisch (Woch. f. Brau., 1905, 22, 17; this J., 1905, 155) first called attention to this fact, and recommended the use of caustic soda or baryta. In confirmation of this I give the results of a number of determinations obtained from a series of beers, with and without the addition of an alkali. In all samples of beer showing a normal amount of acidity, 2.5 c.c. of normal sodium hydroxide solution for 50 c.c. of the sample will be found quite sufficient to prevent the loss of sulphate:—

Sulphuric anhydride in grains per gallon.

Without soda.	With soda.
52.87	63.42
38.16	41.65
20.73	34.81
19.00	38.12
33.27	40.36
16.05	23.28
32.38	36.83
35.04	38.10

In a recent paper in the Analyst (Vol. 32, 84), Ratcliff suggests that the presence of acid phosphates is one of the causes of the loss of sulphuric anhydride on ignition. That this is the case will be seen from the following figures, which are the results of a number of experiments in

which 0.1 gm. of gypsum was ignited with various substances:—

Added substance.	Loss of sulphuric anhydride per cent.
0.1 gm. acid pot. phosphate.....	36.8
0.1 gm. acid pot. phosphate: lower temp.	20.8
0.1 gm. acid pot. phosphate + 0.2 gm. starch.....	38.7
0.1 gm. acid sodium phosphate.....	38.7
0.2 gm. starch.....	3.1
0.1 gm. disodium hydrogen phosphate .	nil.
0.2 gm. silica.....	nil.

Sodium sulphate when ignited at low temperatures with acid phosphates shows no loss of sulphate, but when the temperature is raised by the blowpipe a considerable loss occurs. The loss of sulphuric anhydride by these ignitions is probably due to the formation of acid potassium sulphate, which then decomposes into the neutral sulphate and sulphuric acid. Calcium sulphate and acid potassium phosphate being of the same molecular weight, the quantities used were also molecular.

If the reaction took place according to the following equations,  $\text{CaSO}_4 + \text{KH}_2\text{PO}_4 = \text{CaHPO}_4 + \text{KHSO}_4$ ;  $2\text{KHSO}_4 = \text{K}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ , the theoretical loss would of course be 50 per cent., but as the maximum is rather under this figure the action must partake of the nature of a mass action, the point of equilibrium depending largely upon the temperature at which the reaction takes place.

That the sulphuric acid is actually lost as such was proved by heating some of the mixture in a Rose crucible surrounded by asbestos to prevent access of sulphur from the flame, and drawing the gases evolved through wash bottles containing soda. In this way sulphuric acid was proved to be present and phosphoric acid absent. Another experiment showed that the acid so absorbed was equivalent to a loss of 11 per cent. of sulphuric anhydride.

## II.—ALL MALT AND SUBSTITUTE BEERS WITH SPECIAL REFERENCE TO YEAST NUTRITION AND TOXIC ACTION.

This research was undertaken with a view to determining whether or not it was possible to discriminate by means of chemical analysis between all-malt beers and those brewed with varying amounts of substitutes. Allen (Commercial Organic Analysis, Vol. I., 374) suggests that the nature and proportion of nitrogenous matter would be of material value for this purpose. If all beers were brewed under identical conditions and from malt of similar nitrogen content this might be the case, but when it is remembered that malt varies considerably in composition and that substitute beers are generally brewed under conditions favourable to the extraction of albuminoids, it is not surprising to find that they contain relatively large amounts of nitrogenous matter. The author has met with instances of worts containing as much as 20 per cent. of sugar substitutes which gave an albuminoid figure of over 6 per cent., when calculated on the solids, a figure which is equal to or above the average given by all malt worts.

As malt contains a considerable amount of phosphates and brewing sugars comparatively little, it was thought that the determination of the phosphoric acid in the ash would form a better means of differentiation than the nitrogen content. In the table of analyses it will be seen that in no instance did the phosphoric acid in a substitute beer approach that of one brewed from malt only. In most cases they were at least 30 per cent. lower. It has often been assumed that in a malt wort the phosphates are present in such quantity as to interfere with the stability of the beer. Samples A and B, however, which are brewed practically entirely from malt, and which contain a higher percentage of phosphates, were proved to be of exceptionally good keeping qualities; but the higher alcohol and hop content of these samples must also be taken into account.

Matthews (J. Inst. Brew., 1893, 6, [5]: this J., 1893, 367) states that in his opinion a high residual phosphate content offers a fertile soil for the growth of bacteria, and that when the yeast is not the dominant organism there is risk of deterioration; also, that the presence of phosphates in large quantities is prejudicial to attenuation.

