A Simple Procedure for Decolourisation of Organic Compounds.

By Koshiro ISHIMURA.

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In the course of the investigation on the molecular rearrangement of disubstituted acetaldehydes into the corresponding ketones, the author has prepared a number of aromatic compounds, namely, diaryl ketones, alkyl aryl ketones, their oximes and semicarbazones and benzoyl derivatives of diaryl ethylene glycols and of alkyl aryl ethylene glycols. They have usually been purified by recrystallisation from dilute alcohol, but in every case faintly yellowish or brownish colour could not be removed from the substances by the usual methods, such as changing the solvents, adding animal charcoal or dissolving them in hot alcohol and adding hot water to the solution till it becomes faintly turbid and subsequently leaving it to cool down.(1) In such cases the purification was accomplished with unexpected good results in the following way:—the substance to be purified is dissolved in hot alcohol, into which a large quantity of hot water is poured at a time. An almost colourless flocky precipitate is obtained. It is filtered and recrystallised from dilute alcohol once more in the usual way and thus a completely colourless substance with a well defined crystalline form is easily obtained.

The colouring matters may be some polymerisation or condensation products, possibly with large molecular weights, formed by the side reactions when the above-mentioned substances are synthesised. They are soluble in hot alcohol but not in cold alcohol and water. When hot water is poured into the hot alcoholic solution they may very probably be peptized, forming colloidal solutions, whereas the substances to be purified are precipitated, which are likewise insoluble in water but with much smaller molecular weights and existing in relatively large amount, and thus difficult to form colloidal solutions.

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(1) H. Meyer, "Analyse und Konstitutionsermitterung Organischer Verbindungen", 26, 1931.

Some Methods of Analysis of Commercial Methanol.

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More than ten years ago, when the industry of synthetic methanol did not yet develop in this country, two samples of methanol were offered to the author for analysis from a certain factory of a small pilot-plant scale. The samples were produced while the investigations into the optimum conditions for manufacture were still busily going on, therefore they naturally contained a considerable quantity of various impurities.

Preliminary Examinations. The two samples were designated A and B respectively. They were colourless and their densities were d_4^{20}, 0.8084 and d_4^{20}, 0.7964 respectively.

On distillation, the fractions were obtained from 500 g. of each sample as reproduced in Tables 1 and 2.

Table 1.

Sample A.

Fraction	B. p. (°C.)	Yield		d_4^{20}
		g.	%	
1	Below 65	20.0	4.0	0.7737
2	65 – 67	160.0	32.0	0.7933
3	67 – 70	253.7	50.6	0.8050
4	Above 70	65.0	13.1	—

Table 2.

Sample B.

Fraction	B. p. (°C.)	Yield	
		g.	%
1	Below 63	11.2	2.2
2	63 – 65	101.6	20.3
3	65 – 67	322.7	64.5
4	67 – 70	49.1	9.8
5	Above 70	11.4	2.3

The residue, boiling above 70°C., separated into two layers in each case. The upper layer was light yellow oil (0.44 g. in the case of A), while the lower one was light mobile liquid. 2.8 g. of the former oil and 79.8 g. of the latter liquid, both collected from several runs, were distilled, giving the fractions shown in Tables 3 and 4 respectively.

Table 3.

Fraction	B. p. (°C.)	Temperature of bath (°C.)	Yield (g.)	d_4^{20}
1	Below 102	250	0.1	0.8202
2	Residue	—	2.5	—

Table 4.

Fraction	B. p. (°C.)	Yield (g.)	d_4^{20}
1	70— 75	40.0	0.8218
2	75— 80	18.4	0.8429
3	80— 92	8.8	0.8773
4	92—107	9.0	0.9794
5	107—117	3.6	0.9982
6	Residue	0.1	—

The residue in Table 3 was fractionated under reduced pressure of 38 mm. as shown in Table 5.

Table 5.

