Alcohol in 50 cc.	Reading of standard.	Reading of solution examined.	Salicylic acid indicated in solution. Milligrams.	Remarks.
5	20	20	1.0	
10	18	18	1.0	
15	18	18	1.0	Quality of color not same.
20	20	21	0.95	Color of sample decidedly bluer.
25	20	27	0.74	Color quality identical.
30	20	37	0.54	" " "
35	18	...		Color of sample too light to read.
40	18	...		" " " " " " "

It appears from these results that the presence of more than a small amount of alcohol in the solution used is inadvisable. We, accordingly, have abandoned its use and are now dissolving the ether extract in warm water, cooling, and making to volume.

It is also an improvement to make the tomatoes alkaline with ammonia before adding the milk of lime. When this is done about 15 cc. milk of lime (200 grams quicklime in 2000 cc. water) are sufficient, whereas much more is necessary when the ammonia is not used. These two modifications in the method given above have solved the problem and give us excellent results as is shown by the following figures:

Salicylic acid used. Milligrams.	Salicylic acid recovered. Milligrams.	Recovered. Per cent.
5	4.7	94.0
10	8.0	80.0
10	8.11	81.1
15	13.33	88.8
20	19.20	96.0
25	25.00	100.0
30	26.70	89.0
50	46.9	93.8

[CONTRIBUTIONS FROM THE BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE. SENT BY H. W. WILEY.]

A STUDY OF THE METHODS FOR THE DETERMINATION OF ESTERS, ALDEHYDES AND FURFURAL IN WHISKY.

BY L. M. TOLMAN AND T. C. TRESCOT.

Received August 15, 1906.

IN THE course of an examination of a large number of whiskies made in the Bureau of Chemistry under the direction of H. W. Wiley the following work on the methods for the determination of the ethereal salts, aldehydes and furfural was undertaken, as the methods adopted provisionally by the Association of Official Agricultural Chemists as published in Bulletin 65 of the Bureau of Chemistry were found to be unsatisfactory.

DETERMINATION OF ESTERS.

The provisional method as adopted by the Association of Official Agricultural Chemists in 1903 for the determination of esters is as follows:

Neutralize the residue left after distillation in the fusel oil determination with N/10 sulphuric acid and add an excess of 10 cc. of the acid. Allow to stand five minutes, and make up to 200 cc. Titrate two portions of 25 cc. each, using as indicators methyl orange in the first and phenolphthalein in the second. The difference gives the amount of alkali necessary to neutralize the organic acids in 25 cc. of the sample. By subtracting from this figure the number of cubic centimeters of alkali required for the free acids and multiplying the result by 0.0088, the number of grams of ethereal salts (calculated as ethyl acetate) in 25 cc. of the sample is determined.

The distillation of fusel oil is conducted as follows: Add a small quantity of alkali to 200 cc. of the sample under examination, and distil slowly, till about 175 cc. have passed over; allow the distilling flask to cool, add 25 cc. of water, and distil again till the total distillate measures 200 cc. It was found, however, that it was exceedingly difficult to carry out this method satisfactorily and, further, that it was very inaccurate, not in reality giving any true ester value.

The first objection is that the method does not state that sufficient alkali must be added in the distillation to completely neutralize the acids and saponify the esters. If this is not done, there is a loss of unsaponified esters. Some of the whiskies required as much as 10 cc. of normal alkali to 200 cc. to accomplish this result.

The second objection is the difficulty experienced in the double titration with methyl orange and phenolphthalein in the dark colored whiskies, it being practically impossible to get two titrations agreeing within a reasonable limit of accuracy. It was also found that there is a considerable loss of volatile esters, which come over in the first part of the distillate before they are saponified, even though there be sufficient alkali present, and it was found necessary to boil with a reflux condenser before beginning the distillation. The chief source of error, however, is in the action of the alkali on the caramel and invert sugar present in the whisky.

How much this error may amount to is shown in the following table where caramel prepared from pure cane-sugar was treated in the following manner: A weighed amount of caramel is placed in an Erlenmeyer flask and dissolved in 50 cc. of alcohol (50 per cent. by volume). This is exactly neutralized with N/10 alkali using phenolphthalein as an indicator and then 10 cc. of N/10 alkali are added, the flask connected with a reflux condenser and boiled for one hour, then cooled, and the excess of alkali titrated.

TABLE I.—EFFECT OF ALKALI ON CARAMEL.

