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TRANSACTIONS

1—THE DETERMINATION OF THE ACETIC ACID YIELD OF ACETYLATED CELLULOSES

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A. INTRODUCTION AND SUMMARY

The importance of the mean acetic acid yield of acetylated celluloses in influencing the solubility and the dyeing and electrical properties of the materials has always been realised, and numerous methods for its determination have been advocated. For the most part these rely either on acid hydrolysis of the ester followed by determination of the liberated acetic acid, or on alkaline hydrolysis with subsequent titration of the excess alkali. Summaries of the literature have been presented by Marsh and Wood[1], and Murray, Staud and Gray[2]; more recently Genung and Mallat[3] have compared the Eberstadt alkaline hydrolysis and the Ost distillation methods.

It seems generally accepted that the use of alkali to effect hydrolysis is to be preferred, and most of the recent work is devoted to modifications designed to overcome theoretical objections or to apply to a particular material. The present authors advocate the use of alkali as a hydrolysing agent particularly for routine analysis, and they prefer the methods described below to that published from these laboratories by Parsons[4] in 1933.

The methods employ hydrolysis with sodium hydroxide solution in the presence of sodium chloride for the evaluation of acetate rayons, and hydrolysis with potassium hydroxide in the presence of alcohol for cellulose triacetates or samples difficult to wet or to hydrolyse. Their application to dyed materials which give coloured solutions has been accomplished by the addition of carbon tetrachloride before titration, when in general the dye is absorbed by the carbon tetrachloride, leaving an upper aqueous layer fairly free from colouring matter.

B. EXPERIMENTAL

Method 1. For Undyed Acetate Rayon

The obvious method of hydrolysing the cellulose acetate with a known amount of sodium hydroxide and determining the excess alkali by titration with standard acid was found to be unsuitable owing to absorption of alkali by the cellulose, which resulted in a poor end-point. This was improved by adopting the usual device of adding a known amount of acid, and after a suitable period of time determining the excess acid by back-titrating with standard alkali. Even this modification was not a sufficient improvement owing to the fact that the regenerated cellulose was in a highly swollen condition, being often in the form of gelatinous lumps that retained the reagents and so hindered accurate titration. Glycerol was found to minimise the

swelling, but the addition of sodium chloride eventually proved to be the most satisfactory means of preventing the cellulosic material from losing its fibrous form.

The experimental technique adopted is as follows:—About 0·2-0·4 g. of the acetate rayon is accurately weighed and its dry weight determined either by drying or by making a moisture content determination on a separate sample (drying for at least 3 hours at 110° C. has no effect on the final result). The material is transferred to a stoppered conical flask, 5 c.c. of saturated sodium chloride solution are added, and 10 c.c. of N-sodium hydroxide run in. The conditions of hydrolysis can be varied to suit convenience or urgency, the flask being left either over-night at room temperature or for a shorter time not less than two hours. On completion of the hydrolysis, 10 c.c. of N-sulphuric acid are added, and after half an hour the solution is titrated with N/10-sodium hydroxide, phenolphthalein being used as indicator. Duplicate determinations and blank experiments are run, and the blank value is subtracted from the observed titrations. The normal alkali and acid solutions do not require to be accurately standardised, but to ensure a positive "blank" the acid should be slightly more concentrated than the alkali. The acetic acid yield is defined as the weight of acetic acid produced by the complete hydrolysis of 100 g. of dry cellulose acetate, and is calculated according to the formula:—

$$\text{Acetic acid yield} = \frac{0{\cdot}6 \times f \times (T - t)}{W}$$

where f = factor of the N/10 NaOH

T = actual titre in c.c.

t = blank titre in c.c.

W = dry weight of cellulose acetate used, in grams.

The N/10-sodium hydroxide is standardised against potassium hydrogen phthalate (AnalaR reagent).

Some results obtained by this method are given below, all the figures being the means of duplicate determinations. In order to determine the time required for complete hydrolysis, samples of a commercial acetate rayon were submitted to the standard procedure at 25° C. for various times. The results in Table I indicate that hydrolysis is substantially complete after 2 hours, so that the over-night treatment generally adopted is amply sufficient.

Table I

Time of hydrolysis (hours)	½	1	2	3	6	17½	24	41½
Acetic acid yield, %	45·4	52·5	53·5	53·5	53·1	53·2	53·6	53·3

The method yields accurate results in the analysis of mixtures obtained by adding known amounts of standard acetic acid solution to viscose rayon. Addition of cellulose seemed to increase slightly the apparent amount of acid present in the solution (possibly due to the carboxyl groups in the regenerated cellulose), but the effect is negligible for practical purposes. Table II illustrates these results.

Table II

Weight of dry cellulose added, g.	0	0·0960	0·1832	0·2714	0·3581
Weight of acetic acid added, g.	0·1526	0·1526	0·1526	0·1526	0·1526
Weight of acetic acid found, g.	0·1520	0·1520	0·1519	0·1529	0·1532

In each determination the weight of acid found agrees with that added to within 0·5 per cent., and the experimental error may be regarded as being of this order.

