STUDIES IN OXYCELLULOSE

Part II. The Estimation of -COOH Groups in Cellulosic Materials

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The absorption of different metal ions from aqueous solutions of their salts has been recognized by Witz[1] to be an outstanding property of oxycelluloses. He has also observed the absorption of organic cations from aqueous solutions of basic dyes such as Methylene Blue.

In the case of purified cellulose and oxycelluloses this base exchange capacity can be explained as due to the carboxylic acid groups present and may be represented by the following equilibrium:

$$R.COOH + M^+ \leftrightarrows R.COOM + H^+ \qquad (1)$$

A thorough study of base-exchange properties of cellulose has been made by Walker and Quell[2] and later by Davidson.[3] The latter has found that Methylene Blue ion has got the highest affinity and that silver calcium and barium ions come next.

Though the base exchange reactions are easily reversed,[2] it is found that polyvalent ions are retained with greater tenacity than alkali metal ions.

Perhaps the first attempt to estimate the acidic groups in cellulose has been made by Schwalbe and co-workers,[4] who tried direct titration with dilute caustic soda, as well as absorption of barium from barium hydroxide solutions, the figure being corrected for ash alkalinity.

Instead of titrating the carboxylic acid groups in oxycellulose directly, Lüdtke[5] suspends the oxycellulose in calcium acetate solution and titrates the acetic acid formed with dilute caustic soda using phenolphthalein as indicator. Lüdtke's method has been modified in different ways by subsequent investigators, by Heymann and Rabinov,[6] by Kenyon and co-workers,[7, 8, 9] and by Davidson.[3]

First attempt to determine the acidic groups in cellulose by the conductometric method has been made by Schmidt and co-workers,[10] and later modified by Heymann and Rabinov.[6]

Neale[11] gives sodium chloride preference over calcium acetate and estimates the acid liberated by addition of an excess of dilute alkali followed

by back titration with dilute acid using Bromo-Cresol-Purple as the indicator. Neale and Stringfellow's method has been applied by Nabar, Scholefield and Turner[12] to their studies of hypochlorite oxycelluloses.

The observation of Witz[1] that oxycelluloses possess affinity for basic dyes has led to the development by Clibbens and co-workers[13] of the Methylene Blue absorption method for the estimation of acidic groups in cellulosic materials. Weber[14] has attempted to put this semiquantitative method on a quantitative basis. However, Davidson[3] has shown both by theoretical discussion and practical investigation that the above method is impracticable and has modified it in such a manner that stoichiometric results are obtained.

The other important ion-exchange reaction which has been utilised for the determination of carboxylic acid content of cellulosic materials is that of absorption of silver ions from aqueous solutions of silver salts of weak acids. The method has been first proposed by Sookne and Harris,[15] and later used by Harris and collaborators[16] in their studies of hypoiodite oxidized hydrocelluloses and periodate-chlorite oxycelluloses. In a recent paper, Davidson[3] has studied the absorption of silver ions from aqueous solutions of various silver salts and has given silver meta-nitrophenolate preference over the *o*- and the *p*-isomers.

Evolution of carbon dioxide on boiling oxycelluloses with dilute hydrochloric acid has been first utilized by Heuser and Stöckigt[17] to estimate the carboxylic acid content. Kenyon and coworkers[7, 8, 9] have utilized this method in their studies of nitrogen dioxide oxycelluloses. Nevell,[18] in a recent paper, has studied the rate of evolution and the total amount of carbon dioxide evolved in case of various oxycelluloses, and has shown that in case of dichromate oxycelluloses the carboxylic acid groups present are of the uronic acid type, while in the case of alkaline hypobromite oxycelluloses about 40% of the carboxylic acid groups are of the uronic acid type. He has also shown[18] that, Alginic acid is a polyuronide.

From the foregoing it can be seen that the methods available at present for the determination of carboxylic acid content of cellulosic materials are five, *viz.*, (1) Calcium acetate method; (2) Neale's Alkali titration method; (3) Silver Nitrophenolate method; (4) Methylene Blue absorption method; (5) Carbon dioxide evolution method. Of these the last mentioned only estimates the carboxyl in the 6-position,[7, 8, 9, 17, 18] and therefore is not applicable as a general method.

