The Determination of the Water Content in Acetaldehyde by Means of the Karl Fischer Reagent

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Carbonyl compounds generally interfere with the Fischer titration. This is due to their tendency to form acetals or ketals by the reaction with methanol contained in Karl Fischer reagent, a process accompanied by the production of additional water :[1]

$$RCHO+2CH_3OH \rightarrow RCH(OCH_3)_2+H_2O \quad (1)$$

$$R_2CO+2CH_3OH \rightarrow R_2C(OCH_3)_2+H_2O \quad (2)$$

Mitchell et al.[2] have suggested, therefore, the use of Fischer reagent after converting carbonyl compounds to cyanohydrin with hydrogen cyanide. However, considerable difficulty is encountered in preparing a dried solution of toxic hydrogen cyanide and dioxane or pyridine; moreover, a complicated treatment is required prior to the titration.

Other methods have been proposed for the direct titration of water with modified Fischer reagents containing a great excess of pyridine[3] or containing methyl Cellosolve;[4] these methods are applicable to ketones, but not to aldehydes, in which the precise titration of water cannot be expected because reaction 1 accompanies the reaction 3 of absorbing water from the sample;[5]

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[1] K. Fischer, *Angew. Chem.*, **48**, 394 (1935).

[2] W. M. D. Bryant, J. Mitchell, Jr., and D. M. Smith, *J. Am. Chem. Soc.*, **62**, 3504 (1940).

[3] G. Wernimont, F. J. Hopkinson, *Ind. Eng. Chem., Anal. Ed.*, **15**, 272 (1943).

[4] E. D. Peters, J. L. Tungnickel, *Anal. Chem.*, **27**, 450, (1955).

[5] J. Mitchell, Jr., and D. M. Smith, "Aquametry," Interscience, New York (1948), p. 149.

$$\mathrm{RCHO} + \mathrm{C_5H_5N\cdot SO_2} + \mathrm{H_2O} \rightarrow \mathrm{C_5H_5N}\left\langle \begin{matrix}\mathrm{SO_3CH(OH)R}\\ \mathrm{H}\end{matrix}\right. \qquad (3)$$

In previous papers, the present authors reported methods for the direct titration of water in low polymers[6,7] of formaldehyde and in ketones[8] by using the alcohol-free Karl Fischer reagent SS (Mitsubishi) and by keeping the interfering reactions under control. On the basis of these methods, the authors have now established the present method for the quantitative determination of water in acetaldehyde.

Experimental

Materials.—Special-class reagents of acetaldehyde were used without further purification. Dried acetaldehyde was obtained by the distillation of para-aldehyde. Pyridine was obtained commercially. Propylene glycol was dried by boiling it. The Karl Fischer reagent SS (Mitsubishi), supplied by Mitsubishi Chemical Industries, was used (titer: 3.0 mg. H_2O/ml.)

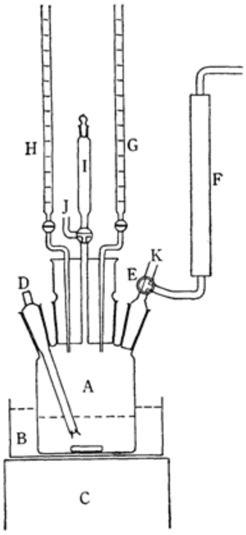

Fig. 1. Apparatus for electrometric titration.
A : Titration flask, 50 ml.
B : Water bath
C : Magnetic stirrer
D : Platinum electrode
E : Three way stop cock
F : Drying tube for nitrogen
G : Buret for Karl Fischer reagent
H : Buret for standard water-methanol
I : Outlet (with drying tube)
J : Outlet for nitrogen
K : Inlet for sample

Apparatus.—The Karl Fischer electrometric titration apparatus, operating by the dead-stop method, was manufactured by the Tsutsui Chemical Instrument Co. The apparatus is illustrated in Fig. 1.

