

## Utilization of Ion Exchangers in Analytical Chemistry. XVIII

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### DETERMINATION OF THE DEGREE OF SUBSTITUTION OF CELLULOSE XANTHATE IN VISCOSE

The possibility of separating high molecular anions from low molecular anions by anion exchangers has been demonstrated in several publications<sup>1-4</sup>. This separation is based on the fact that only the low molecular ions can penetrate into the narrow net-work structure of the ion exchanger and be adsorbed. These investigations have been performed by means of anion exchangers of the weakly basic type which can be used only in acid or neutral media. Recently anion exchange resins of strongly basic type (quaternary ammonium bases) have become available and these resins may be used also in alkaline medium. As a great number of high molecular acids are insoluble in water, or in certain cases, decompose in acid or neutral medium but give stable solutions in alkaline medium, it is of great interest to investigate if this type of anion exchanger can be used for a quantitative separation of high molecular anions from low molecular in alkaline medium.

As an example, the separation of cellulose xanthate from the by-products formed in the preparation of viscose (trithiocarbonate and sulphide) has been studied in the present paper. Based on this principle a new method for the determination of the degree of substitution (D. S.) of cellulose xanthate solutions (viscose) has been investigated.

A great number of methods have been used for the determination of the D. S. of cellulose xanthate in viscose. Most of the older methods are based on the reaction between cellulose xanthate and iodine which results in the formation of disulphide<sup>5</sup>. A number of modifications have been suggested, but the accuracy of all these methods leaves a great deal to be desired.

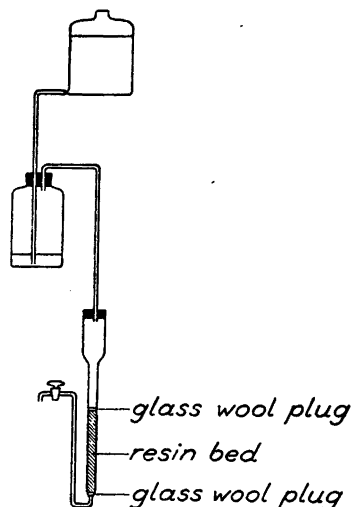


Fig. 1. Ion exchange apparatus.

A well-established method is the precipitation of cellulose xanthate with diethylchloroacetamide according to Fink, Stahn, and Matthes<sup>6</sup>. An insoluble, stable derivative is formed, the nitrogen content of which is determined according to Kjeldahl, and the D. S. calculated from the equivalence between nitrogen and xanthate sulphur. The method gives good reproducibility but the diethylchloroacetamide is an expensive and hazardous chemical.

More recently a volumetric method has been proposed by Barthélemy and Williams<sup>7</sup>. By boiling with sodium zincate solution the sulphur-containing products of viscose (cellulose xanthate, sulphide, and thiocarbonate) are transformed quantitatively into zinc sulphide, which is determined by iodometric titration. In another sample the cellulose xanthate is salted out with a saturated sodium chloride solution and the sulphur content in the filtrate is determined. The difference between the two sulphur determinations corresponds to the xanthate sulphur. The procedure is rather simple and rapid but errors may occur due to incomplete salting out and coprecipitation of trithiocarbonate and sulphide. For most purposes the method may be considered as satisfactory.

#### PREPARATION OF THE ION EXCHANGE COLUMN

The anion exchange resins Dowex 1 and Amberlite IRA-400 were sieved to obtain the particle size 0.36–0.85 mm (air dried). The columns were of ordinary type<sup>8</sup>. The diameter and height were 9 and 150 mm respectively. The flow-rate was kept at a proper level by means of an apparatus which is shown in Fig. 1.

The ion exchanger was transformed into the hydroxyl form by passing 500 ml. 1.5 *N* sodium hydroxide through a column and subsequent washing with distilled water (about 200 ml) until sodium hydroxide could not be detected in the effluent with phenolphthalein. The total time used for these operations was about 2 hours.

After the passage of the diluted technical viscose the columns were emptied and the resin from several columns collected in a beaker and treated with 4 *N* hydrochloric acid. The resin was then collected in a funnel and regenerated with sodium hydroxide as described above. This is less time-consuming than separate regeneration of each column. The treatment with hydrochloric acid was made in a beaker and not directly in the columns because gas bubbles were obtained which would have caused channeling in the columns.

#### PROCEDURE FOR DETERMINATION OF D. S. OF CELLULOSE XANTHATE

About 3 g of technical viscose is used in each experiment. The viscose is diluted with 250 ml ice-cooled distilled water and kept cool during the subsequent percolation through the ion exchange column. If highest accuracy is required the ion exchange column should also be cooled during the experiments. This is especially necessary at very high degrees of substitution of the cellulose xanthate. Afterwards the column is washed with 100 ml water at the same flow-rate as during the adsorption step (5–8 ml/min).

