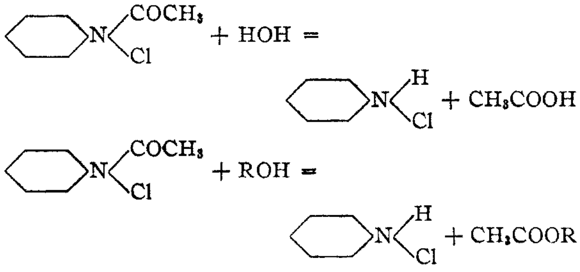
[CONTRIBUTION FROM THE AMMONIA DEPARTMENT OF E. I. DU PONT DE NEMOURS & CO.]

Titrimetric Determination of Water in Organic Liquids Using Acetyl Chloride and Pyridine

BY DONALD MILTON SMITH AND W. M. D. BRYANT

The most frequently used quantitative methods for determining the water content of organic liquids depend upon the measurement of some sensitive physical property of the system. Density, refractive index, critical solution temperature, viscosity and electrical conductivity are among those recommended.[1,2,3,4,5] In these methods the nature and amounts of the organic constituents of the mixture must be known. Other tests of a chemical nature are available but these are mostly qualitative and are restricted to the detection of very small amounts of water. Henle[6] has reviewed some of the earlier methods and has described in detail his own procedure, employing aluminum ethylate. Calcium carbide has long been used in testing for moisture because of the great ease with which it evolves acetylene when exposed to the action of water. The water content of a material may be determined quantitatively by measuring the acetylene formed, either gasometrically,[7] or colorimetrically as cuprous acetylide.[4] According to Weaver[8] the formation of cuprous acetylide is a very sensitive test for water in the presence of many organic materials. The colorimetric procedure is apparently better suited for the determination of traces of moisture. The gasometric procedure is applicable to materials containing appreciable amounts of water, but requires elaborate apparatus for precise work. Two other quantitative procedures have been described recently, one involving the use of α-naphthoxydichlorophosphine,[9] and the other benzoic anhydride.[10] The first, though precise, is not specific for water but reacts with alcohols also. The second gives evidence of good precision and wide applicability, but is much more time consuming than the method reported below.

A rapid quantitative procedure suitable for determining widely varying amounts of water in organic liquids has been developed by the authors. This new method utilizes the fact that acetyl chloride in the presence of pyridine reacts quantitatively with water, producing two moles of titratable acid (actually present as pyridine salts), while when reacting with a dry alcohol, only one mole of available acid is produced



The authors have already described a quantitative procedure for alcoholic and phenolic hydroxyl based on these same reactions carried out in the reverse order.[11]

The reaction is specific for water, and hence is to a large extent independent of the exact nature and composition of the organic solvent. Alcohols, phenols and certain amines which react with acetyl chloride reduce the sensitivity of the method to some extent, but otherwise do not interfere. Even fatty acids can be analyzed for water by this scheme.

The method is about 97–98% stoichiometric and the precision about ±1%. As little as 2 mg. of water can be detected with certainty provided proper control experiments are conducted. Where the solvent does not react with acetyl chloride, volumes of sample up to 10 cc. may be employed, while in the very unfavorable case of methanol, a sample as great as 0.5 cc. may be used. The rapid rate of reaction of water with acetyl chloride in many cases permits the presence of more than the stoichiometric amount of alcoholic hydroxyl in the sample.

Experimental

Chemicals.—The reagent was prepared by mixing 1.5 moles (approx. 118 cc.) of Eastman Kodak acetyl chloride

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(1) N. S. Osborne, E. C. McKelvy and H. W. Bearce, *Bulletin of the Bureau of Standards*, **9**, 327 (1913).

(2) C. Simmonds. "Alcohol, Its Production, Properties and Applications," Macmillan Co., Ltd., London, 1919.

(3) D. C. Jones and S. Amstell, *J. Chem. Soc.*, 1316 (1930).

(4) H. Hartley and H. R. Raikes, *ibid.*, **127**, 524 (1925).

(5) H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

(6) F. Henle, *ibid.*, **53**, 719 (1920).

