	"Peppermint oil"	"Purified peppermint oil"
D ₂₀	0.9010	0.8990
N _D ²⁰	1.4586	1.6379
α_D	-39.60°	-37.30°
Acid No.....	1.52	3.60
Menthyl acetate, per cent.....	9.09	11.47
Ester menthol, per cent.....	7.16	9.03
Ester menthol, per cent.....	58.04	45.38
Total menthol, per cent.....	65.20	54.41
Solubility (70 per cent alcohol at 20° C.)	3 vols.	3 vols.

IMPERIAL TOKYO UNIVERSITY
CARE PROF. T. KAMOI
JAPAN

THE USE OF THE IMMERSION REFRACTOMETER IN EXAMINING AMERICAN BEERS MADE FROM MALT AND UNMALTED CEREALS¹

By ROBERT SCHWARZ

The application of the immersion refractometer to the analysis of numerous chemical solutions and food products has attracted the attention of many investigators, and during the past 12 years quite a few analytical methods based upon the use of this instrument, together with valuable tables, have been published in various chemical journals. A considerable part of this work has been done by fermentation chemists, who quickly recognized the fact that the immersion refractometer was especially well adapted for the analysis of the products obtained by the wine grower, the distiller and the brewer. It is to the work done in the last mentioned field that the author desires to call special attention.

Tornøe,² in 1897, published a method for the analysis of beer which was partially based upon determining the index of refraction, using sodium light and a specially constructed type of differential refractometer. This method, while fairly rapid and quite accurate, did not, however, find wide application.

The introduction of the Zeiss immersion refractometer, which is so extremely simple to manipulate, gave fresh impetus to the study of optical methods for the examination of liquids such as beer. In 1903, Ackermann and Spindler³ published a method for determining the extract by the formula $E = (J - J') 6750$, in which J = index of refraction of the beer, J' = index of refraction of the distillate, and 6750 an empirically determined factor. In this method the index of refraction of the beer and the distillate are calculated from the immersion refractometer reading of these liquids.

In 1905 Ackermann⁴ constructed a calculating machine with which to determine the percentage of alcohol and extract in beer from the density of the decarbonated beer, taken at 15/15° C. and its refractometer reading at 17.5° C. It is not the purpose of this paper to discuss the above publication other than to say that this method is far simpler and much more rapid than the official pycnometer analysis. Ackermann

carefully tested the accuracy of the method by having different analysts send him small samples of beer, together with a statement of their density. From this and the refractometer reading taken by himself, Ackermann calculated the percentage of alcohol and extract with the aid of his machine. Some of the results obtained are discussed below. It must be stated that this calculating apparatus was based upon tables which had been worked out from analytical data obtained by means of the pycnometer, and the corrected alcohol and extract tables of Karl Windisch.⁵

During the same year Barth² published a formula for determining the extract and alcohol in beer from the specific gravity and the refractometer reading of the same. In his article Barth published the results of 16 analyses, and to these we shall again refer below.

In 1910 Danzer³ published a series of tables (also based upon the alcohol and extract tables of Karl Windisch) from which the alcohol and extract of any beer could be calculated from the same determinations as those used in Ackermann's method. As these tables are quite readily accessible, and the calculations involved very simple, they put the refractometric method of beer analysis within the reach of all chemists.

The results published by Ackermann,⁴ and also those given by Barth,⁵ show but small differences between the percentage of alcohol and extract as determined by the refractometer and the pycnometer. It is therefore somewhat surprising that the former method has not come into more general use by brewing chemists. Particularly here in America, has the immersion refractometer failed to receive from the brewing chemists the attention which it so justly deserves.

Although the author has never found any direct written statement to the effect that the method, as published by Ackermann, could not be applied to typical American beers which are brewed from a mixture containing 60-70 per cent malt and 40-30 per cent adjuncts (in most instances unmalted cereals), some of our brewing chemists have informally expressed the belief that the results obtained with the refractometer on such American beers would not be sufficiently accurate to permit the use of this instrument.

The writer, therefore, decided to investigate this matter and examined, with the aid of the refractometer and the Danzer tables, 47 samples of beer and ale which were also analyzed by another chemist, using the official method, namely, distillation and determination of the specific gravity of the distillate and residue with the pycnometer. Attention must be called to the fact that in calculating the percentages of extract and alcohol equivalent to the various densities found, the tables of Karl Windisch, and not those given in Bulletin No. 107, revised, Bureau of Chemistry, U. S. Dept. of Agriculture, were used.

¹ Paper presented before the New York Section of the American Chemical Society, Chemists' Club, June 6, 1913.

² *Z. f. d. ges. Brauwesen*, **20**, 373 (1897).

