

## A NEW METHOD FOR THE ESTIMATION OF CELLULOSE.

(With special reference to jute.)

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### ABSTRACT.

The current methods for the estimation of cellulose in plant materials are critically reviewed. It is shown that none gives true (or  $\alpha$ -) cellulose, or holocellulose, but products containing varying amounts of hemicelluloses including polyuronides. Norman's idea of cellulosan (hexosans and pentosans but not polyuronides) as forming part and parcel of the natural cellulose molecule is found to be untenable. No sharp line of demarcation can possibly be drawn between cellulosans and other hemicelluloses.

A new method, using sodium chlorite, for the cellulose estimation is described, with special reference to jute. It is shown that under suitable conditions, only lignin is removed, leaving behind all other constituents of the fibre intact. The influence of temperature, time, concn., liquor-ratio, etc. have been studied. It is possible to obtain a fibre cellulose with a fairly low copper number and methylene blue absorption value. Full working details of the new method are given.

By far the most important constituent of plants and woods is cellulose; it is the structural framework of their tissues. It is also the main constituent inasmuch as 40-60% of mature plants and woods is cellulose. In fact, it is the most abundant organic compound found in nature, making up not less than one-third of all the vegetable matter in the world. Because of its fibrous structure and other physical and chemical properties, it is extensively used in industry in various forms. Manufacture of rayon, paper, lacquer, etc. to name only a few, constitute quite big industries of the world to-day. But in nature, cellulose seldom occurs in the free state—it is generally associated with other substances such as lignin. Hence the importance of estimation (and isolation) of cellulose. In spite of the enormous progress this branch of chemistry has made during the last three decades (the constitution and molecular size of cellulose are now established facts), it is rather unfortunate that the term cellulose has not yet been satisfactorily defined. Thus Heuser (1944) in his introduction to 'The Chemistry of Cellulose' on the very first page defines cellulose as 'a natural high polymer, the building unit of which is an anhydride of glucose'. It may be noted that he mentions nothing about the degree of polymerisation of such a high polymer. This naturally gives rise to anomaly—for anhydro-glucose in polymerised form may occur as glucosan along with cellulose. This has undoubtedly a lower degree of polymerisation but unless a limit is fixed somewhere, even though arbitrarily, it is difficult to exclude glucosan from the definition of cellulose. Then again, doubts have been expressed in certain quarters about the homogeneity of the cellulose molecule. Some are of opinion that xylan or polyglucuronic acid molecules form links of the cellulose chain just like anhydroglucose. Thus Heuser (1944) in the same book states, 'The aggregate of chain molecules by which the cellulosic substance may be represented may *not* consist exclusively of glucose anhydride chains' (p. 5).

Besides the polymer of anhydroglucose (cellulose and glucosan) bast fibres, mature plants and woods invariably contain varying amounts of other polysaccharides such as hexosans like galactan and mannan, pentosans such as xylan and araban besides lignin, polyuronides (polymers of galacturonic and glucuronic acids), fats and waxes, resins, etc.

The idea of compound celluloses (*e.g.*, ligno-cellulose, pecto-cellulose, adipocellulose, etc.) of Cross and Bevan (1895), pioneer workers in the field, has now been

found untenable as X-ray data are against such a hypothesis. The difficulty of isolation of the cellulose portion from others in woods and plants presumably led to the adoption of such a view. Except in the case of fat and wax and colouring matter which can be extracted by means of suitable solvents more or less completely, the same difficulty remains to-day. No other plant constituent can be isolated by extraction with inert solvents or by any other simple means.

In all research works on cellulose, physical or chemical, cotton cellulose has almost exclusively been employed. Being a seed hair, it hardly bears any close resemblance to the cellulose occurring in plants and woods or even bast fibres. Cotton fibre is unique in the sense that it is *entirely* free from lignin and represents, after a slight purification, 99.8% pure cellulose. This, on hydrolysis, yields glucose almost in quantitative yield; when subjected to X-ray study, evidence for the existence of no other constituent than anhydroglucose is obtained. No conclusive evidence from physical or chemical investigation has yet been available to show that xylan or uronic anhydride molecules form part and parcel of the cellulose molecule as it exists in plants, etc. One fact that seems to be universally established now is that the polysaccharide fractions from different sources contain one constituent (in proportions which vary with the source) which is resistant to the action of 17.5% NaOH at ordinary temperature. Cross and Bevan termed this  $\alpha$ -cellulose; true cellulose or resistant cellulose typified by purified cotton means the same thing.  $\alpha$ -Cellulose from different sources gives identical X-ray diagram and yields, on careful hydrolysis, the same proportion of glucose. But the degree of polymerisation (*i.e.*, molecular weight) of such a product varies with the source even though extreme care is taken for its isolation. The less resistant (*i.e.*, soluble in 17.5% NaOH) portion was termed by them as  $\beta$ - and  $\gamma$ -celluloses. These obviously include the hexosans (other than  $\alpha$ -cellulose), pentosans and polyuronides. The term 'hemicelluloses' was coined by Schulze (1891) for similar bodies—these he regarded as closely related to cellulose. Hemicelluloses are soluble in dilute alkali, and are readily hydrolysed to pentoses and hexoses by warm and dilute mineral acids. These are looked upon by many workers as intermediate stages in the formation of cellulose. Polyuronides, such as galacturonic and glucuronic acids in polymerised form, have been detected in most plants along with hemicelluloses and are included amongst the latter by some investigators.

The mode of combination, if any, between the constituents— $\alpha$ -cellulose, hexosans, pentosans, polyuronides and lignin—may now be regarded more or less a matter of opinion based, of course, upon the kind of experimental difficulties experienced by a particular worker in the isolation of a particular member or members and there are many. Norman (1933, 1937) who has done a lot of work on the subject, for example, classifies the hemicelluloses into two distinct groups, *viz.*, cellulosans (chiefly xylan) and encrusting hemicelluloses, mainly polyuronides. According to him, cellulosans and  $\alpha$ -cellulose should together represent cellulose whilst lignin and hemicelluloses of polyuronide nature are to be regarded as mere encrustants. Norman considers the cellulosans as 'forming a normal integral part of the cellulosic fabric of the plant'. In other words, in Norman's model for cellulose there is no room for a uronic anhydride forming a link in the chain. Though xylan was originally regarded as the only polysaccharide in cellulosan, Norman (1937) later on from hydrolytic studies includes glucosan, polyuronides, etc. as well. He considers the existence of cellulosan as an individual substance impossible.

Irvine and Hirst (1924), however, regard the association of xylan and cellulose in esparto grass as a case of solid solution, because the ratio between the two is variable.

Schmidt *et al.* (1932), on the other hand, consider the union between xylan and cellulose in the wood of red beech to be of ester type, though Lütke (1934) was unable to confirm their view.

Hampton, Haworth and Hirst (1929), however, think differently and regard the association between xylan and cellulose (in esparto grass) as a special case of mixed crystallisation on account of the striking structural similarity between them (both contain amylenic oxide ring and individual units are linked through 1:4-positions). In fact, the only point of difference in molecular structure or configuration of cellulose and xylan is the projecting carbinol group,  $-\text{CH}_2\text{OH}$ , in the former.

The similarity of both structure and configuration between true cellulose, polyglucuronic acid and xylan (these are all identical if the  $-\text{CH}_2\text{OH}$  group in true cellulose and  $-\text{COOH}$  group in glucuronic acid are left out of consideration) and the possibility of one being readily converted into the other by natural oxidation ( $-\text{CH}_2\text{OH}$  of cellulose thus giving  $-\text{COOH}$  of glucuronic acid) or loss of  $\text{CO}_2$  (glucuronic acid will thus yield xylan) have led some to take a still wider view. For example, it is also thought that mixed chains consisting of anhydroglucose, glucuronic acid and xylan units possibly occur in nature (Meyer, 1942).

There are also other complexities such as possibility of a chemical union between lignin and polyuronides, polyuronides and xylan, etc. but these are beyond the scope of the present paper. It will be abundantly clear from what has been stated above that our knowledge regarding the hemicelluloses including polyuronides is very limited indeed and nothing definite has been proved as to the nature of the combination, if any, between true cellulose and other associated compounds such as xylan, etc.

In view of this it would perhaps appear more rational to regard *all* polysaccharides (*i.e.*, pentosans and hexosans including true cellulose) and polyuronides (polymers of galacturonic, glucuronic acids) as jointly comprising 'total cellulose' or holocellulose (and in the case of fibrous materials, 'fibre cellulose') than to define, as Norman does, cellulose as consisting of true cellulose and cellulosan (mainly xylan). For, it has not as yet been possible to extract by means of suitable solvents or to separate by any other simple means completely the encrusting hemicelluloses (polyuronides, pentosans and hexosans) from the natural cellulosic material so as to leave behind only the true cellulose and the cellulosan (comprising the plant cellulose of Norman). In fact, by no existing method of estimation, is it possible to obtain cellulose from plant materials, which will not yield a considerable amount of  $\text{CO}_2$  on distillation with 12% HCl. Norman's definitions of encrusting hemicelluloses and cellulosans are therefore difficult to accept (Preece, 1944).

