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PLANT BIOPOLYMERS

Quantitative Analysis of Cellulose Nitrates by Fourier Transform Infrared Spectroscopy

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Abstract—Quantitative express analysis of nitrogen content in cellulose nitrates by Fourier transform infrared spectroscopy has been developed. The slope of the dependence of the ratio of the band intensity (and area) to sample weight in a tablet, on the nitrogen content in a sample was used to find the reduced extinction coefficients for quantitative analysis of nitrogen content in cellulose nitrate samples by IR spectroscopy. The results were compared with the nitrogen content values in the same samples determined by the ferrosulfate method.

Keywords: nitrogen, cellulose nitrate, Fourier transform infrared spectroscopy

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INTRODUCTION

Cellulose nitrates are among the most widely used cellulose esters, which have been commercially produced since the 19th century. Different fields of application of cellulose nitrates are determined by their specific properties. The high mechanical strength, the possibility of transformation to a plasticized state, high solubility, and compatibility with available plasticizers have ensured high cellulose nitrate outputs for the manufacture of gunpowder, rocket propellants, lacquers, dyes, etc.

Quantitative analysis of cellulose nitration products consists in determining the nitrogen content in the latter. Chemical methods are usually labor-intensive and require hazardous chemicals.

Physical analysis methods are the most promising for studying complex multicomponent polymer compositions. Quite a lot of factual data on the study and interpretation of the IR spectra of basic wood components have been accumulated.

Quantitative analysis of carboxymethyl and benzyl cellulose derivatives by Fourier transform IR spectroscopy, developed at the Chair of Organic Chemistry, Altai State University [1], suggests the possibility of developing a technique for quantitative analysis of cellulose nitration products by the above method.

The goal of this work was quantitative determination of the nitrogen content in cellulose nitration products by Fourier transform IR spectroscopy.

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EXPERIMENTAL

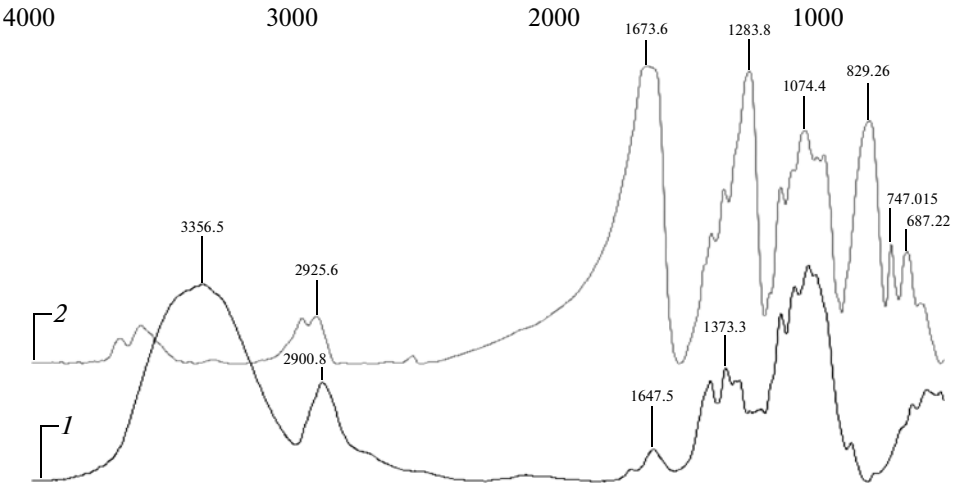
Nitrate samples were obtained by treating wood cellulose with a mixture of nitric and trifluoroacetic acids [2]. A weighed portion (1 g) was placed in an Erlenmeyer flask with a ground stopper, covered with the nitration mixture, and kept for a certain time at 30°C under stirring. After nitration had been completed, the product was separated from the nitration mixture by filtration through a glass filter and stabilized with 1% ammonia solution, then washed again with cold water until neutral reaction of rinsing water. Then the product was dried to a constant weight at 70°C in a desiccator with an open door.

The nitrogen content in the samples was determined by the ferrosulfate method [3] based on saponification of cellulose nitrates by concentrated sulfuric acid and reduction of the formed nitric acid by iron (II) sulfate solution to nitrogen oxide, which under excess nitrogen forms the complex compound $Fe(NO)SO_4$, yielding a yellow-pink color.

Sulfuric acid (25 cm^3) was poured from a pipette over a 0.12-g portion of cellulose nitrate weighed with an accuracy of 0.0002 g. The flask was closed with a stopper and kept in a refrigerator at 3°C until cellulose nitrate was completely dissolved. The resultant solution was titrated with the iron (II) sulfate solution under continuous cooling of the flask in cold water (3°C) until the color changed from yellowish to yellowish pink (on addition of an excess drop, the color changed to pink). The nitrogen content was calculated by the formula

$$N = (VT \times 100\%)/\mathrm{M}, \quad (1)$$

where V was the volume of iron (II) sulfate solution spent on titration of the cellulose nitrate solution, ml;



IR spectra of cellulose (*1*) and cellulose nitrate (*2*) (KBr tablet).