³ *Ibid.*, **26**, 441 (1903).

⁴ *Z. f. d. ges. Brauwesen*, **28**, 33 (1905).

⁵ These tables have been published in numerous journals and text books.

² *Ibid.*, **28**, 303 (1905).

³ *Z. f. d. ges. Brauwesen*, **32** (1910).

⁴ See reference 3.

⁵ See reference 4.

The table for extract in beer, by H. Ellion, given in this Bulletin, gives the same values as the official Balling table, but as the figures in the latter are 0.07 per cent higher than those found in the Windisch table, a correction of -0.07 per cent. in the extract as determined by the refractometer must be made when using either the Ellion or Balling table to convert the specific gravity to percentage of extract by weight. The alcohol table of Gilpin, Drinkwater and Squibb¹ is about 0.02 per cent lower than that of K. Windisch, and therefore the use of the former

warmer months, however, it was found necessary to cool the water bath slightly under 17.5° C. and start taking the refractometer readings when the beers had reached the above temperature. During the time required for testing the samples, the temperature rarely increased more than 0.5° C. The readings were then corrected for an average temperature deviation of 0.25° C., which, according to Stanek and Miskovsky,² involves an addition of 0.05° of the refractometer scale. As 0.1° Ref. is equivalent to 0.006 per cent extract, or to 0.026 per cent alcohol,

TABLE I

Laboratory number	Specific gravity 15/15	Refractometer reading at 17°	Alcohol by pycnometer	Alcohol by refractometer	Difference in 1/100 per cent		Extract by pycnometer	Extract by refractometer	Difference in 1/100 per cent		Original gravity pycnometer analysis	Original gravity refractometer analysis	Difference in 1/100 per cent	
					+	-			+	-			+	-
1	1.01262	42.45	4.26	4.45	..	19	5.05	5.03	2	..	13.25	13.60	..	35
2	1.01146	37.65	3.35	3.42	..	7	4.85	4.37	..	12	12.45	12.50	..	5
3	1.01216	41.00	3.94	3.90	4	..	4.37	4.97	..	..	10.85	10.95	..	10
4	1.00488	34.80	4.25	4.29	..	4	3.11	3.17	..	6	11.30	11.45	..	15
5	1.01222	42.00	4.03	4.09	..	6	4.85	4.77	8	..	12.65	12.65	..	..
6	1.01642	45.40	3.83	3.95	..	12	5.75	5.95	..	20	13.15	13.55	..	40
7	1.01642	42.40	3.10	3.19	..	9	5.53	5.61	..	8	11.50	11.75	..	25
8	1.01648	43.00	3.30	3.30	..	0	5.59	5.66	..	7	11.95	12.05	..	10
9	1.01762	45.35	3.76	3.62	14	..	6.03	6.10	..	7	13.30	13.10	20	..
10	1.02088	46.60	3.17	3.08	9	..	6.54	6.66	..	12	12.65	12.60	5	..
11	1.01190	40.10	3.80	3.74	6	..	4.68	4.72	..	4	12.00	11.95	5	..
12	1.01534	44.35	3.89	3.95	..	6	5.52	5.69	..	17	13.05	13.30	..	25
13	1.01924	46.05	3.29	3.36	..	7	6.32	6.39	..	7	12.70	12.85	..	15
14	1.01296	41.45	3.97	3.82	15	..	5.01	5.02	..	1	12.65	12.40	25	..
15	1.01146	37.40	3.18	3.15	3	..	4.31	4.33	..	2	10.45	10.40	5	..
16	1.01554	41.70	3.25	3.20	5	..	5.31	5.38	..	7	11.60	11.60	..	..
17	1.00458	34.55	4.15	4.20	..	5	3.05	3.10	..	5	11.05	11.20	..	15
18	1.01582	42.75	3.43	3.38	5	..	5.50	5.56	..	6	12.10	12.10	..	..
19	1.01384	40.05	3.36	3.20	16	..	4.96	4.97	..	1	11.45	11.15	30	..
20	1.01394	40.25	3.77	3.74	3	..	5.12	5.20	..	8	12.40	12.40	..	..
21	1.01726	42.75	3.06	3.03	3	..	5.73	5.73	..	0	11.65	11.60	5	..
22	1.01278	41.35	3.79	3.83	..	4	4.92	4.99	..	7	12.25	12.40	..	15
23	1.01434	(a)	4.07	4.04	3	..	5.36	5.48	..	12	13.20	13.25	..	5
24	1.01110	(a)	4.14	4.08	6	..	4.67	4.68	..	1	12.65	12.55	10	..
25	1.01838	(a)	3.66	3.59	7	..	6.18	6.28	..	10	13.25	13.20	5	..
26	1.01542	41.60	3.19	3.21	..	2	5.36	5.35	1	..	11.50	11.55	..	5
27	1.01532	41.60	3.23	3.23	..	0	5.34	5.35	..	1	11.55	11.55	..	..
28	1.01822	46.60	3.79	3.96	..	17	6.33	6.26	7	..	13.65	13.90	..	25
29	1.01246	39.25	3.37	3.37	..	0	4.64	4.68	..	4	11.15	11.20	..	5
30	1.01158	37.25	3.15	3.07	8	..	4.30	4.33	..	3	10.40	10.25	15	..
31	1.01250	40.50	3.78	3.69	9	..	4.81	4.85	..	4	12.10	11.95	15	..
32	1.01024	38.55	4.00	3.87	13	..	4.35	4.32	3	..	12.05	11.80	25	..
33	1.01174	41.00	4.22	4.02	20	..	4.78	4.82	..	4	12.90	12.60	30	..
34	1.01320	41.85	4.03	3.86	17	..	5.03	5.11	..	8	12.80	12.55	25	..
35	1.01472	42.85	3.83	3.73	9	..	5.33	5.42	..	9	11.70	11.60	10	..
36	1.01392	41.50	3.58	3.58	0	..	5.06	5.15	..	9	12.05	12.15	..	10
37	1.01260	41.95	4.14	4.04	10	..	4.98	5.04	..	6	13.00	12.85	15	..
38	1.01700	42.85	3.32	3.12	20	..	5.69	5.71	..	2	12.10	11.75	35	..
39	1.01394	43.70	4.31	4.17	14	..	5.31	5.42	..	11	13.25	13.10	15	..
40	1.01462	42.65	3.60	3.70	..	10	5.31	5.38	..	7	12.25	12.50	..	25
41	1.01256	42.05	4.15	4.08	7	..	4.97	5.05	..	8	12.95	12.90	5	..
42	1.01188	39.60	3.68	3.61	7	..	4.61	4.65	..	4	11.70	11.60	10	..
43	1.01078	39.15	3.90	3.78	12	..	4.38	4.46	..	8	11.90	11.75	15	..
44	1.01842	45.35	3.45	3.41	4	..	6.17	6.20	..	3	12.80	12.80	0	..
45	1.01550	42.30	3.33	3.37	..	4	5.40	5.45	..	5	11.80	11.95	..	15
46	1.01752	43.55	3.21	3.07	14	..	5.83	5.86	..	3	12.00	11.80	20	..
47	1.01462	40.45	3.20	3.12	8	..	5.04	5.11	..	7	11.20	11.15	5	..

