

Washing of Acid from Cellulose Fibers in Connection with the Determination of Carboxyl Groups

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Synopsis

Cellulose samples of bleached sulfite and sulfate pulps have been treated in columns with 0.1*N* radioactive hydrobromic acid and subsequently washed with water. The experiments show that after washing with small amounts of water (about 50 ml./g. sample) the radioactivity of the effluent is very low corresponding to a hydrobromic acid concentration of less than 0.0002 $\mu\text{eq./ml}$. Radioactivity measurements made directly on the cellulose specimen after washing verified that insufficient acid is present in the fibers to affect the titration estimation of the carboxyl groups.

In most methods for the determination of carboxyl groups in cellulose samples the fibers are first treated with acid in order to convert the carboxyl groups into the hydrogen-ion form. Because strong mineral acids, e.g., hydrochloric acid, are used for this purpose, it is naturally important to know how easily the excess acid can be removed from the fibers by washing with water. Careful studies have previously been made on this problem, and the experimental evidence accumulated shows that the acid can easily be washed out of the fibers—at least to such degree that the residue does not significantly interfere with the determination of carboxyl groups.^{1,2} Although opposite conclusions have been drawn from other experiments,³ it was later shown that these conclusions were partly based on an unsatisfactory experimental technique.² In a recently published paper,⁴ however, it was again stated that the washing of acid from cellulose fibers proceeds with great difficulty and quantitatively only if special precautions are taken. Because this conclusion is partly based on a new experimental procedure, we found it pertinent to initiate the present study and also examine the results of Ant-Wuorinen and Visapää.⁴ In order to obtain unambiguous experimental evidence the present measurements were made using a radioactive tracer technique. Hydrobromic acid was used instead of hydrochloric acid because radioactive bromide (Br^{82}) is measurable at much larger dilutions than radioactive chloride (Cl^{36}). Radioactivity measurements were made on the effluents from washing as well as on the final (washed) cellulose samples. It is probable that hydrobromic acid behaves similarly to hydrochloric acid with respect to its retention in

TABLE I
Washing Out of Hydrobromic Acid from Bleached Pulps: Experimental
Data Obtained with a Well-Type Scintillation Counter^a

Fraction volume, ml.	Counts/min.			
	Sulfite pulp		Sulfate pulp	
	Sample A ^b	Sample B ^c	Sample A ^b	Sample B ^c
25	High activity			
25	25,000	2,900	26,400	2,900
45	6,900	2,000	8,600	1,800
30	5,500	1,400	2,100	2,100
50	2,100	1,600	2,200	1,400
50	1,500	900	1,000	1,000
50	1,000	900	1,800	1,000
50	800	1,200	1,000	1,200

^a A sample of 5 ml. was taken for the measurements. The data are not corrected for the background value. The background value was 490 counts/min. The activity of a standard solution, containing 8.0×10^{-8} g. Br, was 8,930 counts/min.

^b Sample A (1.00 g. as moisture-free pulp) was washed with water in equilibrium with atmospheric carbon dioxide.

^c Sample B (1.00 g. as moisture-free pulp) was washed with water free from carbon dioxide.

cellulose fibers. Ant-Wuorinen and Visapää⁴ also used hydrobromic acid in their recent work.

EXPERIMENTAL

Preparation of Radioactive Hydrobromic Acid

A sample of 0.98 g. ammonium bromide (Analar), corresponding to 0.80 g. bromine, was irradiated in the R1 reactor of AB Atomenergi, Stockholm, for 16.5 hr. at a neutron flux of about 1.6×10^{12} n./cm.²-sec. The sample was allowed to stand for 2 hr. after irradiation in order to reduce the activity of Br⁸⁰ which is formed simultaneously with Br⁸². The radioactive salt was then dissolved in 10 ml. water and passed through a cation-exchange column containing about 15 ml. Dowex 50W (50-100 mesh) in the hydrogen-ion form. The column was then washed with water to obtain an effluent volume of 100 ml. The final 0.1N radioactive hydrobromic acid solution, corresponding to about 100 mc. Br⁸², was used for all the experiments.