Procedure.—*Sampling Method.*—A carefully-dried injector (volume, 5 ml.; length of injection needle, about 10 cm.), with a small piece of silicone rubber stuck on the needle tip, was inserted in a polyethylene bag and then placed in an electric refrigerator. The injector thereby cooled and a vessel, which had been similarly stored and which contained the acetaldehyde sample and with a three-way cock for drawing the liquid, were taken out of the refrigerator. The injector was then inserted into the three-way cock in order to draw acetaldehyde from the vessel. The inside of the injector was rinsed twice with the sample, and then, the third time, 5 ml. of cold acetaldehyde was collected in the injector. (Each time after the drawing, the needle tip was wrapped with dry gauze so that the traces of moisture and of the sample which adhered to it were removed.)

Titrating Method.—Five milliliters of a solvent mixture of pyridine-propylene glycol (3 to 1, by volume) was added to a titration flask, which was then subjected to a water bath at 25 to 30°C. While passing dry nitrogen through the three-way cock, E, illustrated in Fig. 1, into this flask at the flow rate of 0.9 l./min., drops of the Karl Fischer reagent SS were added in order to bring it to the dead stop end point. The introduction of nitrogen was then stopped, and the injector was inserted through the three-way cock, E, into the titration flask until the needle tip was soaked in the liquid surface. Then the acetaldehyde was released into the pyridine - propylene glycol mixture as rapidly as possible. Now, while the solution was stirred, nitrogen was again introduced into the flask, and the titration was simultaneously carried out until the end point was obtained, where a drop of the SS (Mitsubishi) reagent kept the magic eye open as long as 50 to 60 sec.

Results and Discussion

Acetaldehyde, among carbonyl compounds, showed the greatest velocity in the interfering reaction 1. Accordingly, an investigation with a view of avoiding this interference was carried out. Because of the difference in the boiling points of acetaldehyde and water, it was possible, after adding an exactly-weighed sample to a titration flask containing the pyridine - propylene glycol mixture solvent which was effective in controlling reaction 1, to evaporate almost all the interfering acetaldehyde with dry nitrogen directed toward the surface of the solution, and to titrate the remaining water in the solvent with the SS reagent. When acetaldehyde was evaporated with nitrogen, a small quantity of the liquid dissolved and remained in the solvent. In order to study any effect of the remaining acetaldehyde on the titration, 0.1, to 0.5 ml.

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[6] K. Muroi and K. Ogawa, This Bulletin, 36, 965 (1963).

[7] K. Muroi and K. Ogawa, ibid, 36, 1278 (1963).

[8] K. Muroi, K. Ogawa and Y. Ishii, *Japan Analyst*, 12, 963 (1963).

TABLE I. EFFECTS OF ACETALDEHYDE IN TERMS OF ITS AMOUNTS EMPLOYED

Amount of sample ml.	Titration temp., °C	Titration value ml.	Interfering reaction	Nature of end point
0.1	25	0.18	Not occur	Distinct
0.2	25	0.37	Not occur	Distinct
0.3	25	0.55	Occurs	Distinct
0.4	25	0.80	Occurs	Indistinct
0.5	25	0.87	Occurs	Indistinct

TABLE II. EFFECTS OF TITRATION TEMPERATURES

Titration temp., °C	Amount of sample ml.	Titration value ml.	Interfering reaction	Nature of end point
10	0.2	0.38	Not occur	Distinct
15	0.2	0.37	Not occur	Distinct
20	0.2	0.39	Not occur	Distinct
25	0.2	0.38	Not occur	Distinct
30	0.2	0.39	Not occur	Distinct

