The Micro-determination of Water*

AXEL JOHANSSON

*Department of Analytical Chemistry, Swedish Forest Products Research Laboratory,
Stockholm, Sweden*

The determination of water content is, in general, no problem with substances that can be heated to over 100° C. On the other hand, substances that decompose upon heating cause difficulty. The procedure generally used for such substances is drying over phosphoric anhydride in a vacuum. In many cases, however, such a moisture determination may take many days. In addition, if there are other volatile substances than water in the sample, both methods are inapplicable. In such cases the Karl Fischer method¹ has found use. It has been adapted by Levy, Murtaugh and Rosenblatt² for use in a micro-scale for the determination of water in *e. g.* penicillin. In work with such small amounts of water, the Karl Fischer reagent's greatest disadvantage, its hygroscopic nature, is greatly pronounced. The method, previously suggested by the author³, in which the Karl Fischer reagent is divided into two negligibly hygroscopic solutions**, should be especially well suited to micro-determinations. In this method, the sample is dissolved or suspended in a solution of sulphur dioxide in pyridine-methanol and titrated with a methanol solution of iodine. In macro-scale these titrations can be carried out in open vessels with negligible error. In micro-determinations, however, the preparation must be accomplished in such a manner that the moisture in the air does not affect the results. In order to achieve still greater accuracy, the method has been further modified so that the hydrogen iodide, formed by reduction of the iodine, is converted into iodic acid by means of bromine. The iodic acid

* This manuscript was completed in October 1947, and submitted to the Royal Institute of Technology, Stockholm.

** Recently, Seaman, McComas, Jr. and Allen⁹ have published a paper in which they, with the present author's previous publication³ as a starting point, propose a procedure for the determination of water. The present author wants to point out, however, that this procedure in all essential points is identical with that previously described³.

is then determined in the usual way by adding potassium iodide to the acidified solution and titrating the liberated iodine with thiosulfate. For every mole of water 12 equivalents of iodine are formed, or, in other words, 1.5 mg water corresponds to 10 ml 0.1 *N* thiosulfate. This procedure has the advantage that the moisture in the air has to be excluded only during the addition of iodine, while the actual titration can be made in a water solution.

It was, however, necessary first to examine the stoichiometry of the Karl Fischer titration. Fischer, himself, expressed the reaction as:

while Smith, Bryant and Mitchell Jr ⁴ maintain that sulfuric acid is not formed, but the reaction proceeds as follows:

In the first case, one mole of iodine consumes two moles of water, while, in the second case, only one mole.

Smith, Bryant and Mitchell Jr., as well as Almy, Griffin and Wilcox ⁵, who have also studied this problem, have not, in practice, been able to come closer to the theoretical value than a ratio of 1 mole of iodine to 0.7 mole water, due to the occurrence of side reactions during the storage of the reagent. Furthermore, part of the discrepancy from the theoretical value is due to the fact that water is taken up from the air. Exactly how much is taken up is difficult to determine by the original Karl Fischer method, and therefore the author's previously mentioned method should give more accurate results, as it reduces, to a large extent, the amount of water absorbed. It is impossible to obtain completely waterfree solutions, but their actual water content can easily be calculated from the water content of the reagents used.

In these experiments two solutions were used. One consisted of a solution of 100 g sulfur dioxide in a mixture of 500 ml pyridine and 500 ml methanol, and the other of 30 g iodine in 1000 ml methanol. The iodine had been dried in a dessicator over phosphoric anhydride. From the water content of the methanol before mixing, the iodine solution was calculated to contain 0.111 mg water per ml solution. The titer of the iodine solution was determined as follows: 20.00 ml of iodine solution was added to a solution of potassium iodide and titrated with 45.23 ml of 0.1047 *N* $\text{Na}_2\text{S}_2\text{O}_3$ solution. The iodine solution was therefore 0.2368 *N*. A confirmatory titration with 15.01 ml iodine solution consumed 33.93 ml of the $\text{Na}_2\text{S}_2\text{O}_3$ solution, which gave an iodine normality of 0.2366 *N*. The average value was therefore 0.2367 *N*.

Iodine solution was added from a burette to 10 ml of the sulfur dioxide solution, until the color changed from yellow to brown, that is, until the water in the sulfur dioxide solution was consumed. After the addition of 0.0536 g water, 26.80 ml of iodine solution

were needed to cause the same color change. Since the iodine solution contained 0.111 mg of water per ml, a total of 0.0566 g of water had been added. The calculated water content, from the iodine consumption, was 0.0571 g. This was calculated on the basis of two equivalents of iodine per mole water, which is in agreement with Smith, Bryant and Mitchell Jr's formel *.