No error was introduced by varying the amount of acetate rayon from 0·1 to 0·4 g. (Table III).

Table III

Weight of dry cellulose acetate used, g.	0·1171	0·1965	0·2843	0·3933
Acetic acid yield, %	54·0	54·5	54·4	54·2

Heating the acetylated cellulose with alkali in order to increase the speed of hydrolysis is not to be recommended because other acidic products are formed, as was also noted by Genung and Mallat[3]. For instance, viscose rayon treated with N-sodium hydroxide at 40° C. and at 70° C. for 1 hour gave apparent acetic acid yields of 1·6 per cent. and 4·8 per cent., respectively, whilst a sample of acetate rayon hydrolysed at 100° C. for 1 hour showed an acetic acid yield of 57 per cent.

The method described above can also be satisfactorily applied to commercial samples of cotton acetylated to approximately 30 per cent. acetic acid yield (Cotopa 30). The figures (obtained at room temperature) given in Table IV illustrate this; it should be noted, however, that with such materials it is not really necessary to add salt, for the fibres do not swell greatly in alkali.

Table IV

Time of hydrolysis (hours) ...	½	1	2	4	6	17	48	168
Acetic acid yield, %	24·2	26·6	26·5	27·6	27·9	27·8	27·5	27·5

Method 2. For Dyed Acetate Rayon

In routine work dyed materials are frequently encountered which on hydrolysis so colour the solution that titration in the ordinary way is impossible. The alternative procedures of stripping the dye from the material before making the determination or of doing an electrometric titration are extremely inconvenient, and the method here described imposes but little alteration of the existing technique and requires no extra time.

The analytical method is identical with that described above for undyed yarns as far as the actual titration stage, when 15 c.c. of carbon tetrachloride are added to the flasks (including the blanks), which are then stoppered, shaken vigorously for about half a minute, and the titration continued as before. Carbon tetrachloride is a dense non-inflammable liquid which generally absorbs practically all the dye from the aqueous solution and forms a separate layer at the bottom of the flask. Further dilution with water may be necessary if complete absorption of dye from the aqueous layer has not taken place. It is helpful in these titrations to support behind the titration flask a piece of mirror so tilted that the flask can be seen from the side; with this arrangement the coloured carbon tetrachloride layer does not interfere with the perception of colour change in the aqueous layer. Phenolphthalein can be used as indicator in all experiments except those in which a pink or red aqueous solution remains after carbon tetrachloride extraction. Here it is advisable to employ Bromthymol Blue (0·5 per cent. solution in 20 per cent. ethyl alcohol, 80 per cent. water) which is yellow in acid solution, passes through green, and then suddenly changes to deep blue. The green colour here serves to indicate the proximity of the end-point.

Application of this method to undyed samples of acetate rayon showed that adding carbon tetrachloride in no way altered the value of the acetic acid yield. The method was then tested on some fifty samples of acetate rayon dyed with representatives of the following classes of dyes:—Artisil, Cellitazol, Celliton, Cibacet, Dispersol, Duranol, Ionamine, Setacyl, Solacet, and S.R.A. Most of the shades were heavy, and with at least half of them the ordinary methods would have failed. Acetate rayons hydrolysed and dyed with direct dyes, samples of vat, azoic, and direct-dyed viscose rayon and cotton, and samples of acetylated cotton dyed with vat and acetate rayon colours have been tested successfully, although in many of these there was but little discoloration of the solution. In addition, however, this method was successfully applied to various samples of acetylated cellulose which gave very dark solutions on hydrolysis. No claim is made that the proposed modification will always allow the end-point of the titration to be detected with a visual indicator, but so far no materials have been encountered to which the method could not be applied.

The used carbon tetrachloride may be purified by the usual methods of distillation, or more simply by shaking with aluminium oxide, activated charcoal, or silica gel, and filtering. A second shaking with the solid will produce a perfectly clear filtrate. Aluminium oxide and activated carbon are more satisfactory than silica gel, and of these the former is to be preferred in that after roasting it may be used again.

Method 3. For Materials Difficult to Hydrolyse

Certain types of acetylated cellulose, such as cellulose triacetates and fibrous, highly-acetylated cottons, are not easily hydrolysed, and it seemed desirable to investigate an analytical method for these materials since they are becoming more widely used, particularly in the electrical insulation field. The experimental technique described below follows the same general principles as Method 1. From work done in these laboratories it has been shown that potassium hydroxide solutions hydrolyse cellulose acetate rayons more rapidly than sodium hydroxide solutions of the same normality, and consequently N-potassium hydroxide is employed in this method as the hydrolysing agent. One other essential requirement is to ensure rapid and complete wetting of the acetylated cellulose, and this is accomplished by dissolving the alkali in a medium composed of equal volumes of water and methyl or ethyl alcohol.

