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FT Raman investigation of sodium cellulose sulfate

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Abstract FT Raman investigation of sodium cellulose sulfates (NaCS) was reported. Different NaCS were prepared by two diverse sulfation methods and their total degrees of substitution (DS) of sulfate groups were determined through either ^{13}C-NMR spectroscopy or elemental analysis. Subsequently, these NaCS were characterized with FT Raman spectroscopy. The caused bands through the introduction of the sulfate groups in cellulose chain were explained and assigned. Additionally, a strong linear correlation between the areas under the bands ascribed to the stretching vibrations of C–O–S groups and the total DS of NaCS was presented. A rapid method of quantifying the total DS of NaCS was established. Finally, sodium sulfate (Na_2SO_4), a salt that is very often produced during the sulfation of cellulose, was found to be analyzable even with a weight content of 0.12% in NaCS. The method of quantifying the content of this salt in NaCS was investigated with Raman spectroscopy.

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Introduction

Besides normally used NMR and IR spectroscopy in cellulose studies, Raman spectroscopy has also been widely applied as a very useful spectroscopic method within the investigation of structures of cellulose and its derivatives. Atalla and colleagues have at first confirmed the advantages of Raman spectroscopy in analyzing cellulose. With this method, they have also determined the molecular conformations and hydrogen bonding patterns of cellulose (Atalla 1976, 1980, 1989; Wiley and Atalla 1987). Moreover, the bands in Raman spectra of cellulose have been explained and assigned (Schenzel and Fischer 2001; Wiley and Atalla 1987).

Recently, the transformation of cellulose polymorphs has been detected by using a combination of NIR FT Raman spectroscopy and X-ray diffraction measurements (WAXS) (Schenzel and Fischer 2001). The degree of crystallinity of cellulose was shown to be determined by Raman spectroscopy with Raman crystallinity index—Xc_{Raman}. The Xc_{Raman} values were comparable with crystallinity parameter from ^{13}C-CP/MAS-NMR spectroscopy (Schenzel et al. 2005). A new study investigated the morphological

and structural changes of mercerized cellulose fibres with combined confocal Raman spectroscopy and atomic force microscopy (AFM) (Eronen et al. 2009). The changes of polymorphic lattice in cellulose fibres treated with 10, 15 or 25% aqueous NaOH solution were analyzed by Raman spectroscopy. Also the uniform polymorphous cellulose structure throughout the cell wall and various microfibril orientations between fibre cell wall layers were detected by Raman spectroscopy. These changes could be confirmed by the AFM images of the same samples.

Besides being used as qualifying method, Raman spectroscopy has been applied in quantifying the properties of some cellulose derivatives. It has been shown, that the DS of two cellulose derivatives and also the reactivity of the cellulose could be determined using FT Raman spectroscopy. The calibration models of DS_{AC} in the range of 0.39–2.00 for cellulose acetate and DS_{CM} between 1.25 and 2.90 for carboxymethyl cellulose were generated, which allowed a rapid prediction of DS values of both cellulose derivatives (Fischer et al. 2005). Raman spectroscopy has been applied in characterizing carboxymethylated cellulose, locust bean gum, guar gum and xanthan gum and quantifying their DS_{CM} as well. Strong linear correlations between the DS_{CM} and area ratios of signals attributed to carboxymethyl groups to signals of polysaccharide backbones in Raman spectrum were observed (Yuen et al. 2009).

Cellulose esters, such as cellulose acetate and cellulose trifluoroacetate, were characterized conventionally with NMR or IR spectroscopy (Deus et al. 1991; Liebert et al. 1996). However, both analysis methods have disadvantages in comparison to Raman spectroscopy. NMR spectroscopy takes a long time for analyzing and can not always guarantee spectra with good resolutions. Although IR spectroscopy is a rapid method, the highly polar bond systems like water resulting in intense infrared bands can interfere with the spectrum of cellulose derivatives. In contrast, Raman spectroscopy represents a rapid method characterizing the cellulose esters without interference of water.