In a similar test using 4.00 ml sulfur dioxide solution and a 0.0522 g water sample, 26.10 ml of the iodine solution was consumed, which corresponds to a water content of 0.0557 g as compared to the actual content of 0.0551 g. The small differences between the calculated and the actual water contents are probably due to the fact that the iodine also contained some moisture and that moisture is taken up by the solutions during mixing.

The titrated solution was diluted with water and neutralized with 99.10 ml of 0.1023 *N* sodium hydroxide solution, using thymolphthalein as an indicator. A blank, using 4.00 ml sulfur dioxide solution, to which iodine had been added to color change, consumed 68.85 ml of the same sodium hydroxide solution. The difference of 30.25 ml was equivalent to 0.0558 g water.

From these experiments it can be seen that the stoichiometry of the Karl Fischer titration is well defined. In order to increase the accuracy in the micro-determination of water, the hydrogen iodide formed is oxidized, as said before, to iodic acid, which is then determined in the usual manner. Naturally, at the same time, the iodine, which was used to convert the water in the sulfur dioxide solution, is also oxidized, yielding a relatively large and considerably varying amount of iodic acid. In order to eliminate this disadvantage a bromine solution can be used to consume this water instead of the iodine solution. It has been found that the bromine first reacts with the water in the same manner as the iodine, but later it also reacts with the sulfur dioxide pyridine solution. An excess of bromine is consequently not detrimental. On the other hand it is impossible to observe when all the water has been consumed. There is no color change, and even the dead-stop method is inapplicable. If, however, a few micro-drops of iodine solution are added first and then the bromine solution, the hydrogen iodide is oxidized to iodine, when all water has reacted, and the end point can be observed.

A p p a r a t u s

Foulk and Bawden's dead-stop method was used to indicate the endpoints. This procedure is based on the fact that if an electrical potential is placed between two electrodes in a solution, in this case in a pyridine and methanol solution of sulphur dioxide, a counter electromotive force is built up, which

* After the completion of this manuscript, Seaman, McComas, Jr. and Allen⁹ have reported the same results concerning the stoichiometry of the reaction.

balances the original potential, providing this is small enough. In a water solution this potential should be 10—15 millivolts, but in the Karl Fischer titration it is possible to go up to a value of 0.3 to 0.4 volts and to use a very simple apparatus (see Fig. 1 in (3)). When iodine is added in excess the electrodes are depolarized and the galvanometer is deflected. The titrating vessel consists of a 10 ml flask with two platinum electrodes fused into the glass. Immediately under the neck of the flask there is a side arm containing the sample. This sidearm may be closed with a ground glass stopper. The flask, itself, is equipped with a ground glass stopper having a 1 mm capillary (see D in Fig. 1). The iodine solution is added through the capillary by means of a glass injection syringe with a platinum needle. The syringe should be graduated in 0.1 ml.

Solutions

1) *Sulphur dioxide*, 100 g, is introduced into a mixture of 500 ml pyridine and 500 ml methanol. All chemicals should be as free of water as possible. The methanol is dehydrated in the usual manner with magnesium, and the sulphur dioxide is dried with silica gel. Water-free pyridine is prepared from a sample of known water content by addition of a little more than the calculated amount of acetyl chloride. The precipitate is removed by filtration through a glass filter. The acetic acid formed does not interfere, nor does the dehydroacetic acid formed from the excess acetyl chloride.

2) *Iodine*, 30 g, which has been dried in a desiccator over phosphoric anhydride, is dissolved in absolute methanol and diluted to 1000 ml.

3) *Bromine*, 0.2 ml, is dissolved in 10 ml absolute methanol.

Procedure

One ml of solution 1) is placed in the titration flask and two micro-drops of iodine solution are added. The sample is weighed in a little tube or any other suitable vessel and placed in the side arm of the flask. Both stoppers are inserted and the platinum electrodes connected to the dead-stop apparatus. The bromine solution is added through the capillary tube by means of a pipette having a capillary point, until the galvanometer gives a constant reading. The flask must be shaken constantly since the galvanometer otherwise returns to zero.

In this manner, all water in solution 1) and all water that may have adhered to the walls of the flask is removed. The sample is then added by inclining the flask. Soluble samples are titrated immediately with solution 2) which is added by means of an injection syringe until the galvanometer again deflects. Insoluble samples should be in a finely divided state so that the water can be

easily extracted. The syringe is read to the nearest 0.1 ml and the content of the titration flask is poured into a 300 ml flask and diluted with water to about 150 ml. Then 5 g sodium acetate and 0.25 ml bromine are added and the solution is strongly shaken until the bromine color remains permanent. The excess bromine is removed with a few drops of formic acid. The precipitate of pyridine bromides reacts very slowly with the formic acid. When the solution has become colorless, the remaining red precipitate, which contains only a very small amount of iodine, may be filtered off. One gram of potassium iodide is added to the filtrate, which is acidified and titrated with 0.1 *N* thiosulfate solution.

