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Determination of the Nitrogen Content of Cationic Cellulose Fibers by Analytical Pyrolysis

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Summary. Analytical pyrolysis in combination with gas chromatography and mass spectrometry or a nitrogen-phosphorus detector, respectively, were used to characterize the quaternization reagent glycidyltrimethylammonium chloride and a cationic cotton fabric. Trimethylamine was shown to be the most abundant nitrogen-containing product in the pyrolysis of glycidyltrimethylammonium chloride and was thus used for the quantification of the nitrogen content of the cationic cotton fabric. The results were compared to those obtained by traditional methods such as *Kjeldahl* and elemental analysis. It could be shown that pyrolysis is well suited for monitoring the nitrogen content of cellulose fibers.

Keywords. Cationic fibers; Cellulose; Nitrogen content; Pyrolysis; Gas chromatography.

Introduction

Cellulose fibers such as cotton or viscose are of prime importance to the textile industry. They are either used as such or as blends with other fibers, mainly polyester. One of the major problems of cellulose in contrast to other fibers is the time consuming dyeing process. Because of the negatively charged backbone (due to OH and COOH groups), cellulose has a natural repulsion towards anionic species such as dyes, fillers, and additives. Dyeing of cellulose needs high concentrations of electrolytes in the dye bath. To reduce electrolyte concentrations, which are an environmental problem, and to enhance cellulose dyeability (so called deep dyeing fibers), positively charged groups are attached to the fiber. Quaternization of cellulose is mostly achieved by derivatization with reactive quarternary ammonium compounds or by incorporation of nitrogen-containing polymers into the fiber. Generally, the application of cationic polysaccharides (cellulose or starch) is not restricted to the textile industry; in paper manufacturing, they are mainly used as flocculants and retention aids [1–4].

A big problem when dealing with this non-level quarternized fabrics with a low degree of substitution is the quantification of the nitrogen content. So far, mainly

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the *Kjeldahl* method, elemental analysis, and polyelectrolyte titration have been used for this purpose [3]. All of these methods give very different results, so accuracy as well as comparability has to be strongly questioned.

Analytical pyrolysis is a method that has been used extensively in the characterization of synthetic polymers [5] and lignin [6–8], but it has already been applied to the characterization of cellulose and several cellulose derivatives [9–13]. The method has also shown potential in the quantitative analysis of cellulose blends and paper additives [14, 15]. *Simkovic et al.* have investigated the possibility of qualitatively characterizing cationic starch with pyrolysis – gas chromatography/mass spectrometry [16].

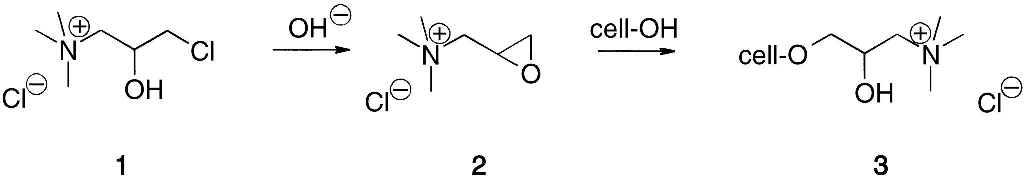
It is the purpose of this work to establish a method for the quantitative determination of the nitrogen content in cotton fibers quaternized with 3-chloro-2-hydroxypropyltrimethylammonium chloride (*CHPT*) or similar reagents.

Results and Discussion

The aim of characterizing cellulose derivatives with analytical pyrolysis is to identify those pyrolysis products which are related to the derivatizing reagent. Since pyrolysis of cellulose results in more than 100 volatile products, this task is often hard to accomplish, especially if the degree of substitution is low. To simplify the search for non-cellulose derived pyrolysis products, the usual procedure is to pyrolyze the derivatizing reagent to determine the main fragments which should then be found in the cellulose derivative as well. This technique is based on the assumption that there is no big difference whether the derivatizing agent is pyrolyzed separately or attached to the cellulose macromolecule. This has been proven to be true at least for organic esters of cellulose as shown by *Schwarzinger et al.* [13].