The technique employed is identical with that described for Method 1 except that N-potassium hydroxide in the water/alcohol solvent is used as the hydrolysing agent, and no salt is added. Dilution with water before titrating is advocated, otherwise the alcohol may cause slight fading of the indicator. This method can of course be used for secondary acetate rayons, and by using it for these materials the time of hydrolysis can be reduced to about 1 hour.

The time required for complete hydrolysis of secondary acetate rayon was found by using the technique of Method 3 on 0·25 g. samples of a commercial material for various times at 25° C. The results in Table V indicate that hydrolysis is substantially complete after half an hour.

Table V

Time of hydrolysis (hours)	½	1	2	3	6	17½	24	40½
Acetic acid yield, %	53·4	54·0	53·5	53·7	53·6	53·6	53·3	53·8

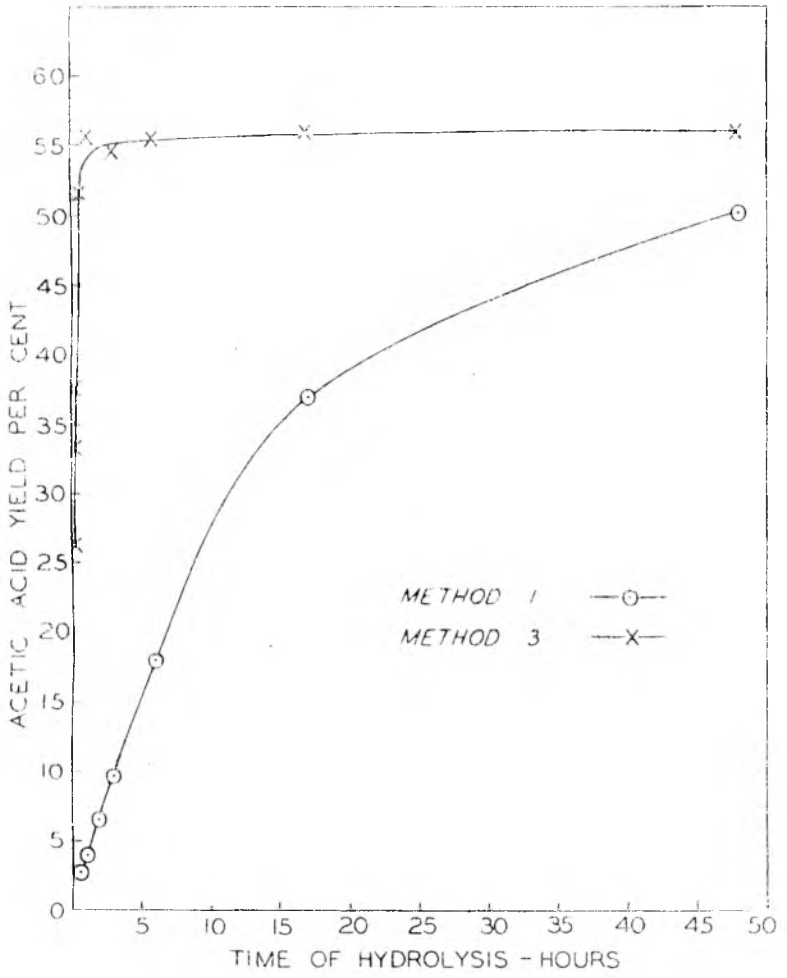

Fig. 1

Method 3 was, however, developed for the rapid hydrolysis of difficultly hydrolysable materials, and to test it for this purpose Methods 1 and 3 have been compared by applying them to a fibrous, highly-acetylated cotton. The results in Table VI and Figure 1 show the great advantage of Method 3 for this purpose, and emphasize the slowness of aqueous sodium hydroxide as a hydrolysing agent in this connection. The results were obtained at room temperature.

Table VI

Method 1		Method 3	
Time (hours)	Acetic acid yield, %	Time (hours)	Acetic acid yield, %
0·5	2·6	0·083	26·5
1·0	4·0	0·167	33·5
2·0	6·6	0·25	37·6
3·0	9·8	0·5	51·7
6·0	18·1	1·0	55·2
17·0	37·2	3·0	54·7
48·0	50·1	6·0	55·4
168·0	55·5	17·0	56·1
		48·0	55·9
		168·0	56·7

From a consideration of Tables I, IV, V and VI it is clear that for secondary acetate rayons and partially esterified cottons Method 1 will cause complete hydrolysis in 2 and 4 hours, respectively, whilst Method 3 needs only 1 hour. It is emphasized that for routine work, however, where samples of different properties are encountered and where dilution of the hydrolysing alkali often occurs through washing the cellulose material down the sides of the flask, an over-night hydrolysis is to be preferred. For such an over-night treatment, dilution with 20 c.c. of water has no effect on the final result.

REFERENCES

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