The first four methods have been critically examined and modified wherever necessary by Davidson[3] and a comparative study has been made on various oxycelluloses. He has also pointed out the limitations of these

four methods and has further stressed that, none of these can be used as a universal method for the determination of carboxyl in cellulose.

It is thus evident that the various methods of carboxylic group determination proposed so far suffer from various handicaps. Even the Methylene Blue absorption method developed by Davidson[3] is very elaborate and gives stoichiometric results only under strictly standardized conditions and it may not be feasible to carry out except in well-equipped laboratories. So it has been found necessary to develop a method which would be simple and at the same time give reproducible results within reasonable limits of accuracy. From this point of view the observation of Lüdtke[5] that iodine is liberated on addition of potassium iodate and iodide to a suspension of an oxycellulose in sodium chloride seems to offer the best starting point. The actual method as developed consists in suspending the cation-free cellulosic material in a solution of KI-KIO_3-NaCl mixture, to which sodium thiosulphate is added to prevent the loss of iodine due to side reactions and vaporization, as also to facilitate the completion of the reaction by removal of the iodine liberated from the sphere of reaction. At the end of the requisite period the excess of thiosulphate is back-titrated with standard iodine solution. In the iodometric method, no alkali is employed and the whole of the reaction takes place[10] at a pH of 7 to 7·3.

The method has been compared with Neale and Stringellow's Alkali titration method,[11] and Davidson's Methylene Blue absorption method[3] and is found to be free from the disadvantages of both the methods. Further this method seems to be applicable to most of the oxycelluloses.

General Details of Experimental Methods

The material used for oxidation is carefully purified and bleached 18's single yarn made from Indian cotton. The following oxycelluloses have have been prepared. Normally a material liquor ratio of 1 : 50 has been maintained.

1. *Alkaline hypobromite oxycelluloses.*—The alkaline hypobromite (0·02 N NaOBr in 0·1 N NaOH) prepared according to the method described by Clibbens and Ridge[20] has been used. The fall in concentration of hypobromite has been found out by estimation of an aliquot portion by the iodimetric method. When the requisite oxygen consumption is reached, the material is washed free from hypobromite, treated with dilute thiosulphate solution and washed. The material is rendered cation free by treating it with 0·5 N HCl for two hours followed by washing with distilled water till the pH of the wash water is the same as that of the distilled water. The material is dried at room temperature and stored carefully.

2. *Periodate oxycelluloses.*—The oxycelluloses have been prepared by oxidizing cotton cellulose with 0·005 M and 0·01 M HIO_4 solutions. The fall in concentration of the oxidizing agent is determined iodometrically. The oxycelluloses are washed with water and then rendered cation free and stored as mentioned previously.

3. *Periodate-chlorite oxycelluloses.*—Periodate oxycelluloses prepared as above are treated with 0·1 M sodium chlorite in 0·5 M phosphoric acid overnight (18 hours) at room temperature (30° C.).[3] The samples are then washed thoroughly and rendered cation free and stored.

4. *Dichromate-oxalic acid oxycelluloses.*—The material is suspended in 2 N oxalic acid solution and to this mixture with rapid stirring, the necessary volume of N dichromate solution and distilled water are added in one lot to give N/5 or 2 N/5 dichromate in N oxalic acid. The mixture is allowed to stand for five hours, then the material is washed, rendered cation free and stored. The oxycelluloses possess a remarkably white appearance and do not show the greenish tinge possessed by dichromate sulphuric acid oxycelluloses.

5. *Chromic acid-chlorite oxycelluloses.*—The chromic acid oxycelluloses are oxidized with chlorite as mentioned under periodate-chlorite oxycelluloses.

6. *Nitrogen dioxide oxycellulose* is prepared by oxidizing cotton cellulose with a carbon-tetrachloride solution of nitrogen dioxide.