Until more precise information leading to conclusive proof is available for the existence of two distinct classes of hemicelluloses, it seems more expedient to consider them all collectively. Plant materials may in that case be considered broadly to consist of total cellulose and lignin, besides fat, wax and resin and traces of mineral and colouring matters. The ideal method for the estimation of cellulose should aim at the *complete* removal of lignin without in any way affecting the other portion. In such a case the percentage figures for lignin and total cellulose should make 100 (within limits of experimental error) on fat-free and ash-free basis; and also the cellulose should have a small copper number and a low methylene blue absorption value as well as only a moderate solubility in caustic alkali. In other words, during the process of delignification, the cellulose should neither be oxidised nor hydrolysed, resulting in shorter chain lengths. Alternatively, we may confine the term cellulose to what is now meant by  $\alpha$ -cellulose (a lower limit of degree of polymerisation, D.P., would however seem extremely desirable) and leave the rest as hemicelluloses. Both the figures (*viz.*, total cellulose and  $\alpha$ -cellulose) are useful in industrial laboratories, the former, for example, in the manufacture of paper and pulp and the latter in rayon manufacture. It will be seen from what follows that the  $\alpha$ -cellulose content of jute remains more or less unaltered whichever method is followed for the separation of cellulose.

A short review of the three current methods, *viz.*, Cross and Bevan's, Norman and Jenkins' and Schmidt's for the estimation of cellulose will now be made.

*Cross and Bevan's method.*—This is the oldest and most widely used method (Cross and Bevan, 1903) for the estimation of cellulose; it has become almost classical. In this process, the cellulosic material is first boiled with 1% NaOH for half-an-hour, washed thoroughly with water and *while still moist*, chlorine gas is passed into it for about 30 minutes. This is next washed with water and boiled for 5 minutes with 2% sodium sulphite solution. The chloro-lignin formed in the previous operation dissolves with a pink colour in the sulphite solution. The process of alternate chlorination and sulphite treatment is repeated until no pink colour is obtained with sulphite solution. The residual material is then bleached with either 0.1% sodium hypochlorite or potassium permanganate solution for a few minutes. The

cellulose thus obtained is washed with water, treated with  $\text{SO}_2$ -water and again washed with water, dried at  $105^\circ\text{C}$  and weighed.

There are two main objections to the above process—firstly, the alkaline boil removes a considerable portion of the hemicelluloses (some of which are believed to be intimately associated with the true cellulose), which is undesirable. In the case of a jute fibre, we have found the total loss to be 12.54%, of which 10.41% represents hemicelluloses and the rest (2.13%) lignin; contrary to our expectation, it was discovered, on analysis of the alkali-boiled fibre that hexosans—but not pentosans (*e.g.*, xylan) or polyuronides are thus mainly removed. Renker (1910) first pointed out that this treatment lowers the yield of cellulose. But this alkali treatment cannot be dispensed with advantageously as otherwise it requires a large number of chlorination and sulphite boiling (particularly in the case of wood) and even then removal of lignin may not be complete. The moist chlorine oxidises the cellulose which is the second objection. The oxidation is considerable if chlorine is allowed to react for a prolonged period. Some oxycellulose is invariably formed during chlorination but by the subsequent treatment with sodium sulphite solution (which is *alkaline*) it is largely removed from the cellulose. In the case of raw jute, the loss on boiling with 3% sodium sulphite comes to about 6.70%. These account for the low figure of Cross and Bevan cellulose (72.55% in the case of jute) which represents neither  $\alpha$ - or true cellulose (60.43%) nor the total or holocellulose (which is 88.60%). That some true cellulose is oxidised and removed during estimation with chlorine is evident from the comparatively low figure for  $\alpha$ -cellulose (56.61%) prepared from Cross and Bevan's cellulose, and calculated on the bone-dry raw material. The hot alkali sulphite solution removes only the carboxyl-type of oxycellulose but not the aldehyde-type. The copper number of Cross and Bevan cellulose is thus appreciable (1.03), but the solubility in alkali is rather low (14.59%) as anticipated. The product is, however, entirely free from lignin (residual lignin being 0.02% which in all probability represents cuticle, etc.). Cross and Bevan's cellulose contains the major portion of the  $\text{CO}_2$ -yielding components (*e.g.*, polyuronides) which obviously resist the oxidation by chlorine. The amount of pentosans (as xylan) present is also rather high. Thus, during Cross and Bevan's procedure, jute loses: (i) Lignin—100%, (ii) hemicelluloses including polyuronides—56.31%, (iii) polyuronides—42.30%, (iv)  $\alpha$ -cellulose—6.31%, of the total. It is clear, therefore, that besides lignin, *all* other constituents of jute fibre are partially removed. The definition must be specially modified if we prefer to call the stuff, obtained by Cross and Bevan's method, 'cellulose'.

Naturally, a number of workers have so far tried to overcome these drawbacks of Cross and Bevan's method. Suggestions have been put forth to make the pre-treatment milder; say, by reducing the time (Dorée recommends 5 minutes instead of  $\frac{1}{2}$  hour) or lowering the temperature (Dorée treats with alkali at room temperature) and also making the action of chlorine less drastic, say, by shortening the period of chlorination, *e.g.*, giving successive short exposures lasting for 3–5 minutes only instead of one or two prolonged ones. These points have been discussed by Dorée (1933, pp. 331–336). But in spite of such modifications, the method is not above criticism even now. The process is neither simple nor elegant—difficulty of working with  $\text{Cl}_2$  gas is an objectionable feature.

*Norman and Jenkins' method.*—Norman and Jenkins (1933) omit the alkali boil altogether in order to avoid the loss of cellulose but boils the material with 3% sodium sulphite solution at the start. This, according to them, ensures thorough wetting of the material and also effects removal of some lignin. Instead of treating with free chlorine, they employ neutral hypochlorite first and then acid hypochlorite, each of the treatments being followed by a boil for 20 minutes with 3% sodium sulphite. This is continued till there is no purple coloration with sulphite solution. The sulphite is removed with hot water, cellulose is dried at  $100^\circ$  and weighed. This method is particularly recommended for cereal straws and woods. The authors claim that 'the method gives results strictly comparable with those of Cross and Bevan determination *without pretreatment* and the product represents as closely as possible the natural cellulosic tissue of the plant freed from encrusting substances'. But unfortunately none of the two primary objectives, *viz.*, complete removal of

lignin and encrustants, retaining all the celluloses as aimed at by Norman and Jenkins, is fulfilled in actual practice. The apparent lignin in the cellulose varies from 0.1 to 3.5% which is not wholly satisfactory. No carbon dioxide estimations have been done on the cellulose isolated, so, there is no evidence to show that the product is free from encrusting polyuronides. It has also not been shown that all the celluloses are intact in the cellulose thus separated.

In the case of jute defatted with alcohol-benzene (1:1), during four sulphite boilings for 20 minutes each, one following the next, the loss comes to 6.70% of which 2.45% represents lignin, 1.28% polyuronides and the rest (2.97%) hexosans and pentosans. As in Cross and Bevan's method, oxidation of cellulose is fairly considerable (alternate boiling with sodium sulphite solution which is alkaline, removes some of the oxycelluloses formed)—the copper number is high (2.69). Lignin is completely removed from jute fibre, but about half of the polyuronides remains associated with the cellulose. Norman and Jenkins' method, as a rule, gives a higher percentage yield of cellulose (77.77%, in the case of jute; of which true cellulose represents 61.15%; hexosans 5.97%; pentosans 8.05% and polyuronides 2.60%). Because both pentosans (xylan) and hexosans (glucosan) can, according to Norman and Jenkins, be derived from dual sources (Ott, 1943)—celluloses or polyuronide hemicelluloses (encrustants)—it is difficult to ascertain, in absence of a satisfactory method for the complete separation of the 'encrustants', the purity of cellulose. But the presence of polyuronides proves definitely that the object of Norman and Jenkins has not been fulfilled. The solubility of their cellulose in boiling caustic alkali (2%) is rather high (30.35%), which indicates the formation of oxycellulose (of the carboxyl type) or shortening of chain length. Norman and Jenkins have not touched upon this point with regard to the quality of the cellulose obtained by their method. The method does not involve the preparation and use of chlorine gas, which is an advantage. It is in reality a tedious method; even in the case of jute (from which all the lignin can be rather easily removed) as many as four treatments with hypochlorite (neutral and acid) and four with sulphite are necessary for complete delignification. Quantitative transfer of the material for 8–10 times undoubtedly introduces some error. It is difficult to accept the statement made by the authors that as many as 16 estimations can be carried out by a single worker per day.

*Schmidt's ClO<sub>2</sub> method.*—Schmidt and co-workers (1921, 1923, 1924) have shown that lignin can be easily removed by means of aqueous chlorine dioxide from lignocelluloses. No pre-treatment with NaOH or Na<sub>2</sub>SO<sub>3</sub> is necessary; a 0.3 to 1.5% solution of chlorine dioxide is generally employed at room temperature. But the time required for complete delignification is from 48 to 96 hours. This is a great drawback of the method. They also recommend washing the residue with 2% hot Na<sub>2</sub>SO<sub>3</sub> solution for the ease of removal of lignin decomposition products.

This method yields the highest amount of cellulose which includes practically all the polyuronides as well. But it does not represent the holocellulose (Heuser and Winsford, 1923). In the case of a jute fibre, the yield is 84.96% and besides lignin (11.80%) about 3% of the polysaccharides is lost, apparently by oxidation for such a long time. This is evident from the high copper number (4.7) of the cellulose obtained, as well as its high solubility (41.01%) in dilute boiling caustic soda. The preparation of chlorine dioxide is a troublesome, if not dangerous, affair. The gas attacks the mucous membrane of the nose and throat and there is also the danger of explosion. Chowdhury and Saha (1930) have found that gaseous ClO<sub>2</sub> passed into the moist jute fibre acts more quickly and is more convenient for the removal of lignin. After-treatment with hot sodium sulphite is also unnecessary. But even then all the holocelluloses cannot be obtained.

