[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WARSAW]

THE ANALYSIS OF MIXTURES OF ETHYL ALCOHOL, ETHYL ACETATE, ACETIC ACID AND WATER

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Determination of Alcohol by Chemical Methods

In the course of work on another problem it became necessary to determine accurately the alcohol content of mixtures of not over a few tenths of a cc. The determination of the alcohol content of such a small quantity of a mixture of volatile compounds, especially if four ingredients are present, must be carried out chemically rather than by physical methods, and in order to find the best method it was necessary to compare all known methods with regard to their accuracy.

Review of the Literature

One direct method for determining alcohol is by oxidation with potassium dichromate and sulfuric acid.[1] The error resulting from the partial oxidation of alcohol to carbon dioxide is considerable in any method using potassium dichromate, but if careful blank tests are carried out the process is applicable.[1j,2] The excess potassium dichromate may be determined by titration with ferrous ammonium sulfate,[1m,n,3] or by iodimetry.[4] Kuriloff and Szebérenyi determined total alcohol plus ethyl acetate in mixtures and found the ester content by saponification. The free alcohol is obtained by difference. Kuriloff's modification seems to be more exact than that of Szebérenyi. Potassium permanganate may be used as the oxidizing agent.[5]

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[1] (a) Bodländer, *Arch. ges. Physiol.* (*Pflügers*) **32**, 398 (1883); (b) Nicloux, *Compt. rend. soc. biol.*, (10) **3**, 841, 1126 (1896); (c) *Ann. chim. anal. chim. appl.*, **1**, 438 (1896); (d) Nicloux and Bauduer, *Bull. soc. chim.*, (3) **17**, 424 (1897); (e) Bordas and Raczkowski, *Compt. rend. soc. biol.*, (10) **3**, 972 (1896); (f) *Compt. rend.*, **123**, 1071 (1896); (g) Pozzi-Escot, *Ann. chim. anal. chim. appl.*, **7**, 11 (1902); (h) **9**, 126, 259 (1904); (i) Nicloux, *ibid.*, **9**, 214 (1904); (j) Landsberg, *Z. physiol. Chem.*, **41**, 505 (1904); (k) Nicloux, *ibid.*, **43**, 476 (1904–5); (l) Widmarck, *Skand. Arch. Physiol.*, **35**, 125 (1917); (m) Yamakami, *Tôhoku J. Exptl. Med.*, **4**, 276 (1923); (n) *Ber. ges. Physiol. exptl. Pharmakol.*, **24**, 106 (1924).

[2] Thorpe and Holmes, *J. Chem. Soc.*, **85**, 1 (1904).

[3] (a) Reischauer (1866), quoted by Röse, *Z. angew. Chem.*, **1**, 31 (1888); (b) Benedict and Norris, THIS JOURNAL, **20**, 293 (1898); (c) Cotte, *Revue internationale des falsifications*, **10**, 206 (1897); (d) Martin, *Mon. sci.*, (4) **17**, 570 (1903); (e) Pringsheim, *Biochem. Z.*, **12**, 150 (1908).

[4] (a) Bourcart, *Bull. soc. ind. Mulhouse*, 558 (1889); abstracted in *Z. anal. Chem.*, **29**, 604 (1890); (b) Kuriloff, *Ber.*, **30**, 741 (1897); (c) Szebérenyi, *Z. anal. Chem.*, **53**, 683 (1914).

[5] (a) Röse, *Z. anal. Chem.*, **1**, 31 (1888); (b) Herzog, *Ann.*, **351**, 263 (1907); (c) Barendrecht, *Z. anal. Chem.*, **52**, 167 (1913).

In Zeisel's method[6] the alcohol is converted to ethyl iodide and the iodine determined as silver iodide. The ethyl iodide may be decomposed and determined by iodimetry.[7] The ethyl alcohol may be converted into iodoform, the iodine fixed as potassium iodide and determined by precipitation with silver nitrate, the excess silver nitrate being titrated.[8] Still another procedure is to convert the alcohol to ethyl nitrite, treat with potassium iodide and determine the iodine.[9] By the method of Grün and Wirth[10] the alcohol is esterified with laurinyl chloride and the excess decomposed with water. The ester is then extracted and determined by saponification. If an ester is present along with the alcohol, this process gives the combined content of ester and alcohol. A procedure given by Wolff[11] involves esterification with acetic anhydride, which is open to the same objection as laurinyl chloride. Wolff esterified 0.5 g. of approximately 90% alcohol with 1 cc. of acetic anhydride by heating them in a sealed tube for an hour in boiling water. The tube was then placed in a bottle containing about 50 cc. of water and broken by shaking. The bottle and contents were then heated for half an hour on a water-bath at 50°. In this way the excess of acetic anhydride was converted into acetic acid, which was then exactly neutralized, phenolphthalein being used as indicator. The ester was determined by saponification with potassium hydroxide. In two analyses given the result was too small by 0.7–1.0%. The method was not applied to mixtures.