Sodium cellulose sulfate (NaCS), as a cellulose ester showing biological potential, has been analyzed with different methods, such as NMR spectroscopy (Hettrich et al. 2008; Nehls et al. 1994). The total DS of NaCS could be determined through either the sulphur content of NaCS from elemental analysis or ^{13}C-NMR spectroscopy (Nehls et al. 1994; Wang et al. 2007). IR spectroscopy was proved to be a good method in analyzing sulfated polysaccharides, such as heparin (Grant et al. 1991), and it was also used in characterizing NaCS (Chaidedgumjorn et al. 2002; Wang et al. 2007). Similarly, Raman spectroscopy has also been applied in detecting the sulfate groups of sulfated polysacchrides, for instance, heparin and other glycosaminglycans in aqueous solutions (Cabassi et al. 1978). Very seldom was Raman spectroscopy applied in analyzing the NaCS. Hettrich et al. (2008) have shown a few Raman spectra of NaCS with different DS and proposed Raman spectroscopy as a potentially useful method for the characterization of cellulose derivatives.

In this paper, NaCS was prepared with two different sulfation methods and the total DS were determined with ^{13}C-NMR according to Nehls et al. (1994) or with elemental analysis. Then we demonstrate Raman spectroscopy as a rapid analytical method in characterizing NaCS. The spectrum of NaCS is analyzed and the bands due to the sulfation are explained. The possibility of quantifying the total DS of NaCS with the bands ascribed to the sulfate half-ester groups is presented. Finally, it will be shown that impurities such as Na_2SO_4 in NaCS can be detected and quantified.

Experimental

Materials

Native cellulose (AC, with 97.0% alpha cellulose) with an average DP of 1180 was purchased from Buckeye Technologies Inc. (Memphis, USA). Microcrystalline cellulose (MCC) with a DP of 275–277 was received from J. Rettenmaier and Söhne GmbH (Rosenberg, Germany). Cellulose-2.5-acetate (C2.5A) was received from M & G Group (Verbania-Pallanza, Italy). The celluloses and C2.5A were used without further treatment. Dimethylformamide (DMF) was freshly distilled and water was deionized before use. Other chemicals were all of laboratory grades and used as received.

Preparation of NaCS and mixtures of NaCS and Na_2SO_4

The synthesis of NaCS was carried out either as acetosulfation of cellulose (Method I) or as direct

sulfation of cellulose and C2.5A (Method II) to obtain products with different DS (Klemm et al. 1997; Hettrich et al. 2008).

For a typical acetosulfation 2.5 g cellulose were suspended in 125 mL anhydrous DMF and the system was kept at room temperature (RT) for over 14 h. The reaction agent consisting of either chlorosulfuric acid or sulfuric acid and acetic anhydride in DMF was dropped into the cellulose suspension under vigorous stirring over a period of 15 min. After that, the temperature was raised to 50 °C and the system was kept at 50 °C for 5 h. Then the mixture was cooled down to RT and poured into a saturated solution of anhydrous sodium acetate in ethanol.

The precipitate was gained through centrifugation and washed with 4% sodium acetate solution in ethanol. After a deacetylation with 1 M ethanolic solution of sodium hydroxide for 15 h the pH value was adjusted to 8.0 with acetic acid/ethanol (50/50, w/w). The product was then washed three times with ethanol, dissolved in water, filtered, dialyzed in deionized water and lyophilized.

For direct sulfation the cellulose or celluloseacetat was at first suspended for 14 h or dissolved in DMF. The sulfating agent was added into the suspension or the solution over a period of 15 min. Then the mixture was kept at RT for a designed duration. After the reaction the mixture was poured into the saturated solution of anhydrous sodium acetate in ethanol and washed with 4% sodium acetate solution in ethanol. The product obtained was dissolved in water and the pH was adjusted to 8.0 with acetic acid/ethanol (50/50, w/w). After washing with ethanol the product was dissolved in water, filtered, dialyzed in deionized water and lyophilized.

Mixtures of NaCS and Na_2SO_4 with various weight ratios were prepared through dissolving both in water under stirring and subsequent drying of the solution. NaCS and Na_2SO_4 are dried at 103 °C for 3 and 24 h, respectively, before use. The details about the composites of the mixtures can be found in Table 2.

^{13}C-NMR spectroscopy

The ^{13}C-NMR spectra were recorded at RT using a Bruker DPX 400 spectrometer at a frequency of 100.13 MHz and with 30° pulse width, 0.3 s acquisition time and a relaxation delay of 3 s. The samples were dissolved in D_2O and Scans between 5,000 and 20,000 were accumulated.

FT Raman spectroscopy

FT Raman spectra of the samples in small metallic discs were recorded on a Bruker MultiRam spectrometer with a liquid-nitrogen cooled Ge diode as detector.

