The Determination of the Water Content of the Low Polymers of Formaldehyde by the Karl Fischer Method. I. The Determination of the Adsorbed Water and Bound Water Formed by the Pyrolysis of the Polymer

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The difficulty in determining the water content in the low polymers of formaldehyde by the vacuum-drying method is that the content of bound water produced by the pyrolysis of the polymer via the reaction,

$$HO-(CH_2O)_n-H \rightleftharpoons nCH_2O+H_2O \qquad (1)$$

and also the content of water physically adsorbed on the polymer are determined at the same time[1]. The determination of the adsorbed water with a high degree of accuracy is, therefore, difficult in this method. The authors have found a new method to determine these two kinds of water separately by using the Karl Fischer method.

Experimental

Materials.—Both commercial grade and a special-class reagent of paraformaldehyde were used without further purification. α-Polyoxymethylene was supplied by our laboratory. Methanol was dried by magnesium metal. Ethylene glycol, butylene glycol and propylene glycol were dried by boiling. The Karl Fischer reagent SS "Mitsubishi", free from methanol supplied by the Mitsubishi Chemical Industries, was used (titer: 0.5 mg. H_2O/ml. and 3.0 mg. H_2O/ml.).

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. A is the container of anhydrous methanol prepared by adding the Karl Fischer reagent drop by drop to the end point. The methanol was used for the extraction of the adsorbed water. The polyethylene bag, H, filled with dry nitrogen was used to keep the titration flask from moisture in the air. The titration flasks J and K were used for the determination of the adsorbed water, and L, for the bound water, in polymers. Figure 2 illustrates the Ward-type automatic buret which was used as the container and the pipet of dry propylene glycol. Dry propylene glycol was treated

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[1] J. F. Walker, "Formaldehyde", Reinhold Publishing Co., New York (1953), p. 129.

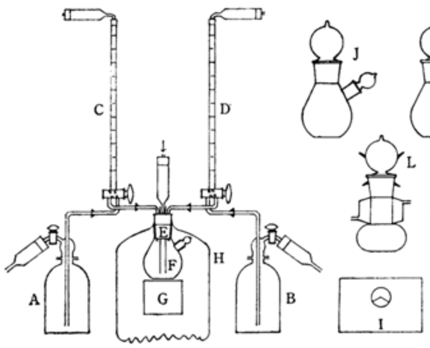

Fig. 1. Apparatus for electrometric titration.

A: Container of methanol
B: Container of the Karl Fischer reagent
C: Buret of methanol, 50 ml., graduated by 0.1 ml.
D: Buret of the Karl Fischer reagent, 10 ml., graduated by 1/50 ml.
E: Ground glass adaptor having two buret inlets, breathing tube and sealed-in electrodes
F: Platinum electrodes
G: Magnetic stirrer
H: Polyethylene bag
I: Indicator of end point
J: Titration flask with a ground glass stopper fitted with a side-arm, 200 ml.
K: Titration flask with a ground glass stopper, 200 ml.
L: Titration flask with a ground glass stopper and a water jacket, 200 ml.

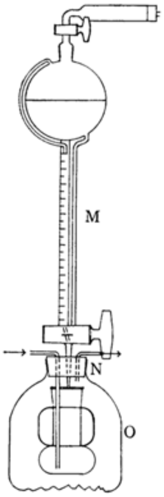

Fig. 2. Automatic buret of propylene glycol.

M: Ward-type automatic buret, 1000 ml.
N: Rubber stopper
O: Polyethylene bag

in the polyethylene bag, O, filled with dry nitrogen.

Procedure.—*The Determination of the Adsorbed Water.—Undried Sample:* The titration flask, J, was attached to E and filled with 25 ml. of anhydrous methanol as exactly measured by the buret, C. After adding the Karl Fischer reagent to the dead stop end point, an exactly-weighed polymer sample was added through a side-arm; the methanol solution was then stored about 10 min. The percentage of adsorbed water, *a %*, is calculated from the titration value of the Karl Fischer reagent (titer 3 mg. H_2O/ml.) for this solution.