(a) Figures for refractometer readings were lost after results had been calculated.

table requires a correction of +0.02 per cent in the refractometer results. The water bath used in at-temperating the decarbonated beers was a large, felt-jacketed enameled pot into which was inserted a revolving umbrella frame capable of holding 12 small beakers. During the winter and spring the temperature at the surface of this water bath would remain unchanged long enough to attemperate the 12 beers and take their refractometer reading. During the

error in the case of the extract is entirely negligible, and in the case of the alcohol so small as to be of practically no importance for commercial or technical analyses.

The results of the analyses of the 47 beers and ales are given in Table I.

Of these samples, Nos. 11, 12 and 13 were beers made from barley malt and hops only; samples Nos. 4, 5, 7, 32 and 39 were top fermented ales, and all the

¹ Bull. 107, revised.

² Z. f. ges. Brauwesen, 33, 145 (1910).

rest typical American beers. The last named, as well as ale No. 39, were brewed from malt and malt adjuncts. Most of these samples were of pale yellow color, but several were of the dark amber type, such as we find in the domestic "Muenchener Style" beer. The darker beers of the "Wuerzburger Type," as well as porter and stout, could not be tested without considerable dilution, and as time was not available to investigate the effect of this procedure on the final results, no very dark beers or ales were taken.

The above figures show the following maximum, minimum and average differences between the results obtained by the official (pycnometer) and the refractometer method.

(In calculating the original gravity, the formula $G = 1.93 A + E$ has been used, and the results rounded off to the nearest 0.05 per cent.)

	Maximum Per cent	Minimum Per cent	Average Per cent
Extract.....	0.20	0	0.063
Alcohol.....	0.20	0	0.081
Original gravity (calculated).....	0.40	0	0.140

While the maximum deviation may seem somewhat large, it must be remembered that the examinations of these beers, both with the refractometer and the pycnometer, were made as regular routine analyses, and that therefore these maximum figures can be accepted as the largest variations likely to result. The differences cannot be entirely attributed to error in the refractometer method, for the results obtained with the pycnometer under the above conditions also involved an error of ± 0.05 per cent.

