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Moisture Determination by Thermal Titrimetry Using the Enthalpy of Reaction of 2,2-Dimethoxypropane with Water

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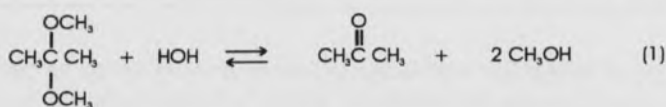
Abstract

Assays for water content can be readily and simply carried out using the technique of thermal titrations. The method is based on measuring the endothermic heat of reaction exhibited when 2,2-dimethoxypropane is brought into contact with water in the presence of an acid catalyst. The apparatus is simple, requiring a constant delivery rate buret, a recording thermistor thermometer, and a stirred, thermally insulated reaction container. The 2,2-dimethoxypropane reagent used for the water assays is environmentally friendly ("green"). It is stable, pleasant smelling and economical. Working curves in three solvents, acetonitrile, tetrahydrofuran and 1,4-dioxane, show excellent precision and linearity with increasing water concentrations to at least 0.07 M. Four different kinds of samples were subjected to this method of water assay to demonstrate its versatility: ethanol, nickel (II) nitrate hexahydrate, concentrated sulfuric acid, and two kinds of fuels. In each case, the method worked accurately and reproducibly with a minimum of time required.

Introduction

The Karl Fischer Method for the quantitative determination of the amount of water in a sample is considered to be the standard method of analysis. This is due to its wide range of applicability compared with numerous other methods available. Substances that react with Karl Fischer reagents, of course, preclude its use. Several excellent discussions of this method and its limitations have been published (Kolthoff and Elving, 1961). We describe a method for moisture determination that also appears to be widely applicable, particularly in some of those cases where the Karl Fischer method fails. Our method involves measuring the heat produced when 2,2-dimethoxypropane reacts with water as described by Equation 1.

Extensive use has been made of 2,2-dimethoxypropane



to dehydrate various samples containing water. The dehydration is easily carried out by pouring an excess of the ketal over the substance to be dried and warming gently. The reaction is driven to completion by removing the low boiling products, acetone and methanol. While in the process of drying various reagents with 2,2-dimethoxypropane, we noted that its reaction with water was accompanied by a considerable absorption of heat. It is a strongly endothermic reaction. We felt that by applying the method of thermal titrations, using 2,2-dimethoxypropane as the analytical

reagent, one could readily quantitate the amount of water in a sample.

There are some obvious benefits to such a method. The reagent, 2,2-dimethoxypropane, is not affected by many substances that interfere with Karl Fischer reagent. For example, ferric and cupric ions interfere in Karl Fischer water analysis. Acids that react to produce esters with the methanol present in Karl Fischer reagents preclude its use. The shelf life of 2,2-dimethoxypropane is much longer than Karl Fischer reagent. Although 2,2-dimethoxypropane reacts with water, it does so only when heated or catalyzed with acid. Moreover, it is not necessary for the concentrations of 2,2-dimethoxypropane to be known in order to determine the amount of water present. The enthalpy of reaction can be used instead. The Karl Fischer reagent is a moisture-sensitive mixture of materials that contains, among other things, the toxic substances sulfur dioxide and pyridine. The 2,2-dimethoxypropane, on the other hand, is a pleasant smelling, harmless, relatively stable liquid that is easily and inexpensively obtainable in pure form.

Earlier investigators proposed methods that used 2,2-dimethoxypropane to accurately determine the amount of water in a sample. For example, Critchfield and Bishop measured the amount of acetone produced after reacting a moisture-containing sample with 2,2-dimethoxypropane (Critchfield and Bishop, 1961). The amount of acetone was determined spectroscopically by measuring its absorbance at 5.87 micrometers. When utilizing their method, one must take into account any carbonyl compounds that also absorb at this wavelength. Other workers have used 2,2-dimethoxypropane to determine the amount of water in a sample with the aid of a gas chromatograph (Badinad et al.,

1965; Martin and Knevel, 1965). Martin and Knevel equilibrated different known amounts of water with 2,2-dimethoxypropane. Aliquots from each of these solutions were withdrawn with a syringe and injected into a gas chromatograph. The peak heights of the ketal were measured on the chromatogram and a relationship between the ratios of these peak heights to the initial water concentration was determined. Once this relationship was known, the amount of water in other samples could be obtained using the same method.

