The Determination of Water Contents in Low Polymers of Formaldehyde by the Karl Fischer Method. II. The Determination of the Total Amounts of Adsorbed Water and Bound Water by the Methanol Absorption Method

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In the previous paper,[1] the present authors reported a method for the determination of adsorbed water and bound water separately in low polymers of formaldehyde by using the Karl Fischer method. Recently, on the basis of the already-established method of determining the trace content of water in gases by Karl Fischer titration,[2] the same authors have developed a simple methanol absorption method for determining the sum of the amounts of adsorbed water and bound water in low polymers of formaldehyde. In the present method, the sample was pyrolyzed in a steam of dry nitrogen; the water vapor thus formed was absorbed in methanol, which was then titrated with a Karl Fischer reagent.

Experimental

Materials.—Both commercial-grade and special-class reagents of paraformaldehyde were used without further purification. The α-polyoxymethylene was supplied by our laboratory. The methanol was dried by magnesium metal. The propylene glycol was dried by boiling. The Karl Fischer reagent SS "Mitsubishi," free of methanol and supplied by the Mitsubishi Chemical Industries, was used (titer: 3.0 mg. H_2O/ml.).

Apparatus and Procedure. — The apparatus is illustrated in Fig. 1. Titration flask, F, was kept at about 10°C by running water through the jacket, G. One hundred milliliters of dry methanol was added to F through a side arm, H. Dry nitrogen, adjusted to a constant velocity of about 0.2 l./min., was passed to A, D and F. The methanol in F was titrated to the dead stop-end point with the Karl Fischer reagent. One to three grams of the sample were added to A through the side arm B. The tubing, D, was heated to about 100°C with a tape heater, E, and then A was heated at 200$\sim$250°C with a mantle heater, C. The water formed by pyrolyzing the sample was absorbed in cool methanol in F, and the water content in methanol was titrated every 5$\sim$10 min. with the Karl Fischer reagent. The dead stop-end point was attained after 30 min.; then the heating of A was stopped. The percentage of water was calculated from the titration value of the Karl Fischer reagent.

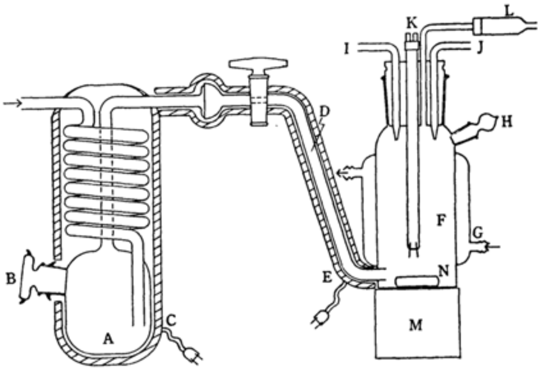

Fig. 1. Apparatus for the methanol absorption method.

A: Pyrolysis flask, 75 ml.
B: Side arm for sampling
C: Mantle heater, 200 W.
D: Conduit tube for gaseous formaldehyde
E: Tape heater, 100 W.
F: Titration flask, 200 ml.
G: Condenser
H: Side arm for methanol
I: Buret for standard water-in-methanol solution
J: Buret for Karl Fischer reagent
K: Platinum electrode
L: Outlet (with drying tube)
M: Magnetic stirrer
N: Stirrer bar

After A had been cooled to room temperature, the sample was added to A again through the side arm B, and the water contents was determined continuously by the same procedures. The bound water content was given by the difference in values between this method and the previously-reported methanol extraction method.[1]

Results and Discussion

In this method, the authors mainly attempted to find an adequate solvent to absorb the gas formed by the pyrolysis of the polymer. Since formaldehyde is known to be readily soluble in alcohols with evolution of heat and is known not to yield formaldehyde gas, the glycol reported in previous paper,[1] which

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

[2] K. Muroi, *Japan Analyst* (*Bunseki Kagaku*), **10**, 847 (1961).

TABLE I. EFFECTS OF INTERFERENCES ON THE DETERMINATION OF WATER IN FORMALDEHYDE AT VARIOUS TEMPERATURE

Titration temp. °C	Nature of end point (visual titration)		Amount of water formed at 10 min's by interfering reaction in end point mg.
	Color change	Stability	
10	Good	Fairly stable	0
20	Good	Fairly stable	0
30	Good	Stable	0
40	Poor	Fades stowly	0.12
50	Very poor	Fades	0.35