Determination of copper number.—In the case of low copper number, the copper number has been determined by Heyes' micro method.[21]

Modified Heyes' method for highly oxidized celluloses.—In this case the weight of the sample has been reduced to 0·1 g. and the volume of the Schwalbe-Brady solution increased to 100 ml. Further, to compensate for the loss of cuprous oxide due to solubility, 10 ml. of 0·04% glucose solution has been added to each 100 ml. of the solution. A blank determination is also carried out under the same conditions to determine the reducing power of 10 ml. of the glucose solution used.

Determination of carboxyl content by Neale's method.[11]—1 g. or 0·5 g. of the cation-free cellulosic material is suspended in a mixture of 25 ml. of 0·02 N caustic soda (CO_3'' free) and 25 ml. of 5% sodium chloride. At the end of the requisite period the excess of alkali is back titrated with 0·02 N hydrochloric acid using Bromo-Cresol-Purple indicator.

Carboxyl content by Davidson's Methylene Blue absorption method.[3]—These determinations have been carried out with a few samples of alkaline

hypobromite and periodate-chlorate oxycelluloses which give correct value for carboxyl content by Neale's method due to their low copper number. The method of colorimetric estimation of Methylene Blue as described by Davidson using a Dubosc type colorimeter having been found to be unsuitable, the estimations have been carried out using a Klett Summerson Photoelectric colorimeter.

Experimental Results and Discussion

It is well known that mineral acids react with a mixture of iodate and iodide with the liberation of iodine thus:

$$6\,H^+ + 5\,I^- + IO_3^- \rightarrow 3\,H_2O + 3\,I_2 \qquad (2)$$

With an organic acid, however, an equilibrium is reached, depending upon the hydrogen-ion concentration.

Lüdtke[4] has proposed and used this method for the estimation of carboxyl groups in cellulose and oxidized celluloses. In his original method, a solution of iodate-iodide is added to a suspension of the cellulosic material in sodium chloride solution and the iodine liberated is titrated against thiosulphate. The advantage of this method is seen in the absence of interfering colloidal phenomena which are present in the use of alkali. The method has only been seldom used, and Lüdtke himself seems to prefer the calcium acetate method.

As already mentioned the reaction as represented in equation (2) does not go to completion in the case of organic acids, and on the assumption that the carboxyl groups in cellulosic materials represent the organic acid an equilibrium will be attained thus:

$$6\,H^+ + 5\,I^- + IO_3^- \leftrightharpoons 3\,H_2O + 3\,I_2 \qquad (3)$$

From (3) it is evident that if the iodine liberated is removed from the sphere of reaction, the reaction will be forced to the right till all the carboxyl groups in the cellulosic material are neutralized. Further, if the free iodine is allowed to remain in contact with the cellulosic material, some of it may be utilized in oxidizing the cellulosic material. There is also the danger of loss of iodine vapour when iodine solutions are allowed to stand for considerable length of time. Further, it has been observed that during the direct titration of the iodine, the end point is very frequently overshot due to the strong retention of iodine and more especially the starch-iodine complex by the cellulosic material.

Kolthoff[19] claims that acids of dissociation constant upto 10^{-6} may be determined by this method and that the pH at the end of the titration is

7 to 7·3. He has recommended[19] that if the reaction with the acid is carried out in the presence of thiosulphate, completion of the reaction is reached in a very short time.

After due consideration of the points mentioned above the following general procedure has been adopted for the development of the Iodimetric method for the estimation of carboxyl groups in cellulosic material.

All the solutions are prepared using carbon dioxide-free distilled water and stored in such a way that they are protected from coming into contact with atmospheric carbon dioxide during storage as well as use, by means of soda-lime traps.