A cw-Nd:YAG-laser with an exciting line of 1,064 nm was applied as light source for the excitation of Raman scattering. The Raman spectra were recorded over a range of 3,500–150 cm^{-1} using an operating spectral resolution of 3 cm^{-1}. A laser power output of 100 mW was used. Every sample was analyzed under the same conditions twice and 400 scans were accumulated. An average spectrum was formed as final spectrum of the corresponding sample and a vector-normalization of the spectrum was executed.

The integration of the peaks was carried out with help of the operating spectroscopy software OPUS Ver. 6.5 (Bruker Optik GmbH, Etlingen Germany). The analysis of the data was executed with OriginPro 7.0 (OriginLab Corporation, MA USA).

Elemental analysis

The sulphur content of the NaCS was measured with Elemental Analyser Eltra CS 500 (Neuss, Germany). The contents of carbon, hydrogen and nitrogen were determined with Elemental Analyser vario El from Elementar (Hanau, Germany). The total DS of NaCS can be calculated as in Hettrich et al. (2008).

Results and discussion

Preparation of NaCS and its characterization

NaCS having various DS were synthesized with two different methods. The obtained NaCS were characterized by ^{13}C-NMR spectroscopy and the DS could also be determined (Nehls et al. 1994). Figure 1 shows the simplified structure of NaCS and Fig. 2 presents the ^{13}C-NMR spectra of three NaCS with different DS.

The carbon atoms of the AGU (anhydro glucose unit) demonstrate different chemical shifts after

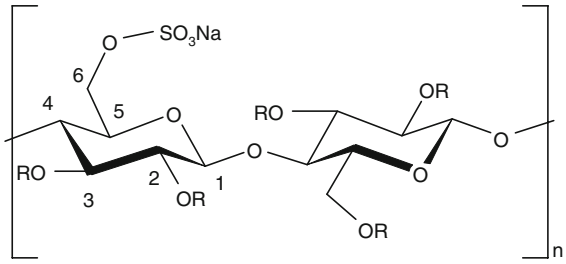

Fig. 1 Simplified structure of NaCS with R = –SO_3Na or –H according to DS

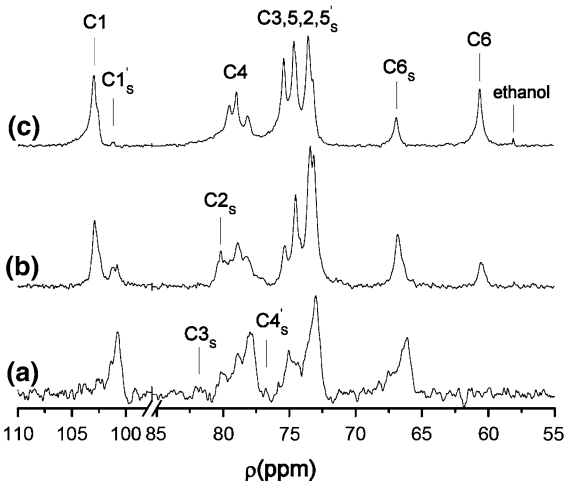

Fig. 2 ^{13}C-NMR spectra (110–55 ppm) of: **a** NaCS20 (DS = 2.15), **b** NaCS15 (DS = 0.97) and **c** NaCS8 (DS = 0.4) in D_2O at RT

sulfation compared to unsubstituted cellulose. From Fig. 2 it can be found that the peak of C6 (carbon 6) lies at 60 ppm and is shifted from 60 ppm to 66–67 ppm after introduction of sulfate groups at 6-*O*-position. With sulfation at 2-*O*-position, a new peak appears at 80 ppm. Because of this sulfation the peak of C1 is split into two peaks: the one at 102 ppm is for C1 without and the other one at 100 ppm is for C1 with the sulfation at 2-*O*-position. If there is sulfation at 3-*O*-position, another new peak for C3 can be found at 83 ppm (Fig. 2a) (Hettrich et al. 2008).

The partial DS at different positions, besides the DS of 3-*O*-position, can be simply calculated with help of the integrated areas under the respective peaks in NMR spectra (Table 1, NaCS1-17). Therefore, the total DS of the NaCS without sulfation at 3-*O*-position can be obtained by addition of the partial DS. In order to calculate the partial DS at 3-*O*-position, the unsubstituted C3-signal or the signals of substituted and unsubstituted C4-signals should be analyzed. However, the analysis of these signals is currently not really accurate due to interferences of other signals, such as that of the C5, C2 and $C2_S$.