(7) R. W. Roberts and A. Fraser, *J. Soc. Chem. Ind.*, **29**, 197 (1910).

(8) E. R. Weaver, THIS JOURNAL, **36**, 2462 (1914).

(9) R. P. Bell, *J. Chem. Soc.*, 2903 (1932).

(10) J. Ross, *J. Soc. Chem. Ind.*, **51**, 121T (1932).

(11) Donald Milton Smith and W. M. D. Bryant, THIS JOURNAL, **57**, 61 (1935).

(No. P-334) with dry J. T. Baker C. P. toluene sufficient to make 1 liter of solution. The above was used in conjunction with dry Baker C. P. pyridine just as employed in the authors' hydroxyl method.[11]

The acetone used in preparing the samples was Baker C. P. grade. The *n*-propanol was "du Pont Propanol" of boiling range 97.2–97.5°. The other solvents used were of the best grades offered by Eastman, J. T. Baker and other manufacturers and were employed without further purification.

Analytical Procedure.—Ten cc. of 1.5 molal acetyl chloride in toluene is pipetted into a dry 250-cc. g. s. volumetric flask (calibration unnecessary), using a Lowy automatic pipet. The flask is then placed in a beaker containing a slurry of finely chopped ice, and after standing for a minute or so, 2 cc. of pyridine is added from a pipet. The mixture is stoppered and shaken. A thin paste of acetyl pyridinium chloride in toluene is formed. The procedure up to this point is identical with the hydroxyl method.

A known weight or volume of sample to be analyzed for water content is added in such proportions that an excess of 0.5 mole of acetyl chloride remains for each mole reacted. The mixture is shaken vigorously to ensure intimate contact between the reagent and the sample. After standing for at least two minutes at room temperature, in which time all of the water present should have reacted, the excess of reagent is decomposed by absolute ethanol (absolute methanol will do, although the hydrolysis of methyl acetate interferes to some extent) added in two installments. The first 1 cc. of absolute ethanol is added from a pipet and followed by vigorous shaking to decompose the major portion of the reagent. Then after at least five minutes, 25 cc. more of absolute ethanol is added to complete the decomposition and produce a homogeneous solution suitable for titration. The solution is allowed to stand an additional ten minutes at room temperature before titration. The addition of absolute alcohol in two portions is necessitated by its small but nevertheless significant water content which would otherwise introduce errors of varying magnitude.

The mixture is then titrated with 0.5 *N* sodium hydroxide solution to a phenolphthalein end-point. At least one blank determination should be made along with each group of samples. The increase in acidity of the sample over the blank is a direct measure of the water present in the sample, one mole of water liberating an extra mole of acid.

Analytical Results

Most of the development work was carried out with solutions of water in *n*-propanol. The use of an alcohol as a solvent is a severe test of the method, since alcohols react with acetyl chloride and so tend to reduce the sensitivity. Table I shows the results obtained with volumetric samples of a wide range of water–*n*-propanol mixtures. Acetone is not reacted upon by acetyl chloride and pyridine, hence is an ideal diluent because of its ready miscibility with both water and organic solvents. The acetone employed in these experiments contained about 0.5% of water which was corrected for by means of controls.

TABLE I

DETERMINATION OF WATER–*n*-PROPANOL MIXTURES (Volumetric Samples)

Vol. per cent. water and *n*-propanol in acetone solution		Water–*n*-propanol ratio	Sample		Per cent. of theoretical water content
H_2O	*n*-Propanol		Cc.	Detn.	
2	0	....	5	9	97.3 ± 1.0
1.96	0.04	49	5	3	97.1 ± 0.4
1.9	.1	19	5	3	97.4 ± .3
3.2	.8	4	2	3	97.0 ± 1.0
3.6	2.4	1.5	2	3	97.4 ± 0.0
3.2	4.8	0.67	2	3	98.6 ± .6
2.0	8.0	.25	2	3	96.1 ± .6
0.8	9.2	.087	2	3	97.3 ± 1.4
.1	9.9	.010	5	3	109 ± 4