Experimental

Two methods were chosen, the one used by Bourcart and Kuriloff and that of Wolff, the former as already used with supposedly great accuracy for determining alcohol in mixtures with ethyl acetate, the latter as suitable, when conveniently modified, for the determining of free alcohol when mixed with ester, which was impossible by any procedure previously followed. Some other methods are delicate but not accurate.

Bourcart-Kuriloff Method.—The following procedure gave the best results. Forty cc. of 0.18 *N* potassium dichromate solution, 4.5 cc. of sulfuric acid (1:5) and a weighed quantity of mixture containing 0.05–0.07 g. of alcohol or about 0.11 g. of ester were placed in a 200cc. flask with a tied-in, air-tight stopper and kept at 100° (in steam) for five to six hours. The flask was then cooled and the contents and washings were poured into a glass stoppered, narrow necked, liter volumetric flask containing about 100 cc. of 1.8% potassium iodide solution, 150 cc. of water and 30 cc. of 1:5 sulfuric

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[6] (a) Prunier, *J. pharm.*, 29, 407 (1896); (b) an abstract in *Z. anal. Chem.*, **35**, 218 (1896); (c) Stritar, *ibid.*, **42**, 579 (1903); (d) *Z. physiol. Chem.*, **50**, 22 (1906).

[7] (a) Klemenc, *Monatsh.*, **34**, 901 (1913); (b) Ripper and Wohack, *Z. landw. Versuchsw.*, **20**, 102 (1917); (c) Wohack, "Handbuch der biologische Arbeitsmethoden," **1921**, I, 3/3, pp. 547–552.

[8] Villedieu and Hébert, *J. pharm. chim.*, (7) **15**, 41 (1917).

[9] Fischer and Schmidt, *Ber.*, **59**, 679 (1926).

[10] Grün and Wirth, *Z. deut. Öl- Fett-Ind.*, **41**, 145 (1921).

[11] Wolff, *Chem. Umschau Fette, Oele, Wachse Harze*, **29**, 2 (1922).

acid. After mixing, the liquid was covered with about 125 cc. of water to prevent evaporation of iodine and the flask was stoppered and allowed to stand for half an hour. The stopper and neck were then rinsed into the flask and a recently standardized, 0.1 *N* sodium thiosulfate solution was run in with continuous shaking, hydrated starch indicator being added when near the end-point. The sodium thiosulfate was standardized by means of an exactly 0.1 *N* solution of potassium dichromate, freshly prepared from dried Kahlbaum's $K_2Cr_2O_7$ "mit Garantie 99.97%." The 0.18 *N* potassium dichromate solution was standardized by means of the sodium thiosulfate solution in the following manner. Forty cc. of the dichromate solution and 4.5 cc. of 1:5 sulfuric acid, after heating for five to six hours (see below), were poured into a mixture of 150 cc. of 1.8% potassium iodide solution, 225 cc. of water and 45 cc. of sulfuric acid (1:5). After mixing, the liquid was covered with 150 cc. of water and titrated after standing for half an hour. Preliminary tests showed that the titer of a quantity of dichromate solution, after heating with sulufric acid as in the oxidation reaction, is lowered by about 1%. This error can be allowed for by using a correction derived from blank runs.

The content of free alcohol found was too large by 0.15–0.5%. The average value found in four determinations of ethyl acetate was 100.0%, the average deviation being ±0.4%. Such discrepancies (considerably larger than Kuriloff supposed) in mixtures containing a large amount of ethyl acetate, as did those analyzed, would give an error of many per cent. in a determination of free alcohol. Therefore, although this method is considerably more accurate than any other chemical method for the determination of alcohol, another procedure was used which is less exact in direct analyses but is suitable for the determination of alcohol in the presence of ester.

Acetic Anhydride Method.—In this process, which is acidimetric, a weighed amount of acetic anhydride is allowed to react with a known weight of alcohol or alcoholic mixture. The reaction may proceed according to either or both of the following reactions

$$(CH_3CO)_2O + C_2H_5OH \longrightarrow CH_3COOH + CH_3COOC_2H_5$$
$$(CH_3CO)_2O + 2C_2H_5OH \longrightarrow 2CH_3COOC_2H_5 + H_2O$$

but the result is the same in either case. The process may be used with mixtures containing considerable water by employing approximately double the amount of acetic anhydride necessary to combine with the alcohol and water. A relatively large amount of acetic anhydride should be used in any case, especially if the composition of the mixture under analysis is unknown. The excess of acetic anhydride is decomposed with water, care being taken not to hydrolyze any of the ester, and the acetic acid produced is determined by titration.