The combined filtrate and washing water is collected in a 500-ml Erlenmeyer flask containing 10 ml of a sodium zincate solution, prepared according to Barthélemy and Williams<sup>7</sup>. The mixture is boiled for 30 minutes and the flask then ice-cooled. After cooling the contents of the flask is washed into a 600-ml beaker containing a cold solution of 50 ml of 1 *M* sulphuric acid and 30 ml of 0.1 *N* iodine. Immediately thereafter the mixture is transferred quantitatively back to the Erlenmeyer flask. After 20 minutes the iodine not consumed is titrated with a 0.1 *N* solution of sodium thiosulphate with starch as indicator. The cellulose content in the viscose is determined according to Jentgen<sup>9</sup> on a separate sample. The D. S. is calculated according to the following formula.

$$\text{D. S.} = \frac{0.0405 \cdot (\text{ml } I_2 \cdot n_1 - \text{ml } Na_2S_2O_3 \cdot n_2)}{\text{g cellulose in the viscose sample}}$$

$n_1$  and  $n_2$  are the normalities of the iodine and thiosulphate solutions respectively.

#### RESULTS AND NOTES ON PROCEDURE

On passing the diluted viscose solution through the anion exchange column the upper layer of column was coloured red. About one day after the adsorption had been performed the layer below the red-coloured one was slightly green. After some time (about 14 days) the colour of both layers had changed to brown. The height of the column was chosen so that the lowest part of the column had the same colour after the adsorption step as before.

The first experiments were performed to study if the retention of thio-carbonate and sulphide in the column was quantitative. The ice-cooled filtra-

tes from the column were immediately titrated potentiometrically with 0.1 *N* mercuric chloride<sup>10, 11</sup>. Sulphide and thiocarbonate could not be detected showing that a quantitative adsorption had been obtained.

Separate experiments were made in order to find out whether the cellulose passes the column quantitatively. 7.9 g technical viscose was diluted with distilled water to 250 ml in a volumetric flask. Two aliquots of 50 ml each were diluted to the same concentration as in the other experiments and filtered through two ion exchange columns (Dowex 1), and after washing with 100 ml distilled water the filtrates were neutralized with hydrochloric acid with methyl red as indicator. After evaporating most of the water ethyl alcohol was added and the precipitated cellulose filtered off on glass filters, washed with water, carbon disulphide, and water again. The cellulose was then dried at 100—105° C for six hours and the crucibles were weighed after cooling in a desiccator. Two other aliquots of 50 ml each were neutralized directly and the cellulose content was determined as described above. The results presented in Table 1 indicate that the cellulose xanthate remains quantitatively in the solution.

Table 1. Determination of cellulose content.

Cellulose content of diluted viscose g/50 ml	
Direct determination	After passage of the ion exchanger
0.1106	0.1110
0.1119	0.1100

The procedure described in the previous section has been tested using three viscoses of different ripeness and two different anion exchange resins, Dowex 1 and Amberlite IRA-400. In order to study the efficiency of the regeneration some experiments were also performed with resins which had previously been used for viscose, and regenerated as described above. The results have been compared with parallel determinations of the D. S. according to Fink, Stahn, and Matthes<sup>6</sup>, as well as Barthélemy and Williams<sup>7</sup>, *i. e.* without use of ion exchangers. The results may be seen from Table 2.

Furthermore, experiments have been performed with direct addition of 0.1 *N* iodine solution (20 ml) to the effluent from the column after neutralization with acetic acid. Excess iodine was back-titrated with sodium thio-sulphate<sup>5</sup>. The method does not give good results. The iodometric titration

has earlier been criticized by many investigators for inaccuracy, and this is confirmed by our own experience.

Table 2. *D. S. of cellulose xanthate determined by different methods.*

Method	Viscose A		Viscose B		Viscose C	
<i>Proposed ion exchange method:</i>						
Dowex 1	37.3	38.0	27.9	27.4	21.7	21.2
Dowex 1, regenerated	37.6		27.3		21.1	
Amberlite IRA-400	37.7	38.1	27.3	27.9	21.7	21.6
Amberlite IRA-400, regenerated	37.2		27.9		21.6	
<i>Fink, Stahn, and Matthes</i>	35.0		24.6		21.6	
<i>Barthélemy and Williams</i>	37.4	36.4	25.8	23.9	22.0	22.4

The influence of the flow-rate and the temperature at which the experiment is performed has been investigated using a fresh viscose sample. The resin Dowex 1 was used in the experiments and the obtained results are presented in Table 3.