Fraction	B. p. (38 mm.) (°C.)	Yield (g.)	d_4^{20}	M. p. (°C.)
1	130—150	0.5	0.7908	2— 6
2	150—160	0.5	0.7825	9—11
3	160—170	0.2	0.7803 d_4^{25})	13—16
4	170—180	0.5	0.7867(d_4^{25})	19—22.5
		0.2	—	30—32.5
5	Residue	0.4	—	—

The fraction 4 in Table 5 was separated into two parts, i.e., one solidified at the ordinary temperature and the other did not solidify.

When the sample A was stocked in the cold place, a small quantity of colourless scales separated out and was proved to be *n*-docosane. It was recrystallised from methyl alcohol and melted at 44–45°C. Found: C, 85.70; H, 15.07. Calculated for $C_{22}H_{46}$: C, 85.62; H, 14.38%. It is very probable that the fraction 4 in Table 5 contains a considerable quantity of *n*-docosane.

Qualitative Analyses. *Higher Alcohols.* The colour reactions with salicyl aldehyde and sulphuric acid and with vanilline and sulphuric acid showed evidently the presence of higher alcohols in the samples, and the boiling points of the fractions in Table 4 suggest that alcohols higher than amyl alcohols may be present, if any, only in very small amounts. The fractions boiling above 70°C. in Tables 1 and 2 gave the colour reaction with vanilline and sulphuric acid, characteristic of propyl or amyl alcohols, when they were carried out according to the informations given by T. Higashi(1). Henville's test(2) for isopropyl alcohol gave a positive result. The existence of ethyl alcohol could not be confirmed.

Aldehydes and Ketones. The samples did not reduce Fehling's solution. But the presence of aldehyde was confirmed by the colour reaction with fuchsine-sulphurous acid and by the formation of a silver mirror as well as of the insoluble compound with resorcine. Formaldehyde was confirmed to exist in the sample by two colour reactions, one with morphine hydrochloride and the other with phenylhydrazine hydrochloride, ferric chloride and concentrated hydrochloric acid. No ketone was found to exist.

Acids and Esters. The samples were neutral to litmus, but acidic to phenolphthaleine.

When the sample was subjected to hydrolysis with a sodium hydroxide solution for one hour on a water bath and then concentrated sulphuric acid was added to it, a gas was found to evolve. It was washed with alkali and passed into a solution of ammoniacal silver nitrate. A brown precipitate was thrown down indicating the evolution of carbon monoxide (Habermann's test(3)) and consequently the existence of formic acid or formic ester in the original sample.

Quantitative Analyses. *Methyl Alcohol.* A large number of methods for the estimation of methyl alcohol have been published; by counting only the principles underlying the methods ten or so will be pointed out, and moreover each method has been followed by its modifications. König's method(4) has been modified by the present author and has been found to be the most suitable for the analysis of the commercial methanol. The principle of this method lies in the fact that methyl alcohol is completely oxidised to carbon dioxide and water by chromic acid mixture under the suitable condition, while the oxidation of the homologous alcohols remains incomplete, only aldehydes or acids being thereby produced.

The estimation of the evolved carbon dioxide will give the amount of methanol. The apparatus used in the present work is shown diagrammatically in Figure 1.

The determination proceeds as follows:— The air free from carbon dioxide is passed into the reaction flask to expel carbon dioxide present in it. The oxidising mixture (15 g. $K_2Cr_2O_7$, 25 c.c. conc. H_2SO_4, 230 c.c. H_2O) is boiled for 15 minutes, cooled and rapidly poured into the flask,

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(1) *Bull. Inst. Phys. Chem. Research* (Tokyo), **7** (1928), 527.

(2) *Analyst*, **53** (1928), 416.

(3) *Z. angew. Chem.*, **5** (1892), 324; F. C. Phillips, *Am. Chem. J.*, **16** (1894), 272.

