

364. *A New Reagent for the Titration of Water.*

By R. BELCHER and T. S. WEST.

A new reagent for the determination of water in inert organic solvents is described. It consists of a solution of sulphur dioxide and bromine in chloroform, and it is used similarly to the conventional Karl Fischer reagent. Dioxan, benzene, pyridine, acetonitrile, and glacial acetic acid are less satisfactory than chloroform as solvent. The results obtained from the new reagent are more nearly stoichiometric than those given by the Karl Fischer reagent, and it appears to be more stable. The change in redox potential at the end-point of the titration is very sharply defined, and a visual end-point depending on the disappearance of the colour of bromine from solution is as satisfactory as the potentiometric end-point. The reagent is cheaper than the Fischer reagent. Its main disadvantage is that alcohols interfere with the determination of water, but in most cases where a preliminary extraction of moisture is necessary, alcohol can be replaced by dioxan. The reaction products formed between pyridine, alcohol, and the reagent have been identified, and an acid-base method for the determination of water, based on these observations, has been suggested.

MANY methods are available for the determination of water, but the only direct titrimetric method which has achieved wide usage is that of Karl Fischer (*Angew. Chem.*, 1935, **48**, 394) in which a solution of iodine, sulphur dioxide, and pyridine in methanol is used. The reaction of this reagent with water may be represented by $I_2 + SO_2 + H_2O \longrightarrow 2HI + SO_3$, but the freshly prepared reagent gives results of only approximately 80% of the theoretical value. After one month the proportion may drop to 50%, and in three months to 40%. This instability is the main drawback to the Fischer reagent.

We have examined some fifty reactions with a view to their development for the determination of water, but only one was found suitable, and this was based on the substitution of bromine for iodine in the Fischer reagent. Although this change had been suggested by Mitchell and Smith ("Aquametry," Interscience Publ., New York, 1948, p. 389) there is no record of its having been examined. The reaction is known to take place in aqueous medium according to the scheme $Br_2 + SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2HBr$, and has been used to dry pyridine before distillation (Johansson, *Acta Chem. Scand.*, 1949, **3**, 1058).

Methanol could not be used as solvent because it reacted vigorously with the other constituents. A pyridine solution of bromine and sulphur dioxide was prepared, which reacted vigorously with all the lower aliphatic alcohols as well as with water. This reagent showed promise, but proved unsuitable: its water equivalence diminished gradually and, after storage overnight even in a dark cupboard, it had entirely lost its reactivity and a highly crystalline, dark brown precipitate had settled. After purification, a light brown compound, $C_{10}H_{10}N_2Br_2$ was obtained which contained bromine and nitrogen, but no sulphur. The crude product $C_{10}H_9N_2Br \cdot H_2O$ decomposed without melting at *ca.* 300°.

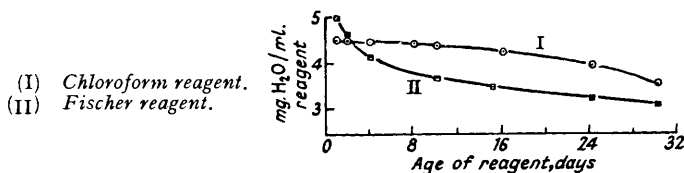
It was apparent from the instability of the reagent containing pyridine that any development of a direct method lay in the use of a solution of bromine and sulphur dioxide in an inert solvent such as benzene or chloroform, and the inclusion of the base in the solution of water to be titrated, rather than directly in the reagent solution as with the Karl Fischer reagent.