A more recent method for the estimation of cellulose in wood is by extraction with monoethanolamine at 168–70°C for 2 hours (Bloom, Jahn and Wise, 1942). The washed residue is finally treated with 0.1% chlorine water at 20°C and successively washed with 0.67% SO<sub>2</sub>-water, water, 2% hot Na<sub>2</sub>SO<sub>3</sub> solution and water. The procedure is to be repeated 2–3 times to ensure complete removal of lignin. It is claimed that a cellulose broadly similar to that by Cross and Bevan's method is thus obtained.

For want of monoethanolamine, this method could not be tried on jute fibre. It, however, does not appear to be a simple process in any case. Neither has it been tested by other workers.

Very recently Shrikhande (1944) has suggested the use of bromine (in place of chlorine) obtained from a bromide-bromate mixture on the plea that bromine is thus more conveniently prepared than chlorine and also that sodium hypochlorite does not keep well in tropics. The residual lignin in the cellulose from paddy straw was between 1.8 to 3.02%. Bromine is less reactive than chlorine, so 1-2 extra exposures are generally required. It may be pointed out that bromine is far more objectionable (and also costly) than chlorine to work with. No figures for  $\text{CO}_2$  or furfural of the isolated cellulose are given. It is not thus possible to evaluate the cellulose obtained by this method.

It will be seen from Table XIX that none of the methods yields the theoretical amount of holocellulose (or fibre cellulose) from jute fibre, the figures for cellulose lie intermediate between those for true (or  $\alpha$ -) cellulose and total cellulose. It seemed worth while to find out a method by which it would be possible to remove only the lignin and colouring matters, if any, leaving the polysaccharides and polyuronides intact. The cellulose obtained should also be least affected by the reagents employed and the method should be easily workable.

*The new method.*—Sodium chlorite,  $\text{NaClO}_2$ , has been found to be such an ideal reagent for the estimation of total cellulose in jute fibre. This compound was first discovered more than 100 years ago by Millon (1843) but it is only recently that the compound has been thoroughly investigated by the chemists of Mathieson Alkali Works, New York, (1940) which firm has succeeded in its cheap and commercial production. The chemical is now being used in the U.S.A. rather extensively for the bleaching of textiles and paper pulp, etc. Solid  $\text{NaClO}_2$  is a stable compound, highly soluble in water. The aqueous solution is quite stable in presence of a little alkali. Light hastens its decomposition. Paper and kraft pulp are now bleached on a commercial scale with chlorite to a high white without loss of strength. No known bleaching agent is so effective in bleaching while preserving the strength. This is attributed to the low oxidation potential of  $\text{NaClO}_2$  compared with other bleaching agents. For example, the value for a 1/142 M solution of sodium chlorite (1 gm. per litre available chlorine) referred to the normal  $\text{H}_2$  electrode is 0.79 volt at pH 4 while that of sodium hypochlorite at the same concentration of available  $\text{Cl}_2$  is 1.2 volt at pH 7-10. For bleaching purposes sodium chlorite is generally used in acid solution. Little or no bleaching takes place in alkaline conditions. The viscosity of cellulose solutions in cuprammonium hydroxide has been found to remain unaltered after bleaching with  $\text{NaClO}_2$  (Mathieson Alkali Works, N.Y., 1942). This evidently shows that  $\text{NaClO}_2$  in acid solution does not attack the cellulose to any appreciable extent.

It was therefore considered worth while to see if sodium chlorite could be used for the estimation of cellulose in plant materials. We have tried it on jute fibre with a view to finding out conditions under which the lignin would be *completely* removed while the fibre cellulose would be left behind practically undegraded.

Sodium chlorite was not available in the market, our efforts to import it from abroad proved futile. We, therefore, prepared it in the laboratory by absorbing chlorine dioxide,  $\text{ClO}_2$ , gas in 10%  $\text{NaOH}$  solution at room temperature. The  $\text{ClO}_2$  was generated in the usual way by warming a mixture of potassium chlorate, oxalic acid and dilute sulphuric acid. The strength was determined by adding excess of  $\text{KI}$  in acetic acid solution and titrating the liberated iodine with decinormal sodium thiosulphate.

For all the experiments described in this paper, only good samples of jute (*capsularis* or *obitorius*), free from bark and specks, were employed. The fibre was conveniently obtained in the sliver form (without, of course, adding any batching emulsion) which was extracted for five hours in a Soxhlet apparatus with a mixture of alcohol-benzene (1:1 by volume) in order to remove the natural fat and wax. The defatted fibre was cut into very small pieces and was used for experiments. Two-gram samples (air-dried) were employed in all cases of estimation of cellulose and ordinarily no pre-treatment with dilute  $\text{NaOH}$  or  $\text{Na}_2\text{SO}_3$ , hot or cold, was

given to the fibre. Analytical data for such a fibre is given in Table I. The influence of concentration of  $\text{NaClO}_2$ , time, temperature, fibre-liquor ratio, etc. was studied one after another, keeping all other conditions unchanged.

TABLE I.

J-160 (defatted sliver).

All figures are expressed on 100 g of bone-dry material.

Lignin	..	..	11.48%	Loss on boiling with 2% NaOH, 4 hrs.	..	..	16.70%
Carbon dioxide	..	..	1.26%	Nitrogen (Kjeldahl)	..	..	0.225%
Furfural	..	..	9.25%	Copper number	..	..	2.09
Ash	..	..	0.79%	Fibre cellulose (by difference, 100 - 11.48)	..	..	88.52%

*Influence of concentration of chlorite on the removal of lignin.*—2 g of finely cut, defatted fibre (J-160) was taken in a conical flask and 40 c.c. of sodium chlorite solution (of various strength) was added to it. The pH of the chlorite was lowered to about 4 by means of acetic acid. The flask was placed in a water-bath maintained at about 65°C for 4 hours, the contents of the flask were stirred with a glass rod frequently. The fibre was filtered through a weighed Jena glass filter, washed with water repeatedly, treated on the filter with 2% sodium bisulphite solution (which improves the colour and is a good antichlor) and finally washed with water 15-20 times. The cellulose was dried in a vacuum evaporator (placed on water-bath) connected to a water pump. When practically all the water is removed, it is connected with a high vacuum pump. The glass filters in tared open weighing bottles were kept over concentrated  $\text{H}_2\text{SO}_4$  under vacuum overnight and weighed next day. The process of drying was repeated until the weight became constant. Residual lignin in the cellulose was estimated with 72%  $\text{H}_2\text{SO}_4$ , after a preliminary boil with 5%  $\text{H}_2\text{SO}_4$  for one hour (Norman and Jenkins' procedure). Duplicate determinations were done in each case—the mean for the two values are given in Table II. All the figures are expressed on 100 g of bone-dry raw jute.

TABLE II.

Expt. No.	% Concen- tration of $\text{NaClO}_2$	% Apparent fibre cellulose.	% Residual lignin.	Colour of the material.	Difference.
	1	2	3		
1	5.3	91.27	0.85	Full white	90.42
2	4.0	92.29	1.65	"	90.64
3	3.5	93.15	2.47	"	90.68
4	2.65	93.69	2.93	Very pale yellow	90.76
5	1.33	95.81	4.41	Pale yellow	91.40
6	0.66	97.05	8.27	Yellow	88.78
7	0.33	97.56	9.67	Light straw	87.89

As the theoretical yield of holocellulose or fibre cellulose of the sample of jute is 88.52% (*vide* Table I), it will be seen that no experiment gave this value. In view of the high percentage of  $\text{NaClO}_2$  used, this would appear to be due to the very low fibre-liquor ratio (1:20) that all the lignin could not be dissolved out. Some lignin decomposition products might adhere to the fibre to make the percentage of cellulose high in experiments 1-5. From the appearance of the fibre it is hardly possible to judge whether it is entirely free from lignin or not. No dependable colour test is available for this purpose. A higher fibre-liquor ratio (1:50) was next tried on a second sample of jute (J-16/P<sub>9</sub>) defatted by extraction with alcohol-benzene, other conditions remaining unchanged. The results are shown in Table III.

TABLE III.

Expt. No.	J-16/P <sub>0</sub> ; Lignin—10·90%		Fibre-liquor ratio—1·50;	
	Holocellulose—(100—10·90)		Temperature—60–70°C	
	=89·10%			
	% NaClO <sub>2</sub>	% Apparent fibre cellulose.	% Residual lignin.	Difference.
	1	2	3	(2-3)
1	4·61	90·86	0·38	90·48
2	4·10	90·86	0·48	90·38
3	3·20	91·46	0·78	90·68
4	2·27	91·65	1·22	90·43
5	1·75	92·55	3·05	89·50
6	1·20	93·10	1·77	91·33
7	0·74	94·43	3·04	91·39

Results in Table III indicate that a higher fibre-liquor ratio effects a better dissolution of lignin from jute fibre even when the concentration of chlorite remains practically the same. Next, a still higher fibre-liquor ratio (1:100) was tried on J-161, defatted. This sample of fibre has 11·80% lignin and so the theoretical yield of fibre cellulose should be 88·20%. It may be pointed out here that jute contains a small amount of cuticle which remains unaffected during reaction with chlorite or 72% H<sub>2</sub>SO<sub>4</sub>. The small residue left after dissolving out the cellulose with 72% H<sub>2</sub>SO<sub>4</sub> has often the appearance of white thin plates; this cannot be dissolved by aqueous solution of ClO<sub>2</sub> as well. This cuticle, being derived from adhering tissues, is not uniformly distributed along the fibre. The percentage of residual cuticle thus varies rather widely even in the same sample of jute. The results with 1:100 fibre-liquor ratio are given in Table IV. Conditions of time, temperature, pH of the chlorite solution, etc. all remaining unaltered.

TABLE IV.