The following solutions are required:

(A) Sodium chloride Analar .. .. .. 50 g.
Potassium iodate C.P. .. .. .. 21·4 g.
Potassium Iodide C.P. .. .. .. 83·0 g.
Carbon dioxide free distilled water to 1 litre

(B) 0·02 N Sodium thiosulphate

(C) 0·02 N Iodine

(D) Starch solution .. .. .. 0·2%

1 g. or 0·5 g. of the air dry cation-free cellulosic material is accurately weighed and transferred to a 250 ml. glass stoppered Pyrex Erlenmeyer flask and washed twice by decantation with carbon dioxide free distilled water. As much of the adherent water as possible is removed by pressing the material with flattened end of a clean glass rod. Then 25 ml. of (A) are delivered into the flask by means of an automatic burette. This is followed by addition of 25 ml. of 0·02 N thiosulphate and 25 ml. of carbon dioxide free distilled water. The flask is stoppered, gently shaken to ensure uniform mixing and the mixture is allowed to stand for the requisite time. At the end of the requisite period, the excess of thiosulphate is determined by back titration with 0·02 N iodine solution using starch solution as indicator. The mixture is kept agitated throughout the course of titration by passage of a current of carbon dioxide-free air. The end point is quite sharp and duplicate results are reproducible within 0·1 ml. of 0·02 N iodine solution. A blank is carried out without using any cotton.

Comparative study of the estimation of carboxyl groups in cellulosic materials by Neale's method and Iodimetric method.—Carboxyl contents of the various oxycelluloses have been determined by Neale's method[11] and Iodimetric method after the oxycelluloses have remained in contact

with the alkali and iodate-iodide-thiosulphate solution respectively, for periods varying from 1 to 32 hours. The results have been tabulated in Table I and represented graphically in the Figure.

TABLE I

Comparative study of the estimation of carboxylic acid groups in cellulosic materials by (a) *Iodimetric method and* (b) *Alkalimetry-Neale's method*

No.	Material	Weight taken for estimation in g.	Carboxyl content milliequivalents per 100 g.								
			Iodimetric Method					Alkalimetry (Neale)			
			(Time in hours)					(Time in hours)			
			1	8	16	24	32	1	8	16	32
1	Bleached cellulose	1	0·354	0·829	1·16	1·21	1·21	0·98	..	..	1·48
2	"1" Treated with chlorous acid	1	0·591	1·06	1·42	1·65	1·77	1·36	..	..	1·73
3	Alkaline hypobromite oxycellulose	1	4·22	4·77	5·50	5·27	5·16	4·93	4·93	5·18	5·18
4	Periodate-chlorite oxycellulose	1	11·50	11·50	12·00	12·00	11·4	11·4	11·2	11·2	11·6
5	Dichromate-oxalic acid oxycellulose	0·5	6·47	7·05	7·82	7·87	7·92	8·58	12·3	18·6	20·2
6	"5" Treated with chlorous acid	0·5	23·3	24·3	25·6	25·6	25·7	24·4	24·4	24·4	24·4
7	Nitrogen dioxide oxycellulose	0·5	14·7	15·4	16·8	17·0	16·8	16·1	16·9	18·6	19·4
8	"7" Treated with periodic acid	0·5	14·3	14·9	16·4	16·5	16·3	49·6	59·9	63·3	65·0
9	Periodic acid oxycellulose	0·5	0·72	1·54	2·41	2·29	2·41	30·1	34·1	39·3	41·6
10	"9" Treated with chlorous acid	0·5	42·9	45·2	46·8	46·6	46·8	46·2	47·0	47·6	47·6

In Table II are given the results of the determination of carboxyl content of various types of oxycellulose by Neale's method[11]—time of contact 1 hour—and by the Iodimetric method as described earlier, time of contact being 24 hours.

From Table II it can be seen that the values of carboxyl content as determined by both methods agree within limits of experimental error in the case of oxycelluloses possessing low reducing power. In the case of oxycelluloses possessing high reducing power Neale's method gives fictitious values, the deviations being much more in the case of periodic acid oxycelluloses as compared with dichromate-oxalic acid oxycelloses.

