442. *A Titration Method for the Determination of Water.*

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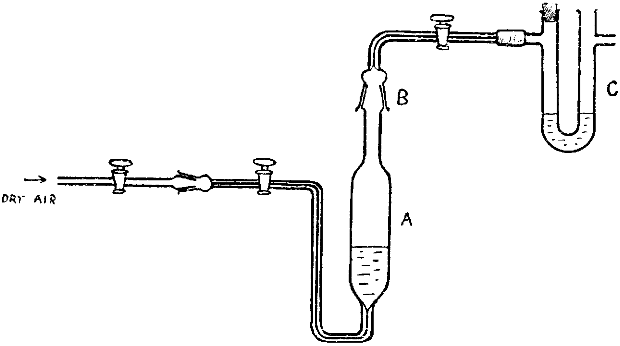
Most methods for determining water depend upon either the gain of weight of hygroscopic substances or the loss of weight of the system investigated. Neither these nor physical methods, applied usually to traces of water in organic liquids, give accurate results for small proportions. Moreover, none of the chemical methods (for references, see Wilson, *J. Amer. Chem. Soc.*, 1921, **43**, 710; Rosenbaum and Walton, *ibid.*, 1930, **52**, 3568) is as accurate and convenient as the one now to be described.

The method depends upon the reaction of water with α-naphthoxydichlorophosphine [referred to subsequently as (N)], $C_{10}H_7\cdot O\cdot PCl_2 + 2H_2O \longrightarrow C_{10}H_7\cdot O\cdot P(OH)_2 + 2HCl$,* the hydrogen chloride being removed by a current of dry air, absorbed in water, and titrated. Other substances, *e.g.*, high-boiling acid chlorides and double compounds of aluminium chloride with organic substances, were not suitable.

The reagent was easily prepared from α-naphthol and PCl_3 (Kunz, *Ber.*, 1894, **27**, 2560), an all-glass apparatus being used throughout. After one distillation in vac. it was obtained as a colourless, non-fuming liquid, b. p. 180° ± 1°/18 mm. Traces of PCl_3 were removed by heating to 100° in a current of air dried with P_2O_5.



When (N) is added to liquid water the reaction is slow, doubtless owing to the small mutual solubility of the two phases, for in C_6H_6 solution the reaction is practically instantaneous.

The apparatus used is shown in the fig. (N), dissolved in a suitable solvent, was contained in the vessel *A*, and the sample to be analysed was introduced

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* The further hydrolysis to $C_{10}H_7\cdot OH + P(OH)_3$ (Kunz, *loc. cit.*) does not occur in presence of excess of (N).

through *B*. The HCl formed was removed by a current of air dried with P_2O_5, and absorbed in H_2O at *C*.

Before a determination, it is necessary to remove any HCl formed by H_2O present in the solvent or apparatus. The air current was passed (50—100 c.c./min.) until the rate of formation of HCl (as measured by periodic titration of the contents of *C*) had decreased to a very small const. value (12—24 hr.), corresponding to the v.p. of (N); several consecutive determinations could then be carried out without refilling with (N). The sample was added and the current of air again passed until a const. rate of HCl formation was reached (this rate is not in general the same as that found before the determination). The amount of H_2O is then given by the total acid titre minus a small correction for the v.p. of (N).

In order to derive this correction, it is necessary to maintain the velocity of the air current approx. const. during the whole of each expt. This was secured (to within 5%) by using a compressed air plant automatically regulated to const. press. The solvent used was PhBr, which does not evaporate appreciably under the conditions of expt. The correction was then calc. by multiplying the const. rate of acid formation at the end of the expt. by the duration of the expt.: it never amounted to more than a few units %, and the results show that this method of calculation is adequate.