TABLE III. EFFECTS OF THE MIXING RATIOS OF PYRIDINE-PROPYENE GLYCOL IN THE SOLVENT

Mixing ratio in the solvent pyridine : propylene glycol	Titration temp., °C	Amount of sample ml.	Titration value ml.	Interfering reaction	Nature of end point
1 : 1	25	0.2	—	Occurs	Indistinct
2 : 1	25	0.2	0.35	Occurs	Indistinct
3 : 1	25	0.2	0.38	Not occur	Distinct
4 : 1	25	0.2	0.39	Not occur	Distinct
5 : 1	25	0.2	0.34	Not occur	Indistinct

of purified acetaldehyde was added to 5 ml. of the 3 : 1 solvent mixture of pyridine - propylene glycol in a flask. The water content in the solution was then titrated with the reagent SS. Tables I, II and III show the results obtained in the investigation of how the interfering reactions were affected by the amounts of acetaldehyde employed, the titration temperatures and the mixing ratios of the solvent components. These tables confirmed that the interference from acetaldehyde was not observed at room temperatures when less than 0.2 ml. of acetaldehyde was contained in 5 ml. of the pyridine - propylene glycol. On the other hand, when a 5 : 1 mixture of pyridine-propylene glycol was employed as the titration solvent for the sample, the end point titration became indistinct because of the pyridine-inhibiting reaction between water and the reagent described. Therefore, the 3 : 1 mixture of pyridine-propylene glycol proved to be the most suitable solvent for the direct titration of water in acetaldehyde.

In determining the amount of the solvent to be employed, 0.1 to 0.5 ml. (both inclusive), of the sample (as in Table I) was added to 20 ml. of the mixture solvent, and then the water content in the solution was titrated. The results obtained show that the sample solvent had not much effect on the attempt to avoid interfering reactions, because acetaldehyde began to interfere when the amount of acetaldehyde present in the mixture exceeded 0.4 ml.

Next, 2 ml. of acetaldehyde was added to 5 ml. of the pyridine - propylene glycol solvent kept at 25°C in a titration flask. While dry nitrogen, adjusted to various velocities of 0.3 to 1.5 l./min., was passed into the flask, the water content in the solution was titrated with the reagent SS. Table IV shows the results obtained. Although acetaldehyde interfered with the titration because of its insufficient evaporation when nitrogen gas was added at a velocity of less than 0.6 l./min., it no longer interfered, because of its good evaporation when nitrogen was passed at a flow rate of

TABLE IV. EFFECTS OF THE VELOCITIES OF NITROGEN GAS

Velocity of nitrogen l./min.	Titration values ml.	Interfering reaction	Nature of end point
0.3	—	Occurs	Indistinct
0.6	4.68	Occurs	Indistinct
0.9	4.67	Not occur	Distinct
1.2	4.57	Not occur	Distinct
1.5	4.45	Not occur	Distinct

more than 0.6 l./min. However, a velocity of more than 1.2 l./min. was found to be undesirable because then the nitrogen tended to drive water from the solvent. Moreover, the amount of acetaldehyde remaining in 5 ml. of the solvent after nitrogen had been passed through at a velocity of more than 0.6 l./min. measured less than 0.1 ml. From this fact, as well as from the afore-mentioned results, it was concluded that a process which involved evaporating the sample by means of nitrogen could have a considerable effect on the elimination of interfering reactions in direct titration.

To 5 ml. of the pyridine-propylene glycol maintained at 25°C 0.2 to 5.0 ml. of acetaldehyde was added. The water content in the solution was then titrated, while nitrogen gas was passed through at a constant velocity of 0.9 l./min. The results, committed to a line graph in Fig. 2, show the rectilinearity and the stable nature of the end point in the titration when 0.2 to 2.50 ml. of acetaldehyde was present in the solvent. However, when more than 3 ml. of acetaldehyde was present, minus errors increased as the titration values increased. On a conjecture that these minus errors might be introduced by the interfering reaction 3, three kinds of reagents, in which molar ratios of I_2 to SO_2 to C_5H_5N were maintained at 1 : 1.5 : 5, 1 : 3 : 10 and 1 : 6 : 20, were then prepared with the reagent SS. After 0.5 to 2.5 ml. of the sample had been added to 5 ml. of the solvent mixture, the water content in the solution was titrated with these modified reagents by directing nitrogen toward the surface of the solution. The results, shown in Fig. 3, indicate that minus errors tended to increase as the molar ratio between SO_2 and C_5H_5N departed further from 1.5 : 5; these results confirmed the early conclusion that these minus errors might result from the interfering reaction 3.