Stern (J. Chem. Soc., March, 1899; see this J., 1898, 1167) draws certain conclusions from his experiments on the nutrition of yeast that may be conveniently summarised as follows:—

*Effect of the addition of inorganic nutriment containing 40–50 per cent. of  $P_2O_5$ .*

Nitrogen content.	Assimilation of nitrogen.	Per cent. of nitrogen in yeast.	Attenuation.	Yeast crop.
Normal or above normal .....	Slight increase.	<i>Nil.</i>	Slight increase.	Increase.
Below normal ....	<i>Nil.</i>	Decrease.	Increase.	Slight increase.

Stern states that when the elements necessary for the growth of yeast are present, 0.025 gm. each of nitrogen (as asparagine) and inorganic nutriment (44 per cent.  $P_2O_5$ ) per 100 c.c. are the largest quantities that could be assimilated by the yeast (0.325 gm.) under the conditions of the experiment. This he calls the "normal supply." The normal, therefore, approximates to 0.090 lb. of nitrogen and 0.037 lb. of phosphoric anhydride per barrel.

It will next be advisable to consider how far these conditions pertain to practical brewing. Taking first the case of an all-malt beer of standard gravity. This would give 14 per cent. of solids, or 50 lb. of solids per barrel (approx.). The solids of the wort contained 0.83 per cent. of nitrogen and 0.65 per cent. of phosphoric anhydride. A barrel therefore contains 0.41 lb. of nitrogen and 0.32 lb. of phosphoric anhydride, or 0.116 gm. and 0.091 gm. respectively per 100 c.c. After fermentation with 1 lb. of yeast per barrel, the beer gave the following figures:—Nitrogen 0.085 per cent. and phosphoric anhydride 0.045 per cent., or 0.30 and 0.168 lb. per barrel. The amounts lost during fermentation would be the equivalent of 0.11 lb. of nitrogen and 0.152 lb. of phosphoric anhydride.

About 7 lb. of yeast, including bottom yeast, per barrel were produced, and contained 0.072 lb. of nitrogen and 0.034 lb. of phosphoric anhydride.

Under these conditions, and assuming the amounts of nitrogen and phosphoric anhydride assimilated by the yeast to be the normal, then the wort before fermentation, assuming that the whole of the nitrogen and phosphoric anhydride is in an assimilable form, would be 4.82 times normal for the nitrogen, and 9.4 times normal for the phosphoric anhydride. As, however, only about 45 per cent. of the nitrogen is so available, and the whole of the phosphate is probably available, then calculated on this basis the wort was 2.17 times normal for nitrogen and 9.4 times normal for phosphoric anhydride. (Ratio  $P_2O_5:N=4.3:1$ ).

Reverting to Stern's experiments, the best result obtained as regards assimilation of nitrogen, attenuation of wort, and increase of yeast, when the nitrogen content was twice normal, was when the phosphoric anhydride content was 10 times normal or 0.25 gm. of inorganic nutriment per 100 c.c. It will thus be seen that the ratio obtained from the all-malt wort approximates to that found by Stern to be most suitable for similar nitrogen contents.

Two samples brewed with the use of about 20 per cent. of invert sugar gave the following results expressed in lb. per barrel:—

	Nitrogen.		Phosphoric anhydride.		Original gravity.
	i.	ii.	i.	ii.	
Before fermentation .....	0.360	0.382	0.173	0.221	i. 1052.8
After fermentation .....	0.277	0.287	0.115	0.141	ii. 1063.2
Assimilated by yeast .....	0.083	0.095	0.058	0.080	

The yeast produced was 6 and 6.5 lb. per barrel, respectively, and contained:—

	I lb.	II lb.
Nitrogen .....	0.055	0.062
Phosphoric anhydride .....	0.031	0.033

If the nutriment actually assimilated is taken as normal, and it is assumed that 45 per cent. of the nitrogen is assimilable, the worts before fermentation are, calculated to normal values:—

	I lb.	II lb.
Nitrogen .....	2.85	2.77
Phosphoric anhydride .....	5.5	6.68
Ratio, $P_2O_5/N$ .....	1.9	2.4

It will thus be seen that whilst an all-malt wort maintains the most favourable ratio of  $P_2O_5/N$  (for yeast nutrition), the substitute worts fall very much below it, and it is therefore evident that no excess of phosphoric anhydride is present in any of the worts. The substitute worts must, in fact, be considered deficient.