Dried Sample: The flask K, containing about 10 g. of a carefully dried sample, was attached to E in bag, H, filled with dried nitrogen. Fifty milliliters of anhydrous methanol was added, and the solution was stored about 10 min. The water content, *a %*, was calculated from the titration value of the Karl Fischer reagent (titer 0.5 mg. H_2O/ml.) for this solution, from which the blank value obtained by the control experiments for a methanol solvent had been subtracted.

The Determination of the Bound Water.—Undried Sample: The titration flask, L, attached to the automatic buret, M, was flushed with dry nitrogen so as to completely remove the adsorbed water from the wall. An exactly weighed sample was added to 25 ml. of propylene glycol in the flask, L, and heated at 160°C about 5 to 10 min., while the jacket around the flask, L, was cooled. The sample was completely dissolved into propylene glycol in this condition. The flask, L, was carefully attached to E so as not to come in contact with moisture in the air by using a dry nitrogen-filled bag, H. The water content in the solution, *b %*, was calculated from the titration value with the Karl Fischer reagent of the titer of 3 mg. H_2O/ml., from which the value for control experiment had been subtracted.

Dried Sample: About 5 g. of a weighed sample in the flask, L, was carefully dried in a vacuum desiccator. The flask, L, was attached to the automatic buret, M, via the joint, N, in a completely dry condition by using the polyethylene bag, O, filled with dry nitrogen. Fifty milliliters of propylene glycol was added to the sample. Again the sample was dissolved into propylene glycol after 5 to 10 min. heating at 160°C. The water content, *b %*, was calculated by the method previously described for the undrid sample. The content of bound water, *c %*, was given by the difference between *b* and *a*; i. e. $c(\%)=b(\%)-a(\%)$.

Results and Discussion

The Elimination of the Effect of Moisture in the Air.—The interference of moisture in the air with the Karl Fischer method and a method of eliminating this interference have been discussed in detail by Bastin et al.[2] and by Loveland and Wester[3]. In the course of the present work, the authors found that the Karl Fischer reagent had a great sensitivity to the moisture in the air and that the water adsorbed on the wall of the flask caused a big error in the determination of a

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[2] E. L. Bastin. H. Siegel and A. B. Bullock, *Anal. Chem.*, 31, 467 (1959).

[3] J. W. Loveland and T. B. Wester, ibid., 31, 30 (1958).

TABLE I. COMPARISON OF THE WATER CONTENTS IN THE DRIED SAMPLE OBTAINED IN A DRY NITROGEN ATMOSPHERE AND IN AIR

	In dry nitrogen		In air		Difference
	H_2O mg.	Error mg.	H_2O mg.	Error mg.	H_2O mg.
	0.49	+0.04	5.07	−0.01	
	0.42	−0.03	5.18	+0.10	
	0.45	0	5.03	−0.05	
	0.50	+0.05	5.09	+0.01	
	0.48	+0.03	5.13	+0.05	
	0.40	−0.05	5.05	−0.03	
	0.43	−0.02	4.99	−0.09	
average	0.45±0.05		5.08	±0.10	+4.63

small amount of water. Table I lists the amount of adsorbed water for the dried sample and the range of error in two cases, one, for the experiment carefully conducted in a dry nitrogen atmosphere and the other, in air. It is obvious that, in the latter case, moisture in the air and the water adsorbed on the glass wall yield much larger values and errors. To eliminate this interference, the authors propose the following two methods:

1) To flush dry nitrogen through a titration flask about 20 min.

2) In the case of the determination of a small amount of water adsorbed on a dried sample, in order to eliminate the repetition of control experiments and also to prevent moisture from entering a flask during the sampling, anhydrous methanol which had been prepared by adding a Karl Fischer reagent to the dead stop point was added to the sample from columns A and C. It would be more effective to put the whole apparatus in a dry box or in a low-humidity room, but in the present work the authors have reported a convenient method for use in an ordinary laboratory.

The Determination of the Adsorbed Water.—Various conditions of the extraction of adsorbed water by dry methanol were studied using the special class reagent paraformaldehyde as a sample. Table II lists the experimental conditions and observed values of water content. It is concluded that the adsorbed water was easily extracted by 25 ml. of methanol after storing the solution for 10 min. Table III lists the values of water content in the various dried samples. An excellent reproducibility is obtained.

