

CLXXVIII.—*A Method for the Estimation of Small Quantities of Water in Alcohol.*

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THE methods at present available for the determination of water in alcohol may be divided into two groups: (1) physical methods, comprising the density method and methods depending on the effect

of water on the miscibility of certain liquids with alcohol, such as Crismer's kerosene method (*Bull. Soc. chim. Belg.*, 1904, **18**, 18; also Curtis, *J. Physical Chem.*, 1898, **2**, 371; Nussbaum, *J. Pharm. Chim.*, 1917, **15**, 230; Jones and Lapworth, *J.*, 1914, **105**, 1804); (2) chemical methods depending on the interaction of the water with substances such as calcium hydride (Worth, *Z. Deut. Oel-Fett Ind.*, 1921, **41**, 147), or calcium carbide (Newman, *J. Soc. Chem. Ind.*, 1924, **43**, 285; also Weaver, *J. Amer. Chem. Soc.*, 1914, **36**, 2462; Hartley and Raikes, *J.*, 1925, **127**, 526). The accuracy claimed for the majority of these processes is not greater than 0.03 unit in the percentage of water. A further disadvantage inherent in nearly all the methods is the necessity for calibration with standard alcohol-water mixtures, the preparation of which is a matter of extreme difficulty where very small percentages of water are concerned.

In view of these considerations, an attempt was made to devise a new method. When the sodium or potassium compound of a hydroxylic substance such as phenol or alcohol is dissolved in aqueous alcohol, it is partly hydrolysed with formation of sodium or potassium hydroxide, an equilibrium being set up. If an ester is present, it will be hydrolysed irreversibly by the free alkali; the equilibrium is thereby disturbed and the reaction proceeds until either the alkali compound, the ester, or the water disappears completely. Provided that the concentration of the water is less than that of the other reactants, conditions can be so chosen that the reaction approaches completion with respect to this component in a relatively short time. It is possible by means of an extrapolation method to find the "limiting titration," *i.e.*, the titre at infinite time, and the difference between this and the initial titration is equivalent to the water concentration. Sodium or potassium ethoxide is employed, prepared by dissolving the metal in the alcohol to be tested, and ethyl acetate as the ester.

#### EXPERIMENTAL.

In carrying out the estimation, it is essential to use perfectly dry apparatus, and to reduce the manipulation of the solutions to the minimum, so as to avoid exposure to the air for more than a few seconds. Hard glass tubes of about 13 c.c. capacity are used as reaction vessels, and are closed with corks soaked in paraffin wax just before use and tied down with string. Finally, the tubes are inverted and dipped into molten paraffin wax for a few seconds, which effectually protects the contents against the possible entrance of water.

Sodium or potassium may be used; if the former, sodium acetate

crystallises in the tubes. This solid does not appear to affect the results, however, the same value being obtained whichever metal is employed.

The solution is prepared as follows : A quantity of the alcohol to be tested (40 to 80 c.c.) is poured into a small, dry, narrow-necked flask. A clean piece of sodium or potassium, large enough to make the solution about  $N/2$ , is cut under the surface of the oil in which it is kept, and rapidly transferred to the alcohol, without removal of the oil film from the surface of the metal, which is therefore not exposed to the air at all. The trace of oil does not interfere with the estimation. The metal is allowed to dissolve, the flask being closed by a calcium chloride tube and, if necessary, cooled in water. A few c.c. of ethyl acetate (dried over sodium) are now added, and immediately 10 c.c. of the solution are withdrawn by means of a dry pipette, and titrated rapidly. The pipette is fitted with a trap, consisting of a narrow glass tube bent into a loop, and filled with fine granules of calcium chloride, to prevent moisture from the mouth finding its way into the solution. This is next delivered into the tubes with the same pipette, care being taken to replace the cork as soon as a tube is charged. When ready, the tubes are sealed with wax as described, and placed in a bath of water at about  $70^{\circ}$ . The water is covered with oil to prevent steam arising, and the tubes are supported in a rack so that the corks are not below the surface of the water. In practice, a thermostat was used, but this is not essential. After 10 to 30 minutes, tubes are withdrawn at intervals and cooled in water, and the contents are titrated. It should be found that successive titration values are constant or decrease slightly. In the latter case, the extrapolation method described below must be applied to find the "limiting titration." The difference between the initial and the limiting titration corresponds to the water in the alcohol. If  $N/8$ -acid is used, this difference, in c.c., multiplied by the factor 0.0225 gives the percentage of water by volume directly.