(4) *Chem. Ztg.*, **36** (1912), 1025.

and then 10 c.c. of the sample are introduced, and meanwhile the air is gently passed in. The sample is prepared by diluting 10 c.c. of the original sample methanol to 100 c.c. The passing of the air is stopped and the mixture is left to stand for 30 minutes. Then it is boiled gently. Carbon dioxide thereby produced is washed with concentrated sulphuric acid, dried with calcium chloride (alkali-free) and absorbed by weighed soda lime. The ends of the two U-tubes containing soda lime are filled with a small quantity of calcium chloride in order to catch water which is to be produced by the reaction between soda lime and carbon dioxide. The boiling is continued for 1 hour and the air is passed for one hour and a half to expel the evolved carbon dioxide completely. The increase in the weight of U-tubes gives the amount of carbon dioxide, from which the amount of methyl alcohol can easily be calculated out. 3.5–4 hours are required for one run of the analysis.

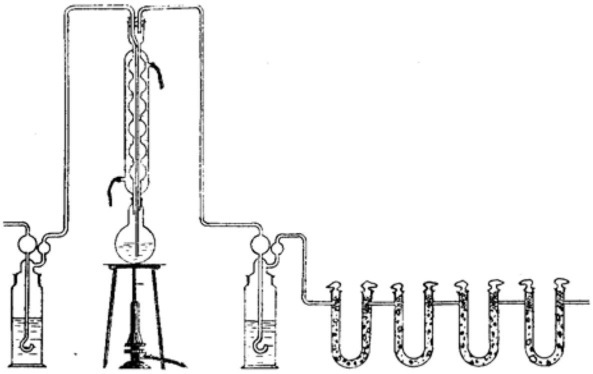

Fig. 1.

It has been found that the following corrections are necessary in the calculation.

(1) A correction for errors due to impurities contained in potassium bichromate, which must be determined by a blank test.

(2) Since some compounds other than methyl alcohol, e.g., formic acid, methyl formate or formaldehyde are also oxidised to carbon dioxide a correction is required.

The content of methyl alcohol was also determined by Zeisel's method of the determination of methoxyl group. The results, given by the two methods, were found to accord very well with each other as shown in Table 6.

Table 6.

Sample	Methyl alcohol (%)	
	By oxidation method	By Zeisel's method
A	89.63, 89.69	89.72
B	94.29	94.43

Acids and Esters. To determine the contents of acids the sample was diluted with equal volume of water and titrated with a 1/10 N sodium hydroxide solution with phenolphthaleine as indicator. It was treated with excess alkali on a water bath for 1 hour and then back-titrated with 1/10 N sulphuric acid in order to estimate the content of esters. Assuming that only formic acid and methyl formate were present, the values shown in Table 7 were obtained.

Table 7.

Sample	Formic acid (%)	Methyl formate (%)
A	0.009	0.13
B	0.08	0.25

Formaldehyde. According to B. H. Smith(5), who has studied comparatively on various methods of the determination of formaldehyde, the method based on the complex formation with potassium cyanide is the most suitable, when formaldehyde is present in a mixture of several substances as in the case of the present experiment.

50 c.c. of the sample were brought into reaction with 20 c.c. of a 1/10 N silver nitrate solution in a 200 c.c. measuring flask, into which 5 drops of concentrated nitric acid were added. The reaction mixture was diluted with water just to 200 c.c., well shaken and filtered through a dry filter paper. 100 c.c. of the filtrate were titrated with a 1/10 N ammonium thiocyanate solution with iron alum as indicator. The required amount of formaldehyde (in g.) was given by twice the difference between the titres of the sample and a blank test, multiplied by a factor 0.0030016. The results are shown in Table 8.

Table 8.