Ordinarily in the analysis of samples containing alcohols or other hydroxylated organic materials in addition to water, a sufficient excess of reagent should be present to combine with all of the alcoholic material as well as with all of the water. It was found, however, that water reacts with acetyl chloride and pyridine so much more rapidly than most alcohols, that it is possible to have an appreciable excess of alcohol present without affecting the water determinations. For example, the regular 10-cc. sample of 1.5 molal acetyl chloride should be completely exhausted by the following approximate weights (volumes) of water and alcohols:

Water	0.27 g.	(0.27 cc.)
Methanol	.48	(.60)
Ethanol	.69	(.86)
Propanols	.90	(1.13)
Butanols	1.11	(1.39)
Pentanols	1.32	(1.65)

In practice it was found that amounts of water up to at least 50 mg. could be determined correctly in the presence of one gram of any of the above alcohols except methanol. On the other hand, methanol, glycol and glycerol interfered with the determination of water when present in greater than the stoichiometric amounts.

Table II contains results of experiments with water–*n*-propanol mixtures in which the samples were measured gravimetrically.

The individual weights of samples 1, 2 and 3 ranged from 0.11 to 0.18 g. Those of samples 4 and 5 ranged from 0.51 to 1.25 g., several exceeding the stoichiometric limit for water plus propanol. The data in column 6 were corrected to the stoichiometric by dividing by the factor 0.975

TABLE II

DETERMINATION OF WATER IN *n*-PROPANOL–WATER MIXTURES

(Gravimetric Samples)

Mixture	Wt. % H_2O in sample	Detns.	Wt. % H_2O found	Per cent. of theoretical water content	Av. wt. % H_2O found × 100/97.5
1	100.00	10	98.0 ± 0.5	98.0 ± 0.5	100.5
2	98.91	6	96.7 ± 1.0	97.8 ± 1.0	99.2
3	98.10	6	95.5 ± 0.8	97.4 ± 0.8	97.9
4	4.71	8	4.62 ± .02	98.1 ± .4	4.74
5	3.00	7	2.91 ± .02	97.1 ± .7	2.98

in order that they might be more readily compared with the weight compositions as prepared (column 2).

Precision and Sensitivity of the Method.—An inspection of Tables I and II shows that the precision of the above method of determining water is about ±1% where the sample contains 50 mg. or more of water, and that the stoichiometric results are approached within 97 to 98%. Due to errors affecting the volumetric measurement of small samples, the gravimetric experiments in Table II are probably more nearly representative of the precision and accuracy to be expected, although the volumetric experiments in Table I were conducted with great care. No extraordinary precautions were taken to remove adsorbed moisture from the reaction flasks in any of the above experiments, since the object of this research was not primarily the determination of minute amounts of water. The flasks were simply dried overnight in an electric oven at 130–140° prior to use.

In order to test the behavior of acetyl chloride and pyridine with water in the presence of a wide variety of organic liquids, two parallel sets of experiments were performed. In the first, volumetric samples (usually 1 cc.) of various organic liquids were analyzed for water by the above method. In the second set of experiments the same quantities of the various liquids were first added, followed closely by 2 cc. of acetone containing 0.0604 g. of water. By proceeding in this manner the first series served as a blank for the second, thus avoiding the necessity of starting with absolutely dry solvents. The experimental results are recorded in Table III. These results are only rough pilot experiments designed to indicate the scope of the method and should not be confused with the precision data in Tables I and II. In most cases only one determination was made with each solvent.