Caramel. Gram.	Amount of N/10 alkali used up. cc.	Time of boiling. Hours.
0.050	0.70	1
0.100	1.85	1
0.150	2.70	1
0.200	3.60	1
0.250	3.80	1
0.250	4.60	2

This table shows that with 0.500 gram of caramel per 100 cc., which gives a color about equal to a dark colored whisky, we would have 7.6 cc. N/10 alkali used up by the caramel, which would be calculated as esters. This would be as much as the volatile esters in most whiskies. If, however, there was also invert sugar present a still larger error would be introduced as is shown in the following table:

TABLE II.—EFFECT OF INVERT SUGAR ON THE ALKALI.

Invert sugar. Gram.	Amount of N/10 alkali neutralized. cc.	Time of boiling. Hours.
0.050	1 2	1
0.050	1.5	2
0.100	2.9	1
0.150	3.6	1
0.250	5.85	1
0.250	6.95	3

This table shows that invert sugar uses up the alkali to a greater degree than caramel. If this reaction of alkali with caramel and invert sugar were quantitative, the figure might have some value, but it is not, so that such a determination can have no value in the presence of these substances.

An illustration of this fact is shown in the following results on some brandies:

TABLE III.—RELATION OF THE SOLIDS AND INVERT SUGAR TO THE FIXED ESTERS.

Solids. Per cent.	Invert sugar. Per cent.	Amount of N/10 alkali used by 100 cc. cc.	Amount of N/10 alkali used by vol. esters in 100 cc. cc.	Amount of N/10 alkali used by fixed esters in 100 cc. cc.
1.2658	0.845	40.4	10.0	30.4
1.1348	0.820	47.6	8.8	38.8
1.0640	0.685	36.2	6.4	28.8
0.9726	0.596	32.2	7.2	25.0
0.7774	0.500	26.0	7.6	18.4
0.6840	0.392	26.6	4.8	20.9
0.6070	0.313	25.0	3.0	22.0
0.0306		18.8	12.4	6.4
0.0200		14.2	11.4	2.8
0.0054	trace	9.6	9.6	0.0
0.0052	"	16.4	15.4	1.0
0.0042	"	10.0	7.4	2.6

This table shows that the fixed esters increase with the sugar and are in fact dependent upon its presence. If it were not for this fact the determination of fixed esters might be of some value, as the following table on pure whiskies indicates.

TABLE IV.—DETERMINATION OF FIXED ESTERS IN PURE WHISKIES.

Solids. Per cent.	cc. N/10 alkali used by 100 cc. of whisky.	cc. N/10 alkali used by Vol. esters. in 100 cc.	cc. N/10 alkali used by Fixed esters. in 100 cc.
0.3264	27.30	8.0	19.30
0.1976	21.20	9.50	11.70
0.1840	18.6	8.00	10.60
0.1690	15.8	5.2	10.60
0.1620	15.10	7.10	8.00
0.1592	13.4	5.8	7.60
0.1356	19.70	7.70	12.00
0.1164	7.70	2.00	5.70
0.0496	6.60	1.80	4.50

It was evident from this work that the provisional method is unsatisfactory and does not give an ester number. It was therefore necessary to determine the esters in a distillate which was prepared in the following manner: Add 25 cc. of water to 200 cc. of the whisky or spirit to be examined and distil off 200 cc.

into a flask guarded with a mercury valve to prevent loss of alcohol. Measure 50–100 cc. of this distillate into a flask, add a few drops of phenolphthalein and exactly neutralize the free acid with N/10 alkali; add 25–50 cc. of N/10 alkali, stopper the flask and allow to stand at room temperature for eighteen to twenty hours, then connect with a single tube condenser and heat nearly to boiling for one-half hour, cool and titrate the excess of alkali with N/10 acid.

The number of cubic centimeters of N/10 alkali used in the saponification multiplied by the factor 0.0088 gives the amount of esters present as ethyl acetate. There should be a considerable excess of alkali to insure the saponification being complete.

The esters may also be determined by connecting the flask with a reflux condenser, instead of allowing them to stand over night, and boiling for one hour, and if only a few determinations are to be made this will be found to be the most satisfactory procedure, but where a large number of determinations are to be made the first scheme is very satisfactory. It was found by experiment that standing over night with the excess of alkali insured complete saponification of the esters without any danger of loss of the volatile esters.