Procedure.—The reaction is carried out in a Pyrex bulb with a capillary tube at least 5 cm. long. The bulb is weighed and then 0.15–0.4 g. of acetic anhydride is placed in the bulb by means of a capillary pipet. The capillary tube is sealed off and the bulb and contents, with the piece removed in sealing, are weighed. The end of the capillary is then broken off, 0.02–0.04 g. of alcohol or alcoholic mixture is added, the capillary sealed and the whole again weighed with the pieces of capillary tube. The bulb and contents are heated in boiling water for an hour. After cooling, the liquid in the capillary is driven back into the bulb with a small flame and the capillary carefully opened. Enough distilled water (0.04–0.1 cc.) to decompose the excess anhydride is introduced from a capillary pipet, the capillary is again sealed and the bulb with contents heated in boiling water for twenty minutes. This length of heating is sufficient to decompose the anhydride without hydrolyzing any of the ester. The bulb is then placed in a flask containing carbon dioxide free water, broken and the acetic acid titrated, taking care not to use an excess of base in order to avoid hydrolyzing any of the ethyl acetate.

The purity of the "Merck" acetic anhydride used in this investigation was determined by the above procedure. The average of the determinations on the pure anhydride was 98.63%, and the average deviation of all determinations, during four months, from the mean was ±0.2%. The method gives no indication as to the nature of the 1.4% of impurity. In all probability it was water, combined as acetic acid. If such was the case, the reagent contained only about 90% of acetic anhydride, but this is of no consequence in the analysis provided an excess is used.

The content of alcohol is calculated from the difference between the amount of acetic anhydride taken and the amount equivalent to the acetic acid found in the reaction mixture, so any error in the value for the alcohol is several times greater than the error in the anhydride. The percentages of alcohol were found to average 3% too low (−6.4– +1.1%). The varying content of water made it impossible to use quantities of anhydride equivalent to the amount of alcohol taken. Therefore, the average deviation of parallel determinations of alcohol in proportion to itself (but not to the whole quantity of mixture) increased, with diminishing alcohol content, from ±0.5% at 40% of alcohol to ±5% when 1.5% of alcohol was present; but in the whole quantity of mixture it was always about ±0.2%. If a mixture contained free acetic acid this, of course, was determined separately.

Determination of Ethyl Acetate.—Chemically pure ethyl acetate was prepared by repeated fractional distillation in the presence of phosphorus pentoxide, and was weighed in sealed Pyrex bulbs. The best results were obtained by hydrolyzing the ester at 60–65° for fifteen to twenty hours with twice the calculated amount of barium hydroxide solution. The average deviation was ±0.09%, the results generally being slightly too high (mean 100.17%).

Determination of Acetic Acid.—In the accurate titration of acetic acid, using phenolphthalein as indicator, carbon dioxide must be carefully excluded. Carbon dioxide free distilled water is used in making up the solutions of barium hydroxide and the hydrochloric acid which is used as a run-back for any excess of base. All flasks, burets, bottles, etc., are filled with carbon dioxide free air and carbon dioxide free air is drawn through solutions which are being titrated. Volumes are read with an accuracy of 0.01–0.02 cc. on standardized burets and corrected for temperature. Benzoic acid was used as a standard and was dissolved in carbon dioxide free alcohol, it having been found that the amount of alcohol used had no effect on the results. Chemically pure, anhydrous glacial acetic acid was employed and was weighed in sealed Pyrex bulbs with an accuracy of 0.03–0.05 mg. The results obtained with this acid showed that the process was sufficiently accurate for the purpose. The influence of the barium acetate on the neutralization point, even in the absence of barium chloride, was neglected. The average deviation was found to be ±0.07%.

Micro Titration of Acetic Acid.—In the analysis of mixtures it was desirable to minimize the relative error of determining each substance. An error of 0.2–0.3% in the quantity of mixture taken is permissible in the determination of alcohol or ethyl acetate when they are the main ingredients, but since acetic acid (except in two analyses) was present only to the extent of 0.25–1.9%, it was necessary to reduce the error to some hundredths or thousandths of one per cent. To attain this accuracy, a micro method was necessary, since not more than 0.1–0.2 g. of mixture could be taken. Hence the acid had to be determined with an accuracy of some hundredths of a milligram.