Anhydrous chloroform was found to be suitable for this purpose, for it dissolved bromine and sulphur dioxide to give a deep red solution which fumed in moist air, and was immediately decolorised on addition of excess of water in pyridine, with evolution of heat. Addition of anhydrous pyridine to the reagent solution caused an immediate diminution in the intensity of its red colour owing to formation of the addition compound between bromine and pyridine, but no further reaction was observed. On potentiometric titration of the reagent into a solution of water in pyridine, a steady potential was recorded after addition of the first few drops of titrant, and this was maintained till the end-point was reached, whereupon there was a sharp change in potential equivalent to 560 mv, and

simultaneous disappearance of the last trace of bromine colour afforded an excellent visual end-point. A reverse titration procedure was used (*i.e.*, the aqueous solution was run into a measured amount of reagent) because a better response was obtained from the polarised bi-platinum system. The spent reagent solution was water-white, and the products were completely soluble in the chloroform and pyridine, whereas, under the reverse conditions, precipitation of the reaction products occurred and a false end-point was sometimes obtained. Consequently, solutions of water of unknown concentration were analysed by careful addition to a measured excess of reagent, and back-titration of the excess with the standard solution of water in pyridine.

Stoichiometry, and Stability of the Reagent.—The reaction between the reagent and a standard solution of water in pyridine was approximately 90% of that required by $\text{Br}_2 + \text{SO}_2 + \text{H}_2\text{O} \longrightarrow 2\text{HBr} + \text{SO}_3$, so the reaction taking place in the organic solvent may be analogous to that shown to take place in the Fischer reaction (Smith, Bryant, Mitchell, *J. Amer. Chem. Soc.*, 1939, **61**, 2407), *viz.*, $\text{C}_5\text{H}_5\text{N}, \text{Br}_2 + \text{C}_5\text{H}_5\text{N}, \text{SO}_2 + \text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O} \longrightarrow 2\text{C}_5\text{H}_5\text{N}, \text{HBr} + \text{C}_5\text{H}_5\text{N}, \text{SO}_3$.

The new reagent therefore possesses the following advantages over the Fischer reagent. (i) It reacts more nearly quantitatively: 90% as compared with 80% for freshly prepared reagents. (ii) The change in potential at the end-point is more sharply defined. (iii) The visual end-point (red to water-white) is more easily observed than that (red-brown to pale brown) with Fischer's reagent. (iv) It has superior stability, as seen from the figure, which shows the change of water equivalence (mg. of water per ml. of reagent)



(I) Chloroform reagent.
(II) Fischer reagent.

with time for both reagents. (v) It is probably more economical, bromine being cheaper than iodine, especially per equivalent.

A selection of results obtained by titration of a standard solution of water in pyridine against the reagent is given below.

Water taken, mg. ...	2.50	5.00	7.50	10.00	12.50	15.00	20.00	25.00	40.00
Water found, mg. ...	2.50	5.02	7.52	10.00	12.50	14.98	20.00	24.99	40.00

In determinations where an alcohol is normally used to extract moisture from the substance under analysis, it would be necessary to substitute dioxan before using the present reagent because of its reactivity towards alcohols. The extract could then be diluted with pyridine, and the analysis carried out on an aliquot of solution. The moisture content of organic solvents not containing hydroxyl groups could be determined similarly by dilution with pyridine and titration against the reagent.

Other Solvents.—A solution of water in pyridine being used for analysis, preparations of the reagent in various organic solvents not containing alcoholic or phenolic groups were examined. In benzene, the reagent solution was deep red and the reaction with the water solution was rapid, the visual end-point being coincident with an excellent potentiometric end-point. The reaction itself was satisfactory, proceeding to the extent of approximately 85–90%, but the insolubility of the products constituted a disadvantage.

Glacial acetic acid readily dissolved bromine and sulphur dioxide together, but titrations of water in pyridine could not be effected because of a reaction between the constituents of the solution on addition of anhydrous pyridine. Titrations of water in glacial acetic acid containing sodium acetate were possible, however, but the reagent solution decomposed more quickly than the chloroform reagent. Although of little use for general purposes, this reaction might be useful for the determination of moisture in acetic acid and its homologues.