Sample	Formaldehyde (%)
A	0.0021
B	0.0046

Water. E. R. Weaver(6) detected the presence of water in various organic solvents by allowing calcium carbide to react with water and by observing the red colour developed on the formation of copper acetylenide. He suggested that by this method it may be detected also in acetone. It has been found, however, by the present author that this is not the case. Hydroxylamine which is used to reduce cupric salt to cuprous salt, reacts with acetone to produce oxime which in its turn reacts with copper acetylenide and thus the red colour disappears. Ketones and aldehydes generally disturb the test; the presence of formaldehyde, benzaldehyde, acetophenone, menthone and furfurol has been found to be the disturbing factor. Besides the oxime-forming substances, acids dissolve copper acetylenide. E. R. Weaver(7) afterwards

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(5) *J. Am. Chem. Soc.*, **25** (1903), 1030.
(6) *J. Am. Chem. Soc.*, **36** (1914), 2462.
(7) *J. Am. Chem. Soc.*, **38** (1916), 352.

succeeded in applying the test to the colorimetric analysis of acetylene but not of water in organic solvents. Although H. Hartley and H. R. Raikes(8) determined water contained in methyl alcohol by this method, no description of the experimental details was given.

According to the present author's experiment the formation of copper acetylenide does not seem to take place quantitatively. The amount of the precipitate of copper acetylenide was determined by R. Willstätter's method(9) and it has been shown that only about 50% of water present in the sample can be detected. But it has been found, that water may be determined quantitatively as well by the colorimetry, if the taken standard solution contains the amount of water not so different from that in the sample.

Following the informations given by E. R. Weaver,(6) grains of calcium carbide, about 3 mm. in diameter, were stocked in absolute alcohol. They were taken out immediately before the experiment and heated with 5 c.c. of absolute alcohol to dryness in order to expel the trace of the occluded acetylene. The sample and the standard methyl alcohol (5 c.c. each) were taken separately in two Erlenmeyer's flasks and two or three grains of the calcium carbide were added to each of them. The flasks were cooled with ice water for 30 minutes, meanwhile the acetylene remained dissolved in methyl alcohol. Cuprous chloride solution was prepared according to Hartley and Raikes' prescription:(8) 1 c.c. each of the following two solutions were mixed immediately before use:—

A. 3 g. of cupric chloride and 6 g. of ammonium chloride dissolved in dilute ammonia (9 c.c. of ammonia, d, 0.88, diluted with 100 c.c. of water).

B. 12 g. of hydroxylamine hydrochloride dissolved in 100 c.c. of water.

The mixing was carried out in a glass tube, about 15 mm. in diameter and about 25 cm. in length, graduated to 0.1 c.c., and a few c.c. of 2% water solution of gum arabic were added to the mixture. Calcium carbide was separated from the sample and the standard solutions by rapid filtration on dry filter papers. According to the content of water, 0.3–1.0 c.c. of the filtrate were added to the cuprous solution. The red colour of the colloidal copper acetylenide developed immediately. Gum arabic served to keep the colloidal solution stable. The colours developed by the sample and the standard solutions were compared with each other by a colorimeter and thus the water content can be calculated. As the standard methyl alcohol Merk's specimen "acetone free, extra pure" was used. The results are shown in Table 9.

Table 9.

Sample	Water content (%)
A	4.1
B	1.3

The reliability of the method above described is shown by the experimental results given in Table 10.

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(8) *J. Chem. Soc.*, **127** (1925), 524.

(9) *Ber.*, . **3** (1920), 939.

Table 10.

Water content in ethyl alcohol (vol. %)		Water content of the standards taken in colorimetry (vol. %)
By density determination	By colorimetry	
0.26	0.27	0.67
0.69	0.62	0.26
0.47	0.47	0.26
0.47	0.43	0.69
1.67	1.73	0.69
1.87	1.85	1.67

Higher Alcohols. Out of a number of methods for analysis of higher alcohols, two have been selected and investigated, i.e., Allen-Marquardt's method⁽¹⁰⁾ and that based on Komarowsky's colour reaction.⁽¹¹⁾

(1) Allen-Marquardt's method. This method consists in extracting higher alcohols with chloroform or carbon tetrachloride and subsequently oxidising to carboxylic acids which are then titrated after being distilled in steam. There are two difficulties in this method. Firstly propyl and butyl alcohols are not extracted quantitatively, and secondly the amount of inorganic acids to be distilled together with the carboxylic acids cannot be accurately known. In the present case the first difficulty need not be taken into account as extractions is unnecessary. The second difficulty can be avoided by carrying out a blank test.