Acid Treatment and Washing

The experimental technique was the same as described earlier.² The cellulose samples consisted of bleached, paper-grade sulfite and sulfate pulps. Each sample, corresponding to 1.00 g. moisture-free pulp, was suspended in water and poured into a column and then treated with radioactive hydrobromic acid (15 ml.). After 1 hr., the sample was again treated

TABLE II
Washing of Hydrobromic Acid from Bleached Pulps

Fraction Volume, ml.	Total amount of hydrobromic acid in each fraction, $\mu\text{eq.}$			
	Sulfite pulp		Sulfate pulp	
	Sample A ^a	Sample B ^b	Sample A ^a	Sample B ^b
25	Large amounts			
25	0.01460	0.00145	0.01540	0.00145
45	0.00684	0.00162	0.00864	0.00135
30	0.00360	0.00066	0.00114	0.00114
50	0.00190	0.00130	0.00200	0.00110
50	0.00120	0.00050	0.00060	0.00060
50	0.00060	0.00050	0.00150	0.00060
50	0.00040	0.00080	0.00060	0.00080

^a Sample A (1.00 g. as moisture-free pulp) was washed with water in equilibrium with atmospheric carbon dioxide.

^b Sample B (1.00 g. as moisture-free pulp) was washed with water free from carbon dioxide.

with hydrobromic acid (10 ml.). Finally, the washing of the sample was started and the effluent collected into fractions. Separate experiments were made with the use of deionized water only and with deionized water in equilibrium with atmospheric carbon dioxide.

Measurements of the Radioactivity

A sample of 5 ml. was taken from each fraction for the measurement of the radioactivity. The standard was prepared by diluting the original solution 10^6 times, and 1 ml. of this diluted solution was measured together with the samples. The measurements were carried out by means of a scintillation detector. The time for 10^4 electrical pulses was registered and then recalculated to counts per minute. The concentration of hydrobromic acid in each fraction was then calculated by means of the standard and background values. After completion of washing, the radioactivity of the cellulose samples was measured as described for the solution.

RESULTS AND DISCUSSION

The experimental data are collected in Table I. The amounts of hydrobromic acid in the fractions have been calculated from these data and the results appear in Table II. It is evident that most of the hydrobromic acid is washed out of the fibers with the first 25 ml. fraction. In the third fraction, only extremely small amounts can be detected, corresponding to a concentration lower than $0.0002 \mu\text{eq./ml.}$ This observation is in good agreement with our earlier results,² which showed that, within the sensitivity limits of the analytical method used ($0.004 \mu\text{eq. HCl/ml.}$), the effluent was free of hydrochloric acid after washing with two portions of 25 ml. of water. On the other hand, our figures are quite different to those

of Ant-Wuorinen and Visapää (Table II in ref. 4). Using our technique, these authors found $0.04 \mu\text{eq. HCl/ml.}$ in the corresponding (third) effluent, which is at least 200 times the amount we found. This substantial disagreement cannot be explained by the differences in the corresponding experiments. For instance, it has been shown that the duration of the acid treatment does not markedly affect the washing step.

Because the radioactive tracer technique employed is specific and extremely sensitive, the present results appear conclusive, indicating that the titrimetric technique used by Ant-Wuorinen and Visapää⁴ led to erroneous conclusions. In their interpretation of the titration data no consideration was given to the following facts. Firstly, bleached pulps contain traces of salts which, during prolonged washing, diffuse from the fibers to the surrounding solution and are simultaneously replaced by the hydrogen ions bound to the carboxyl groups.² Even traces of salts present in the original washing water are exchanged and result in the formation of acids. It is not possible to avoid these impurities completely, even when using water purified by repeated distillations. Secondly, samples of sulfite pulps were used, and these contain xylan which is relatively tightly branched with glucuronic acid units. As shown in a recent investigation,⁵ some of the xylan is easily removed from the pulps. Even if only a very small part of the xylan is washed out of the fibers, this amount will contribute to the consumption of alkali.