Expt. No.	J-161. Lignin—11·80%		Holocellulose—	
			(10—0·11·80)=88·20%	
	% NaClO <sub>2</sub>	% Apparent fibre cellulose.	% Residual lignin.	Difference.
	1	2	3	(2-3)
1	5·2	88·02	0·20	87·80
2	4·5	88·93	0·42	88·51
3	4·0	89·16	0·38	88·78
4	3·5	90·03	0·60	89·43
5	3·0	92·90	2·04	90·86
6	2·5	93·62	2·50	91·12
7	2·0	95·41	4·51	90·90

From the foregoing results, it is observed that 3·5% is the minimum strength of chlorite that may be used in a fibre-liquor ratio of 1:100 for the complete removal of lignin (the residue was found to be cuticle) at a temperature of 60–70°C. In order to fix up a minimum fibre-liquor ratio, at a chlorite concentration of 3·5%, another series of experiments was performed with J-160 defatted sliver. The results are given in Table V. Temperature was 60–70°C, time—4 hours and pH—4 as before, concentration of sodium chlorite being 3·5%.

TABLE V.

J-160 Lignin—11.48%		Fibre cellulose— (100-11.48)=88.52%		
Expt. No.	Fibre- liquor ratio.	% Apparent fibre cellulose.	% Residual lignin.	Difference.
	1	2	3	(2-3)
1	1: 20	93.15	2.47	90.68
2	1: 50	90.23	0.81	89.42
3	1: 75	87.55	0.43	87.12
4	1: 100	88.89	0.43	88.46

With 3.5% sodium chlorite, the safest (minimum) fibre-liquor ratio is thus found to be 1: 75. In all experiments with 3.5% chlorite this or the next higher fibre-liquor ratio, *viz.*, 1: 100 was used.

The influence of time on the delignification was then studied using a chlorite concentration of 3.5%, at a temperature 60–70°C with a fibre-liquor ratio of 1: 100. The results obtained (shown in Table VI) indicate that 4 hours is the minimum period of exposure for the complete removal of lignin from jute fibre. It is interesting to note that more than 60% of the lignin is dissolved out in the first half-an-hour. The rate then falls rapidly.

TABLE VI.

J-160 defatted. Lignin—11.48%		Fibre cellulose—88.52%		
Expt. No.	Time in hours.	% Apparent fibre cellulose.	% Residual lignin.	Difference.
	1	2	3	(2-3)
1	$\frac{1}{2}$	95.86	4.56	91.30
2	1	96.01	4.14	91.87
3	$1\frac{1}{2}$	94.67	3.87	90.80
4	2	92.58	1.88	90.70
5	3	90.80	0.72	90.80
6	4	88.89	0.43	88.46

It is to be noted that frequent stirring of the fibre in the flask during reaction with chlorite is essential for quick and complete removal of lignin. A suspension of minute, white, solid particles is found in the chlorite solution after the fibre is taken out; this deposits as a mud at the bottom on standing overnight. Apparently this comes from the decomposed lignin. Stirring helps mechanically the separation of these particles to a considerable extent.

The next point to be studied was the effect of temperature on the delignification of jute fibre. The rate of decomposition of  $\text{NaClO}_2$  in solution rapidly increases with rise in temperature provided the solution is acid (Mathieson Alkali Works, 1940) so that the concentration of chlorite falls rapidly without being available for the delignification. The results of experiments described below will show that 60–70°C is the optimum temperature for the delignification of jute fibre.

TABLE VII.

Time—4 hours; Chlorite concentration—3.5%; pH—4; Fibre-liquor ratio—1:100.  
J-160 defatted; Lignin—11.48%; Fibre cellulose—88.52%.

Expt. No.	Temp. °C.	%	%	Difference.
		Apparent fibre cellulose.	Residual lignin.	
	1	2	3	(2-3)
1	40-45	96.18	5.13	91.05
2	60-70	88.89	0.43	88.46
3	80-85	79.55	trace	79.55
4	98-99	74.54	trace	74.54

Obviously, a portion of the hemicelluloses is oxidised to water-soluble products at higher temperatures. These include polyuronides, pentosans as well as hexosans. The carbon dioxide value of such a sample is considerably low as also the yield of furfural. But the loss of polyuronides and pentosans does not account for the total loss—the balance is due to hexosans.

High concentration of sodium chlorite rather than high temperature used for the separation of lignin might as well as be responsible for the loss of hemicelluloses and consequent low yield of fibre cellulose. A series of experiments was performed in which the temperature was kept constant, *viz.*, that of the boiling water-bath (98-99°C) but the concentration of chlorite alone was varied. Considering that the rate of decomposition of the chlorite increases with rise in temperature, the treatment was continued for 3 hours only. The results are shown in Table VIII. It will be seen that complete removal of lignin is possible even with a much lower concentration of chlorite at the temperature of boiling water-bath. But in all cases except the last one varying amounts of hemicelluloses are also removed simultaneously.

TABLE VIII.

Temp. 98-99°C; Time—3 hours; pH—4 (with acetic acid); Fibre-liquor ratio—1:50.  
J-16/P<sub>9</sub> defatted; Lignin—10.90%; Fibre cellulose—89.10%.

Expt. No.	Concen-	Apparent	Residual
	tration of chlorite. %	fibre cellulose. %	lignin. %
1	4.10	76.73	Nil
2	3.20	80.72	"
3	2.27	80.83	"
4	1.75	83.81	"
5	1.20	87.35	"
6	0.74	88.22	0.36

The influence of pH of the chlorite solution on the delignification of jute fibre was studied next. For this purpose, 0.7% sodium chlorite was employed at 98-99°C for 2 hours in a fibre-liquor ratio of 1:50. Under these conditions, jute was found to be completely delignified provided the aqueous solution was just acidic. The pH of the chlorite solution was maintained at definite figures by means of buffer solutions (HCl and sodium acetate—Walpole). A very concentrated solution of NaClO<sub>2</sub> (nearly 6%) was neutralised and then diluted with the respective buffer solutions to the required concentration (*viz.*, 0.7% chlorite). For maintaining the solution at pH 7, citric acid and disodium hydrogen phosphate buffer was employed. It may be noted that the temperature (98-99°) was much higher than the one (18°C) for which the buffer is recommended. But as the temperature coefficient of buffer solution is usually low, the alteration in pH due to rise in temperature is expected to be small (no data are available in literature for Walpole's buffers at different

temperatures). In any case, the relative differences are expected to be more or less constant. The results are shown below. The colour of the final stuff appeared to be more or less the same, *i.e.*, almost white.

TABLE IX.

J-160 defatted; Concentration of NaClO<sub>2</sub>—0.7%; Liquor-ratio—1: 50;  
Temp. 98-99°C; Time—2 hours.

Expt. No.	pH of the chlorite solution.	% Apparent fibre. cellulose.	Copper number. *	Methylene blue absorption, in millimoles per 100 g dry stuff.
1	1.09	89.67	1.14	2.50
2	1.99	89.82	1.22	2.54
3	3.09	89.39	1.13	2.53
4	4.19	89.24	1.25	2.54
5	5.20	88.51	1.57	2.76
6	7.0	95.34†		

\* Calculated on bone-dry stuff.

† Lignin content—8.62%

It thus seemed possible to find out conditions for the separation of lignin with a chlorite solution of very low concentration thus avoiding largely the degradation of the cellulose. It has been found that the cellulose prepared with high concentration of NaClO<sub>2</sub> (3.5%) at 60–70° turns pale yellow on heating even on water-bath under vacuum and has also a high copper number, but that obtained with 0.7% chlorite at 98-99° remains almost white and has a lower copper number. The loss on standard alkali boil (with 2% NaOH for 4 hours) is, however, slightly higher in the latter case than in the former. The results obtained with the two sets of conditions are tabulated below for comparison.

TABLE X.

J-160 defatted; Lignin—11.48%; Fibre cellulose—88.52%.

(Figures are expressed on 100 g of bone-dry raw material.)

	With 3.5% chlorite for 4 hrs. at 60–70°C, liquor-ratio—1: 100.	With 0.7% chlorite, for 2 hrs. at 98-99°C, liquor-ratio—1: 50.
Fibre cellulose .. ..	88.89%	88.80%
Residual lignin in cellulose .. ..	0.40%	0.36%
CO <sub>2</sub> yield in cellulose .. ..	1.30%	1.20%
Furfural in cellulose .. ..	8.92%	8.88%
Loss on alkaline boil (with 2% NaOH, 4 hrs.) of cellulose (including lignin)	32.71%	35.48%
Loss on treatment with 5% NaOH (1: 100), 5 hrs. at room temp. 31°C	32.73%	34.42%
α-Cellulose content .. ..	60.71%	61.36%
Ash content of cellulose .. ..	0.60%	0.63%
Copper number of cellulose .. ..	1.97	1.09
Methylene blue absorption in millimoles per 100 g .. ..	2.51	2.54

For the estimation of total cellulose in jute, therefore, 0.7% sodium chlorite may be safely recommended in a fibre-liquor ratio of 1: 50 at the temperature of boiling water-bath for 2 hours, the pH of the chlorite solution should be near about 4. The rate of delignification under these conditions is shown in Table XI.

TABLE XI.

Rate of delignification with 0.7% NaClO<sub>2</sub>; J-160 defatted; Fibre-liquor ratio—1: 50;  
Temp. 98-99°C.

Expt. No.	Time in hrs.	%	%	Difference.
		Apparent cellulose.	Residual lignin.	
	1	2	3	(2-3)
1	½	95.41	5.49	89.92
2	1	93.58	3.52	90.06
3	1½	90.48	1.73	88.75
4	2	88.80	0.36	88.44

It may be noted that about 50% of the lignin present in the fibre is removed during the first half-an-hour; the rate then falls as in the case with 3.5% chlorite at 60-70° (*vide* Table VI). This is interesting from the point of view of jute bleaching. Since prolonged exposure of the fibre to the action of hot chlorite is deleterious, this indicates the possibility of bleaching jute partially (a light cream colour is thus obtained which may be considered quite good for many purposes) for half-an-hour under the above conditions.