Anhydrous dioxan readily dissolved sulphur dioxide and bromine, forming a light

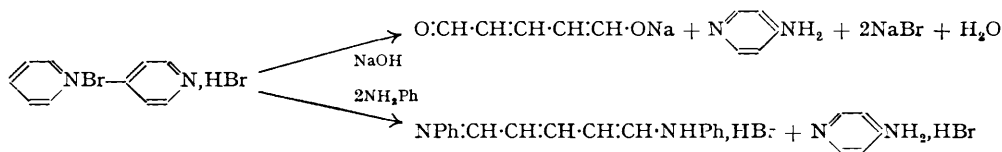
red solution which fumed in moist air. When this reagent was titrated with water in pyridine, two layers were formed : the lower layer appeared to contain most of the pyridine and practically all of the bromine and sulphur dioxide. Normally, dioxan and pyridine are miscible, and the presence of either bromine or sulphur dioxide alone does not cause separation of phases. When the polarised bi-platinum electrode system made contact with the upper layer only, no end-point could be detected potentiometrically until some considerable time after the lower red layer had been decolorised but, when the electrode system penetrated to the lower layer, reproducible electrometric end-points coincident with the visual end-points were obtained. The titration proceeded smoothly and rapidly with a sharp change in potential at the end-point, but the formation of insoluble products was an undesirable feature. The reaction was approximately 90% of the stoicheiometric value.

Anhydrous acetonitrile was the only solvent apart from chloroform which retained the reaction products in solution. The acetonitrile reagent was dark red, and its reaction with water in pyridine was rapid, both visual and potentiometric end-points being excellent and coincident. The spent reagent solution was colourless. Unlike the chloroform reagent, however, this solution of bromine and sulphur dioxide decomposed entirely after a few weeks, forming a black deposit.

All attempts to prepare a composite reagent containing bases other than pyridine (quinoline, quinaldine, aniline, piperidine, and morpholine) failed, the base reacting with the other constituents.

Reaction of the Reagent with Alcohols and Pyridine.—Reaction of the reagent with alcohols might yield a dialkyl sulphate or an alkyl bromide : $\text{Br}_2 + \text{SO}_2 + 2\text{R}\cdot\text{OH} \longrightarrow 2\text{HBr} + \text{R}_2\text{SO}_4$ or $\text{Br}_2 + \text{SO}_2 + 2\text{R}\cdot\text{OH} \longrightarrow 2\text{RBr} + \text{H}_2\text{SO}_4$. Proof that the alkyl sulphate was formed is given on p. 1776.

As stated on p. 1772, a decomposition product of the pyridine-containing solution had the composition $\text{C}_{10}\text{H}_{10}\text{N}_2\text{Br}_2$, which agrees with that of 4-1'-pyridylpyridinium bromide hydrobromide. The corresponding dichloro-compound was prepared by Koenigs and Greiner (*Ber.*, 1931, **64**, 1045, 1049) by reaction of thionyl chloride and pyridine. Our bromo-compound showed the behaviour characteristic of this type of compound, *viz.*, cleavage of the pyridine ring by cold dilute aqueous alkali to form the intensely yellow derivative of glutaconic dialdehyde. Furthermore, on reaction with aniline under reflux in alcohol, it afforded glutaconanil hydrobromide (anil-anilino-form) :



This compound was prepared by Zincke (*Annalen*, 1904, **333**, 317) by a different route. Qualitative tests using α -naphthylamine in place of aniline gave a bright scarlet precipitate, and 4-1'-pyridylpyridinium hydrochloride reacted in identical manner.

This behaviour of the reagent with pyridine and aliphatic alcohols parallels that of sulphuryl chloride with these substances and suggests that a mixture of bromine and sulphur dioxide behaves in certain respects as sulphuryl bromide would be expected to react. Sulphuryl bromide has never been isolated, but might exist to a slight extent in equilibrium in the reagent solution. Sulphuryl iodide would be well nigh incapable of existence in even equilibrium amounts and this sequence of stability may explain why the bromine reagent reacts with alcohols while the conventional Fischer reagent does not.