As indicated earlier, the minimum absolute amount of water detectable is about 2 mg. However, in determining the water content of inert solvents such as hydrocarbons, ethers, esters, weak tertiary amines and ketones, samples up to 10 g. can be used, so that in the most favorable case as little as 0.02% of water could be detected

TABLE III

DETERMINATION OF WATER IN VARIOUS SOLVENTS

(0.0604 g. of Water Added to Each Sample)

Solvent	Sample, cc.	Detns.	Per cent. of theoretical water content	
Methanol	0.5	1	100.0	
Ethanol	1.0	1	97.2	
n-Propanol	1.0	1	96.5	
Isobutanol	1.0	2	94.6 ± 0.4	
s-Butanol	1.0	1	97.2	
t-Butanol	1.0	1	97.2	
Cyclohexanol	1.0 (approx.)	1	95.7	
Isobutyl formate	1.0	1	95.5	(some hydrolysis)
n-Butyl acetate	1.0	1	97.2	
1,4-Dioxane	1.0	1	98.0	
Paraldehyde	1.0	1	98.0	
Methyl isopropyl ketone	1.0	1	97.2	
Ethylene dichloride	1.0	1	97.2	
Acetic acid	1.0	3	94.0 ± 1.3	
Propionic acid	1.0	1	98.0	
Isobutyric acid	1.0	1	97.2	
Caproic acid	1.0	1	95.7	
Oleic acid	1.0 (approx.)	3	97.8 ± 0.9	
Triethanolamine	1.0 (approx.)	2	96.0 ± 0.5	
Aniline	1.0	2	95.0 ± 0.5	
Dimethylaniline	1.0	1	95.7	
Pyridine	1.0	1	96.2	

When the sample contains alcohols or other reactive materials, the use of as much as one gram is usually permissible. The maximum sensitivity would then be about 0.2% water. The most unfavorable materials investigated so far (methanol, ethylene glycol and glycerol) should permit the determination of about 0.5% water. Where the sample is chiefly aqueous, it is possible to detect the presence of as little as 1 to 2% of alcoholic or inert material by difference.

Effect of Moisture in the Reagents.—The presence of small amounts of water in the reagents employed does not affect the accuracy of the results obtained, provided the above analytical procedure is followed in detail. Water in the acetyl chloride solution or pyridine is automatically corrected for by the blank and is harmful only when present in sufficient quantity to reduce seriously the amount of available acetyl chloride.

The presence of as much as 0.1% of water in the absolute ethanol used to decompose the residual acetyl chloride would ordinarily be more serious, because in certain cases (*e. g.*, samples containing alcohols) the analytical results are affected to a varying extent depending upon the amount of unreacted acetyl chloride remaining after the addition of the sample. However, the addition of the absolute ethanol in two successive portions, as recommended in the procedure, effectively eliminates interference from this source. It is probable that no special care in this respect would be necessary if perfectly dry ethanol instead of ordinary absolute material were employed to decompose the unused acetyl chloride.

The advantage of adding absolute ethanol in two successive portions of 1 cc. and 25 cc., respectively, to destroy residual acetyl chloride, instead of a single 26-cc. portion, may not be at once appreciated. The following exposition should clarify this point. The addition of 26 cc. of absolute ethanol containing 0.1% by weight of water means that in the absence of other influences the total titer may be increased by the equivalent of 26 mg. of water. In a blank determination this would be especially true. However, if the sample added contains sufficient alcoholic ingredients, in addition to its water content, to combine with all the residual acetyl chloride, none of the 26 mg. of water added in the later step could react at all, and the difference between the regular analysis and the blank would be erroneously low. If, instead of adding the absolute ethanol in a single portion, 1 cc. of it is added first, all of the unused reagent is destroyed by this amount of alcohol while its water content (1 mg.) is too small to affect the titer of either the blank or the sample. The subsequent addition of 25 cc. more of absolute ethanol has no chemical effect upon the analysis but simply exerts a solvent action upon the mixture.

Interfering Substances.—The data in Table III indicate that the scope of the method is exceptionally wide and that even fatty acids do not in general interfere provided their titer is taken into account. Formic acid, however, is exceptional in that it is instantly decomposed with the evolution of carbon monoxide upon its addition to the acetyl chloride–pyridine reagent; hence it cannot be analyzed for water by this method without modification. The fact that certain higher fatty acids form stable mixed anhydrides with acetyl chloride does not affect the correctness of the water determination since stable anhydrides are indistinguishable from esters in a titrimetric procedure.

Appreciable amounts of aldehydes also interfere, but not to the same extent as in the hydroxyl method.[11] Their action is characterized by a rapidly fading end-point.