To see if a still lower concentration of chlorite would be effective for the complete removal of lignin from jute fibre, a 0.5% solution of NaClO<sub>2</sub> was tried under different conditions. The results are shown in Table XII. It is possible to delignify jute completely even with such low concentration of chlorite provided the fibre-liquor ratio is 1: 100. Very frequent stirring is essential for success of the experiment.

TABLE XII.

J-160 defatted; 2g-samples taken; Temp. 98-99°C; Concentration of NaClO<sub>2</sub>—0.5%; pH—3.4.

Expt. No.	Mode of treatment.	%	%	Difference.
		Apparent cellulose.	Residual lignin.	
		a	b	(a-b)
1	Fibre-liquor ratio—1: 100, 1 hr.	.. 93.48	6.37	86.91
2	Fibre-liquor ratio—1: 100, 1½ hr.	.. 91.75	2.71	89.04
3	Fibre-liquor ratio—1: 100, 2 hrs.	.. 87.86	0.29	87.57
4	Fibre-liquor ratio—1: 100, 3 hrs.	.. 86.71	0.25	86.46
5	Fibre-liquor ratio—1: 100, 4 hrs.	.. 85.61	Nil	85.61
6	Fibre-liquor ratio—1: 75, 2 hrs.	.. 90.31	2.37	87.94
7	Fibre-liquor ratio—1: 50, 2 hrs.	.. 93.47	5.33	88.14

The copper number and methylene blue absorption value for the fibre cellulose obtained in experiment 3 are 1.37 and 2.62 millimoles per 100 g respectively. Both these are somewhat higher than in the case of cellulose obtained with 0.7% chlorite in a liquor-ratio of 1: 50 (*vide* Table X). The latter procedure is therefore preferred to the former.

It may now be definitely said that by means of sodium chlorite complete removal of lignin from jute fibre is quite possible and therefore, the first desideratum in a method for cellulose estimation is thus achieved. We have now to see whether or not all other constituents of the fibre are intact, and the cellulose has suffered any degradation during the process of isolation. The figures for the percentage yield of cellulose (either at 60-70°C or at 98-99°C) under optimum conditions will show that there has apparently been no loss of any of the constituents by degradation inasmuch as they strictly conform to the theoretical values, *viz.* (100—% lignin). The percentages of mineral and nitrogenous matter in the separated cellulose remain more or less the same showing thereby that the small amounts of mineral and protein matter remain almost wholly associated with the fibre cellulose itself. The analytical figures for the raw (defatted) jute and the fibre cellulose obtained by the sodium

chlorite method, both calculated on 100 g of bone-dry raw material, are given in Table XIII whence it will appear that the polyuronides and the pentosans also remain intact. The constancy of the values of  $\text{CO}_2$  and furfural for raw and delignified jute at once indicates that very little, if any, oxycellulose (of the -COOH type) has been formed, for, the latter (glucuronic acid) would yield additional amounts of both  $\text{CO}_2$  and furfural. The copper number is not low as expected, but this does not appear to be due to the oxidative action on the cellulose material alone inasmuch as raw fibre itself has a fairly high copper number. The lower hemicelluloses presumably possess reducing property; boiling water extract of jute fibre reduces Fehling's solution. This is further corroborated by the observation that the copper number of cellulose (79.62%) obtained from jute after a very mild preliminary treatment of the raw fibre for half-an-hour with 0.5% NaOH solution (1:100) at room temperature (30°C) is 0.49 while the original fibre had a copper number 2.09. The loss suffered by the fibre during this pre-treatment with alkali is 5.10%.

TABLE XIII.

J-160 defatted.

The figures are expressed on 100 g of bone-dry raw material.

	Raw jute defatted.	Defatted jute delignified with 0.7% sodium chlorite.
Lignin .. .. .	11.48%	0.36%
$\text{CO}_2$ .. .. .	1.26%	1.20%
Furfural .. .. .	9.25%	8.88%
Nitrogen .. .. .	0.225%	0.163%
Ash .. .. .	0.79%	0.63%
Loss on alkali boil—(2% NaOH, 4 hrs.) .. .. .	16.70%	35.48% (includes lignin— 11.48%)
Copper number .. .. .	2.09	1.09
Methylene blue absorption value, millimoles per 100 g .. .. .	2.22	2.54

The only point of difference is the high loss the fibre cellulose suffers on alkaline treatment. This is not apparently due to the formation of oxycellulose (of the carboxyl type) since the  $\text{CO}_2$ -value is practically constant as also the furfural yield. Shortening of chain length may also be ruled out in view of the facts that the copper number is low and that the yield of  $\alpha$ -cellulose is practically the same, no matter which method of isolation of cellulose is followed provided it is not assumed that shortening of chain length by hydrolytic breakdown occurs equally in *all* the methods. It may be that the lignin serves as a protective coating for the hemicelluloses—as soon as lignin is removed, the latter dissolve freely in the caustic alkali. A lignin-hemicellulose combination theory has been put forward to account for this behaviour (Norman, 1937).

*Action of chlorite on pure cellulose.*—In order to ascertain to what extent, if at all, pure cellulose is attacked by the chlorite under conditions of experiment (for the isolation of fibre cellulose from jute fibre) quantitative filter paper (Whatman No. 42), cut into very small strips, was subjected to exactly the same treatment under identical conditions. The results obtained are given below. It will be seen that the effect of the chlorite on the cellulose of filter paper is hardly significant. That the oxidative action of the chlorite on the cellulose is the minimum becomes evident from the low copper number and low solubility in alkali of the treated material. The methylene blue absorption value of the filter paper treated with chlorite (3.5 or 0.7%) is, however, somewhat higher.

TABLE XIV.

Quantitative filter paper, Whatman No. 42. 2g-sample taken for each experiment.

*Results are expressed on 100 g of the bone-dry material.*

(a) Loss on treatment with 3.5% sodium chlorite solution at 60–70°C for 4 hrs. at pH 4, in solid-liquor ratio 1:50	0.61%
(b) Loss on treatment with 0.7% chlorite at 98–99°C for 2 hrs. at pH 4, in solid-liquor ratio 1:50	0.40%
(c) Copper number of sample treated as in (a)	0.52
(d) Copper number of sample treated as in (b)	0.33
(e) Copper number of original sample	0.38
(f) Loss on treatment of the original sample with 5% NaOH at room temp. (32°C) for 5 hrs. in solid-liquor ratio 1:100	0.57%
(g) Loss on treatment of the sample treated as in (b) with 5% NaOH at room temp. for 5 hrs. in solid-liquor ratio 1:100	0.60%
(h) Methylene blue absorption value of original filter paper (in millimoles per 100 g dry material)	1.01
(i) Methylene blue absorption of filter paper treated as in (a)	1.42
(j) Methylene blue absorption of filter paper treated as in (b)	1.43

The high copper number of raw jute (it has been found to vary between 2.0 and 3.6) is not apparently due to oxidation or hydrolytic degradation suffered by the fibre, for, carefully retted fibres also give a high value. Jute fibre has a fairly high percentage of hemicelluloses—pentosans and hexosans of comparatively low degree of polymerisation (as evident from their solubility in dilute caustic soda solution). These short chain molecules seem to be responsible for the high copper number. Jute fibre treated with boiling 2% NaOH gives a copper number which is about  $\frac{1}{4}$  of the original value. Approximately half the value is obtained when the fibre is extracted with 5% NaOH or soda ash or even lime water at room temperature. Not the true cellulose but these components of the fibre seem to be attacked by sodium chlorite in acid solution to some extent during delignification; but this is not reflected in the copper number of the separated cellulose, which is lower than that of the raw jute fibre. These turn yellow on heating or on prolonged storage. This after-yellowing is a characteristic feature of the cellulose obtained by Schmidt's method (using  $\text{ClO}_2$ ) as well as by the new method, both of which aim at the removal of lignin alone, retaining all other components. In Cross and Bevan's or Norman and Jenkins' method, however, such after-yellowing does not occur presumably due to the treatment with boiling 3% sodium sulphite solution (this is alkaline) in both cases. The latter removes the portion responsible for after-yellowing. In Cross and Bevan's method, pre-treatment with caustic soda also removes a fairly large portion of these bodies. It may be noted here that the yield of cellulose by either method is considerably lower than by the  $\text{ClO}_2$  or  $\text{NaClO}_2$  method, though the  $\alpha$ -cellulose calculated on the raw material from any of the four celluloses is practically the same (that from Cross and Bevan's method cellulose is, however, slightly lower in percentage).

It has not been possible to separate a holocellulose from jute (by treatment with  $\text{NaClO}_2$  alone), which will not turn yellow at all on heating or on storage. By using very mild conditions this after-yellowing can be minimised, no doubt, but cannot be averted altogether. Various pre-treatments were therefore given to the fibre before reacting with chlorite in order to obtain a cellulose which will not turn yellow on heating or on storage. The results are shown in Table XV. All the fibre celluloses were entirely free from lignin but the percentage of cellulose was somewhat lower in every case.

It is to be noted that the fibre cellulose, obtained in all cases in which pre-treatment with fairly strong NaOH even at room temperature was given, was obtained in the form of a pulp (like that in Norman and Jenkins' or Cross and Bevan's method). In order to retain the original fibrous structure, any pre-treatment with alkali must therefore be very mild, say, with 0.5% NaOH at room temperature. The fibre cellulose, obtained from jute by means of chlorite without alkali pre-treatment, loses its fibrous structure as soon as it is treated with dilute NaOH even at room temperature. This leads to the conclusion that it is the hemicelluloses

TABLE XV.