Acid-Base Method for Determination of Water.—Although water liberates 4 equivs. of acid per molecule of reagent (the SO_3 behaves as a dibasic acid on addition of water), alcohols liberate only two. We have applied this reaction in developing an alternative, simple alkalimetric method using a common acid-base indicator. An excess of reagent was allowed to react with the solution of water in pyridine, and the excess was destroyed by addition of an excess of anhydrous alcohol. The acid thus formed was titrated with

standard alkali, and from this titre was deducted the titre obtained from reaction of an identical amount of reagent with excess of anhydrous alcohol. The net titres thus obtained were strictly proportional to the weights of water taken.

The reagent solution used for this determination contained an excess of bromine, since it was difficult to titrate accurately the weak sulphurous acid formed by the excess of sulphur dioxide present in the former reagent solution. The excess of bromine then remaining in the solution was destroyed by addition of phenol before titration.

The method is advantageous in that only simple apparatus is required and that titration follows conventional lines; its drawbacks are the necessity to prepare anhydrous alcohol to react with the reagent, and the fact that the titre for water is obtained as a small difference between two relatively big titres. This is due to the stoichiometry of the reactions, for the excess of reagent produced 4 equivs. of acid per mole of bromine in reaction with water, whereas the blank produced 2 equivs. of acid per mole of bromine on reaction with alcohol. Since a two-fold amount of reagent was used, the equivalence of one mole of water was found as the difference between (4 + 2) and 4 equivs. of acid.

Other Reactions investigated.—The following reaction is cited as an example of others that we examined for suitability for the determination of water. Cupric salts are reduced by aqueous sulphur dioxide as follows: $2\text{CuCl}_2 + \text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Cu}_2\text{Cl}_2 + 2\text{HCl} + \text{H}_2\text{SO}_4$. A reagent prepared to contain anhydrous cupric chloride and an excess of sulphur dioxide in certain proportions of anhydrous methanol and pyridine reacted quite rapidly with a solution of water in methanol. Although reaction was slower than that with the Karl Fischer reagent under similar conditions, excellent end-points were obtained both visually and potentiometrically and titrations were reproducible. The speed of reaction with water decreased as the reagent solution aged, however, and after 5 days it was useless.

EXPERIMENTAL

Preparation of Reagent.—In chloroform dried by redistillation from phosphoric oxide, pure bromine was dissolved (15 ml. in 750 ml.) and the tightly stoppered container was chilled in ice-salt. Liquid sulphur dioxide (20 ml.) was added rapidly, with gentle shaking, and the volume of the solution adjusted to approx. 1 l. with anhydrous chloroform; 1 ml. of this solution was equivalent to approx. 5 mg. of water.

The water solution was prepared by dissolving 5 g. in 1 l. of anhydrous pyridine (prepared by distillation of pure reagent from phosphoric oxide). The equivalence of this solution was checked in the normal way by titration with a solution of Karl Fischer reagent which had been standardised against sodium acetate trihydrate

Titration Procedure.—The reagent and the water solution were placed in the reservoirs of a conventional Fischer-type apparatus. A Mullard "magic-eye" potentiometer unit was used to record the end-point of the titration in conjunction with an electrode system of two stout platinum wires led into the titration vessel through a ground-glass stoppered side arm. Stirring of the solution was effected by dry nitrogen. An appropriate amount of reagent solution was slowly delivered into the titration vessel from the burette mounted on the reagent reservoir, and the potentiometer system was connected to the mains supply with the switch in the polarising position. A few drops of the water solution were added slowly, and the solution gently stirred. Over-rapid addition of reagent to the titration vessel or of pyridine solution to the reagent caused loss of bromine by volatilisation due to the heat of reaction; once sufficient pyridine is present, however, there is no danger of loss of bromine in this way. The potentiometer unit recorded a steady potential as more water solution was added, and the colour slowly faded to pale yellow. The titration was finished dropwise, the solution being thoroughly stirred with dry nitrogen after the addition of each drop. At the end-point, the "eye" of the potentiometer unit closed sharply and could only be opened by applying a balancing voltage of some 560 mv. Simultaneously the last trace of yellow colour disappeared, leaving a transparent, colourless solution.