In order to compare the above differences between the pycnometer and the refractometer method, the average differences found by Ackermann¹ and by Barth² have been tabulated with those given above:

	Extract	Alcohol	Original gravity
Ackermann (44 samples).....	0.026	0.061	..
Barth (16 samples).....	0.157	0.055	0.14
Author (47 samples).....	0.063	0.081	0.14

In the case of Ackermann's figures only those have been taken in which the two analyses were made by different chemists. As regards Barth's figures, all those given in his communication were taken, but it is not known whether the tests were made by different analysts. The results of Ackermann show a slightly better agreement than those of the author, but as compared with Barth, the latter figures show decidedly less deviation in the case of extract. Taken on the whole, the results must be considered as very good and as showing that, on the average, there is but little difference between the results obtained by means of the refractometer and the pycnometer.

Besides the analyses given in Table I, the refractometer was used to check the percentage of extract and alcohol by taking the refractometer reading of the distillate and beer residue. As Mohr³ had shown that for laboratory worts of 8° Balling, 1° Ball. is equivalent to 4° on the refractometer scale, and Lalin⁴ had shown

the same relationship for the products of the hydrolysis of starch in cereals, the author determined to test this relationship in regard to the beer residue left after distilling off the alcohol. That the relationship should approximately hold true was theoretically based on the fact that on the average over 75 per cent of the extract in a finished beer consists of the products of starch hydrolysis. The extract, therefore, was determined by the formula of Mohr $E = \frac{R - 15}{4}$,

where R = the refractometer reading of the residue at 17.5° C. and 15 = the refractometer reading of pure water at the same temperature.

The results obtained in this way are given below.

TABLE II—DETERMINATION OF EXTRACT IN DE-ALCOHOLIZED BEER

No.	Extract by pyc- nometer	Extract by refrac- tometer $E = \frac{R - 15}{4}$	Difference in 1/100 per cent	
			+	-
1.....	4.68	4.64	4	..
2.....	5.52	5.62	..	10
3.....	6.32	6.30	2	..
4.....	6.55	6.52	3	..
5.....	5.73	5.62	11	..
6.....	6.07	5.96	11	..
7.....	5.01	4.94	7	..
8.....	4.31	4.19	12	..
9.....	5.31	5.22	9	..
10.....	3.05	3.06	..	1
11.....	5.50	5.50	0	..
12.....	4.96	4.87	9	..
13.....	5.12	5.12	0	..
14.....	5.36	5.39	..	3
15.....	4.67	4.67	0	..
16.....	6.18	6.19	..	1

It will be noticed that the average difference in the first eight or nine analyses is considerably greater than in the later determination. This is due to the fact that the former were made in rapid succession without any correction for temperature or any time given for the prism on the refractometer to regain the standard temperature after having taken up heat from the hand of the operator who had to carefully dry the prism between the immersions. As readings at higher temperature (the temperature of the prism plays just as important a part as that of the liquid) require a plus correction, these first determinations gave low results. In the later analyses the temperature was carefully held at 17.5° C. and the prism given about 2 minutes in each beaker to regain the normal temperature.

In determining the alcoholic strength of the distillate by means of the refractometer, the table of Ackermann and Steinmann⁵ was used (Table III).

In these tests the necessity of giving the prism an opportunity to regain the normal temperature is strongly brought out by the difference in the average variation in the first seven and last seven determinations, each of which series was made under the difference of conditions described above. Taking in each instance the results of the determinations made in the correct manner, it is seen that the refractometer used with the formula $E = \frac{R - 15}{4}$ and the table of Ackermann and Steinmann, *Z. f. d. ges. Brauwesen*, 28, 259 (1905).

¹ See reference 3.

² See reference 4.

³ *Woch. f. Brauerei*, 23, 136 (1906).

⁴ *Z. f. d. ges. Brauwesen*, 32, 231 (1909).

⁵ Ackermann and Steinmann, *Z. f. d. ges. Brauwesen*, 28, 259 (1905).

TABLE III—DETERMINATION OF ALCOHOL IN DISTILLATES FROM BEER

Number	Alcohol by pyc- nometer Per cent	Alcohol by refrac- tometer Per cent	Difference in 1/100 per cent	
			+	-
1.....	4.00	3.87	13	..
2.....	4.22	3.99	23	..
3.....	4.03	3.84	19	..
4.....	3.82	3.67	15	..
5.....	4.14	4.00	14	..
6.....	3.32	3.20	12	..
7.....	4.31	4.25	6	..
8.....	3.60	3.64	..	4
9.....	4.15	4.10	5	..
10.....	3.68	3.67	1	..
11.....	3.45	3.41	4	..
12.....	3.33	3.30	3	..
13.....	3.21	3.15	6	..
14.....	3.20	3.15	5	..

mann and Steinmann checks the pycnometer quite well.