Besides ^{13}C-NMR, the elemental analysis offers us another possibility in determining the total DS of high sulfated NaCS. The measured total DS of the synthesized NaCS (NaCS18-20) can be found in Table 1. Moreover, the partial DS on 3-*O*-position can be calculated based on the difference between the total DS and the partial DS at 2-*O*- and 6-*O*-position which can be determined by elemental analysis and ^{13}C-NMR spectroscopy, respectively.

According to the Fig. 2 and the results in Table 1, the selective sulfation of the applied sulphating agents can be concluded. The 2-*O*-position and especially the 6-*O*-position were preferred sulfated in contrast to 3-*O*-position, in spite of the sulfation method as direct sulfation (Fig. 2, spectrum a) or as acetosulfation (Fig. 2, spectrum b and c) of cellulose.

FT Raman spectroscopy of NaCS

The cellulose and NaCS were analyzed by Raman spectroscopy and the chosen spectra can be found in Fig. 3.

First of all, the spectra of NaCS demonstrate several peaks known from spectra of cellulose. These peaks reveal the vibrations of cellulose backbone and can be well explained and assigned (Wiley and Atalla 1987; Schenzel and Fischer 2001).

By comparing the spectrum of cellulose and NaCS, we can observe the appearance of new bands in the spectrum of NaCS which are attributed to the presence of sulfate groups. These new bands are located at 417, 589, 1,274 cm^{-1}, between 825 and 843 as well as between 1,068 and 1,076 cm^{-1}, respectively. Among them, it is distinguished between the signals of vibrations of C–O–S and sulfate half-ester groups.

The band at 417 cm^{-1} could be assigned to the deformation vibration of SO_3 groups (Colberg 2001). Another band at 589 cm^{-1} is ascribed to the deformation vibration δ(O=S=O) (Socrates 2001). The bands at 417 and 589 cm^{-1} occur as triplets.

The band between 825 and 843 cm^{-1} is attributed to the C–O–S stretching vibration υ(C–O–S) (Cabassi et al. 1978; Grant et al. 1991). In addition, this band is

Table 1 Total DS of synthesized NaCS and the areas under the bands between 825 and 843 cm^{-1} (the bands of υ(C–O–S)) within the Raman spectrum of the corresponding NaCS

Samples	Sulfation method	Starting material	Total DS	Areas under the bands of υ(C–O–S)
MCC	–	MCC	0	0
NaCS1	Method I	MCC	0.21	0.291
NaCS2	Method I	MCC	0.215	0.33
NaCS3	Method I	MCC	0.235	0.312
NaCS4	Method I	MCC	0.24	0.315
NaCS5	Method II	C2.5A	0.31	0.55
NaCS6	Method I	MCC	0.34	0.518
NaCS7	Method I	AC	0.34	0.582
NaCS8	Method I	MCC	0.4	0.387
NaCS9	Method I	MCC	0.41	0.463
NaCS10	Method I	MCC	0.42	0.532
NaCS11	Method I	MCC	0.43	0.417
NaCS12	Method I	AC	0.43	0.529
NaCS13	Method I	MCC	0.47	0.536
NaCS14	Method I	MCC	0.51	0.949
NaCS15	Method I	MCC	0.97	1.533
NaCS16	Method II	MCC	1.52	2.372
NaCS17	Method II	MCC	1.69	3.025
NaCS18	Method II	MCC	2.01	3.978
NaCS19	Method II	MCC	2.1	4.073
NaCS20	Method II	MCC	2.15	4.103

shifted to higher wave number with increasing total DS of NaCS (Fig. 3).

The band in the range of 1,068–1,076 cm^{-1} is the dominant one within the spectrum and it is assigned to the symmetric stretching vibration υ_s(O=S=O). The maximum of this signal is shifted to higher wave number with increasing total DS, in the way as the band of υ(C–O–S). Another peak at 1,274 cm^{-1} is the signal of the asymmetric stretching vibration υ_{as}(O=S=O) (Cabassi et al. 1978; Chaidedgumjorn et al. 2002).

Based on the spectra it is clear that the intensities and the widths of these new peaks rise with increasing total DS. Moreover, the bands of υ_s(O=S=O) and υ(C–O–S) lie at the positions with higher wave numbers with increasing total DS, which means, that a more intensified sulfation resulted in a shift of the both vibrations to slightly higher wave numbers, because the content of sulfate groups within AGU rises with increasing total DS and therefore, the signal of the sulfate groups becomes more dominant. Meanwhile, the intensities of the bands in the range of 1,140 and 1,098 cm^{-1} within spectrum of cellulose, which represent the symmetric ring breathing vibration and glycosidic υ_s(COC), are growing weaker within spectren of NaCS with increasing total DS. The introduction of the sulfate groups in the glucose ring should have influenced the vibration modes of the total ring and the glycosidic bonds, so that the intensities of the bands drop or the bands even disappear, and only one signal with maximum at 1,122 cm^{-1} and a shoulder at higher wave number can still be found.