Further, as can be seen from Table II, the radioactivity of the effluent at the end of the washing is approximately the same as the background value, which means that not more than $0.00001 \mu\text{eq. HBr/ml.}$ is present in the last fractions. It appears also that washing with water containing carbon dioxide results in effluents free from hydrobromic acid.

Finally, the results from measurements on the pulp samples are shown in Table III. The observed radioactivity corresponds to a hydrobromic acid content of about $0.01 \mu\text{eq. HBr/g. sample.}$ It is possible that the pulp contains traces of basic groups originating from proteins and these are able to bind anions. Also, it is possible that part of the radioactivity is attributable to the elemental bromine which is formed during neutron

TABLE III
Determination of Hydrobromic Acid in the Pulp after Washing

	Sulfite pulp		Sulfate pulp	
	Sample A ^a	Sample B ^b	Sample A ^a	Sample B ^b
Radioactivity, counts/min.	1.1×10^6	1.3×10^5	1.1×10^5	1.0×10^5
Carboxyl content, meq./100 g. pulp	4.7	4.7	5.3	5.3
Residual HBr				
$\mu\text{eq./g. pulp}$	0.013	0.016	0.013	0.012
% of the carboxyl content	0.03	0.03	0.02	0.02

^a Sample A (1.00 g. as moisture-free pulp) was washed with water in equilibrium with atmospheric carbon dioxide.

^b Sample B (1.00 g. as moisture-free pulp) was washed with water free from carbon dioxide.

irradiation of ammonium bromide.⁶ However, even if it is assumed that all the radioactivity originates from the hydrobromic acid, the amount left in the fibers is negligibly small. Thus, compared with the carboxyl content of the samples, the error caused by the acid is smaller than 0.03%. It can further be concluded that the error due to the residual acid is also negligible after the fibers have been washed with about 50 ml. water subsequent to the acid treatment. The washing out of acid from the fibers thus proceeds very easily, in agreement with earlier results.^{1,2}

Ant-Wuorinen and Visapää⁴ have also used viscosity measurements and an x-ray emission spectrography method for the detection of residual acid in the fibers. The aim of this work, as well as that of our earlier investigation,² has been to establish if the acid-treated pulp after washing with water contains sufficient acid to interfere with the determination of carboxyl groups. It has now been verified that this is not the case and it is beyond the scope of our work to investigate whether or not traces of acid under this limit are present. However, in order to clarify the problem it may be appropriate to interpret the viscosity data found by Ant-Wuorinen and Visapää.⁴ These authors measured the viscosities of the washed samples after drying them overnight at 105°C. It was observed that when acid-treated samples were shaken eight times with 100-ml. portions of water under nitrogen, the viscosities of the final dried samples were nearly identical to those of the original samples after drying. However, the samples which were washed in columns eight times with 25-ml. portions of water showed lower viscosities after drying. Because depolymerization occurred under drying, the authors concluded that the fibers after washing in a column still contain traces of acid. Surprisingly enough, it was found that batch-wise washing results in a completely acid-free sample only if the experiments are carried out in an atmosphere free from carbon dioxide (under nitrogen), whereas carbon dioxide does not affect the washing when the column-technique is used.

If the last traces of acid would lead to a depolymerization of cellulose during drying, then the hydrogen ions originating from the carboxyl groups must have a catalytic effect on the depolymerization. In view of the extremely low hydrobromic acid content in the fibers after washing (Table III), it can be concluded that most of the hydrogen ions originate from the carboxyl groups. This is even the case if only a very minor part of the carboxyl groups, say 1%, is dissociated. It is therefore surprising that no decrease in viscosity was obtained when the samples were washed batch-wise. Perhaps, even more surprising is the finding that the viscosities of the dried samples were about the same when they were washed in a column once or eight times, (Table I in ref. 4) as, after the first washing with 25 ml. water, considerable amounts of acid are present in the fibers.