The quantitative determination of the amount of water in a sample by thermal titrimetry is not new. Greathouse et al. determined the amount of water in acetic acid by reaction with acetic anhydride (Greathouse et al., 1956). A known amount of excess acetic anhydride was titrated with small increments of water in a dewar flask until no further temperature rise was observed on a thermometer. Alternatively, acetic anhydride and the sample were mixed in a Dewar flask and the temperature noted. Then catalyst was added that allowed the hydrolysis reaction to take place quickly. The maximum temperature was observed and compared with a working curve of temperature rise versus water content. This latter technique was a precursor of what is now termed Direct Injection Enthalpimetry, DIE (Wasilewski et al., 1964). Spink and Spink used DIE to determine the amount of water in organic liquids (Spink and Spink, 1968). Their method involved injecting 80% wt/wt sulfuric acid into a dewar flask containing the sample and noting the temperature rise. A working curve was prepared relating the amount of water to the temperature rise. It is interesting to note that the heat produced by the addition of water to sulfuric acid was used by Somya to determine the water content of sulfuric acid (Somya, 1927). Finally, Wasilewski and Miller used DIE to do moisture analysis (Wasilewski and Miller, 1966). They used the heat produced when water is added to Karl Fischer reagent. First, they added a known excess of Karl Fischer reagent to the sample and noted the temperature. Next, they added an excess of water. The remaining Karl Fisher reagent reacted with the water producing -16.1 kcal per mole of water reacted.

The analytical method of thermal titrations is not widely recognized as a useful method for many types of determinations. Two monographs give an in-depth explanation of the method along with several examples (Barthel, 1975; Bark and Bark, 1969). In addition a theoretical derivation of thermal titration thermograms obtained can be found in Wilson (Wilson, 1968).

The intent of this paper is to describe a method to determine the amount of water in samples by thermal titrations using 2,2-dimethoxypropane as the analytical reagent. As will be shown, this method is very quick, simple, precise, and relatively accurate as far as instrumental methods are concerned. It is also environmentally friendly.

Materials and Methods

Two thermal titration systems were used for these analyses. The system used for obtaining calorimetry data and some of the water calibration measurements have been described in detail (Wilson, 1968). The remaining measurements were made using a FACTS Titration System, composed of a Sanda Dual Titration Station, F.A.C.T.S. Ce2010 Data Processing Module, National Instruments Lab-PC 1200 Control Board and PC computer (Sadtler, 1999). This latter instrument was used to make the majority of measurements. The instrumentation in both cases is similar in that what is required is an accurate constant rate delivery buret, a stable, sensitive thermistor thermometer, a stirred titration vessel that is thermally insulated, and a means of recording the resulting thermogram. The FACTS system is particularly useful because of the sophisticated data handling that produces a thermogram on which the temperature versus milliliters of titrant is plotted along with the first and second derivatives of temperature versus milliliters. The derivative plots greatly enhance the ability to measure the endpoint of the thermogram accurately without having to resort to graphical extrapolations.

In order to determine the amount of water in a sample by thermal titration with 2,2-dimethoxypropane, it is necessary to have a solvent capable of dissolving both the sample to be analyzed and the 2,2-dimethoxypropane. Ideally, one would like to have a solvent with low vapor pressure, no unpleasant odor, a low cost, and one that would dissolve a wide variety of inorganic and organic materials. Acetone and methanol are unsuitable because they are the products of the reaction between water and 2,2-dimethoxypropane. Moreover, alcohols, ketones, acid anhydrides, and acid chlorides, as well as amines cannot be used since they may react with the 2,2-dimethoxypropane (Killian et al; Baum and Hennion, 1938; Kreevoy and Taft, 1955; Hock, 1934). Consideration of the preceding criteria narrowed the choice of suitable solvents to three. These are acetonitrile, tetrahydrofuran, and 1,4-dioxane.

Acetonitrile, the most polar of the three, dissolves many inorganic salts, and hydrated salts readily. When used as a solvent, acetonitrile many times will become colored as the reaction proceeds. This is due to its polymerization. As the results show, this does not appear to pose a problem. It occurs after the titration has been completed in most cases. The other two solvents show no such effect.

Results

Table 1 provides a summary of our ability to establish a working curve for the determination of the amount of water in acetonitrile. In these analyses, water was added to ACS Reagent Grade acetonitrile over a range of 0.025 M to 0.078

Table 1. Thermal Titration of Water with 2,2-Dimethoxypropane

mMole H ₂ O Added	mMole H ₂ O Found
Acetonitrile Solvent	
5.98	6.41
11.96	12.60
17.95	18.92
23.92	25.31
mMole H ₂ O = 0.9490 mMole 2,2-DMP - 0.0514	
Tetrahydrofuran Solvent	
0.00	1.73
5.83	7.05
11.66	12.49
17.49	18.18
mMole H ₂ O = 1.0638 mMole 2,2-DMP - 1.7469	
1,4-Dioxane Solvent	
0.00	3.87
5.76	9.64
11.52	15.58
17.28	21.21
mMole H ₂ O = 0.9935 mMole 2,2-DMP - 3.8530	

M. Titrations were then performed on each solution with 2,2-dimethoxypropane, using methane sulfonic acid catalyst. Table 1 also contains the results obtained when tetrahydrofuran and 1,4-dioxane were used as the solvents for the water analysis.

