Application Note – Colloid Analysis

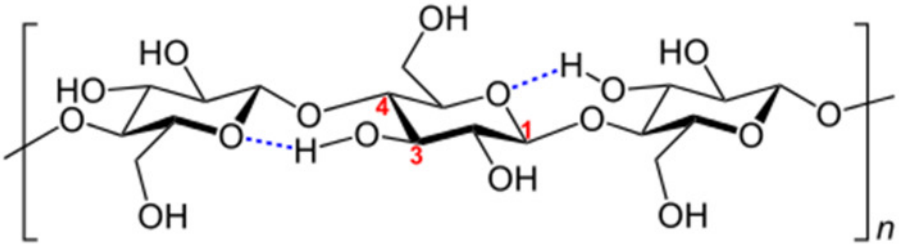
Quantitative determination of the acid groups of cellulose and nanocellulose with polyelectrolyte titrations

Due to their universal availability, remarkable properties and outstanding biocompatibility, nanocellulose materials are currently at focus of research. Numerous branches of industry are engaged developing new products or environmentally friendly replacements for existing products based on cellulose.

In the field of life science there are many applications, such as wound dressings, drug delivery, adsorption and fixation of proteins and enzymes, as well as medical nanomaterials, to name but a few [1]. Nanocellulose is also used as a rheological additive in the food sector to improve the mechanical properties of plastics, in electronics as an insulator, in the packaging industry and in the production of building materials.

Depending on the manufacturing process, a distinction is made between cellulose nanocrystals (CNC or NCC), cellulose nanofibers (CNF) and bacterially produced nanocellulose.

From a chemical point of view, cellulose is a polysaccharide whose properties are largely determined by hydroxyl groups.



Cellulose basic unit

Modification of the acid groups

For most applications, however, it is necessary to modify the surface in order to obtain the desired properties. Depending on the desired property, this can be done by adsorption, i.e. non-covalent bonding, or by covalent bonding.

Of particular interest here is the establishment of acid groups on the surface which are negatively charged at neutral pH values and thus can either enable the adsorption of positively charged molecules or be esterified.

The two main acid groups produced on the surface of cellulose are carboxylic acids and sulfonic acids. The latter is a very strong acid (comparable to sulfuric acid, pks-value <1), whereas the carboxylic acids are weaker acids, whose pks-value is about 4.

While sulfonic acids are mostly formed during the purification of celluloses with sulfuric acid, carboxylic acids are produced by targeted oxidation of the hydroxyl groups on the cellulose (on the primary alcohol). An important process is the so-called TEMPO oxidation, which specifically oxidizes the primary alcohol but is very sensitive to the reaction conditions.

Quantification of the acid groups

Therefore, a precise quantification of the acid groups actually present or newly produced on the powder is of crucial importance for reaction management and quality control. The acid number is also an important parameter for further esterification or for the determination of adsorption sites.

IR spectroscopy

IR spectroscopy is suitable for the qualitative determination of functional groups, but quantification is very inaccurate.

Conductometric titration

Another frequently used method to determine the acid groups is conductometric titration, in which cellulose is mixed with a defined amount of HCl and then titrated using NaOH [2,3]. The quantification of the carboxylic acids is determined by the buffering effect (which is shown by plateau formation when applying conductivity to pH). Unfortunately, this method also contains some sources of error:

1.) Sulfonic acids on the surface are not detected because they are too strong and are not protonated by HCl on the one hand, and have no buffering effect on the other hand.

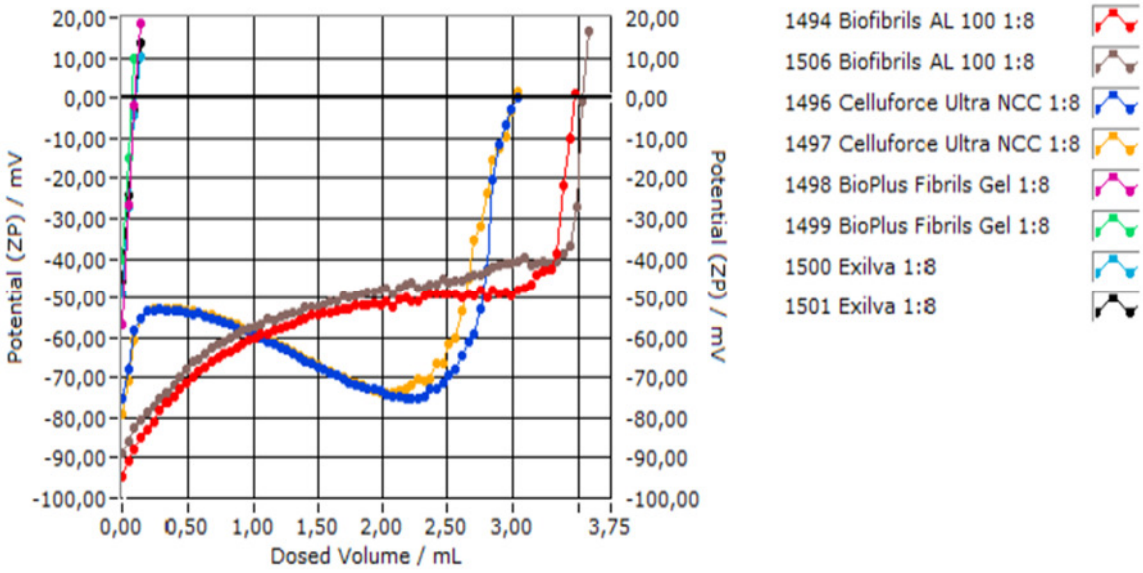
2.) The graphical evaluation for plateau determination using applied tangents leads to very large errors.