The obtained signals ascribed to sulfate half-esters, are all located at the positions with higher wave numbers than the corresponding signals of heparin and other glycosaminglycans (Cabassi et al. 1978). Various factors could attribute to this fact. First, NaCS were measured in this study as solid material, and it should present different analysis conditions than in aqueous solution. Due to the ionic structure of the sulfate groups, a dissociation of these function groups can take place if heparin and other sulfated

glycosaminglycans are dissolved in water. Consequently, analysis with Raman spectroscopy resulted in a shift of the signals to lower wave numbers. In addition, the backbone of the polysaccharide should have an influence on the sulfated polysaccharide. There are not only glucose units but also many other sacchride components in heparin and some other glycosaminglycans, while the cellulose is only consisting of glucose units.

Furthermore, the changes of few peaks of cellulose can be found. The signal at 1,481 cm^{-1} with a small band at 1,458 cm^{-1} of cellulose which indicates crystalline cellulose I is replaced by a peak at 1,460 cm^{-1} that occurs typically within the Raman spectra of cellulose II (Schenzel and Fischer 2001). The appearance of the peak at 1,460 cm^{-1} is ascribed to the sulfation process of cellulose. During the sulfation, the cellulose was dissolved into the solvent and the product was then precipitated. According to the spectra in Fig. 3, it can be concluded that the sulfation process decreased the crystallinity of starting cellulose I and a cellulose II-analogue polymorphous structure was formed.

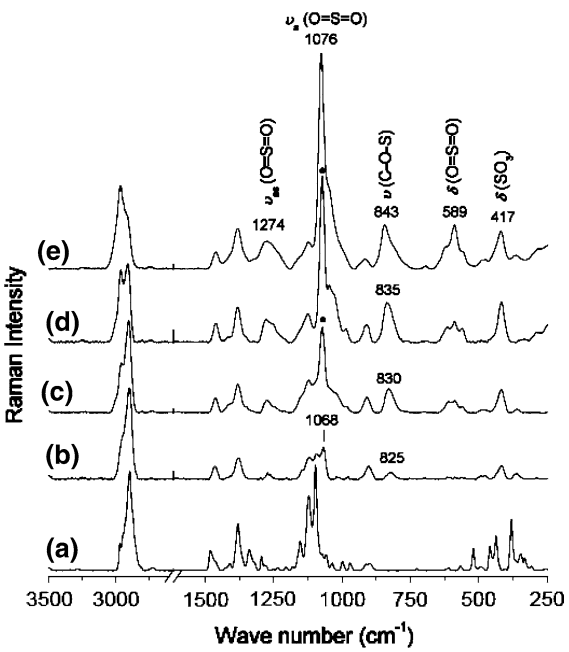

Fig. 3 Raman spectra (3,500–250 cm^{-1}) of **a** cellulose, **b** NaCS8 (DS = 0.4), **c** NaCS15 (DS = 0.97), **d** NaCS17 (DS = 1.69) and **e** NaCS20 (DS = 2.15). * The peaks' maxima of ν_s(O=S=O) of **c** and **d** lie both at 1,072 cm^{-1}

Besides, the intensities of the peaks at 2,896 and 2,969 cm^{-1} of cellulose that reflect the CH and CH_2 stretching vibrations change their relationship after diverse sulfation. The peak at 2,896 cm^{-1} of CH vibration is, within the spectrum of cellulose, the dominant one and is obviously higher than that of CH_2 vibration (Fischer et al. 2005). But after the sulfation, the intensity of the peak of CH_2 vibration rises with the increasing total DS of NaCS. In the spectrum of NaCS20 the peak of CH vibration is actually not a real peak any more. The peak of CH_2 stretching vibration is now prevalent and can be found at 2,964 cm^{-1}. As a result, it can be said that the sulfation of cellulose changes the intensities of the CH and CH_2 vibrations. The relationship of the intensities of their signals depends on the total DS of NaCS. The intensity of the signal of the CH_2 vibration rises with increasing total DS, while that of the CH vibration of NaCS with a total DS as high as 2.15 presents only as a shoulder.