Micro acidimetry, as generally used, is a delicate but not very accurate proceeding. The ability to work in a closed space is an important advantage of the apparatus of Pilch,[12] which consists of two micro burets with horizontal tubes at the lower ends which are sealed into the sides of a sphere of some 20cc. capacity. At the top the sphere has a long neck with a glass stopper for the introduction of material to be titrated, and at the bottom an outflow tube. Both side tubes and the outflow tube have stopcocks very close to the sphere so as to avoid any large amount of dead liquid space in the tubes. The side stopcocks permit additions of standard solution in as small amounts as 0.001 cc. The upper ends of the burets are fastened to a board by means of a string. Stirring is effected by shaking the whole apparatus.

When somewhat modified, the apparatus was used for determining acetic acid. The dead spaces in the side tubes were eliminated by lengthening both tubes into the sphere, as shown in Fig. 1. In this way only that part of the solution which actually flowed from the tips was used in the titration. During the titration the liquid was continually agitated so as to rinse the tubes and wash in any small drops adhering to the tips. Diffusion from the solution in the tubes during the moments of rinsing was negligible, and even when the ends of the tubes were covered, as was the case in several titrations, the results did not differ from those in which they were not. The dead space in the lower tube was filled with carbon dioxide free distilled water. This water remained neutral throughout the reaction, as is shown by the fact that it exhibited no color even during the vigorous agitation of an intensely pink solution above it.

Care was taken to avoid contamination from carbon dioxide during micro titration. The neck of the sphere was short and fitted with a ground in stopper with a small air

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[12] Pilch, *Monatsh.*, **32**, 21 (1911); see also Emich, "Lehrbuch der Mikrochemie," Wiesbaden, **1911**, pp. 8–10.

channel. The burets were filled through side tubes connected with the solutions, which were stored in liter bottles. The burets were of 2cc. capacity, graduated to 0.02 cc. and were read (after several minutes' drainage) to 0.002 cc. Above the scale the burets were enlarged into bulbs the tops of which were protected with soda lime tubes. Portions of solution which had been in the burets for a day or more were rejected, and the standard solutions (barium hydroxide and hydrochloric acid) were not kept for more than a few weeks, as it was found that the titer changed slowly on standing. The solutions were always shaken and standardized before using. Before titration the sphere was filled with carbon dioxide free air and then 5–20 cc. of carbon dioxide free water and 2–3 drops of 0.03% phenolphthalein were introduced. During the titration the sphere was placed before a white background in order to facilitate the observing of the end-point (very pale pink color). An accuracy of 0.005–0.01 cc. of 0.01 N barium hydroxide solution could be attained.

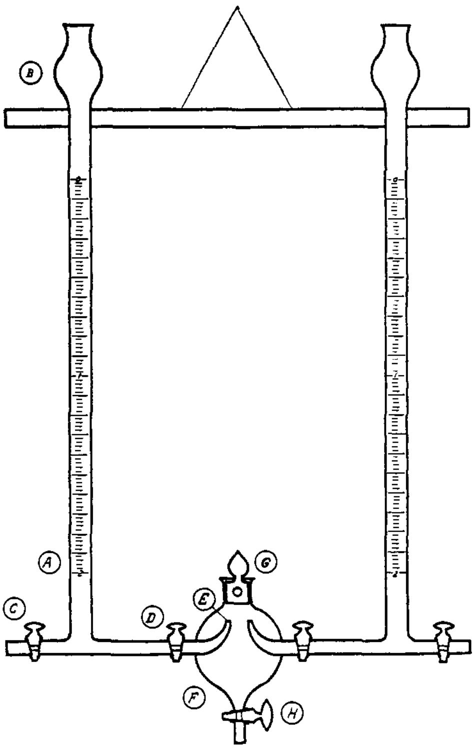

Fig. 1.

Titrations were always begun by determining the correction for the acidity of the water, that is, the smallest amount of barium hydroxide solution which would produce a faint pink color in 1 cc. of carbon dioxide free water. In practice this was done by adding alkali to 10–20 cc. of pure water until a faint pink appeared. The volume of the liquid was then ascertained by measuring it in a graduated cylinder. The correction as found from several concordant determinations was equivalent to 0.0015–0.0020 cc. of 0.01 N barium hydroxide solution. In all later analyses, both in standardizing and in actual analysis, the final volume of liquid was measured and the correction subtracted. This correction eliminates any error which might result from a difference in volumes of the solutions.