Table 2 gives the results of the analysis of the amounts of water in various solvents and fuels:

Ethanol measurements.--25.00 mL of freshly opened pure alcohol plus 0.50 mL methanesulfonic acid catalyst were placed into the titration vessel and titrated with 2,2-dimethoxypropane. As a comparison, 25.00 mL of the same pure ethanol was taken from a laboratory wash bottle that had been exposed to the air for some time. Again, 0.50 mL of methanesulfonic acid catalysts was added. No additional solvent was needed because all components were mutually soluble.

Gasoline and Aviation Fuel.--Gasoline and aviation fuel are not soluble with the methanesulfonic acid catalyst. All are soluble in tetrahydrofuran. Because these solvents generally contain only small amounts of water, the 2,2-dimethoxypropane was first diluted 1:5 with tetrahydrofuran for the water analysis. This helped to improve the precision of the experiment. First a blank had to be obtained to find the amount of water in the tetrahydrofuran solvent. Five replicate titrations were performed on 50.00 mL ACS Reagent Grade tetrahydrofuran to which 0.50 mL methanesulfonic acid catalyst had been added. The titrations were made using the diluted 2,2-dimethoxypropane described

Table 2. Analytical Results of Thermal Titrations Using 2,2-Dimethoxypropane (DMP)

Sample	No. Replications	mL DMP	Grams H ₂ O Found	%H ₂ O
"New" Ethanol	5	4.3±0.2	0.62±0.03	2.5±0.1
"Old" Ethanol	5	5.2±0.3	0.76±0.04	3.0±0.2
Acetonitrile	5	1.52±0.02	0.223±0.003	0.45±0.01
Tetrahydrofuran	5	1.05±0.06	0.153±0.009	0.31±0.02
87 Octane, Exxon, Sat'd	5	0.46±0.09	0.07±0.01	0.13±0.03
"Old" C152 Aviation Fuel	5	0.192±0.009	0.028±0.001	0.056±0.002
H ₂ SO ₄ , Conc.	3	1.4875±0.0	0.21785±0.0	0.43570±0.0
"New" Ni(NO ₃) ₂ ·6H ₂ O	4	2.13±0.03	0.311±0.005	39.4±0.6
"Old" Ni(NO ₃) ₂ ·6H ₂ O	4	2.42±0.07	0.35±0.01	45±1

All results expressed in % vol/vol except for nickel samples which are in % wt/wt

earlier. This established the blank to be subtracted from all the analyses involving the two fuels. Each of the fuels was analyzed for water by measuring 50.00 mL gasoline or aviation fuel, 50.00 mL tetrahydrofuran, and 0.50 mL methanesulfonic acid catalyst. Five replicate titrations were performed on the gasoline and on the aviation fuel. The gasoline was Exxon 87 octane that had been equilibrated with water to saturate the sample. The aviation fuel was an old sample of C152 fuel taken from an aircraft, and it was already saturated with water.

Sulfuric Acid.--One of the most remarkable and useful applications of this analytical method is that sulfuric acid can be easily and quickly assayed for water content. Since the sulfuric acid provides the hydrogen ion catalyst needed in the reaction, the titrations were carried out directly on 50.00 mL samples of fresh, ACS Reagent Grade concentrated sulfuric acid. Because the results were so precise, only three replicate determinations were required.

Inorganic Salts.--The assay for water in inorganic salts is quite useful. The water of hydration of these salts can be measured. Also, those salts that have adsorbed various amounts of water from exposure to humid air can be analysed. Because of this, many reagent bottles with water logged samples can be salvaged because the concentrations of the salts can be established. Acetonitrile was found to be the best solvent for water assays of inorganic salt samples. Five replicate titrations of 50.00 mL of acetonitrile plus 0.50 mL methanesulfonic acid were carried out to determine the amount of water in the solvent. The salt samples were massed, 3.95 g, into a 250.00 mL volumetric using acetonitrile solvent. Then 50.00 mL aliquots of the solution were titrated after adding 0.50 mL methanesulfonic acid catalyst to each. Four replications were performed on the two salt samples studied.

Discussion

As Table 1 shows, the amount of water determined by thermal titrimetry was close to the amount of water added to the sample. The reason more water was detected is that the solvents themselves were found to contain a small amount of water. This fact is evidenced in Table 2 for the titrations of neat acetonitrile (0.44% v/v H₂O) and tetrahydrofuran (0.31% v/v H₂O). The data in Table 1 were plotted to establish a working curve for each solvent. Linear least squares fitting of the data gave the values shown in Table 1 for each solvent. It must be emphasized that the solvents must be titrated each day to find the water content for that time and batch of solvent. The water assays for each of the solvents in Table 1 also reveal that the working curves for all three solvents are very precise and linear to approximately 0.07 M water concentration.