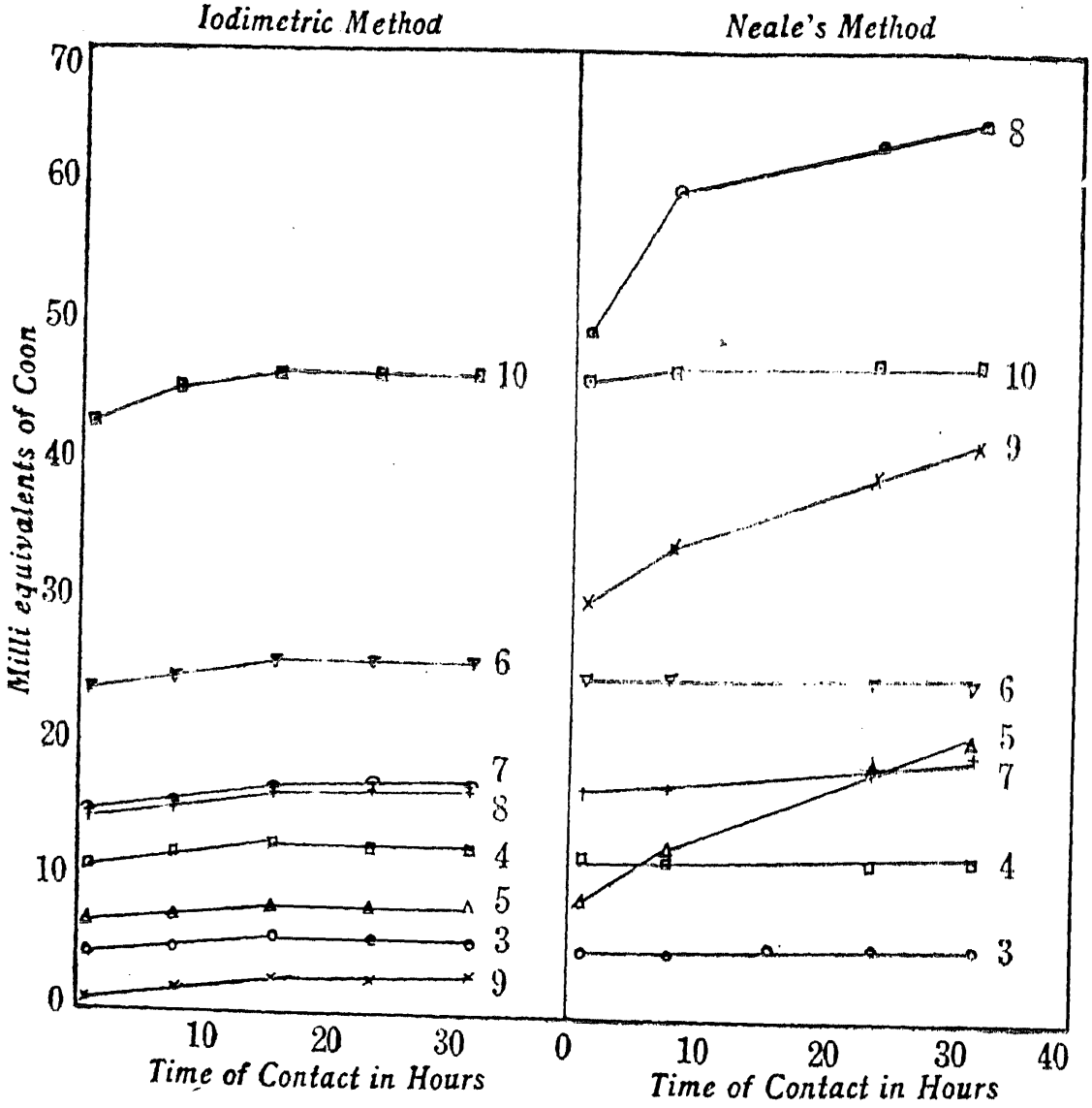

FIG. 1. Comparative study of Neale's and Iodimetric methods of Estimation of –COOH in cellulosic material. Numbers against curves refer to Table I

A few oxycelluloses have been analyzed for carboxyl content by Davidson's Methylene Blue[3] absorption method and the results are tabulated in Table III, together with the values obtained by Neale's method[11] as well as the Iodimetric method.

From Table III the fair agreement between the various values obtained by all the three methods is quite evident in the case of periodate-chlorite and alkaline hypobromite oxycelluloses. With the dichromate oxalic acid oxycelluloses, however, the Methylene Blue absorption gives values for carboxyl content which are higher than those obtained by Iodimetric method and lower than those obtained by Neale's method.

