Gal and Werner: *C. R.*, **103**, 1141 (1887); Abstr. in **J. Chem. Soc.*, **52**, I., 206.

Peratoner :* *Chem. Ztg.*, **21**, I., 40 (1897).

Peratoner and Tamburello: *Gazz. Chim. Italiana*, **33**, II., 233 (1903); Abstr. ***Centrbl.*, 1904, I, p. 45.

The stars indicate the publications in which the articles were available to us. Double stars indicate articles with especial reference to salts of meconic acid or bearing upon salt formations. In general, it may be said that the literature before Liebig's discovery in 1833[1] of the true relationship between meconic, comenic and pyrocomenic (synonymous with pyromeconic) acids is of little importance except historically.

Beilstein (Vol. II, p. 2041) gives a reference[2] to an article by Liebig which is incorrect. The reference given is to an article by Blanchet and Sell on an entirely different subject and there is no other article in that volume by Liebig on meconic acid. The above list includes some references to comenic and pyrocomenic acids which were examined for information on the parent acid.

MALLINCKRODT CHEMICAL WORKS,
ST. LOUIS.

[CONTRIBUTION FROM THE DEPARTMENT OF FOOD AND DRUG INSPECTION OF THE MASSACHUSETTS STATE BOARD OF HEALTH.]

THE DETECTION AND DETERMINATION OF ETHYL AND METHYL ALCOHOLS IN MIXTURES BY THE IMMERSION REFRACTOMETER.

BY ALBERT E. LEACH AND HERMANN C. LYTHGOE.

Received June 14, 1905.

THE USE of wood alcohol in various preparations which come within the domain of the public analyst for examination is apparently on the increase. It is especially to be looked for as an adulterant in medicinal preparations, liniments, tinctures, and in all varieties of flavoring and other extracts high in alcohol. In Massachusetts we have found methyl alcohol in various pharmaceutical preparations, such as tincture of iodine, and in lemon and orange extracts.

Existing methods for the detection of wood alcohol, with one or two exceptions, are extremely unsatisfactory. Most of the older methods such, for example, as the potassium permanganate

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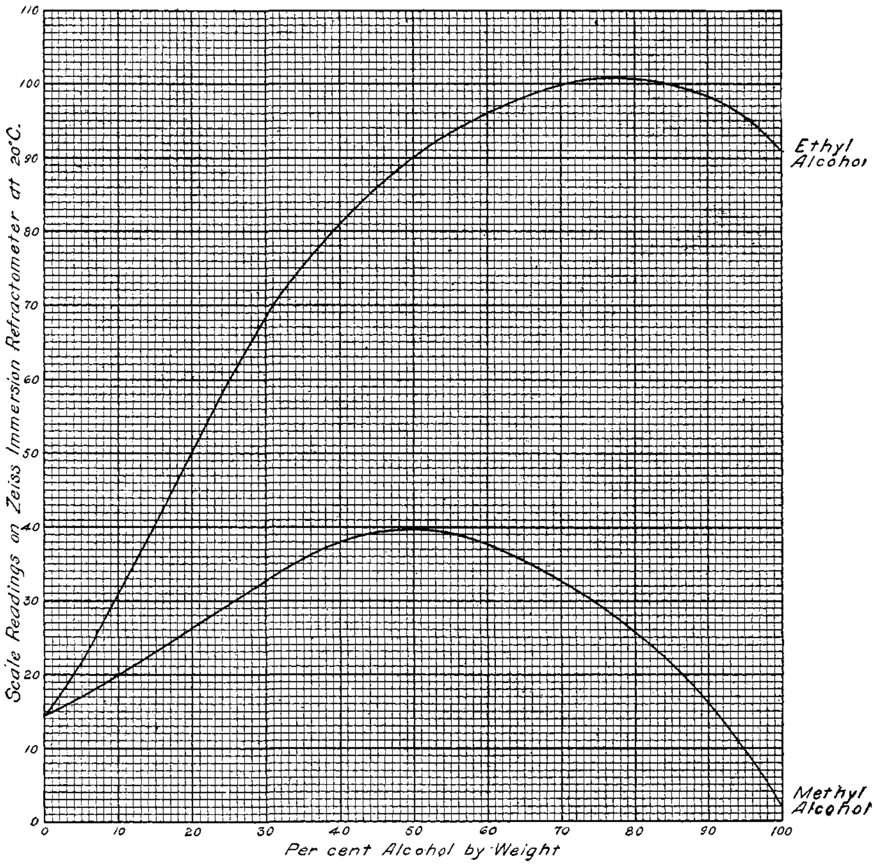
[1] *Ann. Chem.*, **7**, 237.