Calculations

$$\text{H}_2\text{O (mg)} = 1.501 A \cdot N - B \cdot W$$

A = ml thiosulfate

N = normality of thiosulfate

B = ml iodine solution

W = water content of iodine solution in mg/ml.

The water content of the iodine solution may, as mentioned above, be obtained from the water content of the methanol used. Since, however, the water content of the iodine solution may change during storage, the actual value may be determined in the following manner: Iodine solution is added to 5 ml sulfur dioxide solution until a brown color is obtained and then 20 ml methanol of known water content (about 0.2 %) are added. More iodine solution is added until another color change is observed. The titer of the iodine solution is determined by titration with 0.1 *N* thiosulfate. The water content of the iodine solution is then obtained as the difference between the amount of water added and the amount of water calculated from the titer of the iodine solution.

As can be seen from the above, it is not necessary to know the titer of the iodine solution. The accuracy of the procedure, however, depends on the exactness with which the iodine can be added to cause the change in potential. One drop from an injection syringe can be made very small, about 0.005 ml, depending upon how fine a needle is used. This volume corresponds to about 0.01 mg water. It is scarcely possible by this method to obtain a greater accuracy. As can be seen from the table below, the errors are generally somewhat larger.

Table 1. Micro-titration of water.

Substance	Added amount		Found mg H ₂ O	Difference
	mg	mg H ₂ O		
H ₂ O	3.92	3.92	3.88	— 0.04
„	4.36	4.36	4.34	— 0.02
„	2.80	2.80	2.82	+ 0.02
NaOAc, 3H ₂ O	8.31	3.30	3.26	— 0.04
„	1.94	0.77	0.80	+ 0.03
3CdSO ₄ , 8H ₂ O	2.67	0.50	0.51	+ 0.01

Example

Two micro-drops of iodine solution 2) were added to 1.0 ml of solution 1) and then bromine solution 3) was added until the potential changed, 0.2 ml were used. Water, 4.36 mg, weighed in a capillary tube, was introduced from the side arm of the flask. In reobtaining the change 2.30 ml of iodine solution were consumed. The contents of the flask were then treated as described above and titrated with 30.80 ml 0.1006 *N* sodium thiosulfate solution. This value corresponded to 4.65 mg water ($30.80 \cdot 0.1006 \cdot 1.501$). Since the water content of the iodine solution was 0.135 mg/ml, the found amount of water was $4.65 - 0.31 = 4.34$ mg.

The water content of the iodine solution was determined as follows: 10.00 ml of the solution, added to 10 ml of water containing a few grams of potassium iodide, consumed 23.42 ml 0.1006 *N* sodium thiosulfate. The normality of the solution was therefore 0.2356 *N*. For the titration of 20.00 ml methanol containing 56.94 mg water (2.847 mg/ml) 28.65 ml of the iodine solution were consumed. The water content of this solution was, therefore, as follows:

$$\frac{28.65 \cdot 9.008 \cdot 0.2356 - 56.94}{28.65} = 0.135 \text{ mg/ml}$$

AUTOMATIC TITRATION

As was stated before, the accuracy of the determination is completely dependent upon the exactness with which the amount of the iodine solution equivalent to the water content can be added. In order to facilitate this addition of iodine an apparatus was constructed in which the plunger in the syringe was operated by a motor. Furthermore, the dead-stop apparatus was so arranged that it stopped the supply of iodine solution after all water was consumed.

Description of apparatus

The worm-gear motor A (see Fig. 1), which together with the screw B operates the plunger in the syringe, is equipped with a double wound armature, so it can rotate in both directions. This was used to make the motor to stop instantaneously. If one electrical circuit is left in the system and the other is closed, the motor stops much more rapidly, than if all current is switched off

Fig. 1. Apparatus for automatic titration.

A. Motor	R_4 .	Resistance	2500 ohm
B. Plunge operator	R_5 .	»	20 000 ohm
C. Injection syringe	R_6 .	»	500 ohm wire wound
D. Titrating vessel	R_7 .	»	4000 » » »
E. Wheel for manual screw operation	R_8 .	»	150 » » »
F_1 . Condensor 0.1 micro F	R_9 .	»	150 » » »
F_2 . Electrolytic condensor 8 micro F	R_{10} .	Relay with	400 ohm resistance coil
G. Connection contacts	V_1 .	Tube	6F5
H. Lamp 6V, 0.3A	V_2 .	»	25L6
R_1 .	V_3 .	»	25Z6
R_2, R_3, R_9	S_{1-3}	Switches	

from the armature. By this method there is only a movement of a few degrees after the circuit has been closed. The screw, which has a one mm thread, rotates at a rate of 19 r. p. m. The screw can be uncoupled from the motor and manually operated with the wheel (E), to facilitate the filling of the syringe