J-160 defatted; 2g-samples are used in all cases.

*All results are expressed on 100 g of bone-dry raw material.*

Pre-treatment.	Mode of extraction of cellulose.	% Cellulose.	Copper number.	Colour on heating at 105°C, 10 hrs.	Remarks.
1. Boiled with 1% NaOH (200 c.c.), $\frac{1}{2}$ hr.	3.5% NaClO <sub>2</sub> (200 c.c.) at 60-70°C, 4 hrs.	73.79	..	Practically white.	Loss in pre-treatment—12.54%.
2. With 1% NaOH (200 c.c.), (2+2) hrs., 31-32°C.	0.7% chlorite (100 c.c.) at 98-99°C, 2 hrs.	76.90	0.33	..	Loss in pre-treatment—6.77%.
3. With 1% NaOH (200 c.c.), 1 hr., 31-32°C.	Do. ..	78.05	..	..	....
4. With 1% NaOH (200 c.c.), $\frac{1}{2}$ hr., 31-32°C.	Do. ..	78.23	..	..	....
5. With 5% NaOH (200 c.c.), (2+2) hrs., 31-32°C.	Do. ..	73.13	..	..	On pre-treatment: CO <sub>2</sub> —0.81% Furfural—6.94%.
6. With $\frac{1}{2}$ % NaOH (200 c.c.), (2+2) hrs., 31-32°C.	Do. ..	77.35	0.38	..	Loss in pre-treatment—6.49%.
7. With $\frac{1}{2}$ % NaOH (200 c.c.), 2 hrs., 31-32°C.	Do. ..	77.11	0.40	..	On treatment: CO <sub>2</sub> —1.20% Furfural—9.23%.
8. With $\frac{1}{2}$ % NaOH (200 c.c.), 1 hr., 31-32°C.	Do. ..	78.80	..	..	....
9. With $\frac{1}{2}$ % NaOH (200 c.c.), $\frac{1}{2}$ hr., 31-32°C.	Do. ..	79.62	0.39	..	Loss in pre-treatment—5.10%.
10. With 1% Na <sub>2</sub> CO <sub>3</sub> (200 c.c.), 2 hrs., 31-32°C.	3% NaClO <sub>2</sub> at 60-70°C ..	88.29	..	Yellow	Residual lignin—0.85%.
11. Boiled with 2% Na <sub>2</sub> SO <sub>3</sub> (100 c.c.), for 20 mins.	0.7% NaClO <sub>2</sub> ..	85.16	..	Pale yellow	....
12. With $\frac{1}{2}$ % NaOH (200 c.c.), 4 hrs., +1.6% HCl, 4 hrs. at 32°C.	3.5% NaClO <sub>2</sub> at 60-70°C ..	77.00	0.48	White	....
13. Nil ..	0.7% NaClO <sub>2</sub> and extracted with 2% Na <sub>2</sub> SO <sub>3</sub> .	81.21	..	Pale yellow	....

(hexosans particularly) which bind the ultimate cells in jute fibre, but not lignin—as is generally believed. It therefore seems possible to remove the lignin and yet retain the strength of the fibre. The interesting point in this connection is that by pre-treatment with very dilute alkali at room temperature and subsequently reacting with 0.7% chlorite at the temperature of boiling water-bath, we obtain near about the same percentage of cellulose as by Norman and Jenkins' method. The very low copper number of such product indicates that it has not suffered oxidation. This aspect of the problem of cellulose estimation has not received the attention it deserves. Complete removal of lignin is as important as protection of the cellulose from oxidation or hydrolysis. With sodium chlorite it is now possible to remove *all* the lignin from jute fibre and obtain the holocellulose in quantitative yield and with minimum degradation. Work is in progress to find out a procedure by which it may be possible to arrest the after-yellowing of the fibre cellulose completely. It is likely that the lower hemicelluloses (which dissolve readily in dilute NaOH even at room temperature) are responsible for this development of yellow colour on heating or storage. Whether or not this is due to the formation of protein chloroamine remains an open question. It has not been found possible to remove the small amount of nitrogenous matter from the fibre by extraction with neutral solvents or by any other simple means without removing the hemicelluloses partially. It has been found that the amounts of nitrogen in the raw and delignified jute (calculated on raw jute) are only slightly different (0.225% for raw and 0.163% for jute delignified with 0.7% chlorite), showing thereby that the nitrogenous matter is not severely attacked and largely removed during treatment with chlorite. Pre-treatment with 0.5% NaOH for half-an-hour at room temperature (32°C) followed by delignification with 0.7% chlorite resulted in a greater reduction in the percentage of nitrogen (0.082%) in the final product.

*Polyuronides in jute fibre.*—One very interesting observation has been made in connection with the jute fibre cellulose obtained with sodium chlorite. Unlike in the case of ClO<sub>2</sub>-cellulose, it is not possible to extract with 0.5% ammonium oxalate or 2% sodium fluoride solution (both excellent solvents for pectin) any appreciable amount of CO<sub>2</sub>-yielding components present therein. It was expected that the removal of such bodies by this means would be an easy task after the complete separation of lignin. It seems, therefore, that polyuronides are not mere encrustants (as Norman holds) existing separately. A lignin-polyuronide combination theory appears to be inconsistent with the fact for, in that case, after the removal of lignin, polyuronides would be free to be extracted by solvents. It may be that the polyuronides and polysaccharide hemicelluloses form links of the same chain, and that oxalate or fluoride solution can extract the free polyuronide but not the combined ones. The extraction with 0.5% ammonium oxalate was done for four hours—changing the solution at the end of every hour, in the fibre-liquor ratio of 1:100, at 80–85°C. With 2% fluoride, the extraction was done under the same conditions but at the temperature of boiling water-bath. The results are shown below (Table XVI).

TABLE XVI.

J-160 defatted.

*All figures are expressed on 100 g of bone-dry jute fibre.*

Description of sample.	% CO <sub>2</sub> .
(a) Raw fibre defatted with alcohol-benzene .. .. .	1.26
(b) Raw fibre defatted and delignified with 0.7% NaClO <sub>2</sub> .. .. .	1.20
(c) Sample (b) extracted with 0.5% ammonium oxalate .. .. .	1.04
(d) Sample (b) extracted with 2% sodium fluoride .. .. .	1.12
(e) Sample (a) delignified with ClO <sub>2</sub> .. .. .	1.60
(f) Sample (e) extracted with 0.5% ammonium oxalate as in (c) .. .. .	0.55

*Applications of the chlorite method to other lignocelluloses.*—An attempt was next made to see if the procedure worked out for the estimation of fibre cellulose in jute could be successfully applied to other lignocelluloses. The method was

tried on paddy straw (cut into very small pieces, preferably ground into a powder) and pine wood (in the form of sawdust). Both were previously extracted with alcohol-benzene. 0.7% sodium chlorite at 98-99°C for two hours at a solid-liquor ratio of 1:50 was used in both cases with and without any pre-treatment with boiling caustic soda. The results are given in Table XVII.

TABLE XVII.

The figures are expressed on 100 g of the bone-dry material. 2g-samples were taken in each case.

Material.	Pre-treatment.	% Holo-cellulose.	% Residual lignin.	Remarks.
Paddy straw	.. Nil .. .. .	70.18	0.56	*
Paddy straw	.. Boiled with 200 c.c. of 1% NaOH for ½ hr. . . .	52.93	0.22	..
Pine wood (Ash—0.45%)	Nil .. .. .	79.41	8.94	..
..	.. Boiled with 200 c.c. of 1% NaOH for ½ hr. . . .	65.02	5.66	..

\* Ash of the original material—10.09%. Some of this ash comes with the lignin appearing white. It is readily soluble in dil. NaOH. Residual lignin is obtained by treating this apparent lignin with chlorite solution and filtering. The difference is 0.56 only.

It is clear that complete removal of lignin by means of sodium chlorite is possible in case of paddy straw without any pre-treatment with boiling alkali but not so in the case of pine wood even after an alkali treatment. It may be noted here that Jayme (1942) also could not completely delignify beech or spruce wood with NaClO<sub>2</sub>; the cellulose obtained from both contained 3% of lignin which is considered to be 'particularly resistant'. By using bromide-bromate mixture Shrikhande (1944), however, was unable to remove all the lignin from paddy straw (2.72% remained with the cellulose). It seems therefore that the chlorite method would be better than Norman and Jenkins' (by which also Shrikhande could not remove all the lignin from paddy straw) or Shrikhande's.

The lignin in jute fibre or paddy straw, both of which are annual plants, seems to be less highly polymerised and so less complex and less resistant than various wood lignins.

Cellulose has been prepared by the three current methods and also by the new one, from the same sample of jute, strictly following the recommended procedures in each case. The celluloses thus obtained have been analysed for their quality in the usual manner. The results are shown in Table XIX. The analytical constants of the sample of jute (J-161) used for the purpose are given below.

TABLE XVIII.

J-161 defatted; Lignin—11.80%; CO<sub>2</sub>—1.30%; Copper number—1.91;  
Furfural—8.50% (ppt. washed with alcohol).  
Loss in alkali boil (2% NaOH for 4 hours)—18.40%.

It would appear from the Table given below that only by the sodium chlorite method it is possible to obtain *all* the constituents of the fibre free from lignin, *i.e.*, one can obtain the holocellulose. The ClO<sub>2</sub> method of Schmidt gives a cellulose which has not only the highest copper number but also the highest loss on alkaline boil (as also the highest % CO<sub>2</sub>)—indicating thereby the degradation it has suffered during the process of isolation. It may be noted that by Norman and Jenkins' method, it is not possible to remove *all* the polyuronides (which are regarded by them as encrustants). In Cross and Bevan's method some of the α-cellulose is lost presumably due to the oxidising action of moist chlorine. Some pentosans are removed in both methods—Norman and Jenkins' as well as Cross and Bevan's—during the alternate treatment with boiling sodium sulphite which is alkaline.