Reaction Products formed with Ethanol and with Pyridine.—*Isolation of ethyl sulphate.* Equivalent amounts of bromine and sulphur dioxide were added to anhydrous ethanol. A slight excess of sulphur dioxide was added if necessary to discharge the colour of bromine from the solution, and the excess of sulphur dioxide and alcohol was removed at a low temperature under reduced pressure. When water was added to the residual liquid, a pale yellow, oily layer separated, which was washed several times with dilute alkali and distilled water, dried

(Na_2SO_4), and distilled *in vacuo*. The purified liquid had the characteristic odour of ethyl sulphate; b. p. 208° (decomp.) [Found: C, 31.1; H, 6.6; S, 20.6. Calc. for $(\text{C}_2\text{H}_5)_2\text{SO}_4$: C, 31.2; H, 6.5; S, 20.8%].

Isolation of 4-1'-pyridylpyridinium bromide hydrobromide. This substance was obtained from a reagent solution of 15 ml. of bromine and 20 ml. of sulphur dioxide in 1 l. of pyridine as a dark brown, crystalline deposit after the solution had been kept overnight. These crystals were insoluble in all the common solvents except alcohol and water, in which they were extremely soluble. Recrystallisation from alcoholic hydrobromic acid (charcoal) afforded pale brown needles, m. p. 160° (decomp.) (Found: C, 37.8; H, 3.1; N, 8.7; Br, 50.4. $\text{C}_{10}\text{H}_{10}\text{N}_2\text{Br}_2$ requires C, 37.8; H, 3.2; N, 8.8; Br, 50.3%). When an alcoholic solution of equivalent amounts of the above *compound* and aniline were refluxed for $\frac{1}{2}$ hr., an intensely red solution was obtained which deposited red crystals on cooling. Recrystallised from alcohol several times, these had m. p. 168° . Zincke (*loc. cit.*) gave m. p. 167° (Found: C, 62.1; H, 5.1; N, 8.4; Br, 24.3. Calc. for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{Br}$: C, 62.0; H, 5.2; N, 8.5; Br, 24.3%).

Acid-Base Method for Determination of Water.—The reagent used for this determination was prepared as described previously except that the quantities of bromine and sulphur dioxide were 28 and 16 ml., respectively, per l. Ethanol was rendered anhydrous by distillation from calcium. A measured excess of the reagent was delivered into a dry iodine flask and a few ml. of the solution of water in pyridine were carefully added. The flask was stoppered, and the contents gently mixed; after 1 min. anhydrous ethanol (1–2 ml.) was added, and the mixture vigorously shaken till the fumes in the flask had redissolved. The solution was then freed from bromine by addition of a few crystals of phenol, and the total acidity was found by titration with a solution of sodium ethoxide in ethyl alcohol, with phenolphthalein as indicator. (Under these conditions, the added phenol showed no acidity and could not be titrated either thus or by use of a pH meter.) The blank value was found by titration of an identical amount of reagent treated similarly, but without addition of the water solution. The difference in the two titres gave the titre equivalent to the amount of water reacting.

Thanks are offered to Mr. D. Skidmore and Miss E. Fowler for carrying out the organic microanalyses, and to Monsanto Chemicals Ltd. for a grant in aid of this research.

CHEMISTRY DEPARTMENT, THE UNIVERSITY,
EDGBASTON, BIRMINGHAM, 15.

[Received, September 2nd, 1952.]