It is occasionally found that one (or more) of the tubes gives an abnormally low titre, owing to the introduction of a trace of water. Such a reading may be neglected. When the amount of ethyl acetate added exceeds about 1 c.c., the volumes of ester and alcohol are measured approximately and allowance is made for the slight increase in the volume of the solution on addition of the ester. It is assumed that the addition of the alkali metal does not alter the volume.

Two methods have been used for finding the "limiting titration" : (1) the titrations are plotted against time, and the slope of the curve at various points is calculated. The slopes are then plotted against

the corresponding titration values, yielding a nearly straight line which can be extrapolated to zero slope, and the "limiting titration" read off; (2) the titrations are plotted against the reciprocal of the time, giving a similar curve which can be extrapolated to zero  $1/\text{Time}$  in the same way. The two methods agree well, the values for percentage of water not differing by more than 0.004%. The second is the simpler and more trustworthy and was used in most cases.

A further modification, which was developed towards the end of the research, allows of still greater simplification. It consists in using a considerable excess of potassium or sodium, and also of ethyl acetate, so that, when the water has nearly disappeared, the concentrations of ethoxide and ester are still large ( $N/4$  to  $N/2$ ).

Under these conditions, the reaction is extremely rapid, and proceeds to completion, as nearly as can be estimated, in 10 to 40 minutes at  $70^\circ$ . Thus there is no necessity for extrapolation, and also less material is required, for it is only necessary to take sufficient for two or three tubes, the contents of which are titrated after  $\frac{1}{2}$  hour or 1 hour, and should, of course, give the same titration value. Moreover it is not necessary to heat the tubes in a thermostat, since a constant temperature is not necessary. In this form, the method may be described as an indirect titration of water with standard acid. The process is extremely delicate and the accuracy attainable is limited, not by lack of sensitiveness, but by the difficulty of preventing the entry of further traces of moisture into the alcohol during the course of the estimation.

*Results.*—The following experiments are typical, the first of a case where extrapolation had to be applied, and the second of a case where this was unnecessary.

#### Sample D.

Sodium used.	Water added, 0.335%. Ester volume correction, 3%.									
Time (mins.) ...	0	5	10	23	35	58	92	155	$\infty$	
Titre ( $N/8$ -acid)	28.3	14.1	11.4	9.7	9.3	9.05	8.8	8.7	8.6	
	Diff. = 28.3 - 8.6 = 19.7 c.c.									
	% Water = 19.7 $\times$ 0.0225 $\times$ 1.03 = 0.457%.									

#### Sample F.

Potassium used.	No water added. Ester volume correction, 5%.				
Time .....	0	10	43	63	113
Titre ( $N/4$ -acid).....	15.55	13.25	13.2	13.2	13.2
	Diff. = 15.55 - 13.2 = 2.35 c.c.				
	% Water = 2.35 $\times$ 0.045 $\times$ 1.05 = 0.111%.				

The degree of accuracy attainable in this estimation was only to be arrived at by repeating it several times with the same sample

of alcohol. A further check could be obtained by adding a known quantity of water and estimating the total amount present.

The following results have been obtained :

## Sample D.

Expt.	% H <sub>2</sub> O added.	% H <sub>2</sub> O found.	% H <sub>2</sub> O originally in alcohol.
1	—	0.117	0.117
2	—	0.122	0.122
3	0.335	0.457	0.122

## Sample H.

Expt. ....	1	2	3
% H <sub>2</sub> O in alcohol .....	0.151	0.162	0.157

## Sample I.

Expt.	% H <sub>2</sub> O added.	% H <sub>2</sub> O found.	% H <sub>2</sub> O originally in alcohol.
1	—	0.022	0.022
2	0.158	0.164	0.006
3	0.164	0.176	0.012
4	0.218	0.229	0.011

These results show that it is possible to estimate the water in alcohol by this process to 0.01%. This is, therefore, one of the most accurate processes yet devised for the estimation of small quantities of water in alcohol, and also one of the simplest if the final modification is employed. Moreover, it possesses one outstanding advantage over almost every other method in that the result can be calculated directly from the readings obtained and there is no necessity for calibration against alcohol-water mixtures of known composition.

The author wishes to express his thanks to Dr. Crocker for the great interest he has taken in this research, and to the London County Council for a grant which enabled the work to be undertaken.

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[Received, April 4th, 1927.]