do not react with formaldehyde below about 100°C, were first used as absorbing solvents of the gas; it was found, however, that the glycols did not absorb the gas completely. Then methanol, which has the strongest affinity for formaldehyde among primally alcohols, was used. The interference of formaldehyde with the Karl Fischer titration was studied. Mitchell et al.[3] have reported that formaldehyde does not interfere with the direct titration of an ordinary Karl Fischer reagent. On the contary, Iliceto et al.[4] have reported that formaldehyde interfered with the results of the Karl Fischer titration. To study the interference of the formaldehyde which was adsorbed in methanol, 3 g. of paraformaldehyde was pyrolyzed and absorbed in 50 ml. of methanol. Then the methanol solution was titrated with a Karl Fischer reagent at various temperatures. The water content thus measured and the nature of the titration end point visually observed are listed in Table I. It was found that the formaldehyde reacted with methanol very slowly above 30°C, and that it did not react at all below 30°C. From these results, as well as from the fact that the rate of the vaporization of methanol on the bubbling of a dry nitrogen carrier decrease with a decrease in the temperature, the methanol solution in flask F was kept at 10°C. Though the time necessary for analysis procedure not depended on the flow rate of the dry nitrogen carrier gas but, rather, mainly on the heating temperature of flask A, the optimum flow rate for reducing the vaporization loss of methanol was found to be 0.2 l./min. Table II lists the water content values in the various types of low polymers of formaldehyde determined by this method. An excellent reproducibility was obtained. Table III lists the water content values in the same samples as determined by this method and by the propylene glycol dissolution method reported in the previous paper.[1] The agreement between the two methods was remarkably good. When this method was compared with the propylene glycol dissolution method, it was found that this method had these advantages:

1) The operation of this method is simple, it is not affected by the moisture in the air, and the reproducibility is good.

2) The propylene glycol dissolution method can not be applied to samples pyrolized above about 170°C, but this method is applicable to such samples.

3) It has been found that the propylene glycol dissolution method is interfered with the small amount of an alkali component contained in commercially-available paraformaldehyde, but in this method, this small

TABLE II. RESULTS OF DETERMINATION OF WATER CONTENTS BY METHANOL ABSORPTION METHOD FOR VARIOUS TYPE OF LOW POLYMER FORMALDEHYDE

Sample	Water content %
Commercial grade paraformaldehyde	13.64 13.56 13.73
Special grade reagent paraformaldehyde	2.30 2.31 2.31
α-Polyoxymethylene	0.61 0.61 0.61

TABLE III. COMPARISON OF WATER CONTENTS IN VARIOUS TYPE OF LOW POLYMER OF FORMALDEHYDE DETERMINED BY METHANOL ABSORPTION METHOD AND PROPYLENE GLYCOL DISSOLUTION METHOD

Sample	Water content, %	
	Methanol absorption method	Propylene glycol dissolution method
85% Paraformaldehyde	13.64	13.68
95% Paraformaldehyde	3.45	3.46
Special grade reagent paraformaldehyde	2.31	2.31
α-Polyoxymethylene	0.61	0.61

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

[4] A. Iliceto and S. Bezzi., *La Chemica e I. Industria*, **42**, 728 (1960).

TABLE IV. RESULTS OF CALCULATIONS OF THE DEGREES OF POLYMERIZATION FROM THE CONTENT OF BOUND WATER

Sample	Water content, %		Bound water %	Degree of polymerization
	Methanol absorption method	Methanol extraction method		
85% Paraformaldehyde	13.58	7.86	5.72	10
95% Paraformaldehyde	3.45	0.53	2.72	21
Special grade reagent paraformaldehyde	2.31	0.30	2.01	30
α-Polyoxymethylene	0.61	0.24	0.37	162

TABLE V. RESULTS ON THE VARIATION OF WATER CONTENTS IN PARAFORMALDEHYDE IN AIR

	Days on shelf					
	0	1	3	5	7	10
Adsorbed water, %	8.1	7.8	7.6	6.6	4.2	2.7
Bound water, %	6.1	7.7	4.3	3.1	3.0	2.9

amount of an alkali component remains in the pyrolysis flask A and does not enter into the titration flask F; therefore, titration is not interfered with alkali. Table IV lists the adsorbed water content value and the summed content of adsorbed water and bound water in various types of low polymers of formaldehyde as determined by the methanol extraction method and by this method. The difference in the values corresponds to the content of bound water in the polymers from which the average degree of polymerization was calculated. Table V lists the results of the variation of adsorbed water and bound water in paraformaldehyde in air with time. At first, both adsorbed and bound water decreased rapidly. After 5 days, while bound water was stabilized at the value of about 3% (n=about 20), adsorbed water was still decreasing slowly. The authors are now studying the processes of the depolymerization of paraformaldehyde from the variation of adsorbed and bound water.

Summary

The summed content of adsorbed water and bound water in low polymers of formaldehyde has been determined by the following method: (1) The sample is pyrolized in a steam of dry nitrogen. (2) The water thus formed is absorbed in methanol. (3) The water content of the methanol solution is determined by titrating with a Karl Fischer reagent. A comparison between the present method and the propylene glycol dissolution method reported in the previous paper has made it evident that the present method is easy in its operations and is applicable to polymers having a wide range of polymerization. It has also been found that formaldehyde does not react with methanol below 30°C.

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