Because in comparison to cellulose, the principle difference in the NaCS is the presence of the sulfate groups which are linked to the cellulose chains through ester bonds. The hydrogen atoms in the hydroxyl groups were substituted by sulfated groups and the hydrogen bonds which are linked to these hydrogen atoms were destroyed. Consequently, the modes and intensities of the CH and CH_2 vibrations could be altered according to the total DS of NaCS.

Apart from characterizing NaCS with Raman spectroscopy, a new method estimating the total DS of NaCS should be developed. According to the above elucidation the peaks of the vibrations attributed to the sulfation can be taken into account. But the related peaks besides the peaks of υ(C–O–S) lie all in the range where the signals of cellulose also occur, while between 825 and 843 cm^{-1} there is no peak of cellulose to be found at all. On account of this, the peaks between 825 and 843 cm^{-1} of the chosen NaCS were integrated after a normalization of the Raman spectra and the areas under these peaks were obtained, which can be found in Table 1.

The relationship between the areas under the bands of υ(C–O–S) and the total DS (Table 1) of the chosen NaCS was plotted and the result was presented in Fig. 4. A strong linear correlation with a coefficient of 0.9925 between areas under the bands of υ(C–O–S) and the total DS of NaCS is obtained, which confirms the feasibility of Raman spectroscopy for quantifying

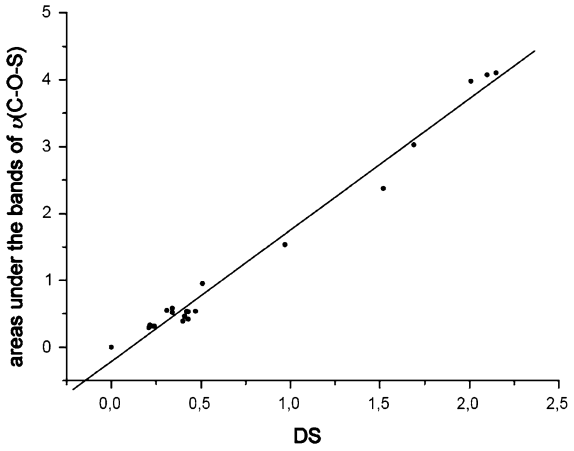

Fig. 4 Correlation between the total DS of NaCS and the areas under the bands of υ(C–O–S). Linear regression is $Y = -0.21209 + 1.96422 * X$ with $R = 0.9925$

the total DS between 0 and 2.15. Using this quantifying method the total DS of unknown NaCS can be determined within a few minutes.

Analysis and quantification of Na_2SO_4 in NaCS

Raman spectroscopy can not only be used in qualifying NaCS and quantifying its total DS, but it can also be applied to analyse impurities in NaCS, such as inorganic salts.

The NaCS is normally synthesized with sulfating agents. The sulfate salts, especially sodium sulfate, is a very common salt in the NaCS product after the sulfation. Otherwise, sodium acetate is also formed in considerable amount after the acetosulfation of the cellulose. These impurities in NaCS could change the real content of the latter and change its properties like water solubility. Therefore, it is meaningful that the presence of these salts is detected and the amount estimated.

Based on a model experiment, it is possible to find out the correlation between the contents and the Raman signal of sodium sulfate as the salt in NaCS. For this purpose the mixtures of NaCS and Na_2SO_4 were prepared and the details are listed in the Table 2.

Figure 5 presents a comparison between the Raman spectra of NaCS14, M6 and Na_2SO_4. The Na_2SO_4 alone has characteristic peaks within its Raman spectrum, but these peaks are mostly covered by the peaks of NaCS within the spectrum of the mixture. Only the peak at 997 cm^{-1} is still visible,

Table 2 The compositions of the mixtures consisting of NaCS and Na_2SO_4

Samples	Salt contents in wt%	Areas under the Raman bands between 1,027–968 cm^{-1}
NaCS14	0	0.057
M1	0.12	0.142
M2	0.96	0.146
M3	2.58	0.247
M4	4.09	0.257
M5	9.87	0.643
M6	20.94	1.464
M7	49.70	6.321