The above deduction is supported by the figures in the table where it will be observed that, when calculated to original gravity, the higher the phosphoric anhydride content, the lower the amount of unassimilated albuminoids. In further confirmation of this, a wort was prepared containing 40 per cent. of sugar extract, and divided into two parts. To one part 0.1 per cent. of acid potassium phosphate was added. Both samples were then pitched with equal quantities of the same yeast fermented, and the albuminoids estimated. The sample with the addition of phosphate contained 0.203 per cent. as against 0.269 per cent. in the other portion. Further, the table shows that there is no general material difference in the results of the analyses of all-malt and substitute beers; in fact, the only difference is in the percentage of phosphoric anhydride, and this is so small, even in the former, that no real nutritive value (as regards the human system) can be attached to it. The purchaser of samples brewed with the use of substitutes is therefore clearly not prejudiced by a deficiency or addition of any substance.

The products obtained from sugars and raw grains that are not present in malt are, according to Allen, (1) The acid decomposition products such as tyrosine and leucine, and (2) humin bodies. As regards the former, it is very uncertain that such products are peculiar to acid decomposition, as enzyme action produces amino bodies which are similar to, if not identical with tyrosine and leucine. Again, such bodies even if present would not be found in the wort after fermentation. Humin bodies, on the other hand, may possibly be found in the beer, but as little is known as to their toxic action and the quantity present can only be very minute, their presence is of no importance. Humic acid, the acid corresponding to these humin bodies, is probably present in all upland water supplies, and as no toxic action has been ascribed to this acid *per se*, it is extremely probable that the bodies from which it is derived are also harmless. Many of the unpleasant symptoms due to excessive use of beer have been attributed to the substitutes that may or may not have been used in its production, but it will be seen from the above that such an allegation is baseless. The physiological effects produced by beer, apart from the alcohol, must be due to the hop principles, and it is interesting to compare the amounts of the various principles present in beer with the medicinal doses of the same. The general constituents of *Humulus lupulus* (vide Hale White's Materia Medica) are (1) Lupulin, a liquid alkaloid; (2) lupinic acid, a bitter crystalline principle; (3) valerol, 1 per cent., an aromatic oil giving the odour; (4) resin; (5) tannin; (6) a sesquiterpene,  $C_{15}H_{24}$ . Griseb and Harrow have also proved the presence of choline in beer. The official preparations of *Humulus lupulus* are:—*Infusum lupuli*, 1 in 20 (boiling water); dose 1–2 fluid ounces. *Tinctura lupuli*, 1 in 5 (alcohol, 60 per cent.); dose  $\frac{1}{2}$ –1 fluid drachm. *Lupulinum*: dose, 2–5 grains. Taking the infusion as the preparation most closely approximating to beer, the proportions are:—

Results are in grms. per 100 c.c. except where otherwise denoted.	100% malt. A.	Malt. B.	14% M. 10% I. C.	28% I. 10% R. D.	20% I. E.	15% I. F.	25% I. G.	35% I. H.
Original gravity .....	1002.1	1001.7	1051.2	1039.1	1049.6	1053.1	1051.1	1060.3
Present gravity .....	1012.1	1005.8	1010.1	1009.5	1013.0	1006.1	1013.3	1021.3
Absolute alcohol by weight .....	5.30	6.02	4.51	3.32	4.08	5.07	3.78	5.10
Apparent attenuation, per cent. ....	80.5	90.6	82.2	75.7	73.8	88.5	73.9	64.6
Extract: total solids .....	5.25	3.81	4.35	4.04	5.02	3.53	3.23	5.30
Extract (3.80) .....	5.40	3.08	4.54	3.89	—	3.78	3.45	5.51
Ash .....	0.35	0.32	0.27	0.19	0.21	0.28	0.18	0.24
Potash (K <sub>2</sub> O) .....	0.0107	0.029	0.027	0.021	0.024	0.026	0.022	0.025
Nitrogen .....	0.083	0.077	0.057	0.042	0.067	0.078	0.053	0.075
Albuminoids (N × 6.3) .....	0.523	0.485	0.359	0.264	0.422	0.493	0.334	0.473
Phosphoric anhydride .....	0.045	0.041	0.022	0.014	0.019	0.028	0.023	0.022
Volatile acidity calc. as acetic acid...	0.012	0.012	0.012	0.020	0.018	0.018	0.024	0.014
Residual acidity calc. as lactic acid ..	0.132	0.115	0.117	0.130	0.120	0.115	0.136	0.127
Chlorine calc. as sodium chloride, grains per gall. ....	20.70	17.32	27.17	32.34	28.87	50.52	50.82	63.52
Sulphuric anhydride, grains per gall. ....	63.42	41.65	38.02	37.34	36.13	18.48	23.42	21.21
Albuminoid nitrogen calc. as percentage of total nitrogen .....	75	77	—	—	—	—	—	—
Albuminoids × 10,000—original gravity .....	84	78	70	67	85	93	65	79
Phosphoric anhydride × 100,000—original gravity .....	72	66	43	36	39	52	45	36