[2] *Ibid.*, **5**, 286 (1833).

test, depend upon the presence of acetone in the methyl alcohol. With the improved refining processes used at the present day wood alcohol is readily obtainable free from more than traces of acetone, so that it is impossible to distinguish it from ethyl alcohol by its odor. Crude wood alcohol with acetone present in marked degree is frequently capable of being indicated even in mixture with ethyl alcohol by the sense of smell. It is the refined or deodorized methyl alcohol, sold under a variety of trade names, such as Columbian spirits, Hastings spirits, Colonial spirits, purified wood alcohol, etc., that one finds as an adulterant of tinctures, extracts and beverages.



The most practical method hitherto used for the detection of methyl alcohol is that of Mulliken and Scudder,[1] which depends on the oxidation of the methyl alcohol in the sample to formaldehyde by the use of a red-hot spiral of copper wire, using, however, the hydrochloric acid and milk test for the detection of formaldehyde in the oxidized solution.[2]

Attention is further called to the German official process of Windisch,[3] a color reaction depending on the transformation of the methyl alcohol to methyl violet.

Methods for the quantitative determination of wood alcohol are even more rare. Duprey[4] has suggested a method of concentrating the alcohol by repeated distillation, after which part of the final distillate is oxidized to acetic acid, the latter being titrated with alkali, while the alcohol is determined in the other portion of the distillate from the specific gravity. Both methods with pure ethyl alcohol should give concordant results, whereas in presence of methyl alcohol a lower result is obtained by the oxidation process.

The specific gravity of absolute methyl and ethyl alcohol is practically identical, and it is also true that when mixed with varying proportions of water the specific gravity of both alcohols is so nearly the same (with the same proportions of water in each) that the same tables for computation of percentage of alcohol from the specific gravity may be used in one case as in the other.

A very important physical constant, however, which we have found to differ most widely in the two alcohols is the index of refraction, and it is on this property that we base our method for the detection and determination of methyl alcohol.

We use for this purpose the immersion refractometer of Zeiss. This instrument was fully described in a former paper by us.[5] To illustrate the wide difference in refraction between the two alcohols, the strongest commercial ethyl alcohol found on the market (the alcohol of the U. S. Pharmacopoeia, which contains 91 per cent. of absolute alcohol by weight) gives a reading with the immersion refractometer of 98.3° at 20° C., while the reading of methyl alcohol of 91 per cent. strength by weight is 14.9°. Fifty per cent. ethyl alcohol by weight has a refraction on the immersion re-

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[1] *Am. Chem. J.*, **24**, 444 (1900); this Journal, **27**, 892.

[2] Ann. Rept. Mass. State Board of Health, 1897, p. 558; Leach: "Food Inspection and Analysis," p. 666.

[3] *Vereinbar. z. Unters. v. Nahr. u. Genussm.*, Heft II, p. 130.

[4] *Analyst*, 1, p. 4.

[5] This Journal, **26**, 1196 (1904).

TABLE I.—PERCENTAGE BY WEIGHT OF ETHYL AND METHYL ALCOHOLS CORRESPONDING TO SCALE READINGS ON ZEISS IMMERSION REFRACTOMETER AT 20° C.