25 g. of potassium bichromate dissolved in 100 c.c. of water were introduced into a 300 c.c. round flask and 2 c.c. of the sample was added to the solution. The flask was connected with a condenser with a ground joint. 30 c.c. of concentrated sulphuric acid was added drop by drop from the top of the condenser, and the reaction mixture was heated for 8 hours on a water bath. Carboxylic acids produced by the oxidation were then subjected to steam distillation. Inorganic acids, distilled out thereby, were determined by a blank test as stated above. When the progress of the distillation was adjusted so as to give 1 litre of distillate for 4 hours, the distillate in the blank test consumed 2.64 c.c. of a 1/10 N sodium hydroxide solution.

Preliminary tests, carried out with known amounts of butyl and amyl alcohol dissolved in methyl alcohol, gave satisfactory results as shown in Table 11.

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(10) Allen and Chattaway, *Analyst*, **16** (1891), 102; Ph. Schidrowitch, *J. Soc. Chem. Ind.*, **21** (1902), 814; *Analyst*, **31** (1906), 181; *J. Am. Chem. Soc.*, **29** (1907), 561; E. A. Mann, *J. Soc. Chem. Ind.*, **25** (1906), 1125; W. L. Dudley, *J. Am. Chem. Soc.*, **30** (1908), 1271; Adams, *J. Assoc. Official Agr. Chem.*, **1** (1915), 143.

(11) Komarowsky, *Chem. Ztg.*, **27** (1903), 807; Th. von Fellenberg, *Mitt. Lebensm. Hyg.*, **1** (1910), 791; W. Müller, *ibid.*, **14** (1923), 105.

Table 11.

	Present in 2 c.c. of methyl alcohol (g.)	Found (g.)
Butyl alcohol (b.p., 104–110°)	0.07276	0.07408 0.07345 0.07104
Amyl alcohol (b.p., 128–131°)	0.08102	0.07911 0.08073

The results of the analysis of the methanol samples carried out under the same condition are shown in Table 12.

Table 12.

Sample	Higher alcohols (%) (calculated as butyl alcohol)
A	0.62, 0.57
B	1.20, 1.08

(2) *Colorimetric method.* Purple red colour is developed when higher alcohols are brought into contact with salicyl aldehyde. The colour reaction is known as Komarowsky's reaction. When applied to the quantitative analysis, it also has two disadvantages. First the depth of the colour depends upon the kind of alcohols and consequently the generally adoptable standard cannot be prepared, and secondly a linear relation does not always hold between the depth of the colour and the concentration of the alcohols and therefore the reaction can not be applied except when the concenrations of alcohols in samples and the standards are not greatly different. These disadvantages, however, can be turned into advantages, if they are appropriately treated. Thus it has been found by the present author that not only the total quantity of butyl and amyl alcohols but also the ratio between them can be determined at a time.

Standard solutions were prepared with the following reagents:—

(1) Butyl alcohol, b.p., 100–106°C.; d_4^{20}, 0.8084. Amyl alcohol, b.p., 125–131°C.; d_4^{20}, 0.8137. The two alcohols were Merk's "extra pure" quality, of which 0.0330 g. each was dissolved in 100 c.c. each of pure methyl alcohol (d_4^{20}, 0.7918).

(2) Salicyl aldehyde was synthesised by Reimer- Tiemann's method. It boiled at 196°C. It was confirmed to be pure enough for the purpose by Kreis' method(12). 0.6767 g. of the aldehyde was dissolved in 100 c.c. of pure methyl alcohol.

The sample methanols were treated with silver oxide on the water

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(12) *Chem. Ztg.*, **32** (1908), 149.

bath for 3 hours to remove any aldehyde completely according to Fellenberg's informations(13), as the presence of aldehyde would interfere with the reaction.