It is apparent that more experimental evidence is needed to explain the viscosity data of Ant-Wuorinen and Visapää.⁴ However, it is possible, that the increasing viscosities are due to a partial replacement of the hydrogen ions of carboxyl groups by metal ions. Also, as mentioned, some of the acidic xylan is dissolved during water treatment, which will lead to a

TABLE IV
Influence of the Ionic Form on the Pulp Viscosity after Drying^a

Sample	Treatment	Intrinsic viscosity, cm. ³ /g. ^b
1	50 ml. 0.1N HCl + 250 ml. water + 50 ml. 0.1N NaCl + 50 ml. water	1065
2	50 ml. 0.1N HCl + 250 ml. water	380
3	50 ml. 0.1N NaCl + 50 ml. water	1033
4	100 ml. water containing CO ₂	900

^a Samples corresponding to 1.00 g. moisture-free pulp were treated in columns and then dried overnight at 105°C. according to Ant-Wuorinen and Visapää.⁴

^b Method of Scandinavian Pulp, Paper and Board Testing Committee.⁷

higher degree of polymerization of the pulp. The risk of xylan dissolution as well as replacement of hydrogen ions is naturally greater in those experiments where large amounts of water have been used with simultaneous mechanical treatment of the pulp.

In order to prove the hypothesis as to whether the free carboxyl groups influence the viscosity, samples of sulfite pulp were pretreated with dilute hydrochloric acid and sodium chloride solution, respectively. After being washed with water, some of the acid-treated samples were then treated with sodium chloride solution in order to replace the hydrogen ions by sodium ions. The results from these experiments appear in Table IV. As can be seen the viscosity of sample 2 (only HCl-treated) is considerably lower than the viscosities of the other samples. However, the viscosity of sample 1 (HCl-NaCl-treated) and sample 3 (NaCl-treated) are practically identical. It can further be seen that a partial replacement of sodium ions with CO₂-water also results in decreased viscosity (sample 4).

These observations strongly support the view that the decrease in viscosity found by Ant-Wuorinen and Visapää⁴ is rather a positive indication of the presence of free carboxyl groups than due to the presence of mineral acid.

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Résumé

Echantillons de la cellulose d'une pâte blanchie de sulfite et sulfate ont été traités en colonnes avec un acide hydrobromique radioactif de 0,1N, après quoi ils ont été lavés avec de l'eau. Les expériences ont montré qu'après un lavage avec de petites quantités d'eau (environ 50 ml pour 1 g d'échantillon), la radioactivité du liquide écoulé était très faible, correspondant à une concentration d'acide hydrobromique de moins de 0,0002 / μ équiv./ml. Les mesurages de l'échantillon de cellulose faits directement après lavage ont vérifié l'insuffisance d'acide dans les fibres pour interférer l'estimation du titrage des groupes de carboxyl.

Zusammenfassung

Celluloseproben, bestehend aus gebleichtem Sulfit- und Sulfatzellstoff, wurden in Kolonnen mit 0,1N radioaktiver Bromwasserstoffsäure behandelt und dann mit Wasser gewaschen. Die Experimente zeigten, dass schon nach Waschung mit kleinen Wassermengen (ungefähr 50 ml pro 1 g Probe) die Radioaktivität des Durchlaufs sehr niedrig war entsprechend eine Konzentration der Bromwasserstoffsäure weniger als 0,0002 μ Äquiv./ml. Die Messungen der Radioaktivität direkt an dem Cellulosepreparat zeigten, dass die Mengen an zurückgehaltener Bromwasserstoffsäure so klein sind, dass sie nicht die titrimetrische Bestimmung der Carboxylgruppen stören.

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