The use of the immersion refractometer for the direct analysis of beer according to the method of Ackermann or Danzer is the last question to be discussed. Do the results published herewith, as well as those made public by the authors cited, justify the adoption of the rapid, short refractometer method in place of the decidedly longer and more cumbersome pycnometer analysis? We believe that it has been shown that the agreement between the results of the two analyses is practically as good for American beers made from malt and adjuncts as it is for European all-malt beers. In Europe, it is to-day the opinion of most brewing chemists that the results obtained with the refractometer are perfectly reliable for factory control. Where questions of law, or exact food chemistry are involved, opinions differ considerably. Even in such cases, however, the variations between results obtained by the two methods rarely exceed the limits which must be permitted even in a judicial controversy. It seems, therefore, that the brewing chemist here in America is amply justified in adopting the refractometer method of beer analysis, and only reverting to the old method in legal cases or controversies between analysts.

In conclusion, the author wishes to acknowledge his thanks to Mr. Theodor Ihnen, chemist for the First Scientific Station for the Art of Brewing, for numerous beers analyzed in gathering material for this paper.

CHEMICAL LABORATORY
FIRST SCIENTIFIC STATION FOR THE ART OF BREWING
NEW YORK

CALCIUM THIOARSENATE AS A SPRAY

S. H. KATZ AND P. D. BUCKMINSTER

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Since the inception of this work, Ellis has patented (U. S. Pat., No. 1,002,247) "a composition for agricultural spraying purposes, comprising a soluble form of alkali or alkaline earth polysulfids preferably in conjunction with a thioarsenate or other thioarsenical compound as a strengthening material and preferably with a binding or adhesive material." Parsons¹

¹ THIS JOURNAL, 4, 185.

has said of arsenic, "It is used in large quantities in combination with lead as an insecticide and it would seem worth while to have experiments inaugurated to determine if arsenic sulfid or calcium sulfarsenite, both of which are probably quite harmless to plants, may not be substituted as an insecticide, giving a much cheaper material, using more arsenic and conserving lead. It should be noted particularly that any proposed insecticide must be effective as a poison but must not injure the foliage of the plant upon which it is placed."

The above expresses in part the original purpose of this work, but it was also hoped to produce a substance which would be effective as a fungicide as well as an insecticide and scalecide, for calcium thioarsenate resembles, at least in chemical composition, the polysulfids of calcium, which, as the lime-sulfur solutions, are now used as fungicides. Calcium thioarsenate is a soluble substance, and it is well known that soluble arsenic in the arsenicals now used as sprays is injurious to foliage. But the thioarsenates are quite different in their chemical nature from the arsenites or arsenates and it was expected that there might be a corresponding difference in their physiological action on foliage. Also the thioarsenic compounds readily decompose on exposure, yielding in part insoluble arsenic trisulfid. From these considerations it was hoped that the material could be safely used as a spray. In his patent, Ellis¹ stated that his invention is particularly for the treatment of citrus trees but has to say in this regard, "Ordinarily the soluble compounds of arsenic, especially if used in effective strength for insects, have a defoliating action, but in the present case, by exposure of a solution of, for example, potassium thioarsenate, oxidation and carbonation take place more or less in the case of the polysulfid, thereby throwing out of the solution to a very considerable degree the previously dissolved sulfid of arsenic, and rendering the arsenic comparatively harmless to vegetation. This action is especially marked in the case of the polysulfid of calcium."

A solution was prepared by dissolving precipitated arsenic trisulfid in a lime-sulfur solution of 1.310 specific gravity, together with a little gelatin which seemed to aid in the solution and would serve as an adhesive when the material was sprayed. The proportion of 25 grams of arsenic trisulfid to 100 cc. of the lime-sulfur solution to 0.5 gram of gelatin agitated on a shaking machine till reaction was complete, gave on filtering a clear, deep yellow solution of 1.37 specific gravity. Exposed to air, this solution decomposed and formed a yellow gel, which, on drying, adhered tenaciously to the surface supporting it.

On analysis this solution yielded the results given in the table following. The figures for theoretical solutions of calcium thioarsenite and calcium thioarsenate having 7.51 per cent of calcium are given for comparison.

From the analyses the solute is seen to approach the composition of calcium thioarsenate which salt must be present in large quantity.

¹ Loc. cit.