In order to test the accuracy of the method, known amounts of H_2O were added from a weight pipette. The results were :

	(*a*).	(*b*).	(*c*).	(*d*).
H_2O, added (g.)	0·0623	0·0416	0·0364	0·0251
H_2O, found (g.)	0·0624	0·0413	0·0365	0·0250

Determinations (*a*) and (*b*) were carried out successively with the same (N), and (*c*) and (*d*) with a fresh portion. After addition of the drop of water, the apparatus was kept for 30 min. with occasional gentle shaking before passage of the air current, in order to ensure complete solution. The details for determination (*a*) follow :

> 1 c.c. (N) + 5 c.c. C_6H_5Br in apparatus. Air passed for 24 hr. HCl absorbed during last 4 hr. = 0·25 c.c. of 0·1027*N*-NaOH = 0·06 c.c./hr. Water added; successive titres then :

Time, hr.	2	6	12	24	34
Titre, c.c.	27·30	6·15	1·05	0·75	0·65
Rate, c.c./hr.	13·65	1·03	0·18	0·063	0·065
				0·064	

> Total titre after 12 hr. = 34·50; correction = 12 × 0·064 = 0·77; corr. titre = 33·73. Water found = 0·03373 × 0·1027 × 18·02 = 0·0624 g.

As an example of the application of the method to the determination of yet smaller quantities of H_2O in solution, some results obtained with moist C_6H_6 are given. In order to obtain const. H_2O content, the C_6H_6 was rotated with Na_2SO_4 and $Na_2SO_4,10H_2O$ for 48 hr. at 20°. Samples were then removed by a pipette (delivering 8·81 ± 0·02 g. of C_6H_6 at 20°) fitted with a cotton-wool plug, suction being applied through a $CaCl_2$ tube. The vol. of liquid was kept approx. const. by saturating the air with C_6H_6 vapour at room temp. before it entered the P_2O_5 tube.

	(*a*).	(*b*).	(*c*).	(*d*).	(*e*).
H_2O found (mg.)	4·03	4·03	4·06	4·05	4·06
Correction applied (%)	14·6	26·7	8·2	14·8	2·5

In (*a*), (*b*), (*c*), and (*d*) the correction was made unnecessarily large, by using a large excess of (N) and a large vol. of PhBr, but the concordance of the results shows that no systematic error is introduced thereby. The mean value obtained for the concn. of H_2O in equil. with $Na_2SO_4,10H_2O + Na_2SO_4$ (0·00405 g. per 8·82 g.) can be employed to calculate the solubility of H_2O in C_6H_6 at 20°, the v.p. of H_2O over the solution being assumed to be proportional to its concn. over the small range in question. The v.p. of the hydrate pair being 13·38 mm. (Baxter and Lansing, *J. Amer. Chem. Soc.*, 1920, **42**, 419; cf. Wilson, *loc. cit.*), the value obtained is 0·0601 g. per 100 g., which lies between the two most accurate previous determinations, 0·0608 (Hill, *ibid.*, 1923, **45**, 1143) and 0·0573 (Rosenbaum and Walton, *loc. cit.*).

When this work was completed, it was found that Lindner (*Z. anal. Chem.*, 1925, **66**, 305) had described a similar method for determining the H_2O formed in ultimate analysis. He used α-naphthyldichlorophosphine oxide, $C_{10}H_7{\cdot}POCl_2$, at 100°, but this compound (L) is not so suitable as (N). For instance, at room temp. it reacts with H_2O dissolved in C_6H_6 so slowly that only a few units % of the theor. amount of acid are formed after 12 hr., and the use of a higher temp. is inconvenient with such a solvent. α-Naphthoxydichlorophosphine oxide ($C_{10}H_7{\cdot}O{\cdot}POCl_2$; Kunz, *loc. cit.*) also reacted much too slowly.

A few rough expts. were carried out to discover whether H_2O vapour present in a current of gas could be quant. converted into HCl by using (N) at room temp. in place of the more difficultly accessible (L) at 100°. A measured vol. of air satd. with H_2O vapour at room temp. was passed through a solution of (N) in PhBr in the apparatus described, and the evolved HCl absorbed in H_2O. The remainder of the HCl formed was removed by a current of dry air, and the amount of H_2O calc. as before. Three expts. with 500 c.c. of air satd. at 21·3° gave 9·80, 10·80, and 10·03 mg. of H_2O. In the first two expts. 1 c.c. of (N) was dissolved in 5 c.c. of PhBr, and in the last, 0·3 c.c. in 5 c.c. The calc. H_2O content of the air is 9·95 mg., so that, in spite of the short period of contact between the gas and the solution, the yield of HCl was quant. within the limits of uncertainty as to the exact vol. and humidity of the air.

For an approx. determination of the H_2O content of an organic liquid, it is sufficient merely to pass the air current for a few hours, and titrate the HCl thus evolved without applying any correction. The method can, of course, only be used with non-hydroxylic solvents.

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