Scale reading. 20° C.	Per cent. alcohol by weight. Methyl alcohol.		Per cent. alcohol by weight. Ethyl alcohol.	Scale reading. 20° C.	Per cent. ethyl alcohol by weight.	Scale reading. 20° C.	Per cent. ethyl alcohol by weight.	
0...				40...	14.73	80...	38.82	
1...				41...	15.23	81...	39.64	
2...		100.00		42...	15.73	82...	40.64	
3...		99.33		43...	16.23	83...	41.64	
4...		98.69		44...	16.73	84...	42.75	
5...		98.06		45...	17.23	85...	43.75	
6...		97.44		46...	17.73	86...	44.75	
7...		96.80		47...	18.23	87...	46.00	
8...		96.13		48...	18.73	88...	47.25	
9...		95.42		49...	19.23	89...	48.38	
10...		94.71		50...	19.73	90...	49.62	
11...		94.00		51...	20.25			
12...		93.28		52...	20.77	91...	50.87	100.00
13...		92.55		53...	21.29	92...	52.66	99.00
14...		91.75		54...	21.81	93...	54.00	98.00
15...	1.34	90.92	0.33	55...	22.33	94...	55.80	97.00
16...	3.00	90.08	1.00	56...	22.85	95...	57.60	96.00
17...	4.67	89.25	1.62	57...	23.38	96...	59.60	95.00
18...	6.34	88.45	2.25	58...	23.90	97...	61.75	94.00
19...	8.00	87.64	2.93	59...	24.43	98...	64.00	91.60
20...	9.67	86.73	3.56	60...	24.94	99...	66.75	88.50
21...	11.34	85.80	4.19	61...	25.50	100...	70.00	85.50
22...	13.00	84.80	4.82	62...	26.06	101...	75.00	
23...	14.67	83.60	5.39	63...	26.60			
24...	16.17	82.40	5.94	64...	27.15			
25...	17.72	81.20	6.50	65...	27.71			
26...	19.33	80.00	7.06	66...	28.29			
27...	20.93	78.75	7.58	67...	28.88			
28...	22.47	77.43	8.09	68...	29.44			
29...	23.96	76.00	8.64	69...	30.00			
30...	25.50	74.57	9.20	70...	30.71			
31...	27.18	73.14	9.76	71...	31.47			
32...	28.67	71.50	10.32	72...	32.21			
33...	30.33	70.00	10.87	73...	32.93			
34...	32.00	68.00	11.43	74...	33.69			
35...	33.50	66.00	11.99	75...	34.43			
36...	35.16	64.00	12.54	76...	35.09			
37...	37.00	62.00	13.10	77...	35.99			
38...	40.00	59.75	13.64	78...	37.00			
39...	43.93		14.19	79...	37.90			

fractometer of 90.3°, while the same strength (50 per cent.) of methyl alcohol refracts on the instrument at 39.8°, all readings being made at 20° C. From this wide variation it is readily seen that there is no trouble in detecting even small amounts of methyl alcohol in mixtures. Table I shows the percentage by weight at 20° C. of the two alcohols corresponding to each degree of scale reading on the refractometer.

The difference in refraction between the two alcohols varies considerably for different strengths. In the case of methyl alcohol, starting at zero (or water containing no alcohol) at which the reading on the immersion at 20° is 14.5, the refraction gradually increases with increasing strength of methyl alcohol up to about 50 per cent. of the latter by weight, where the refraction reaches its maximum, after which for higher strengths of methyl alcohol it drops quite rapidly until at 100 per cent. the refraction is but 2.0.

In the case of ethyl alcohol, starting, as before, with pure water and increasing the strength of the solution in alcohol, the refraction increases quite rapidly up to solutions of about 75 per cent. strength, where it then drops slightly, but by no means to such an extent as in the case of methyl alcohol. It will thus be seen that by far the widest variations in refraction between the two alcohols take place above 50 per cent. in strength.

From the peculiar shape of both alcohol curves, rising gradually to a maximum and then falling, no confusion should be caused by the fact that in some cases one scale reading may correspond to two different percentages of strength of the same alcohol.

The detection of wood alcohol by this method is comparatively simple and consists in submitting to refraction with the immersion refractometer the distillate which one makes for the determination of ethyl alcohol in the regular manner in alcoholic beverages, essences, tinctures, extracts, or whatever may be the nature of the substances to be examined. If the refraction of the liquid shows the percentage of alcohol agreeing with that obtained from the specific gravity in the regular manner, it may safely be assumed that no methyl alcohol is present. If, however, there is an appreciable amount of methyl alcohol the low refractometer reading will at once indicate the fact. If the absence in the solution of other refractive substances than water and the alcohols is assured this qualitative test by difference in refraction is conclusive, but if there is doubt a confirmatory test by the Mulliken and Scudder method[1] should be made.

TABLE II.—SCALE READINGS ON ZEISS IMMERSION REFRACTOMETER AT 20° C. CORRESPONDING TO EACH PER CENT. BY WEIGHT OF ETHYL AND METHYL ALCOHOL.