The question as to whether complete saponification could not be obtained in the cold by standing eighteen to twenty hours at room temperature with the excess of alkali was thoroughly tested in the following manner: Duplicates were measured into flasks and the excess of alkali added and stoppered and allowed to stand over night. In the morning one was titrated and the other was heated for one hour with the tube condenser on the water-bath, cooled and titrated. In 30 cases there was no difference between these titrations and the average on 171 determinations was for the cold titrations 4.1 cc. N/10 alkali for 50 cc. of sample and 4.2 cc. N/10 for 50 cc. of the sample that was heated, which indicates that practically complete saponification takes place at room temperature and that the heating for one hour is not necessary, but in a few cases the titration of the cold saponified sample would be low, showing that complete saponification had not taken place. In our experience, therefore, it is safer to complete the saponification by heating as directed in the method.

The samples that were heated on the water-bath always had a little more color than the samples which were not heated, indicating a little more resinification of the aldehydes, which may account for the slightly higher results obtained by heating.

In order to check up the method of distillation the esters were determined in some artificial brandies before and after distillation. The results of four determinations on the original showed that 9 cc. of N/10 alkali were needed to saponify the esters in 100 cc. while, according to the average on 20 determinations on the distillate, 8.9 cc. were required for 100 cc., which shows that where the esters present are ethyl acetate, as they were in this sample, all are found in the distillate.

This experiment was repeated on five samples of new colorless whiskies with the same result, showing that the method of distillation is satisfactory and that the esters are distilled over completely although this does not prove that in the old, aged whiskies there are not formed esters which are non-volatile but it is impossible to distinguish them from coloring-matters and resinous materials which are affected by boiling with alkali, as has been shown.

ALDEHYDES.

By L. M. Tolman.

The method for the determination of aldehydes as provisionally adopted by the Association was found to be entirely unreliable and in fact the reagents as given were not correct, as they reacted with alcohol free from aldehydes. The reason for this was that there was not enough sulphur dioxide in the solution. The amount of sulphur dioxide in the solution greatly affects its sensitiveness and the main point to be determined was how to prepare a solution that would not react with pure alcohol and was still sensitive enough. By experimenting with a number of mixtures it was found that a reagent that contained 5 grams of sulphur dioxide to the liter gave only the slightest tinge of color with the pure alcohol and was sensitive to 0.0001 gram of aldehyde in 50 cc. From this it can be seen that it is very necessary that the amount of sulphur dioxide present should be accurately determined and that the use of a solution of sodium bisulphite of a definite specific gravity is not to be relied on in preparing this reagent. If the sulphite is to be used, its strength in sulphurous acid should be determined by use of a standard solution of iodine. Another objection to the Association method was the fact that the test is made in a 30 per cent. alcohol solution. The objection to using this strength of alcohol is that when most pure whiskies are diluted to this alcoholic strength they are turbid, and this turbidity greatly interferes with the reading of the amount of aldehydes in the colorimeter. The following are the reagents and method finally adopted for our work.

DETERMINATION OF ALDEHYDES.

Reagents.

(1) *Alcohol Free from Aldehydes.*—This is prepared by first redistilling the ordinary 95 per cent. by volume alcohol over caustic soda or potash and then adding 2 to 3 grams per liter of *m*-phenylenediamine hydrochloride, and digesting at ordinary temperature for several days or with an upright condenser on the steam-bath for several hours and then distilling slowly, rejecting the first 100 cc. and the last 200 cc.

(2) *Sulphite-Fuchsin Solution.*—Take 0.500 gram of pure fuchsin and dissolve in 500 cc. of water, then add 5 grams of sulphur dioxide dissolved in water, make up to a liter and allow to stand until colorless.

This solution should be made up in small quantities, as it retains its strength for only a very few days.

(3) *Standard Acetic Aldehyde Solution.*—Prepared as directed in Vasey.[1]

Aldehyde ammonia is taken as the starting point. Grind this in a mortar with ether and decant the ether, repeating the operation several times, then dry the purified substance in a current of air and finally in a vacuum over sulphuric acid. Dissolve 1.386 grams of this purified aldehyde ammonia in 50 cc. of 95 per cent. by volume alcohol, to this add 22.7 cc. of normal alcoholic sulphuric acid and then make up to 100 cc. and add 0.8 cc. to compensate for the volume of the ammonium sulphate precipitate. Allow this to stand over night and filter. This solution contains 1 gram of acetic aldehyde in 100 cc. and will retain its strength.

The standard found most convenient was 2 cc. of this strong aldehyde solution diluted to 100 cc. with 50 per cent. by volume alcohol. One cc. of this solution is equal to 0.0002 gram of acetic aldehyde. This solution should be made up fresh every day or so as it loses its strength.

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[1] "Analysis of Potable Spirits," p. 30.