3.) Acidification with HCl can lead to reactions on the surface of the cellulose or even to a change in the structure, in which case the result does not correspond to the actual number of acid groups on the surface.

Polyelectrolyte titration

An elegant method which allows the quantitative determination of anionic (or cationic) surface groups without these complications is the measurement of the streaming potential during titration with a cationic polyelectrolyte (e.g. PolyDADMAC). In contrast to conductometric titration, it is possible to determine the number of anionic surface groups without changing the pH value. By determining the isolelectric point, sulfonic acid groups can also be detected and differentiated from the carboxylic acid groups.

This method is particularly suitable for comparing and selecting suitable cellulose, but also for monitoring the quality of different batches. Figure 1 shows the titration curves of some commercially available celluloses with 0.0025 n PolyDADMAC.

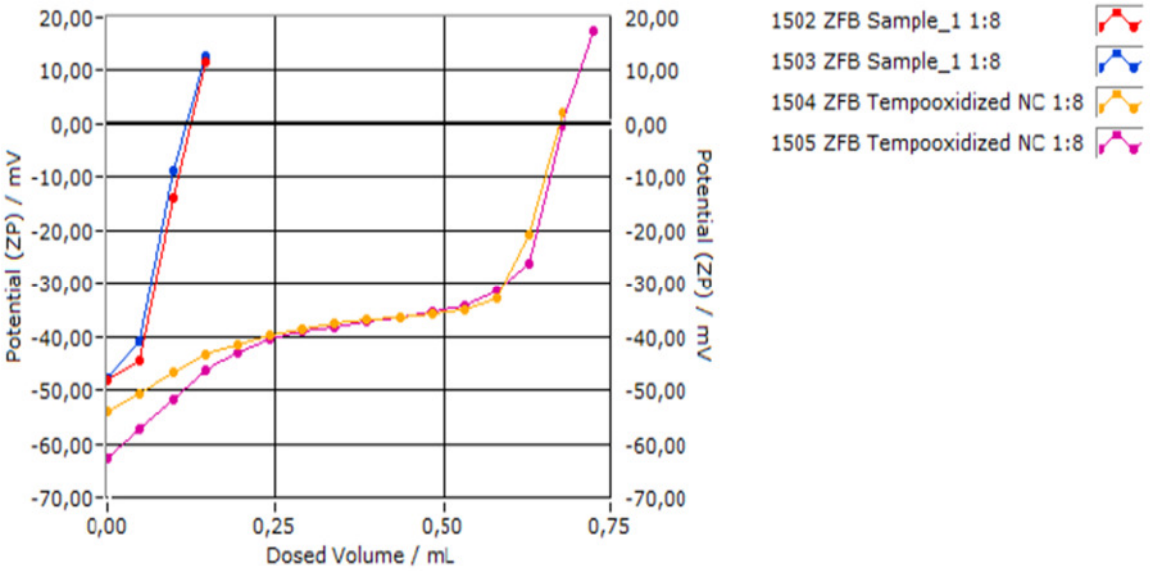


Cellulose	Volume Titrand (mL)	Charge (C/g)	Charge (meq/g)
Biofibril AL 100	3.51	56	0.583
Cellulose Ultra NCC	3.04	48.5	0.505
BioPlus Fibris Gel	0.09	1.44	0.015
Exilva	0.11	1.75	0.018

Figure 1: Charge titration of different commercially available celluloses

The measurement results indicate that the two celluloses Bioplus Fibris Gel and Exilva are non-oxidised celluloses, while the types Biofibril Al 100 and Cellulose Ultra NCC have a high charge density.

Furthermore, charge titrations allow the quantification and optimization of the reaction conditions during the oxidation of celluloses. Figure 2 shows the charge titration of a cellulose before and after TEMPO oxidation.



Cellulose	Volume Titrand (mL)	Charge (C/g)	Charge (meq/g)
Nanocellulose unmodified	0.12	1.91	0.022
Nanocellulose oxidized	0.68	10.84	0.113

Figure 2: Charge titration of Nanocellulose before and after TEMPO-Oxidation

The charge density could be significantly increased by oxidation.

Conclusion

The combination of streaming potential measurement and charge titration makes it possible to quantitatively record the existing surface groups. Thus, not only oxidation reactions can be optimized, but also different celluloses can be investigated with regard to their possible applications.

Literature

[1] N. Lin, A. Dufresne, „Nanocellulose in biomedicine: Current status and future prospect“, European Polymer Journal, 59 (2014), 302-325.
[2] D.S. Perez, S. Montanari, M. R. Vignon, „TEMPO-Mediated Oxidation of Cellulose III“, Biomacromolecules 4 (2003), 1417-1425.
[3] T. Saito, A. Isogai, „TEMPO-Mediated Oxidation of Native Cellulose. The Effect of Oxidation Conditions on Chemical and Crystal Structures of the Water-Insoluble Fractions“, Biomacromolecules 5 (2004), 1983-1989.