It will be observed that the weak aromatic and heterocyclic nitrogen bases do not exert any disturbing influence upon the method. However, bases strong enough to affect phenolphthalein must not be present. Triethylamine, for example, cannot be analyzed by this method. On the other hand, the weaker triethanolamine does not interfere.

Substances which are readily hydrolyzed do not give very reliable results. Formic esters lower than the butyls are unsatisfactory and even isobutyl formate must be corrected by means of a control.

The success of the above method for determining water when applied to alcohols and amines depends to a large extent upon the more rapid rate of reaction of water; hence the maximum amount of sample to be used should always be predetermined by control experiments.

Summary

1. A rapid and specific quantitative method for the determination of water in organic liquids, based upon the use of acetyl chloride and pyridine,

has been developed. The procedure is adapted to the analysis of liquids of widely varying water content.

2. It has been found that the reaction of acetyl chloride and pyridine with water is much more rapid than the corresponding reactions with alcohols and amines. Consequently a moderate excess of alcohol or amine over the stoichiometric amount generally does not interfere with the determination of water.

3. By means of the new method water has been determined successfully in over twenty different organic compounds including fatty acids.

4. Substances known to interfere with the method are discussed.

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A Modified Iodimetric Method of Determining Copper

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The iodimetric method of determining copper consists essentially in treating a solution of the cupric salt with a soluble iodide which precipitates cuprous iodide and liberates iodine. The latter can be titrated with thiosulfate. The method has, however, certain difficulties which are familiar to those who have used the method, and which limit its accuracy. In particular, the reaction on which the method depends, $2CuI_2 \longrightarrow 2CuI + I_2$, which is reversible, does not run quite to completion when the iodine is titrated. This appears to be due partly to adsorption of iodine by cuprous iodide, which in consequence is distinctly colored instead of white at the end-point. The fact that cuprous iodide is not extremely insoluble also contributes to the difficulty of obtaining complete reaction. The method is, however, widely used on account of its speed but is hardly to be classed in accuracy with a number of other iodimetric methods. When used, the thiosulfate should be standardized with copper under rather definite conditions because of the lack of an exact stoichiometric relation between copper and iodine in the reaction.

A modification of this method was proposed by Bruhns[1] with the object of using less iodide than is necessary by the usual method. The modification consists in adding potassium thiocyanate along with the iodide, which precipitates the more insoluble cuprous thiocyanate instead of cuprous iodide. This modification has been shown repeatedly to give unreliable results and recently[2] the reasons for the failure of the method have been investigated in considerable detail. Briefly, the modified method gives low results because both iodine and thiocyanogen are liberated simultaneously to a certain extent, and react on each other.

In principle, however, the Bruhns method has one advantage, since cuprous thiocyanate is more insoluble than cuprous iodide, thus tending to make the reaction more complete due to the more complete removal of cuprous ion. As we have found in the present investigation, moreover, cuprous thiocyanate does not adsorb iodine at low concentrations of the latter, but becomes white as the free iodine is removed by titration, which makes the end-point exceedingly sharp in the presence of starch. It appeared probable that the undesirable side reactions occurring in the Bruhns method could be eliminated by adding the soluble thiocyanate late in the course of the titration. In that case the method should have greater accuracy than the usual method. The qualitative effect of adding a thiocyanate can be shown very easily. If this salt is added, during a titration, just as the end-point is reached by the usual method, the starch iodide color is markedly intensified. Quantitatively, the additional iodine liberated when the thiocyanate is added at this point amounts to about 0.15 cc. of decinormal thiosulfate.

Experimental

The copper used in the determinations given below containing 99.955% of the metal, was kindly furnished us by the Department of Metallurgy of this University. The impurity consisted chiefly of oxygen. The two thiosulfate solutions used were standardized by means of resublimed iodine and the equivalent in copper calculated.

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[1] Bruhns, *Z. anal. Chem.*, **58**, 128 (1919); **59**, 337 (1920).

[2] Krüger and Tschirch, *ibid.*, **97**, 161 (1934). These writers also give complete references to the literature regarding the modified method of Bruhns.