The method of determining aldehyde is as follows: 5 or 10 cc. of the distillate as prepared for the determination of esters are placed in one of the colorimeter tubes and made up to 50 cc. with aldehyde-free alcohol, strength 50 per cent. by volume, placed in a water-bath kept at 15° until it reaches the temperature of the bath. Then 25 cc. of the sulphite-fuchsin solution, which is also at 15°, is added; the two solutions are thoroughly mixed and allowed to stand in the bath held at 15° for fifteen minutes and then compared in the colorimeter with standard aldehyde solutions.

Standards containing 0.0005, 0.0010 and 0.0015 gram of acetic aldehyde are prepared at the same time and under the same conditions. The standard which matches the sample nearest is used for comparison in the colorimeter. If the color of the sample is stronger than any of the standards, less of the sample must be taken, as colors deeper than that produced by 0.0015 gram of acetic aldehyde cannot be compared with accuracy.

The regulation of the temperature at which the test is made is of the greatest importance, as the accuracy of the method is entirely dependent on the temperature being held constant at about 15° during the reaction. If this is not done, the color developed in the blank which should be run with every determination, will be so strong as to interfere with the method. In fact it is impossible to do anything with the method quantitatively without controlling the temperature exactly.

The comparisons in the colorimeter must be made as quickly as possible, as the color rapidly deepens if the room temperature is much above 15°. The standard aldehyde solution may be checked against the color glasses of the Lovibond tintometer. In our work, following the exact conditions given above, red No. 5 and blue No. 1.25 combined gave the color developed by 0.0005 gram of acetic aldehyde in 50 cc., looking through 42 mm. depth of solution. This, however, should not be taken as a standard but each analyst should compare his reagents, under the conditions under which he is working with the standard glasses. This will be found to be a valuable check on the solutions.

TABLE V.—CALCULATION OF ALDEHYDES FROM COLORIMETER READINGS.

Sample reading.	0.0005 gram standard. Reading 15. Mg.	0.0005 gram standard. Reading 25. Mg.	0.0010 gram standard. Reading 10. Mg.	0.0010 gram standard. Reading 20. Mg.	0.0015 gram standard. Reading 10. Mg.
10		0.80	1.00	1.50	1.50
11		0.76	0.94	1.40	1.40
12		0.72	0.89	1.30	1.30
13		0.69	0.83	1.25	1.25
14		0.67	0.79	1.20	1.20
15	0.50	0.65	0.76	1.15	1.15
16	0.48	0.62	0.73	1.10	1.10
17	0.465	0.60	0.70	1.08	1.06
18	0.45	0.59	0.685	1.05	1.03
19	0.43	0.575	0.67	1.03	1.00
20	0.415	0.56	0.655	1.00	0.97
21	0.40	0.55	0.64		
22	0.38	0.54	0.62		
23	0.365	0.525	0.61		
24	0.35	0.515	0.59		
25	0.33	0.50	0.58		
26	0.315		0.565		
27	0.30		0.55		
28	0.29		0.535		
29	0.28		0.52		
30	0.27		0.50		
31	0.265		0.49		
32	0.255		0.485		
33	0.245		0.48		
34	0.235		0.47		
35	0.23		0.465		
36	0.22		0.46		
37	0.21		0.455		
38	0.20		0.45		
39	0.195		0.445		
40	0.19		0.44		
41	0.185		0.435		
42	0.18		0.43		
43	0.175		0.425		
44	0.17		0.415		
45	0.165		0.41		
46	0.16		0.405		
47	0.155		0.40		
48	0.15				
49	0.145				
50	0.14				

The amount of color developed by acetic aldehyde under these conditions is not in direct proportion to the percentage of aldehyde present. A standard containing 0.001 gram develops about three times as much color as a standard 0.0005 gram and about one-half the color of a standard containing 0.0015 gram. This necessitated the preparation of a number of curves from which the table as given above was prepared:

This table is used in the following manner: The colorimeter tube containing the standard solution is placed in the colorimeter at a definite reading, say at 25. The tube containing the sample is now placed in the instrument and compared with the standard by moving it up and down until the colors match, which is at say 19. Now suppose the standard contained 0.0005 gram of aldehyde and was set in the instrument at a reading of 25, then look in the column under the 0.0005 gram reading 25 until you come to the place opposite the reading of the sample and there find the milligrams of aldehyde which, in this case, is 0.575. The colorimeter used in this work was that described by Schreiner[1] and it was found to be very satisfactory and convenient, being preferred in this work to the Soleil-Dubosq instrument, as it gives a much wider range of comparison. Schidrowitz[2] does not use the distillate for this determination but clarifies the whisky with basic lead acetate, colors his standard slightly with tincture of galls to match the color of the decolorized whisky, and then treats with the reagent, but this method, while it is applicable to pure whiskies light in color, cannot be applied to whiskies that are colored with caramel, as caramel is not removed by lead acetate. Hence, in order to obtain comparable results, it is necessary to work on the distillates in all whiskies.