A solution of hydrochloric acid was used as a run-back and was standardized against the barium hydroxide. The barium hydroxide was compared with a determinate solution of acetic acid, the comparison being carried out as follows. Approximately 0.10–0.12 g. of chemically pure glacial acetic acid was weighed out in a sealed Pyrex bulb. The bulb was then placed in a small cylinder with carbon dioxide free distilled water, broken and the solution diluted to 100 cc. in a measuring flask. This solution was always made up just before use as colonies of microörganisms were observed in a solution which had been allowed to stand for a week. One cc. of this acid was taken in a carefully calibrated, 1cc. pipet and run into the titrating sphere, which already contained a small amount of water and indicator. The stopper was then inserted and the titration begun. This method has the advantages that the acid and base dissociate about equally in solution, the titer of the 0.01 N barium hydroxide solution used is in strict proportion to that of the 0.1 N solution actually standardized, and the necessary accuracy is obtained without a micro balance. For the determination of acetic acid in unknown mixtures, several hundredths of a gram (in one case 0.1–0.2 g.) of the unknown is weighed in a glass bulb. The bulb is then broken in carbon dioxide free water in a cylinder and the solution and washings are poured into the titrating sphere, water and phenolphthalein already having been placed in it. Control tests carried out with pure ethyl acetate showed that acid could be titrated with 0.01 *N* barium hydroxide in the presence of ester with no observable hydrolysis, provided the solution is shaken and excess of base is avoided.

Determinations showing any great deviation from the normal (not rare in the case of micro titration) were rejected. The mean of the average deviation of all series of parallel titrations was ±1.0% in standardizing hydrochloric acid, ±0.8% in standardizing barium hydroxide solutions and ±1.4% in the determination of acetic acid in unknown mixtures. When known quantities of acid were determined the average results in four mixtures, in proportion to acid content, were 1.7–2.8% too high (in one case too high by 4% and in another 2.4% too low). These errors, and also deviations from the mean values (mentioned above) in proportion to the quantity of mixture, were equal to 0.02–0.08% (in one case +0.16%) when 3–4% of acid was present; 0.003–0.007% with 0.25% of acid.

The mixtures analyzed were not in equilibrium and some changes in composition during analysis could therefore occur. Such changes, however, would produce no error in the process as long as the free acetic acid was determined immediately. In calculating the content of ester from the results of the saponification, the initial content of acid, of course, is allowed for, and even though some hydrolysis may have taken place the content of acid in the solution could not change. The same is true in the case of the alcohol. Esterification or hydrolysis would change the amount of acetic anhydride used up, but would produce an equivalent change in the amount of acid found.

The content of water was found by difference. The error in its determination, in proportion to the whole amount of mixture, would be obtained by adding (with the right signs) the errors in determining ester and alcohol and reversing the sign of the sum (the error in determining acid is very small in proportion to the amount of mixture). The maximum error may be found approximately from the average deviation in alcohol content. In general it was about 0.2% of the mixture. With an error in the content of ethyl acetate, if both were of the same sign, it would not be more than approximately 0.5%. In the least favorable of all the cases in which the methods were applied, with only 6.7% of water, the relative error was several per cent. It would be even greater if mixtures containing smaller amounts of water were analyzed.

Complete Analysis of a Known Mixture.—In order to test the accuracy of the separate determinations, a complete analysis was made of a mixture containing all four ingredients. The following results were obtained.

TABLE I

RESULTS OF COMPLETE ANALYSIS

	Acid, %	Alcohol, %	Ester, %	Water, %
Taken	0.253	9.74	81.61	8.40
Found	0.260	9.69	82.00	8.05

The author wishes to express his indebtedness to Dr. W. Swietoslawski, Professor at the Polytechnical School in Warsaw, both for suggesting this study and for his benevolent support in pursuing it.

Summary

1. The methods given in the literature for the determination of alcohol have been compared with regard to their accuracy.

2. A method involving oxidation of alcohol with potassium dichromate and sulfuric acid, with subsequent iodimetry, has been tried out and the conditions have been improved upon. Results were accurate to about 0.3% of the alcohol present.

3. A method for the determination of free alcohol in the presence of ethyl acetate by esterification with acetic anhydride and subsequent decomposition and titration of the excess has been developed. The results are accurate to about 0.2% of the amount of mixture taken.

4. Procedure is given for determining acetic acid with an accuracy of about 0.07% and ethyl acetate to 0.17%.

5. Micro titration of acetic acid in a modified Pilch apparatus has been carried out with 0.01 *N* solutions and necessary precautions are given. An accuracy of some hundredths or thousandths of the quantity taken was attained.

6. The processes were applied successfully to the analysis of mixtures of all four ingredients.

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