The left side of the diagram consists mainly of an electronic relay, cf.⁷ A potential of approximately 0.2 volts exists between the electrodes in the titration vessel as long as all the water has not been consumed. However, as soon as there is an excess of iodine, and the electrodes depolarize, the negative grid potential decreases in the tube V_1 . The resulting increase in the plate current in the same tube causes an increased voltage drop in the resistances R_3 and R_4 . This voltage drop causes a decreased negative grid

potential in the tube V_2 and thus an increased plate current, which causes the armature of the relay to close the motor circuit. The relay is of the ordinary telephone type with two contacts. One contact closes one of the circuits of the motor and the other opens the short circuit at the lamp H.

Procedure

Titration with this apparatus can be accomplished in the following manner. One ml of sulphur dioxide solution is placed in the flask D and the electrodes are connected to G. Both switches S_1 and S_2 should be open. Two micro-drops of iodine solution are added and then bromine solution until the lamp H lights. The sample is introduced, whereby the relay moves and the light goes out. The needle of the syringe is inserted through the capillary tube into the titration vessel and the switches S_1 and S_2 are closed. The syringe should be inserted far enough so that the needle enters the solution. The motor then forces out the iodine solution as long as the relay is disconnected. After all water has been consumed the relay engages and the motor stops. This generally tends to occur first, just before the end-point is reached, due to a local excess of iodine. However, after this has been consumed the motor starts again. This generally occurs a few times before the motor stops definitely at the true endpoint. For determination of water in substances that are insoluble in the titrating liquids, it is convenient to use magnetic stirring and to let the apparatus add the iodine solution as the water is extracted from the sample. To prevent the syringe from leaking it is good to moisture the plunger with a drop of iodine solution. When the motor has stopped definitely, the contents of the vessel are removed and treated in the aforementioned manner.

By use of the automatic procedure it is possible to omit the determination of iodine by oxidation to iodic acid. The volume of iodine solution used can be obtained with great accuracy from the scale on the screw, which moves the plunger in the syringe. As was said before, each thread on the screw is 1 mm. Furthermore, the screw is provided with a scale, which makes it possible to read parts of a revolution. A suitable syringe volume is approximately two milliliters, which, in the syringe used by the author, corresponded to about 40 mm. Each revolution of the screw is therefore equivalent to 0.05 ml, and if twentieth parts of a revolution are read a satisfactorily accurate determination of volume will be obtained. The calibration may be accomplished by weight-delivery experiments or by determination of the plunger's area⁸. The diameter of the plunger should be measured in several directions, and an average value taken. The volumes calculated from these two methods coincide quite well.

The titration can, therefore, be accomplished in the following manner: One ml of sulfur dioxide solution is introduced into the titration vessel, whereafter the iodine solution is added until the relay makes contact. The scale is then read and the sample introduced. The titration is continued until the motor stops, and then the scale is read again. The iodine solution is standardized by titration of a weighed amount of water or measured volume of methanol of known water content. This standardization is conveniently accomplished in a macro-scale.

SUMMARY

A method for the micro-determination of water with a modified Karl Fischer method is proposed. The hydrogen iodide formed by this reaction is oxidized by bromine to iodic acid, which is determined in the usual way by titration, in water solution, with sodium thiosulfate solution. For every mole of water, twelve equivalents of iodine are formed, *i. e.* 1.5 mg water corresponds to 10 ml 0.1 *N* thiosulfate.

REFERENCES

1. Fischer, K. *Angew. Chem.* 48 (1935) 394.
2. Levy, G. B., Murtaugh, J. J., and Rosenblatt, M. *Ind. Eng. Chem. Anal. Ed.* 17 (1945) 193.
3. Johansson, A. *Svensk Papperstidn.* 50, no. 11 B (1947) 124.
4. Smith, D. M., Bryant, W. M. D., and Mitchell, Jr, J. J. *Am. Chem. Soc.* 61 (1939) 2407.
5. Almy, E. G., Griffin, W. C., and Wilcox, C. S. *Ind. Eng. Chem. Anal. Ed.* 12 (1926) 392.
6. Foulk, C. W., and Bawden, A. T. *J. Am. Chem. Soc.* 48 (1926) 2045.
7. Serfass, E. J. *Ind. Eng. Chem. Anal. Ed.* 12 (1940) 536.
8. Shaffer, Jr, P. A., Farrington, P. S., and Niemann, C. *Anal. Chem.* 19 (1947) 492.
9. Seaman, W., McComas, Jr, W. H., and Allen, G. A. *Anal. Chem.* 21 (1949) 510.

Received August 31, 1949.