Results are in grms. per 100 c.c. except where otherwise denoted.	20% R. 15% I. I.	40% I. J.	15% M. 10% I. K.	10% G. 15% I. L.	B.P.G. and I. M.	I. N.	I. O.
Original gravity .....	1036.3	1037.2	1053.5	1052.7	1050.5	1048.8	1058.6
Present gravity .....	1004.6	1007.3	1009.8	1009.7	1009.9	1013.3	1016.2
Absolute alcohol, by weight .....	3.40	3.32	4.70	4.64	4.45	3.84	4.51
Apparent attenuation, per cent. ....	87.3	80.3	81.6	81.6	80.4	72.7	72.3
Extract: total solids .....	1.97	3.11	4.31	4.30	4.40	5.22	6.33
Extract (3.80) .....	2.61	3.30	4.68	4.63	4.47	5.28	6.43
Ash .....	0.36	0.20	0.38	0.32	0.22	0.23	0.24
Potash (K <sub>2</sub> O) .....	0.021	0.020	0.023	0.024	0.020	0.021	0.023
Nitrogen .....	0.053	0.030	0.059	0.050	0.053	0.054	0.064
Albuminoids (N × 6.3) .....	0.333	0.245	0.371	0.315	0.333	0.339	0.403
Phosphoric anhydride .....	0.014	0.014	0.031	0.027	0.025	0.024	0.029
Volatile acidity calc. as acetic acid .....	0.016	0.012	0.013	0.018	0.014	0.015	0.013
Residual acidity calc. as lactic acid .....	0.130	0.124	0.130	0.125	0.120	0.124	0.118
Chlorine calc. as sodium chloride, grains per gall. ....	26.56	47.36	48.71	46.37	48.34	43.67	44.88
Sulphuric anhydride, grains per gall. ....	33.00	20.31	35.18	34.81	36.75	38.12	37.91
Albuminoid nitrogen calc. as percentage of total nitrogen .....	30	38	45	48	47	40	57
Albuminoids × 10,000—original gravity .....	91	65	60	60	61	69	69
Phosphoric anhydride × 100,000—original gravity .....	38	37	50	51	50	40	50

B.P.G.=Beane's Patent Glat. G=Glucose. I=Invert sugar. M.=Malzo. R.=Rice.

infusion, 1 in 20; beer, 1.75 in 360 (approx.), or 1 in 200. The amount of beer to be taken to obtain the medicinal dose of the infusion would be 10 to 20 fluid ounces, or, roughly,  $\frac{1}{4}$ —1 pint. Choline is stated to be present in very small quantities, and considering the intensely poisonous effects of the administration of choline chloride, the statement is probably correct.

The general physiological effect of hops is stomacheic and carminative (due to the volatile oils and bitters), and also, as a whole, soporific. When taken in excess hops act as a narcotic.

It is thus evident that, even assuming the toxicity of humin bodies and their presence in substitute beers, their effect can be so little compared with that of the hops normal to all classes of beers as to be quite negligible.

In conclusion the author wishes to thank Mr. Raymond Ross, F.I.C., F.C.S., for the facilities granted during the preparation of this paper and for many valuable suggestions. He is also indebted to Mr. William Duncan, F.I.C., F.C.S., for many hints that have proved invaluable.

#### DISCUSSION.

THE CHAIRMAN thought the figures showing the difference between malt beers and substitute beers were rather disappointing; still, it was gratifying to know that substitute beers were not prejudicial to health. Was an inferior quality of hops used in brewing the poorer class of beers, and had they any ill-effect on health?

Mr. RAYMOND ROSS said that, with regard to the differentiation of beer by means of albuminoids and phosphoric acid, they had for many years regarded these figures as of primary importance in distinguishing malt vinegars from sugar vinegars. Far more notice had always been taken of the phosphoric acid than of the albuminoids. The causes of this could be seen by a reference to a paper by Allen. (Analyst, Vol. 19.) Phosphoric acid might be added with the intention to deceive. He thought that the character of the albuminoids might have more to do with the stability of beers than either the amount of albuminoids or phosphoric acid. Mr. Race had taken 45 per cent. of the albuminoids as assimilable. The albuminoid figure might be useful in determining the available nitrogen, as the compounds most easily broken down would be the most easily assimilated. It had been shown that each constituent of whiskey, excepting water, increased for many years on keeping (J. Amer. Chem. Soc., 1908, 30; this J., 1908, 173). It was well known that old whiskey was more beneficial than new, yet all the secondary products had increased. It was therefore evident that something else had a prejudicial effect on the system. Might not this be due to the presence of certain humin substances, the composition of which was by no means definite? One authority stated that he found 3 per cent. of nitrogen in them. Was it not possible that in the process of manufacture a great proportion of the hop alkaloids was lost? Only minute quantities of choline had been found in beer; to what extent it was present in hops he did not know. The fact that beers were dry hopped to give additional flavour supported the above contention.