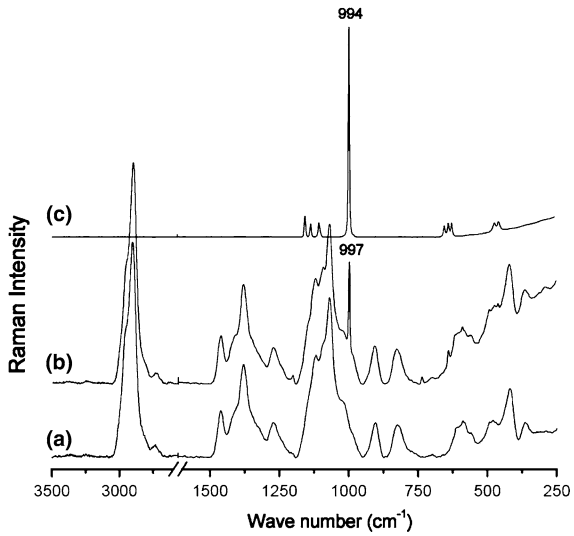

Fig. 5 Raman spectra (3,500–250 cm^{-1}) of **a** NaCS14 (DS = 0.51), **b** M5 and **c** Na_2SO_4 in comparative demonstration

which allows a characterization of this salt and the measurement of its content in the mixtures.

Figure 6 shows the spectra of mixtures with different mass contents of Na_2SO_4 in NaCS. It is obvious that the intensity of the peak at 997 cm^{-1} increases with the rising content of Na_2SO_4 within the mixture. M1, the mixture with 0.12% Na_2SO_4 still presents a detectable signal between 1,000 and 988 cm^{-1} in the Raman spectrum. With increasing content of Na_2SO_4 the peak at 997 cm^{-1} is more apparent. In addition, within the spectrum of M7 another characteristic peak of this salt appears at

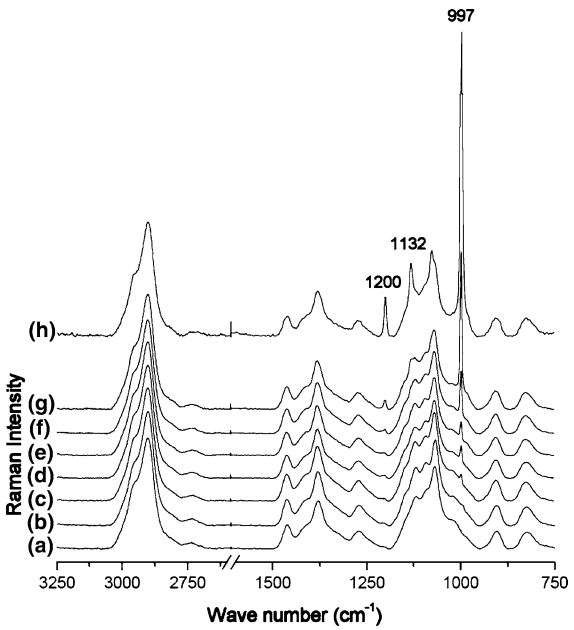

Fig. 6 Raman spectra (3,250–750 cm^{-1}) of the mixtures of NaCS and Na_2SO_4 with different mass contents of the latter: **a** NaCS14 (DS = 0.51), **b** M1, c M2, **d** M3, **e** M4, **f** M5, **g** M6, and **h** M7

1,132 cm^{-1}. Also, the intensity of another new signal at 1,200 cm^{-1} rises with increasing content of Na_2SO_4 in mixtures.

The areas under the Raman bands between 1,027 and 968 cm^{-1} were obtained for all mixtures and NaCS14 after a normalization of the Raman spectra and integration of these Raman bands. The data can be found in Table 2. With these data, an almost linear correlation with a coefficient of 0.9944 is attained between the areas and the content of Na_2SO_4 in mixtures up to 21%.

If the mixture—M7 with 49.7% salt is also taken into consideration, the coefficient of the correlation between the areas and the content of the Na_2SO_4 is just 0.9782, which indicates a weaker linear correlation. The reason could be the strong influence of the Na_2SO_4 due to its high content.

Conclusions

NaCS with different DS were synthesized and their total DS were calculated with the help of ^{13}C-NMR spectroscopy or elemental analysis.

Raman spectroscopy demonstrates a rapid and valid method in characterizing NaCS and determining its total DS. A few new bands at 417, 589, 1,274 cm^{-1}, between 825 and 843 cm^{-1} as well as in the range of 1,068–1,076 cm^{-1} due to the sulfation of cellulose are observed. These new bands are assigned to different vibrations of sulfate half-ester groups and their widths rise with increasing total DS. The bands between 825 and 843 cm^{-1} are ascribed to the stretching vibrations of C–O–S groups (υ(C–O–S)). A strong linear correlation between total DS up to 2.15 and the areas under the bands of υ(C–O–S) between 825 and 843 cm^{-1} was revealed. Thus, the total DS of unknown NaCS can be simply measured.