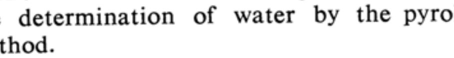
TABLE II. RESULTS OF DETERMINATION OF ADSORBED WATER ON *p*-FORMALDEHYDE BY METHANOL EXTRACTION

Sample weight g.	Methanol ml.	Time of extraction min.	Water mg.	Content %
0.6539	50	5	4.51	0.69
0.5972	50	10	4.18	0.70
0.8133	50	20	5.62	0.70
0.7156	50	40	5.08	0.71
0.6734	50	60	4.75	0.70
0.9114	50	120	6.65	0.73
0.8227	10	10	5.59	0.68
0.7955	25	10	5.81	0.73
0.8023	50	10	5.62	0.70
0.8154	100	10	5.87	0.72

TABLE III. RESULTS OF THE REPRODUCIBILITY TEST FOR DETERMINATION OF ADSORBED WATER OF DRIED SAMPLES

Sample	Water content, %
Paraformaldehyde	0.098
	0.095
	0.095
α-Polyoxymethylene A	0.025
	0.021
	0.020
α-Polyoxymethylene B	0.019
	0.019
	0.019

The Determination of the Summed Amount of Bound Water and Adsorbed Water.—Iliceto and Bezzi discovered the reaction of formaldehyde with methanol and suggested the use of the Karl Fischer reagent after changing formaldehyde to cyanohydrine by treating it with hydrogen cyanide[4]. The authors have tried to find a better solvent than methanol. Dimethylformamide, *o*-chlorophenol, dioxane, *m*-cresol and ethylene glycol, propylene glycol, and butylene glycol were used as solvents. First, the solubility of samples in these solvents was studied. The samples had low solubility in dimethylformamide, *o*-chlorophenol, *m*-cresol and diethylene glycol, even at 120°C. They had a high solubility in hot dioxane, but a low value at room temperature. It was concluded from the solubility tests that ethylene glycol, propylene glycol and butylene glycol were good solvents. Formaldehyde reacts readily with glycols and yields water in the presence of acid catalysis or at a high temperature via the reaction:



$$\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix} + HCHO \rightarrow \begin{matrix}CH_2O\\ |\\ CH_2O\end{matrix}\!\!>CH_2 + H_2O \qquad (2)$$

The water thus formed might interfere with the determination of water by the pyrolysis method.

Table IV lists the variation in water content of paraformaldehyde at various conditions of pyrolysis in dry ethylene glycol. The sample is insoluble below 60°C, when only the

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[4] A. Iliceto and S. Bezzi, *La Chimica e l'Industria*, 42, 728 (1960).

adsorbed water was extracted. The water content reached a constant value in the temperature region 120～150°C within 10 minutes heating. At 170°C the same constant value was obtained in 3 minutes heating. At 150°C, the water content increased with the heating period, which suggests the occurrence of reaction 2. The reaction of formaldehyde with propylene glycol and butylene glycol was also studied, because it is well known that the rate of esterification decreases in the order of primary, secondary and tertiary alcohols. Figure 3 illustrates the results. It is concluded that propylene glycol is the best solvent because it gives an almost constant value of water content during the heating period studied. The dependence of the value of water content on the ratio of the amount of propylene glycol to that of sample was studied. Table V lists the value of water content with various amounts of sample and solvent. It is suggested that about 5 g. of a sample in 25 ml. of propylene glycol is suitable for conducting experiments. Table VI lists the value of the summed content of adsorbed water and bound water in various types of low polymers of formaldehyde determined by the pyrolysis method in dry propylene glycol. Table VII lists the value of adsorbed water content for the samples determined by the methanol extraction method. The difference in values corresponds to the content of bound water in the polymers. The average degree of polymerization was calculated from the content of bound water.