Dr. G. H. BAILEY said he could endorse what Mr. Race had stated with regard to the loss of sulphuric acid, unless precautions were taken. Mr. Race said he used barium carbonate and obtained a black ash. A common practice was to saturate the organic substance with sodium carbonate, but the difficulty in using carbonates for this purpose was that if too little were used there might still be loss, and if sufficient were used, the burning off of the carbonaceous matter was slow and incomplete, involving difficulty when extraction was made for the determination of chlorine and sulphuric acid by precipitation. He had found that sodium nitrate was most useful, but it was usually too impure to be employed without further purification. His practice was to moisten the material with concentrated nitric acid, and then pour on a solution of bicarbonate until this was neutralised. He then found that the ash would burn quite readily on heating, and on igniting there was no loss of chlorine or sulphuric acid.

Mr. RACE, in reply to the Chairman, said that it was not usual to use an inferior quality of hops for the cheaper beers. A stronger variety was used, so that a smaller

quantity would be required to obtain the desired effect. In reply to Mr. Ross, he pointed out that if the albuminoid ammonia as estimated by Graham's method were any criterion of the nitrogenous matter readily available for yeast nutrition, the all-malt samples would not contain nearly the whole of their nitrogen in that form. These samples were highly attenuated, and fermented under conditions favourable to the assimilation of nitrogen, so that it might reasonably be expected that the albuminoids remaining were not readily assimilable. Peptone, which was generally considered an excellent nutrient for yeast, yielded only about 30 per cent. of its nitrogen by Graham's process, so that that method was useless for the estimation of the substances available for yeast nutrition. Although it was possible that humin bodies were present in whiskey, it seemed improbable, as the only point at which the materials could be contaminated was during the curing of the malt, and even then it would only apply to those districts where pent was used for that purpose. Mr. Ross's hypothesis would also necessitate the humin body being volatilised from the fuel, condensed on the malt, and soluble in water. Beer, however, could not be contaminated in that way, as no pent was used for curing. H. T. Brown had stated that tyrosine and leucine must be, regarded as of comparatively low fermentability. Ehrlich however, had shown that under ordinary brewing conditions they were assimilated, and that leucine was probably the primary factor in the production of amyl alcohol, the esters of which were important as regards flavour. Tyrosine, which had actually been isolated from yeast, when fermented by yeast in the presence of sugar, yielded hydroxyphenylethyl alcohol, a crystalline body generally found mixed with the succinic acid after the extraction of fermented liquids with ether. This body had an intensely bitter flavour, and would certainly contribute to the bitterness of the beer (Ehrlich). In reply to Dr. Bailey, he pointed out that barium carbonate was only used for the estimation of the chlorides. Caustic soda was used for the sulphates, the ash being burnt perfectly white.

#### THE ESTIMATION OF ALCOHOL AND EXTRACT IN SPIRITS BY MEANS OF THE REFRACTOMETER.

BY JOSEPH RACE, A.I.C.

Experiments were first made to ascertain if the method of E. Reigler (Analyst, 21, 133; this J., 1896, 223) were applicable to the examination of such spirits as brandy and whiskey. To obtain comparative results, and to make the figures obtained as accurate as possible, all observations were made at the same temperature, viz., 15.5° C., and for the sodium line. The observations were made with a Pulfrich instrument provided with an arrangement for keeping the temperature constant. The amount of alcohol in the mixtures was found by determining the specific gravity and reference to alcohol tables.

The following table sets forth the results obtained from a few mixtures of pure alcohol and water.

$c$  = the refractive index of redistilled water = 1.33350 :—

Percentage of alcohol by weight = $a$ .	Refractive index of mixture = $b$ .	$\frac{b-c}{a} \times 100,000$
5	1.33645	50
6	1.33714	61
7	1.33785	82
8	1.33856	93
9	1.33928	104
10	1.34001	115
11	1.34074	125.8
12	1.34146	136.3
13	1.34219	146.9
14	1.34293	157.2
15	1.34368	167.8
16	1.34443	178.3
17	1.34517	188.7
18	1.34591	199.0