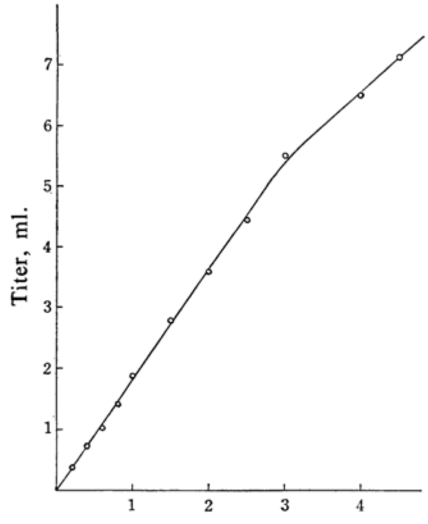


Fig. 2. Effects of amounts of acetaldehyde.

Accordingly, it may be suggested that a restriction should be imposed upon titration values in order to eliminate the interference thoroughly. Moreover, a restriction on the titration value (i. e. $C_5H_5N\cdot SO_2$ concentration in the reagent) involves a restriction of water content in the solvent employed. Therefore, for our present purposes, the effects of water content on the interfering reaction were studied. To 5 ml. of the 3 : 1 mixture of pyridine and propylene glycol containing various quantities of water, 0.2 ml. of the

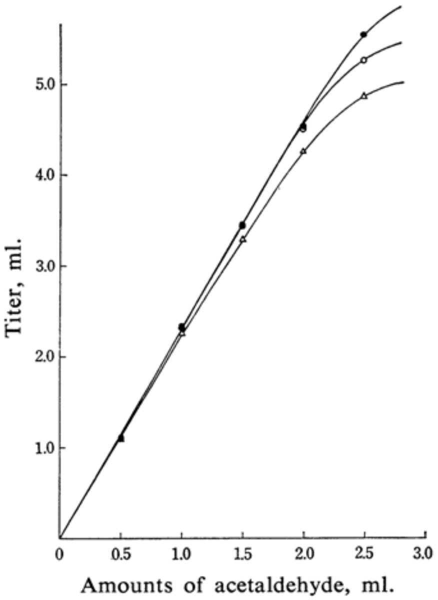
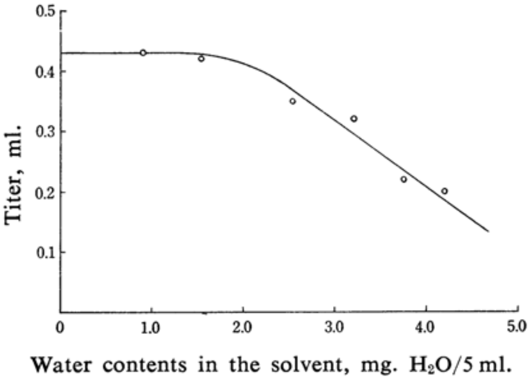


Fig. 3. Effects of molor ratios of I_2 to SO_2 to C_5H_5N in the reagent.
△, 1 : 6 : 20 ○, 1 : 3 : 10 ●, 1 : 1.5 : 5



Water contents in the solvent, mg. H_2O/5 ml.

Fig. 4. Effects of water contents in the solvent.

TABLE V. RESULTS OF THE TOTAL ANALYSIS

Sample	Acetaldehyde %	Water %	Impurities %	Total %
Commercial grade reagent	88.7	10.1	1.0	99.8
Acetaldehyde purified and distilled from the reagent	99.5	0.67	0.08>	100.2

sample was added. The results of the titrations, suggest that more than about 1.5 mg. (about 0.03%) of water in 5 ml. of the solvent caused minus errors (Fig. 4). Morever, the use of a large quantity of the solvent necessitated an increase in the amount of the reagent consumed for it, so it was found profitable to carry out the titration with the least possible amount of the solvent mixture.