T was the titer of iron(II) sulfate solution; and *M* was the weighed portion of potassium nitrate, g.

The IR spectra of tested samples were recorded on an Infralum FT-801 spectrometer in the frequency range of 550–4000 cm^{-1}. For recording of spectra, the tablets were pressed in potassium bromide at a cellulose nitrate/potassium bromide ratio of 1 : 150.

RESULTS AND DISCUSSION

The IR spectra of initial cellulose and cellulose nitrate are shown in the Figure.

In the IR spectrum of cellulose nitrate, an absorption band appears in the region of 1500–1700 cm^{-1}; there are several overlapping bands in this region. According to the literature data [4–8], the band at 1660 cm^{-1} corresponds to vibrations of nitrate groups at the $C_{(2)}$ and $C_{(3)}$ of the elementary unit of cellulose macromolecule. According to the authors of [6], the band at 1630 cm^{-1} is related to asymmetrical valence vibrations of ONO_2 groups at $C_{(6)}$. In the region of 1281 cm^{-1}, a band appears that corresponds to symmetrical valence vibrations of nitrate groups, while the bands at 829, 745, and 686 cm^{-1} correspond to vibrations of the nitrate group: valence $\nu(NO_2)$, wagging $\gamma_w(NO_2)$, and scissoring $\delta(NO_2)$, respectively. A decrease in the band intensity of OH groups is observed as well.

The quantitative analysis is based on the Lambert–Beer law [1]:

$$A = \xi \times c \times W, \qquad (2)$$

where *A* is the band intensity (area (I, cm^{-1})); ξ is the reduced extinction coefficient; *c* is nitrogen concentration, %; and *W* is sample weight in a tablet, mg. Thus, after calculating ξ of a certain band by the spectrum of a sample with the known content of the functional group, we can quantitatively analyze a number of similar compounds.

To calculate the reduced extinction coefficients, cellulose nitrate samples with nitrogen contents of 3 to 13% were obtained. Reduced extinction coefficients ξ(A) and ξ(I) were calculated for "pure" bands at 1660 and 1280 cm^{-1} (Table 1).

Reduced extinction coefficients were used to determine the nitrogen content in cellulose nitrate samples. The results were compared with the values of nitrogen content in the same samples determined by the ferrosulfate method (Tables 2–3).

The nitrogen content values obtained from the spectral data agree well with the chemical analysis data. The relative measuring error is 0.9 to 5.2%. As a whole, quantitative analysis can be performed with the reduced extinction coefficients calculated by both intensities (A) and areas (I) of absorption bands.

Table 1. Values of reduced extinction coefficients

ν, cm^{-1}	$\xi(A) \times 10^2$, mg^{-1}	$\xi(I)$, cm^{-1} mg^{-1}
1660	2.5 ± 0.4	2.2 ± 0.3
1280	2.6 ± 0.3	0.95 ± 0.04

Table 2. Nitrogen content (%) in cellulose nitrate samples determined by Fourier transform IR spectroscopy by the band at 1660 cm^{-1}

No.	Nitrogen content determined by the band of 1660 cm^{-1}		Nitrogen content determined by the ferrosulfate method ($X \pm 0.1$)
	A	I	
1	10.9 ± 0.8	10.9 ± 0.6	10.4
2	11.2 ± 0.6	11.0 ± 0.3	10.8
3	11.3 ± 0.6	10.8 ± 0.7	11.4
4	12.9 ± 0.5	12.8 ± 0.4	12.5

Table 3. Nitrogen content (%) in cellulose nitrate samples determined by Fourier transform IR spectroscopy by the band at 1280 cm^{-1}

No.	Nitrogen content determined by the band of 1280 cm^{-1}		Nitrogen content determined by the ferrosulfate method ($X \pm 0.1$)
	A	I	
1	10.7 ± 0.9	10.9 ± 0.6	10.4
2	10.4 ± 0.8	10.9 ± 0.5	10.8
3	10.7 ± 0.7	11.1 ± 0.4	11.4
4	13.0 ± 0.4	12.7 ± 0.5	12.5

The found nitrogen content values by the band at 1280 cm^{-1}, as well as the data by the band of 1660 cm^{-1}, agree wll with the chemical analysis data. The measurement error in relation to the ferrosulfate method is 0.9 to 6.1%. The quantitative analysis by the 1280 cm^{-1} band can be performed with the reduced extinction coefficients calculated by both intensities (A) and areas (I) of absorption bands.

CONCLUSIONS

An express method for quantitatively determining the nitrogen content in cellulose nitrates by Fourier transform IR spectroscopy has been developed [9]. The nitrogen content in cellulose nitrate samples was determined: by the band of 1660 cm^{-1} responsible for symmetrical valence vibrations of nitrate groups, with a relative error of 5.2% compared to the ferrosulfate method, and by the band of 1280 cm^{-1} corresponding to symmetrical valence vibrations of nitrate groups with a relative error of 6.1% compared to the ferrosulfate method.

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