The procedure of the analysis is as follows:— 1–4 c.c. of the sample solution is taken in a small glass cylinder, about 50 c.c. in volume, to which 1 c.c. of the salicyl aldehyde solution is added. If the total volume is less than 5 c.c., it is made just to 5 c.c. by adding pure methyl alcohol. Then 5 c.c. of distilled water is added, shaken, cooled with water and 20 c.c. of concentrated sulphuric acid is added drop by drop. Care must be taken not to allow the temperature of the mixture to rise unduly high. It is well shaken and left to stand for 20 hours. The red purple colour developed thereby is compared with that of the standard solution which has been similarly treated.

It has been found that not only the amount of higher alcohols but also that of salicyl aldehyde influences the depth of the colour as shown in Figure 2.

Now, the relation between the concentration of butyl or amyl alcohol (x, the unit of which is chosen arbitrarily as follows:— 0.0330 g. of the alcohol dissolved in 1 c.c. methyl alcohol) and height of the liquid column (y, expressed in mm., which should give the same depth of the colour as that of 5 mm. of the standard solution of the unit concentration) has been found to be capable of being expressed by the following equation:—

$$(5-y)^2 = p(x-1) \qquad (1)$$

which represents parabola, p a parameter, being a constant depending upon the kind of alcohol.

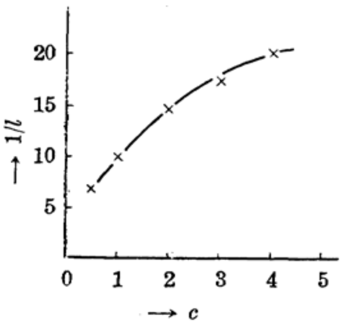

Fig. 2.

l: Height of liquid column,
c: Concentration of salicyl aldehyde; 0.006767 g. of the aldehyde dissolved in 1 c.c. of methyl alcohol is taken arbitrarily as unit.
Amount of butyl alcohol: 0.0660 g. dissolved in 1 c.c. of methyl alcohol, that is, $x = 2$.

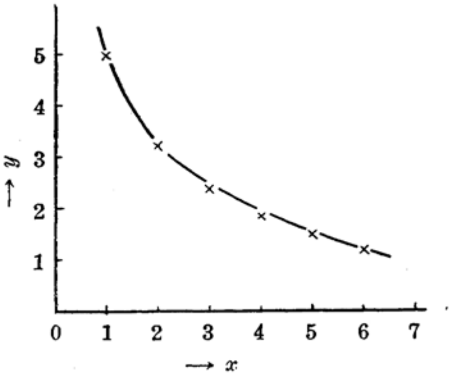

Fig. 3.

In the case of butyl alcohol, p is 3.15 and the theoretical curve and the found values are shown in Figure 3.

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(13) *Loc. cit.*

Similarly in the case of amyl alcohol 1.75 has been found as the value of the parameter and Figure 4 was obtained.

Next, the equal amount of the two alcohols were mixed and the mixed solution was examined similarly. The value of the parameter, in this case, must be the mean of the two values given to the two alcohols. The theoretical curve and the found values are shown in Figure 5.

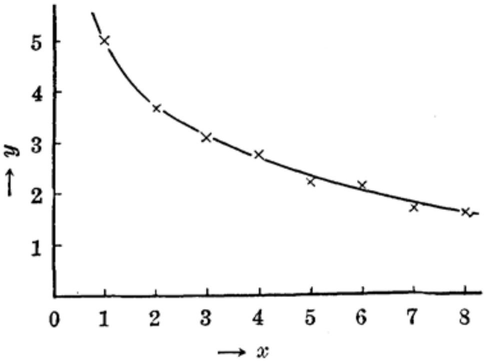

Fig. 4.