The results indicate that a flow-rate of 5—8 ml/min is necessary in order to prevent decomposition of the cellulose xanthate during the experiment. For the same reason the ice-cooling cannot be excluded.

Table 3. *D. S. of cellulose xanthate determined at different flow-rates and temperatures.*

Temp.	Flow-rate ml/min	Viscose 1	Viscose 2
The viscose and the ion exchange column ice-cooled	8		45.9
	5		45.8
	2		45.0
The viscose ice-cooled	5	49.0	45.5
	2	45.7	44.1
Room temp.	5	46.1	44.3
	2	43.6	42.3

As a complement, resin beds of different heights have been investigated as well as the influence of an addition of sodium sulphite. The results presented in Table 4 were made using a fresh viscose sample. The resin Dowex 1 was used in these experiments. The experiments were in other respects made according to the procedure described in the previous section. As can be seen from the Table a height of 80 mm is sufficient for complete adsorption under the conditions in question. Furthermore it is obvious that sulphite ions do not interfere with the determination.

Table 4. D. S. of cellulose xanthate determined under different conditions.

Height of resin bed mm	Addition of Na <sub>2</sub> SO <sub>3</sub> g	D. S.
150	0.105	49.6
150	—	49.4
80	0.112	49.6
80	—	49.1
50	—	52.1

#### DISCUSSION

The experiments presented above show that the sulphur-containing by-products present in viscose (trithiocarbonate and sulphide) are quantitatively retained in a column filled with an anion exchange resin of the strongly basic type, whereas the cellulose passes the column. In the purified cellulose xanthate solution obtained the degree of substitution can be easily determined in a reproducible manner according to the zincate method. The method can be applied to viscoses containing sulphite.

The figures obtained are slightly higher than for corresponding analyses performed on the same viscose according to Fink, Stahn, and Matthes<sup>6</sup>. As the adsorption of by-products in the ion exchange column has been shown to be complete there is no reason to believe that the ion exchange method should give too high values. Therefore the conclusion must be drawn that the method to Fink, Stahn, and Matthes<sup>6</sup> gives values which are slightly lower than the correct value.

A comparison between the proposed method and the method devised by Barthélemy and Williams<sup>7</sup> shows that rather good agreement has been obtained. The ion exchange method is, however, superior not only from the theoretical point of view but gives also better reproducibility. The procedure is simple and rapid, the time required for the determination being about two hours. Several analyses can be performed simultaneously.

## SUMMARY

In the present paper a new method for the determination of the degree of substitution of cellulose xanthate solutions (viscose) has been investigated. The method is based on the possibility to separate low molecular anions from high molecular anions by anion exchangers. The procedure is simple and rapid and gives more accurate values than other methods for the same determination.

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## REFERENCES

1. Samuelson, O. *Svensk Papperstidn.* **46** (1943) 583.
2. Samuelson, O. *Svensk Kem. Tid.* **56** (1944) 343.
3. Samuelson, O. *Svensk Kem. Tid.* **61** (1949) 76.
4. Williams, K. T., and Johnson, C. M. *Ind. Eng. Chem.* **16** (1944) 23.
5. Cross, C. F., Bevan, E. J., and Beadle, C. *Ber.* **26** (1893) 1090.  
Cross, C. F., and Bevan, E. J. *Ber.* **34** (1901) 1513.  
Jentgen, H. *Kunststoffe* **1** (1911) 165.  
de Wyss, G. *Ind. Eng. Chem.* **17** (1925) 1043.  
d'Ans, J., and Jäger, A. *Kunstseide* **8** (1926) 17; *Cellulosechemie* **16** (1935) 22.  
Faust, O., Graumann, E., and Fischer, E. *Cellulosechemie* **7** (1926) 165.  
Bernhardt, R. *Kunstseide* **8** (1926) 173, 259.  
Heuser, E., and Schuster, M. *Cellulosechemie* **7** (1926) 27.  
Geiger, E. *Helv. Chim. Acta* **13** (1930) 296.  
Berl, E., and Dillenius, H. *Cellulosechemie* **13** (1932) 8.
6. Fink, H., Stahn, R., and Matthes, A. *Angew. Chem.* **47** (1934) 602.
7. Barthélemy, H., and Williams, L. *Ind. Eng. Chem., Anal. Ed.* **17** (1945) 624.
8. Samuelson, O. *Diss. Kungl. Tekniska Högskolan*, Stockholm (1944).
9. Jentgen, H. *Laboratoriumsbuch für die Kunstseide- und Ersatzfaserstoffindustrie*, Halle (1923).
10. Eckert, P., and Huan, R. *Kleppzig's Textil-Z.* **41** (1938) 205.
11. Samuelson, O. *Cellulosa och papper*, Stockholm (1948) p. 301.

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