Besides the appearance of new peaks, the intensities of the bands attributed to CH and CH_2 stretching vibrations at 2,896 and 2,969 cm^{-1} and their relationship are found to be changed depending on the total DS of NaCS.

In addition, the impurities in NaCS, such as Na_2SO_4 can be analyzed quickly and its quantification is also possible. This salt can be detected in NaCS with a weight content even as small as 0.12%. An almost linear correlation between the areas under the bands between 1,027 and 968 cm^{-1} and the salt contents up to 21% in the mixtures consisting of NaCS and Na_2SO_4 was established. A content of this salt in such mixture as high as 49.7% impairs slightly this almost linear correlation.

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References

Atalla RH (1976) Raman spectral studies of polymorphy in cellulose Part I: Celluloses I and II. App Polym Symp 28:659–669

Atalla RH (1989) Patterns in aggregation in native celluloses: implication of recent spectroscopic studies. In: Kennedy JF, Phillips GO, Williams PA (eds) Cellulose. Ellis Horwood, Chichester

Atalla RH, Whitmore RE, Heimbach CJ (1980) Raman spectral evidence for molecular orientation in native cellulosic fibers. Macromolecules 13:1717–1719

Cabassi F, Casu B, Perlin AS (1978) Infrared absorption and Raman scattering of sulfate groups of heparin and related glycosaminglycans in aqueous solution. Carbohyd Res 63:1–11

Chaidedgumjorn A, Toyoda H, Woo ER, Lee KB, Kim YS, Toida T, Imanari T (2002) Effect of (1 → 3)- and (1 → 4)-linkages of fully sulfated polysacchrides on their anticoagulant activity. Carbohyd Res 337:925–933

Colberg CA (2001) Experimente an levitierten $H_2SO_4/NH_3/H_2O$-Aerosolteilchen: Atmosphärische relevanz von letovizit. dissertation (ETH No. 14331), Swiss federal institute of technology (ETH) Zuerich

Deus C, Friebolin H, Siefert E (1991) Partiell acetylierte cellulose–synthese und bestimmung der substituentenverteilung mit Hilfe der 1H NMR-Spektroscopie. Makromol Chem 192:75–83

Eronen P, Österberg M, Jääskeläinen A-S (2009) Effect of alkaline treatment on cellulose supramolecular structure studied with combined confocal Raman spectroscopy and atomic force microscopy. Cellulose 16:167–178

Fischer S, Schenzel K, Fischer K, Diepenbrock W (2005) Applications of FT Raman spectroscopy and micro spectroscopy characterizing cellulose and cellulosic biomaterials. Macromol Symp 223:41–56

Grant D, Long WF, Moffat CF, Williamson FB (1991) Infrared spectroscopy of heparins suggests that the region 750–950 cm^{-1} is sensitive to changes in iduronate residue ring conformation. Biochem J 275:193–197

Hettrich K, Wagenknecht W, Volkert B, Fischer S (2008) New possibilities of the acetosulfation of cellulose. Macromol Symp 262:162–169

Klemm D, Heinze T, Philipp B, Wagenknecht W (1997) New approaches to advanced polymers by selective cellulose functionalization. Acta Polymerica 48:277–297

Liebert T, Klemm D, Heinze T (1996) Synthesis and carboxymethylation of organo-soluble trifluoracetates and formates of cellulose. JMS-Pure Appl Chem A 33(5):613–626

Nehls I, Wagenknecht W, Phillip B, Stscherbina D (1994) Characterization of cellulose and cellulose derivatives in solution by HR ^{13}C-NMR spectroscopy. Prog Polym Sci 19:29–78

Schenzel K, Fischer S (2001) NIR FT Raman spectroscopy—a rapid analytical tool for detecting the transformation of cellulose polymorphs. Cellulose 8:49–57

Schenzel K, Fischer S, Brendler E (2005) New method for determining the degree of cellulose I crystallinity by means of FT Raman spectroscopy. Cellulose 12:223–231

Socrates G (2001) Infrared and Raman characteristic group frequencies, 3rd edn. Wiley, England

Wang ZM, Li L, Zheng BS, Normakhamatov N, Guo SY (2007) Preparation and anticoagulation activity of sodium cellulose sulfate. Int J Biol Macromol 41:376–382

Wiley JH, Atalla RH (1987) Raman spectra of celluloses. ACS Symp Ser 340:151–168

Yuen S-N, Choi S-M, Phillips DL, Ma C-Y (2009) Raman and FTIR spectroscopic study of carboxymethylated non-starch polysacchrides. Food Chem 114:1091–1098