In order to further develop the results shown in Table IV that water content, as well as acetaldehyde, tended to be evaporated when nitrogen was passed through at a velocity of more than 1.2 l./min., we attempted to determine the most suitable time for passing through nitrogen and for beginning the titration after acetaldehyde was added to the pyridine-propylene glycol. The results obtained show that the vaporizasion of water was not observed when nitrogen was introduced shortly after the beginning of titration, whereas it was obviously observed when nitrogen was passed through for more than about 30 sec. prior to the titration, and the resulting titration values were found to involve minus errors. When nitrogen was introduced almost at the end of the titration, interference from the acetaldehyde was observed because the acetaldehyde dissolved in about 4 ml. of the reagent was consumed, increasing the amount of it present in the solvent. Accordingly, in order to avoid evaporating the water, it was necessary to pass nitrogen through simultaneously with the titration, and to titrate the water content while the acetaldehyde was being evaporated.

The optimum conditions for the determination of the water content in acetaldehyde were established as follows:

Solvent: Five milliliters of 3:1 mixture (by volume) of pyridine-propylene glycol (water content, less than 0.03 per cent).

Titration Temperature: 25 to 30°C.

Velocity of the Nitrogen Passed: 0.8 to 1.0 l./min.
(Pass nitrogen into a titration flask simultaneously with the beginning of titration.).

Sample: Sample so that the titration value with the reagent (3 mg. H_2O/ml. titer) is approximately 4 ml. (equivalent to 12 mg. of water); for example, about 0.1 g. of the sample when it contains 10 per cent water; about 1 g. of the sample, when it contains 1 per cent water, and less than about 10 g. of the sample when it contains less than 0.1 per cent water.

In order to confirm the accuracy of the present method, quantitative determinations of acetaldehyde and the other impurities were made by means of the acid sodium sulfite method and by chromatography, and the values calculated were added to those of the water content. The results shown in Table V suggest the adequacy of the present method for the determination of the water content of acetaldehyde.

TABLE VI. RESULTS OF THE DETERMINATION OF A SMALL AMOUNT OF WATER IN REFINED ACETALDEHYDE

Sample ml.	Titration value ml.	Water content	
		mg.	%
1	0.14	0.42	0.053
3	0.41	1.23	0.052
5	0.65	1.95	0.050
7	1.06	3.17	0.057
10	1.32	3.95	0.050

TABLE VII. RESULTS OF THE DETERMINATION OF WATER IN REFINED ACETALDEHYDE CONTAINING A KNOWN AMOUNT OF WATER ADDED

Sample ml.	Pyridine added ml.	Theoretical amount of water mg.	Water content value measured mg.	Difference from theoretical value mg.
5	—	—	1.95	—
5	0.1	2.07	2.10	+0.03
5	0.2	2.18	2.16	−0.02
5	0.4	2.41	2.40	−0.01
5	0.6	2.64	2.67	+0.03
5	0.8	2.87	2.88	+0.01
5	1.0	3.10	3.05	−0.05

A small quantity of water in pure acetaldehyde prepared with para-aldehyde was determined by the present method. The water content values indicated in Table VI show a reproducibility. Moreover, from the water content values indicated in Table VII for 5 ml. of purified acetaldehyde determined in the presence of a fixed amount of pyridine containing a known quantity of water, it was reaffirmed that the determination of a minimal amount of water in acetaldehyde was carried out with accuracy by the present method.

Summary

Approximately 5 ml. of the sample has been added to 5 ml. of a 3 : 1 solvent mixture of of pyridine - propylene glycol in a titration flask. The difference in boiling point between acetaldehyde and water made it possible to evaporate almost all the interfering acetaldehyde from the solution with nitrogen gas passed into the flask at a velocity of about 0.9 l./min. The water remaining in the solution was titrated with the Karl Fischer reagent SS (Mitsubishi).

Because this reagent is free from alcohol, which would show an interfering reaction in Eq. 1, and because it is somewhat lower than the general Karl Fischer reagent in its concentration of $C_5H_5N \cdot SO_2$, which is the main component responsible for the interfering reaction in Eq. 3, it proves to be the most satisfactory for the present titration method.

A small quantity of water in purified acetaldehyde was determined by the present method, and subsequent anlysis of water content values showed an excellent reproducibility.

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