Compared with the existing methods for the estimation of cellulose the new method, particularly when 0.7% chlorite is used at 98-99°C, is far less time-consuming.

TABLE XIX.  
J-161 defatted.

Method.	% Cellulose on raw jute.	% Residual lignin in cellulose.	%CO <sub>2</sub> .	% Furfural.	Copper No.	% α-Cellulose	% α-Cellulose on raw jute.	% Cellulose + lignin.	% Loss.*
Cross and Bevan's	72.55	0.02	1.04	8.94	1.03	78.01	56.61	84.35	14.59
Chlorine dioxide	84.96	0.20	1.67	9.27	4.70	70.88	60.22	96.76	41.01
Norman and Jenkins'	77.77	0.18	0.86	7.20	2.69	78.65	61.15	89.57	30.33
Sodium chlorite (3.5%) at 60-70°C	89.03	0.40	1.46	9.85	1.48	68.15	60.43	100.83	30.23

The analytical figures in columns 1, 7, 8 and 9 are expressed on 100 g of bone-dry raw jute and the rest on 100 g of bone-dry fibre cellulose.

\* Loss on 2% NaOH boil for 4 hours.

Furthermore, it requires the least amount of personal care and attention. Unlike Cross and Bevan's or the  $\text{ClO}_2$  method, it does not involve the application of obnoxious gases which are troublesome to work with. One has to be extremely active throughout the whole working day in giving alternate treatments with  $\text{NaOCl}$  and hot  $\text{Na}_2\text{SO}_3$ , transferring the material *quantitatively* a good number of times and so on in the case of Norman and Jenkins' method. Nothing of the sort is required here. No hot alkaline treatment (with  $\text{NaOH}$  or  $\text{Na}_2\text{SO}_3$ ), before or after, is necessary in this case. The method, as it is, may be called neat, simple, quick and accurate.

*Action of chlorite in bleaching.*—It is as yet not definitely established how sodium chlorite acts during bleaching. The actual oxidizing agent may be sodium chlorite itself, chlorine dioxide which it readily liberates, or chlorous acid,  $\text{HClO}_2$ , which is set free when  $\text{NaClO}_2$  is acidified. Or, the bleaching action may be due to the combined effect of any two or all of them. Jeanes and Isbell (1941) carried out a large number of quantitative experiments on the action of chlorites on carbohydrates and concluded that chlorous acid was the oxidant. White, Taylor and Vincent (1942) observed that the majority of the consumption of the chlorite in the presence of paper pulps was by direct reaction of the chlorite ion. They, therefore, corroborate the findings of Jeanes and Isbell. None consider chlorine dioxide to be the bleaching agent.

It is a well-known fact that sodium chlorite bleaches only in acid solution; in neutral or alkaline solution, it is hardly reactive. Results with acid solution of sodium chlorite, so far as delignification of jute is concerned, have already been reported. Two experiments with the same sample of jute (*viz.*, J-160 defatted) and 0.7% of sodium chlorite at 98-99°C for 2 hours at a fibre-liquor ratio of 1:50 were carried out, one at pH 8 and another at pH 7 (buffered). The results, which are shown in Table XX, indicate that only a very small amount of lignin can be removed by this means. The loss in weight with pH 8 (alkaline) is apparently due to the removal of some of the hemicelluloses. The figure for lignin in the residue is fairly high.

In all probability, therefore, sodium chlorite itself is not the active agent in the delignification of jute fibre.

TABLE XX.

J-160 defatted; Lignin—11.48%; Holocellulose—88.52% (100—11.48).

pH of the chlorite solution.	% Apparent cellulose.	% Residual lignin.	Difference.
	a	b	(a-b)
5.2	88.51	0.36	88.15
7.0	95.34	8.62	86.72
8.0	93.57	10.35	83.22

That  $\text{ClO}_2$  also is not the real bleaching agent appears from the following considerations:—

(1) The solubility of the gas ( $\text{ClO}_2$ ) is only 1.26% at room temperature (31°C) and normal barometric pressure. But at 98-99°C, it is only 0.02%. It is extremely unlikely that such a low concentration of  $\text{ClO}_2$  would be able to dissolve out lignin completely.

(2) The rate of decomposition of sodium chlorite in acetic acid solution is rather slow, with a 0.7% solution in contact with jute fibre (fibre-liquor ratio 1:50) the final strength is usually found to be 0.3% after two hours at 98-99°C. And at every stage of the reaction it is the chlorite that predominates in solution and not  $\text{ClO}_2$ . This has been determined by estimating the total—chlorite plus  $\text{ClO}_2$ —first; and then only the chlorite, after blowing off with air all the  $\text{ClO}_2$  (the chlorite solution then becomes practically colourless). The results of one typical experiment with J-160 in chlorite solution (1:100) are given in Table XXI.

TABLE XXI.

Rate of decomposition of chlorite in solution at pH 3.4.

Initial concentration—3.5%, temperature 60–70°C.

Time interval.	c.c. N/10 thio consumed by 1 c.c. of chlorite + ClO <sub>2</sub> .	c.c. N/10 thio ≡ 1 c.c. same solution after ClO <sub>2</sub> has been blown off.
Nil	14.70	14.65
1 hr.	14.10	14.0
2 hrs.	13.20	13.10
3½ hrs.	12.3	12.45

It has been observed that in presence of acetic acid the chlorite decomposes much more slowly than when H<sub>2</sub>SO<sub>4</sub> or HCl is present. With the latter, therefore, it is difficult to effect complete delignification under otherwise identical conditions. The results in Table XXII below will show why acetic acid has all along been employed to lower the pH of the chlorite solution. The copper number of the cellulose obtained in the latter two cases is also higher, though the methylene blue absorption value is practically the same. Very dilute HCl or H<sub>2</sub>SO<sub>4</sub> is employed to acidify the chlorite solutions and only small quantities are added at a time, otherwise, ClO<sub>2</sub> gas comes out in much greater proportion and bleaching becomes almost wholly ineffective.

TABLE XXII.

J-160 defatted; Concentration of chlorite—0.7%; Liquor-ratio—1:50;

Temperature 98–99°C; Time—2 hours.

Chlorite solution acidified

	With H <sub>2</sub> SO <sub>4</sub>	With HCl	With acetic acid.
% Cellulose .. ..	90.93	91.45	88.80
Copper number .. ..	1.71	1.37	1.09
Methylene blue absorption value (millimoles/100 g)	2.54	2.53	2.54

## EXPERIMENTAL.

*Preparation of sodium chlorite.*—Though the Mathieson Alkali Works of New York have been making sodium chlorite on a commercial scale for some years past, it is not available in the Indian market as yet. Due to war conditions, our attempts to import the chemical from abroad proved futile. We, therefore, prepared it by generating chlorine dioxide gas and absorbing the latter in 10% caustic soda solution. Chlorine dioxide was obtained by gently warming on water-bath an intimate mixture of finely powdered potassium chlorate (90 g) and oxalic acid crystals (75 g) with dilute sulphuric acid (45 c.c. conc. acid in 150 c.c. of water). The reaction, once started, goes on by itself and a slow stream of ClO<sub>2</sub> is obtained for about 24 hours. The gas is very slowly absorbed by NaOH solution and so the process is both lengthy and tedious. It is important to see that the liquid remains alkaline; as soon as all the NaOH disappears, sodium chlorite begins to decompose. The process is not efficient, as half the chlorine dioxide is lost in the formation of sodium chlorate:  $2\text{ClO}_2 + 2\text{NaOH} = \text{NaClO}_2 + \text{NaClO}_3 + \text{H}_2\text{O}$ . Furthermore, CO<sub>2</sub> consumes a fairly large proportion of the NaOH and forms sodium carbonate and bicarbonate. Oxalic acid has got to be used with potassium chlorate, for CO<sub>2</sub> liberated therefrom makes the ClO<sub>2</sub> less liable to explode. The less soluble sodium chlorate and bicarbonate separate out, after about 48 hours—the chlorite remaining in solution. A stock solution containing 4–6% NaClO<sub>2</sub> could thus be made. This was diluted with the requisite quantity of water for various experiments.

*Estimation of sodium chlorite.*—This was done by iodometric titration. 1 c.c. of the chlorite solution was diluted to about 20 c.c., an excess of KI (about 2 g) was added and the solution was acidified with acetic acid. The liberated iodine was titrated with N/10 thiosulphate solution in the usual manner. The presence of sodium chlorate in the chlorite solution does not interfere with the estimation of NaClO<sub>2</sub>. This has been verified by performing a blank experiment with pure NaClO<sub>3</sub> under identical condition. The chlorite solution invariably contains a little ClO<sub>2</sub> when acidified. If the acidification is carefully done with acetic acid and a slight excess of the acid be present, the amount of the ClO<sub>2</sub> gas in the solution is very small indeed. This gas also liberates I<sub>2</sub> from KI under conditions of estimation. It may be expelled from the solution by blowing air. At room temperature, the rate of liberation of ClO<sub>2</sub> from NaClO<sub>2</sub> due to the action of acetic acid is rather slow and so it is possible to estimate the chlorite after removal of ClO<sub>2</sub>. But for practical purposes this step was found to be unnecessary, the difference between the two titrations being very small.