The four water assays chosen illustrate some of the wide applicability and usefulness of the method of thermal titra-

tions using 2,2-dimethoxypropane. The first assays, summarized in Table 2, compare the amount of water found in a freshly opened bottle of pure ethanol with a sample of ethanol taken from a laboratory wash bottle that had been exposed to the air for a period of time. As expected the aged ethanol sample had absorbed some water from the air in the laboratory.

An interesting application of this method is its use to determine water of hydration of hydrated salts. A sample of nickel (II) nitrate hexahydrate from a freshly opened bottle of ACS reagent grade material was analyzed for water content. The theoretical weight percent water in this compound is 37.16% wt./wt. This compares well with the analysis, which showed 39.3% wt./wt. The larger value indicates that the sample contained a small amount of excess moisture. Another nickel (II) nitrate hexahydrate sample was taken from a reagent bottle that had been on the shelf for several years and had absorbed so much water that it was syrupy. This sample had absorbed an additional 7.84% wt./wt. water.

Astonishingly, concentrated sulfuric acid can be easily assayed for water content. A bottle of freshly opened ACS Reagent Grade sulfuric acid contained a trace of water as shown in Table 2. In this assay, the amount of heat produced during titration per mole of 2,2-dimethoxypropane added was large enough to increase the signal to noise ratio to the point where there was no scatter in the replicate measurements.

Finally, the amount of water was assayed in two samples of fuel. The original sample of gasoline had less water than the detection limits for this method. In order to test the method, the gasoline was first saturated with water. Therefore, the value for the amount of water given in Table 2 in the Exxon gasoline represents the saturation solubility of water in gasoline. In the case of the aviation fuel, a sample was removed from the sump in the tanks of a small, private aircraft. Again, the water content was quite low.

Conclusions

Assay of samples for water content is easily accomplished by the method of thermal titrations using 2,2-dimethoxypropane as the analytical reagent. It takes less than five minutes to carry out a single titration. This method should be a strong candidate for automation. The components of the system are robust and not contaminated, and the single analytical reagent needed is environmentally friendly. The method can be applied to virtually any sample provided it can be brought into a solution that allows for mutual miscibility of the sample, acid catalyst, and 2,2-dimethoxypropane.

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Literature Cited

- Badinad, A. C. Quincy, and R. J. Guilluy.** 1965. *J. Pharm. Belg.* 20:397 ff.
- Bark, L. S. and S. M. Bark.** 1969. *Thermometric Titrimetry* Pergamon Press, Oxford.
- Barthel, J.** 1975. *Thermometric Titrations* John Wiley & Sons, New York.
- Baum, A. A. and G. F. Hennion.** 1938. *J. Am. Chem. Soc.* 60:568 ff.
- Critchfield, F. E. and E. T. Bishop.** 1961. *Anal. Chem.* 33:1034 ff.
- Greathouse, L. M. H. J. Janssen, and C. M. Haydel.** 1956. *Anal. Chem.* 28:357 ff.
- Hoch, J.** 1934. *Comt. rend.* 199:1428 ff.
- Killian, D. B. G. F. Hennion, and J. A. Nieuwland.** 1935. *J. Am. Chem. Soc.* 57:544 ff.
- Kolthoff, I. M. and P. J. Elving.** 1961. *Treatise on Analytical Chemistry*, p. 69-206, Vol. Part II., Vol. 1. Interscience, New York.
- Kreevoy, M. M. and J. Taft, R. W.** 1955. *J. Am. Chem. Soc.* 77:5590 ff.
- Martin, J. H. and A. M. Knevel.** 1965. *J. Pharm. Sci.* 54:1464 ff.
- Sadtler, T.** 1999. SANDA F.A.C.T.S Ce2000 Operational Manual. SANDA Corporation, 4005 Gypsy Lane, Philadelphia.
- Somiya, T.** 1927. *J. Soc. Chem. Ind. (Japan)* 30:106 ff.
- Spink, M. Y. and C. H. Spink.** 1968. *Anal. Chem.* 40:617 ff.
- Wasilewski, J. C. and D. C. Miller.** 1966. *Anal. Chem.* 38:1750 ff.
- Wasilewski, J. C. P.T.-S. Pei, and J. Jordan.** 1964. *Anal. Chem.* 36:2131 ff.
- Wilson, E. W., Jr.** 1968. *Thermometric Titration of Water with 2,2-Dimethoxypropane.* Dissertation, University of Alabama, Tuscaloosa.