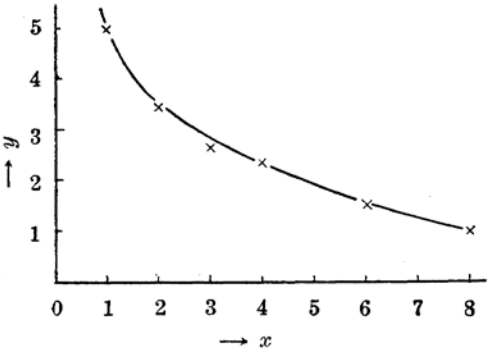

Fig. 5.

Thus the ratio of the amounts of the two alcohols and the corresponding value of the parameter can easily be calculated as shown in Table 13.

Table 13.

Butyl alc./Amyl alc. (g.)	10/0	9/1	8/2	7/3	6/4	5/5	4/6	3/7	2/8	1/9	0/10
p	3.15	2.99	2.84	2.69	2.54	2.40	2.26	2.13	2.00	1.87	1.75

The depth of the colour to be developed by the same concentration of butyl and amyl alcohols differs considerably. At the unit concentration the ratio of the depths was found to be 5.00/3.53. The ratio at any concentration will be obtained by a simple calculation by adopting this value and by applying it to equation 1. In Table 14 are shown the values of the ratio thus calculated together with the found values.

Table 14.

Concentration (x)		1	2	3	4
Ratio of depth of colour	Calculated	—	5.00/3.09	5.00/2.81	5.00/2.52
	Found	5.00/3.53	5.00/2.97	5.00/2.79	5.00/2.60

It is clear from the above consideration that the analysis of one of the two alcohols above mentioned, when it is present alone in methanol, may be carried out simply and accurately. When, however, both the alcohols co-exist, several standard solutions must be prepared and several curves must be described from the mixtures of the two alcohols in arbitrary proportions and it must be examined which of these curves accords with that of the sample. In the present case the state is more complicated. It is not known whether there are higher alcohols other than the above mentioned two or not. Even if only the two alcohols are present, our standards may not be used at once, as they are not prepared from pure substances but from mixtures of isomers.

A mixed standard was prepared from 7 parts of the butyl alcohol and 3 parts of the amyl alcohol, which gave the curve shown in Figure 6.

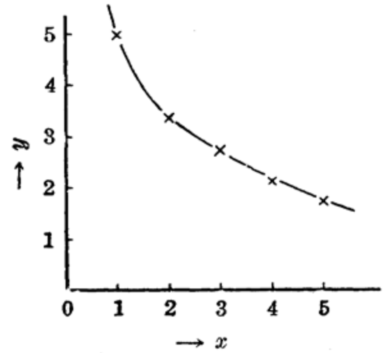

Fig. 6.

If the sample methanols contain only butyl and amyl alcohols which are identical with and in equal ratios to those of the mixed standard, the results of the colorimetry with the samples can be put in accordance with the curve given in Figure 6 by adopting the suitable concentrations of the samples to be analysed.

It has been found, in carrying out the experiment as stated above, that the samples actually contain the two alcohols in the proportion of 7:3. The values thus obtained are denoted by crossed marks in Figure 6. The total quantity of the two alcohols can easily be estimated, for the mixture can be thus treated as a single substance. The results are compared with those obtained by the oxidation method as shown in Table 15.

Table 15.

Sample	Higher alcohols (%)	
	By oxidation	By colorimetry
A	0.62, 0.57	0.53
B	1.20, 1.08	1.34

The results of the total analysis of the two sample methanols are summarised as shown in Table 16.

Table 16.

Sample	A (%)	B (%)	Sample	A (%)	B (%)
Methyl alcohol	89.68	94.34	**Formic acid**	0.009	0.08
Butyl alcohols	0.40	0.87	**Methyl formate**	0.13	0.25
Amyl alcohols	0.17	0.31	**Formaldehyde**	0.0021	0.0046
Water	4.1	1.3	**Total**	94.49	97.21

The rest may be considered as hydrocarbons, being calculated as 5.51 and 2.79% in A and B respectively.

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