From the foregoing results it can be seen that the Iodimetric method gives reproducible and reliable values for the carboxyl content of various types of oxycelluloses. While, as has already been observed by Davidson,[3] and as shown also in Tables I and II, it is evident that Neale's method gives

TABLE II

Estimation of carboxyl content of cellulosic material by Iodimetry and Alkalimetry

No.	Material	Weight taken for estimation in g.	Copper Number	Carboxyl content milliequivalents per 100 g.					
				Iodimetry (Time of contact 24 hours)			Alkalimetry (Neale) (Time of contact 1 hour)		
				1	2	Mean	1	2	Mean
1	Bleached cotton cellulose	1	0·04	1·21	1·21	1·21	0·98	0·98	0·98
2	" 1" Treated with chlorous acid	1	0·04	1·60	1·70	1·65	1·36	1·36	1·36
3	Alkaline hypobromite oxycellulose No. I	1	0·29	5·11	5·21	5·16	4·93	4·93	4·93
13	" " " No. II	1	0·32	5·46	5·46	5·46	5·22	5·42	5·32
14	" " " No. III	1	0·25	8·35	8·45	8·40	8·12	8·32	8·22
4	Periodate-chlorite oxycellulose No. I	1	0·40	11·9	12·1	12·0	11·4	11·4	11·4
15	" " " No. II	1	0·35	7·01	7·01	7·01	7·29	7·29	7·29
16	" " " No. III	1	0·37	8·68	8·58	8·63	8·46	8·46	8·46
5	Dichromate-oxalic oxycellulose I	0·5	20·2	7·8	7·95	7·87	8·48	8·68	8·58
6	" 5" Treated with chlorous acid	0·5	2·54	25·6	25·6	25·6	24·4	24·4	24·4
17	Dichromate-oxalic acid oxycellulose II	0·5	11·73	4·82	5·02	4·92	5·40	5·60	5·40
18	" 17" Treated with chlorous acid	0·5	1·53	15·3	15·3	15·3	16·0	16·0	16·0
9	Periodic acid oxycellulose I	0·5	19·0	2·29	2·29	2·29	30·1	30·1	30·1
10	" 9" Treated with chlorous acid	0·5	1·53	46·7	46·8	46·8	47·5	47·7	47·6
19	Periodic acid oxycellulose II	0·5	10·2	2·66	2·66	2·66	12·6	12·8	12·7
20	"19" Treated with chlorous acid	0·5	1·02	25·31	25·31	25·31	25·1	25·3	25·2

TABLE III

Comparison of Iodimetric method and Neale's method with Davidson's Methylene Blue absorption method

Material	Carboxyl content milliequivalents per 100 g. of cellulose		
	Iodimetry	Alkalimetry (Neale)	Methylene Blue absorption (Davidson)
Periodate-Chlorite Oxycelluloses			
I	12·0	11·4	11·6
III	8·63	8·46	8·36
Alkaline Hypobromite Oxycelluloses			
II	5·15	4·93	4·80
III	8·40	8·22	8·25
Dichromate-oxalic acid Oxycelluloses			
I	4·92	5·50	5·24
II	7·87	8·58	8·0

fictitious values for the carboxyl content of reducing oxycelluloses. Davidson's Methylene Blue absorption method suffers from the disadvantage that it has to be carried out under strictly standardised conditions and cannot be carried out except in a well-equipped laboratory. It suffers from the further disadvantage that due to the low concentrations of the Methylene Blue solutions employed for the determination, the weight of oxycellulose of high carboxyl content required for analysis becomes inconveniently small. Further the colorimetric estimation of Methylene Blue by visual colorimeters is a tedious process requiring long practice for accurate results. The method requires more or less the same time as the Iodimetric method. On the contrary the Iodimetric method is simple and strightforward and does not require any special equipment. Further, as the reaction throughout takes place[19] at a pH of 7 to 7·3 no complications occur with alkali sensitive oxycelluloses.

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