White, Taylor and Vincent (1942) do not precisely indicate in their analysis of chlorite solutions how the estimation is to be done. From the analytical data of Jeanes and Isbell (*loc. cit.*) it is found that—

5 gm NaClO<sub>2</sub> (in 100 c.c.)   ≡ 22.0 c.c. N/10 NaHSO<sub>3</sub> solution,  
 which is—                           ≡ 22.0 c.c. N/10 iodine solution,  
 whence, 1 litre of N solution of I<sub>2</sub>   = 22.61 g NaClO<sub>2</sub> (mol. wt. 90.45).  
 So that, 1 mol NaClO<sub>2</sub> reacts with 4I,  
           or,   NaClO<sub>2</sub> + 4KI + 4CH<sub>3</sub>COOH  
   = NaCl + 2I<sub>2</sub> + 4CH<sub>3</sub>COOK + 2H<sub>2</sub>O.  
 ∴ 1 c.c. N/10 I<sub>2</sub> (or thiosulphate) = 0.00226 g NaClO<sub>2</sub>.

*Treatment of fibre with chlorite.*—It is essential that the fibre should be very finely cut and uniformly distributed in the liquid. Lumps should not be allowed to form. Frequent stirring with a glass rod facilitates the process of delignification—a finely divided, white solid deposits at the bottom thereby and the chlorite can act better. For preventing the loss of water due to evaporation during the reaction, the experiments were usually done in conical flasks fitted with tall air condensers. The flasks were shaken from time to time—stirring with a glass rod being inconvenient. Alternatively, a funnel placed on the mouth of the conical flask served the same purpose.

The jute fibre was extracted for 5 hours in a Soxhlet apparatus with a mixture of alcohol-benzene (1:1 by volume) to remove fat and resinous matter (and also varying amounts of chlorophyll) before treatment with chlorite. With fibre thus defatted, the penetration of chlorite solution was better and the action consequently quicker.

After treatment with chlorite, the fibre was collected on a Jena sintered glass crucible (1G3) and thoroughly washed thereon with water and then with 2% sodium bisulphite solution and finally with water. The very pale yellow colour of the fibre becomes milky white on washing with bisulphite solution. This solution being acidic, no loss of hemicelluloses occurs as with sodium sulphite solution. The drying of the fibre was done in a vacuum evaporator on water-bath, first with a good water pump and then with a hyvac cenco pump. The crucibles were kept overnight over fresh concentrated H<sub>2</sub>SO<sub>4</sub> under vacuum in a vacuum desiccator and weighed the next day. This was done mainly to avoid yellowing of the fibre in air at 105°C. The hemicelluloses seem to get oxidised in air and turn yellow. The bone-dry fibre being hygroscopic, the weight was invariably taken in weighing bottles (tared with a similar one).

*Estimation of lignin.*—Lignin was determined on one-gram samples of the defatted finely cut jute fibre and on the material obtained from two-gram samples of the same (moisture determined on a separate sample). In every case, the sample was first treated with 100 c.c. of 5% H<sub>2</sub>SO<sub>4</sub> on boiling water-bath for one hour according to the procedure recommended by Norman and Jenkins (1934). To the washed and dried fibre, taken in a stoppered flask, was then added 25 c.c. (40 c.c. in the case of the material from a 2g-sample) of 72% H<sub>2</sub>SO<sub>4</sub> and shaken in a shaking

machine for about one hour. This was kept overnight in a refrigerator (temp. below 10°C). Next day the contents were diluted to about 3% H<sub>2</sub>SO<sub>4</sub>, boiled for two hours and allowed to settle. The supernatant liquid was siphoned out and passed through a weighed sintered Jena glass filter (1G3). The residue was next filtered, washed and dried.

This lignin is almost invariably contaminated with varying amounts of cuticular matter. It can be readily separated by suspending the lignin in water and passing ClO<sub>2</sub> gas into it. The lignin thus dissolves completely leaving behind the cuticle, the amount of which scarcely exceeds 0.5%. The residue left after ClO<sub>2</sub> treatment is not cellulose, for, it does not dissolve in 72% H<sub>2</sub>SO<sub>4</sub>.

*Determination of furfural.*—Both polyuronides and pentosans yield furfural on boiling with 12% HCl but none quantitatively. Some amount of hydroxymethyl furfural is liberated by hexosans under the same circumstances. The estimation is further complicated by the fact that formaldehyde, set free by boiling mineral acids from lignin, condenses with phloroglucinol to form an insoluble compound. Some workers wash the precipitate of phloroglucide with hot alcohol to dissolve out the last two but in such a case Kröber's tables cannot be used, for, it was never meant for such a procedure (Angell, Norris, Resch, 1936). We have, therefore, preferred to omit the washing with alcohol in view of the fact that the actual amount thus removed is rather small. We have in general followed the procedure of A. W. Schorger as outlined by Dorée (1933, p. 361) for the estimation of furfural. 2g-samples of jute were taken and the estimation was done in duplicate. Instead of 40 c.c. of the phloroglucinol solution, we added 50 c.c.; it was found that the yield of phloroglucide increased slightly in the latter case. The precipitate had to be filtered under very mild suction, otherwise a portion of the precipitate passed out through the sintered Jena glass filter. The washing with water was done very carefully to avoid the formation of a colloidal solution which again passed through the glass filter. By using a special type of distilling flask (after Kullgren and Tydén) the effects of bumping could be nullified.

*Estimation of carbon dioxide.*—Unlike furfural, the yield of CO<sub>2</sub> from polyuronides is quantitative. The procedure of Nanji, Paton and Ling (1925) was followed in the determination of CO<sub>2</sub>. The details are given by Dorée (1933, p. 371). The small amount of CO<sub>2</sub> given by lignin under the conditions of experiment was ignored and the whole of it was attributed to uronic acid anhydrides. 2g-samples of jute were taken for the purpose and the experiment was done in duplicate. From time to time a blank experiment was performed to test if the apparatus was free from leakage. In calculation, the blank titre was deducted. The frothing in the U-tube containing aniline hydrochloride solution was prevented by putting some glass wool into it. With this modification, the estimation could be done without any difficulty.

(1) % Uronic anhydride = % CO<sub>2</sub> × 4 (Nanji, Paton and Ling, *loc. cit.*).

(2) Uronic anhydrides give 23.50% of their weight of furfural (Norris and Resch, 1935).

From the above two relationships, it is possible to find out the amount of polyuronides present in jute as well as the quantity of furfural actually yielded by this amount of polyuronide. The balance of the total furfural is derived from pentosans.

From Kröber's tables,  $\frac{\text{Furfural}}{\text{Xylan}} \times 100 = 64.50$ , whence the amount of pentosan (as xylan) can be calculated.

From the total hemicelluloses (extracted by caustic soda) one can find out the amount of hexosans by subtracting the polyuronides and pentosans.

*Estimation of copper number.*—The method of Schwalbe-Braidy, as modified by Clibbens and Geake, was followed. The details are to be found in 'The Methods of Cellulose Chemistry' (Dorée, 1933, p. 38). It may be pointed out that the cellulosic material should be very thoroughly spread out beforehand. The reaction is incomplete and results are discordant if this is not done. While in the water-bath the flasks should be occasionally shaken. 2g-samples of raw fibre or the material obtained therefrom were taken for each experiment and duplicates always

done. 35 c.c. of iron alum solution and 50 c.c. of  $H_2SO_4$  were used to dissolve and wash the  $Cu_2O$  deposited on the fibre. The titration of the ferrous solution was done as quickly as possible. A blank determination with the same amount of chemicals used in the actual test was made and a correction applied.

*Methylene blue absorption value.*—This was determined according to procedures suggested by Clibbens and co-workers (1926). The dye solution was buffered to pH 7.0. The fibre (2 g of raw jute of known moisture content or the material derived therefrom) was very carefully spread out into a conical flask and 100 c.c. of the dye solution (0.4 millimoles per litre) was poured upon it, well shaken and left uncorked. The absorption is almost instantaneous. The titration of the exhausted dye bath with Naphthol-Yellow-S could not be done for want of the chemical. Colorimetric method was therefore followed—a Duboscq colorimeter being employed for the purpose. A general turbidity in the exhaust liquor made the colour match rather difficult. The shades appeared different. So, the decanted liquid was centrifuged at high speed and the clear liquid used for comparison.

Two interesting observations have been made in this connection that the absorption of the dyestuff by jute fibre (defatted) is, under otherwise identical conditions, dependent on the concentration of the dye solution; secondly, with raw jute the colour of the dye solution, when not exposed to air, is gradually discharged, presumably due to the reducing substances present in the fibre.

*Estimation of nitrogen.*—This was done by the well-known Kjeldahl method. In view of the small percentage of nitrogen present in jute, 10 g of the fibre, finely cut, was used for each estimation with 10 g of potassium sulphate, about 0.3 g of  $CuSO_4$  and 60 c.c. of pure concentrated  $H_2SO_4$ . The contents are intimately mixed together by gentle shaking and first placed over a small flame, cautiously shaking until copious frothing and evolution of white fumes have ceased. 25 c.c. (or more, depending on the nitrogen content) of N/10 acid is taken to absorb the liberated  $NH_3$ . The distillation was carried on with 100 c.c. of 60% NaOH and a few granules of zinc to prevent bumping and back-rush. A blank experiment was done to ascertain the purity of the chemicals used and a correction applied.

*Estimation of  $\alpha$ -cellulose.*—The fibre cellulose (about 1.5 g or the material obtained from 2 g of raw jute) is triturated with 50 c.c. of 17.5% by weight of NaOH solution at room temperature (30°C), allowed to stand for 30 minutes, diluted with 50 c.c. of water and filtered through a sintered Jena glass filter, washed with hot water. The material is next steeped into 100 c.c. of 10% acetic acid, then filtered in a tared glass crucible, washed and dried to constant weight at 105°C.

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