Per cent. alcohol by weight.	Scale readings. Methyl alcohol.	Scale readings. Ethyl alcohol.	Per cent. alcohol by weight.	Scale readings. Methyl alcohol.	Scale readings. Ethyl alcohol.	Per cent. alcohol by weight.	Scale readings. Methyl alcohol.	Scale readings. Ethyl alcohol.
0...	14.5	14.5	34...	35.2	74.4	68...	34.0	99.4
1...	14.8	16.0	35...	35.8	75.8	69...	33.5	99.7
2...	15.4	17.6	36...	36.3	76.9	70...	33.0	100.0
3...	16.0	19.1	37...	36.8	78.0	71...	32.3	100.2
4...	16.6	20.7	38...	37.3	79.1	72...	31.7	100.4
5...	17.2	22.3	39...	37.7	80.2	73...	31.1	100.6
6...	17.8	24.1	40...	38.1	81.3	74...	30.4	100.8
7...	18.4	25.9	41...	38.4	82.3	75...	29.7	101.0
8...	19.0	27.8	42...	38.8	83.3	76...	29.0	101.0
9...	19.6	29.6	43...	39.2	84.2	77...	28.3	100.9
10...	20.2	31.4	44...	39.3	85.2	78...	27.6	100.9
11...	20.8	33.2	45...	39.4	86.2	79...	26.8	100.8
12...	21.4	35.0	46...	39.5	87.0	80...	26.0	100.7
13...	22.0	36.9	47...	39.6	87.8	81...	25.1	100.6
14...	22.6	38.7	48...	39.7	88.7	82...	24.3	100.5
15...	23.2	40.5	49...	39.8	89.5	83...	23.6	100.4
16...	23.9	42.5	50...	39.8	90.3	84...	22.8	100.3
17...	24.5	44.5	51...	39.7	91.1	85...	21.8	100.1
18...	25.2	46.5	52...	39.6	91.8	86...	20.8	99.8
19...	25.8	48.5	53...	39.6	92.4	87...	19.7	99.5
20...	26.5	50.5	54...	39.5	93.0	88...	18.6	99.2
21...	27.1	52.4	55...	39.4	93.6	89...	17.3	98.9
22...	27.8	54.3	56...	39.2	94.1	90...	16.1	98.6
23...	28.4	56.3	57...	39.0	94.7	91...	14.9	98.3
24...	29.1	58.2	38...	38.6	95.2	92...	13.7	97.8
25...	29.7	60.1	59...	38.3	95.7	93...	12.4	97.2
26...	30.3	61.9	60...	37.9	96.2	94...	11.0	96.4
27...	30.9	63.7	61...	37.5	96.7	95...	9.6	95.7
28...	31.6	65.5	62...	37.0	97.1	96...	8.2	93.9
29...	32.2	67.2	63...	36.5	97.5	97...	6.7	94.0
30...	32.8	69.0	64...	36.0	98.0	98...	5.1	93.0
31...	33.5	70.4	65...	35.5	98.3	99...	3.5	92.0
32...	34.1	71.7	66...	35.0	98.7	100...	2.0	91.0
33...	34.7	73.1	67...	34.5	99.1			

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[1] *Loc. cit. supra.*

Not only can methyl alcohol be thus readily detected, but the amount may be approximately and in some cases very accurately determined. Addition of methyl to ethyl alcohol decreases the refraction in direct proportion to the amount present. Hence the quantitative calculation may be readily made by interpolation in Table II, which follows, using the figures for pure ethyl and methyl alcohol of the same alcoholic strength as the sample. The degree of accuracy of this calculation varies with the strength of alcohol. For instance, with an alcoholic strength of 10 per cent. there is less exactness than at 50 per cent. strength, where 1 per cent. or even less can be readily determined. From this point on the delicacy of the process naturally increases, until at 90 per cent. strength 0.1 per cent. of methyl alcohol may be determined with accuracy.

Table II shows the refraction on the immersion refractometer corresponding to each percentage of alcohol, both ethyl and methyl by weight, all readings being taken at exactly 20° C. This table will show at a glance whether a solution of given strength of alcohol as determined from the specific gravity contains ethyl or methyl alcohol, or is a mixture of the two.

The fact should be borne in mind that in the examination of flavoring extracts it is difficult to so completely separate out the volatile oils as to prevent minute traces from appearing in the distillate. These, and indeed any volatile substances present in marked degree, appreciably affect the accuracy of the quantitative results, though mere traces do not cause serious error. The presence of notable amounts of acetone exercises also a marked effect, but the purified wood alcohol commonly used as an adulterant contains so little acetone that it may ordinarily be neglected in expressing approximate results. Pure acetone refracts considerably lower than ethyl alcohol.

Two or three examples of actual cases as found in the routine inspection of foods and drugs in Massachusetts will best illustrate the method of calculation. For determination of total alcohol from the specific gravity, Hehner's alcohol tables were used.

(1) A lemon extract found by the polariscope to contain 4.9 per cent. of lemon oil by volume and 90.20 per cent. of alcohol by volume at 15° was freed from lemon oil by diluting four times with water, treating with magnesia in the regular manner and filtering.

A measured portion of the filtrate was then distilled and the distillate made up to the measured portion taken. This distillate was found to have a specific gravity of 0.9736, corresponding to 18.38 per cent. alcohol by weight,[1] and to have a refraction of 35.8 on the Zeiss immersion refractometer.