The claim that aldehydes are formed in the distillation is not substantiated by our experiments on 150 samples of new brandies in which the determination of aldehydes was made on the original sample and on the distillate. The average on the original was 172 mg. per liter while the average on the distillate was 173 mg. per liter. These results show several things. First, that the method gives comparable results and results that can be duplicated, as in this work the determination on the original was made on one day and the determination on the distillate the next day. Second, that there is no loss or gain in aldehydes by distillation.

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[1] This Journal, 27, 1192–1203 (1905).

[2] J. Chem. Ind. 21, 814–819 (1902).

Third, that it is an exact method as is shown by the close agreement of results.

FURFURAL.

BY L. M. TOLMAN.

Schidrowitz does not use the distillate for this determination but follows the same procedure in the determination of furfural as in the determination of aldehydes. The same objection holds in this method, however, as in the aldehyde determination, namely, that the method cannot be applied to all the whiskies on account of the impossibility of removing caramel when present, so that it is better to use the distillate in all cases.

The following are the reagents and the method used for the determination of furfural: Colorless aniline, hydrochloric acid (sp. gr. 1.125), alcohol free from furfural. The aniline was obtained by redistilling the ordinary dark colored aniline. This must be kept in the dark or it will soon become colored. The ordinary 95 per cent. by volume alcohol redistilled over caustic soda or alkali is practically free from furfural.

Standard Furfural Solution.—Prepare the standard furfural solution by weighing 1 gram of redistilled furfural and dissolving it in 100 cc. of 95 per cent. by volume alcohol. This strong solution will keep. Standards for use are made by diluting 1 cc. of this solution to 100 cc. with 50 per cent. by volume alcohol. One cc. of this solution contains 0.0001 gram of furfural.

The method for determining furfural is as follows: 10 or 15 cc. of the distillate as prepared for the determination of esters is placed in a colorimeter tube and diluted to 50 cc. with 50 per cent. by volume alcohol free from furfural. The tube is placed in a water-bath kept at 15° and allowed to remain until it reaches the temperature of the bath. Then 2 cc. of the aniline and 0.5 cc. of the hydrochloric acid are added and the whole thoroughly mixed. The tubes are left for fifteen minutes in the bath at 15°, and then taken out and read in the colorimeter against standard furfural solutions.

Standards containing 0.0001, 0.0002 and 0.0003 gram of furfural are prepared and treated in the same manner. The standard which matches nearest the color in the sample is used for comparison in the colorimeter.

The amount of color developed by the furfural solutions is in direct proportion to the amount of furfural present, so that calculations can be made directly from the readings.

The temperature greatly affects the reaction and it should be carefully regulated.

Hydrochloric acid was used instead of acetic acid on account of the fact that the acetic acid available gave a very decided color reaction, which interfered with the test. Another advantage of hydrochloric acid is that it is more uniform in quality than acetic acid and in these color tests it is necessary that the conditions shall remain constant in order to obtain comparable results. The occurrence of furfural in acetic acid or some substance that gives a similar color reaction with this reagent seems to be quite common, as it has been noted by a number of observers. The substance that gives the test can be destroyed by heating the mixed reagent, but this interferes with its sensitiveness.

In order to settle the question whether all the furfural will be found in the distillate and also whether there is any formation of furfural in distillation, the determination was made on a number of samples of slightly colored and colorless spirits, in the original and in the distillate.

The results on 120 samples gave an average of 23.4 mg. per liter on the original and of 23.2 mg. per liter on the distillate. This shows that there is no loss or gain of furfural by distillation; it also shows that the method is reliable, as the same conditions held in these determinations as in the work on aldehydes.

MOISTURE IN COAL.[1]

By E. E. Somermeier.

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THE determination of moisture in a sample of coal is apparently simple and a result is easily obtained. The proper relation that this result bears to the original sample is, however, not so easily determined. Variations in this relation directly affect the application of all analytical work done upon the sample and the possibility of unaccounted-for moisture losses during the taking, shipping and preparing of the sample for chemical analysis too often receives little or no attention.

The method of determining moisture recommended by the

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[1] Published by permission of the Director of the U. S. Geological Survey.