The determination of the degree of polymerization of the low polymer of formaldehyde is rather difficult, and only a few methods have been reported[5,6]. Recently, Iliceto and Bezzi[4] have determined the degree of polymerization from the water content by the Karl Fischer method, but they have not determined bound water and adsorbed water separately, as the present authors have now done. In the other works, since the calculation was based on the summed amount of bound and adsorbed water, the accuracy of

Table IV. Results of the determination of water formed by pyrolysis at various temperatures

Condition of pyrolysis Temperature °C	Time min.	Water content %
20	20	0.57
40	20	0.54
60	20	0.57
80	20	1.37
110	20	2.86
120	20	3.03
130	20	3.08
150	10*	3.08
150	30*	4.03
150	60*	6.14
170	3*	3.05

* The heating time after a sample dissolves completely in solvent.

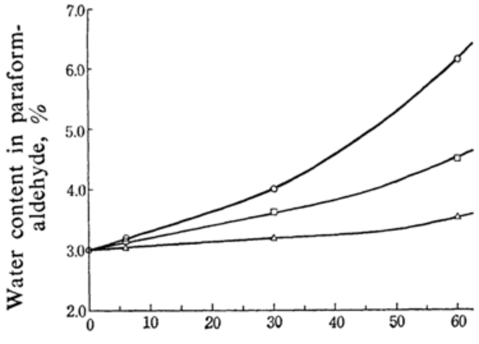

Fig. 3. Variation of the water content with heating period of paraformadehyde in various solvents.

Table V. Water content in various concentrations of the sample in propylene glycol

Weight of sample %	Propylene glycol ml.	Water content %
2.0056	25	0.42
3.1643	25	0.45
4.5315	25	0.41
1.9881	50	0.44
3.0624	50	0.42
5.3211	50	0.40

Table VI. Results of the determination of the water contents by the pyrolysis method for various types of the low polymers of formaldehyde

Sample	Temperature of dissolution °C	Water content %
Commercial grade paraformaldehyde	150	3.32
	150	3.28
Dried commercial grade paraformaldehyde	150	2.58
	150	2.56
α-Polyoxymethylene	170	1.65
	170	1.66
Dried α-polyoxymethylene	170	0.45
	170	0.45

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5) J. Löbering and K. P. Jung, *Monatsh. Chem*, 70, 281 (1939).

6) J. F. Walker, " Formaldehyde ", Reinhold Publishing Co., New York (1953), p. 121.

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

Sample	Water content %		Bound water %	Degree of poly-merization
	By propylene glycol dissolution method	By methanol extraction method		
Commercial grade paraformaldehyde	3.30	0.60	2.70	22
Dried commercial grade paraformaldehyde	2.57	0.09	2.48	24
α-Polyoxymethylene	1.64	1.05	0.59	102
Dried α-polyoxymethylene A	0.44	0.02	0.42	143
Dried α-polyoxymethylene B	0.45	0.02	0.43	140

TABLE VIII. RESULTS OF THE TOTAL ANALYSIS

Sample	Formaldehyde %	Methanol %	Water %	Total %
85% Paraformaldehyde	87.2	0.70	11.9	99.8
95% Paraformaldehyde	95.8	0.50	3.4	99.7
Paraformaldehyde special-class reagent	96.6	0.30	2.7	99.6
α-Polyoxymethylene	99.2	—	0.6	99.8
Dried α-polyoxymethylene	99.5	—	0.4	99.9

the determination of the degree of polymerization was not very high. The method reported in the present work can be used for the determination of the degree of polymerization of formaldehyde with a high degree of accuracy. To verify the accuracy of the determination of bound water, formaldehyde and methanol in polymer were determined independently. The former was determined by the sodium sulfite method, and the latter, by gas chromatography. Table VIII lists the percentage of formaldehyde and methanol thus determined, together with that of bound water. The sum of these three components is almost 100%, thus establishing the accuracy of this method.

Summary

The adsorbed water of the low polymer of formaldehyde was determined by extraction with dry methanol and Karl Fischer titration. The sum of the adsorbed water and the water formed by the pyrolysis of the sample was determined by titration with the specially prepared Karl Fischer reagent SS, after the sample had been dissolved in propylene glycol by heating. The method of the separation and the determination of the two kinds of water was thus established. When the average numerical degree of polymerization of the polymers was calculated from the content of bound water determined by this method, satisfactory results were obtained. To verify the accuracy of the determination of water content, formaldehyde and methanol were determined independently; their sum was found to be almost 100%.

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