By interpolation in Table II the readings of ethyl and methyl alcohol corresponding to 18.38 per cent. alcohol are 47.2 and 25.4 respectively, the difference being 21.8. $47.2 - 35.8 = 11.4$. $(11.4 \div 21.8)100 = 52.3$. In this case 52.3 per cent. of the alcohol present was methyl.

(2) An orange extract was found with 1.5 per cent. of orange oil and 83.2 per cent. of alcohol by volume at 15° C. The specific gravity of the one-fourth strength distillate, freed from oil as in the case of the lemon extract, was 0.9754, corresponding to 16.92 per cent. alcohol by weight Refraction of the distillate at 20° C. was 42.0. Readings of ethyl and methyl alcohol of 16.9 strength are, according to Table II, 44.3 and 24.5 respectively. Difference, 19.8. $44.3 - 42 = 2.3$. $(2.3 \div 19.8)\ 100 = 1.2$. Thus, 1.2 per cent. of the alcohol present was methyl.

(3) 6.3 cc. of tincture of iodine, after titration with N/10 sodium thiosulphate (in the regular manner for determining its strength according to the U. S. Pharmacopoeia), were neutralized with N/10 sodium hydroxide and distilled, collecting 25.2 cc. of the distillate, corresponding to a dilution of 1 :4 of the sample. The distillate contained 20.92 per cent. alcohol by weight, refraction 27.5 at 20° C., indicating 99 per cent. of the alcohol to be methyl. There is no doubt that the alcohol in this case was entirely methyl, the slightly high refraction of the distillate being due to the presence of a slight amount of volatile substance, formed by decomposition of the tincture of iodine.

The accuracy of the method is shown in a general way by a series of experiments, the results of which are tabulated as follows:

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[1] Our methyl-ethyl alcohol tables being most conveniently worked out on the weight-per cent. basis, the per cent. by weight rather than by volume of the dilute distillate is here taken. Percentage of total alcohol in the extract as well as of lemon oil we commonly express by volume. In this case, the specific gravity 0.9736 corresponds to 22.55 per cent. alcohol by volume. The per cent. by volume of total alcohol in the extract, 90.20 at 15° C., is found by multiplying 22.55 by 4 to correct for the dilution.

TABLE III.—READINGS OF EXPERIMENTAL MIXTURES OF METHYL AND ETHYL ALCOHOLS.

			Methyl alcohol.		Ethyl alcohol.	
Sp. gr. 15° C.	Per cent. alcohol by weight.	Scale reading. 20° C.	As prepared. Per cent.	As found. Per cent.	As prepared. Per cent.	As found. Per cent.
0.8190	91.36	33.9	68.52	69.88	22.84	21.48
0.8190	91.36	54.9	45.68	47.41	45.68	44.95
0.9239	47.41	51.9	35.56	35.42	11.85	11.99
0.8190	91.36	76.3	22.84	23.75	68.52	67.61
0.9326	43.43	62.4	21.71	21.38	22.71	22.05
0.9643	25.64	37.2	19.23	19.76	6.41	5.88
0.9207	48.86	77.5	12.21	11.77	36.65	37.09
0.9753	17.00	34.0	8.50	8.92	8.50	8.08
0.9666	23.92	50.2	5.98	6.48	17.94	17.44

SOME OBSERVATIONS ON THE DEPOSITION OF ALLOYS FROM MIXED SOLUTIONS.[1]

BY CHARLES B. JACOBS.

Received June 17, 1905.

RECENTLY the writer had occasion to make a simultaneous deposition of two metals, zinc and nickel, under conditions in which it was impossible to use any of the well-known methods.

The current strength permitted could not be great enough to prevent secondary action of the electropositive metal on the solution of the other, for it would then have resulted in a pulverulent deposit, and the physical structure of the deposit required prohibited anything but a strongly adherent, finely crystalline metal. Neither could cyanide solutions or alkaline solutions of any kind be used, as the deposited alloy was intended to receive a lithographic transfer, and any trace of cyanide solution or alkali acted on the transfer ink and destroyed the fine dots and lines of the work. If the deposited metal were washed sufficiently to rid it of the last traces of cyanide or alkali it became oxidized in spots. These oxidized spots refused to permanently hold the ink from the transfer paper.

Moreover, the composition of the alloy required did not permit of having a small proportion of the more electronegative metal in the bath.

It therefore became necessary to devise a means of plating zinc and nickel simultaneously without the use of cyanide solu-

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[1] Read at the Buffalo Meeting of the American Chemical Society.