Since pyrolysis does not only yield volatile products but also a certain amount of char, it can not be assumed that all the nitrogen bonded to the fiber will be transferred to a single volatile pyrolysis product. Therefore, the system has to be calibrated with an external standard. For our measurements, glycidyltrimethylammonium chloride (**2**), the active intermediate in the preparation of cationic cellulose (**3**) with 3-chloro-2-hydroxypropyltrimethylammonium chloride (**1**), was chosen as reference compound (see Scheme 1). The pyrolysis products are listed in Table 1, trimethylamine and chloromethane being the most abundant ones, which coelute under the given conditions.

To simulate matrix effects and the chemical surrounding of the cationized cotton, glycidyltrimethylammonium chloride was transferred to a short piece of cotton yarn prior to pyrolysis. The amount of glycidyltrimethylammonium chloride (35 to 60 μg) was chosen to minimize the weighing error but being still in a



Scheme 1

Table 1. Pyrolysis products obtained from glycidyltrimethylammonium chloride and cationized cotton

No.	Origin[a]	Compound[b,c]
1	*G*	Chloromethane
2	*G*	Trimethylamine
3	*G*	Acroleine
4	*G*	Dimethylaminoacetone
5	*G*	Chloroacetone
6	*G*	$m/z = 128, 113, 88, 84, 58$
7	*G*	$m/z = 170, 144, 125, 82, 58$
8	*C*	CO_2
9	*C*	2,3-Butandione
10	*C*	H_2O
11	*C*	Hydroxyacetone
12	*C*	2-Cyclopenten-1-one
13	*C*	1-Hydroxy-2-butanone
14	*C*	Propanal
15	*C*	2-Furfural
16	*C*	Pyruvic acid methyl ester
17	*C*	Dihydro-(3*H*)-furan-2-one
18	*C*	Furfuryl-2-alcohol
19	*C*	(5*H*)-Furan-2-one
20	*C*	2-Hydroxy-3-methylcyclopentan-2-one
21	*C*	3-Ethyl-2-hydroxycyclopentan-2-one
22	*C*	$m/z = 87, 57, 44, 43, 29$
23	*C*	1,4:3,6-Dianhydro-α-*D*-glucopyranose
24	*C*	5-Hydroxymethyldihydrofuran-2-one
25	*C*	5-Hydroxymethyl-2-furfural

[a] G: Glycidyltrimethylammonium chloride, C: Cellulose; [b] identification based on comparison of the mass spectra with electronic libraries; [c] for unidentified compounds the major mass fragments are listed

Table 2. Initial weights and pyrolysis–GC/NPD results of glycidyltrimethylammonium chloride and cationic cotton

	Mass (μg)	Area	$g(N) \cdot kg(cotton)^{-1}$	Deviation (%)[a]
GlyTMAC	57.8	33946		0.56
	37.5	21604		−1.35
	44.8	26371		0.79
Mean value	46.7	27307		
Cotton	251.2	2753	1.73	0.58
	219.0	2339	1.69	−1.74
	276.4	3208	1.83	6.40
	232.9	2405	1.63	−5.23
Mean value	244.9	2676	1.72	

[a] Refers to the mean values

reasonable range for the comparison to cationized cotton. For quantification, the area of the trimethylamine peak in the chromatogram obtained with a nitrogen-phosphorus detector (NPD) was measured (Table 2). The linearity of the NPD response for glycidyltrimethylammonium chloride, or exactly its main pyrolysis product trimethylamine, was tested in the range of 25 to 100 µg and was found to be satisfactory.

For the analysis of the quaternized cotton a rather high amount of sample was used to produce a trimethylamine signal with a good signal-to-noise ratio in the NPD chromatogram. Figure 1a shows the TIC chromatogram of a sample where all major compounds known to be produced in the pyrolysis of cellulose can be found. In Fig. 1b, the NPD chromatogram of the same sample is shown. The only peak

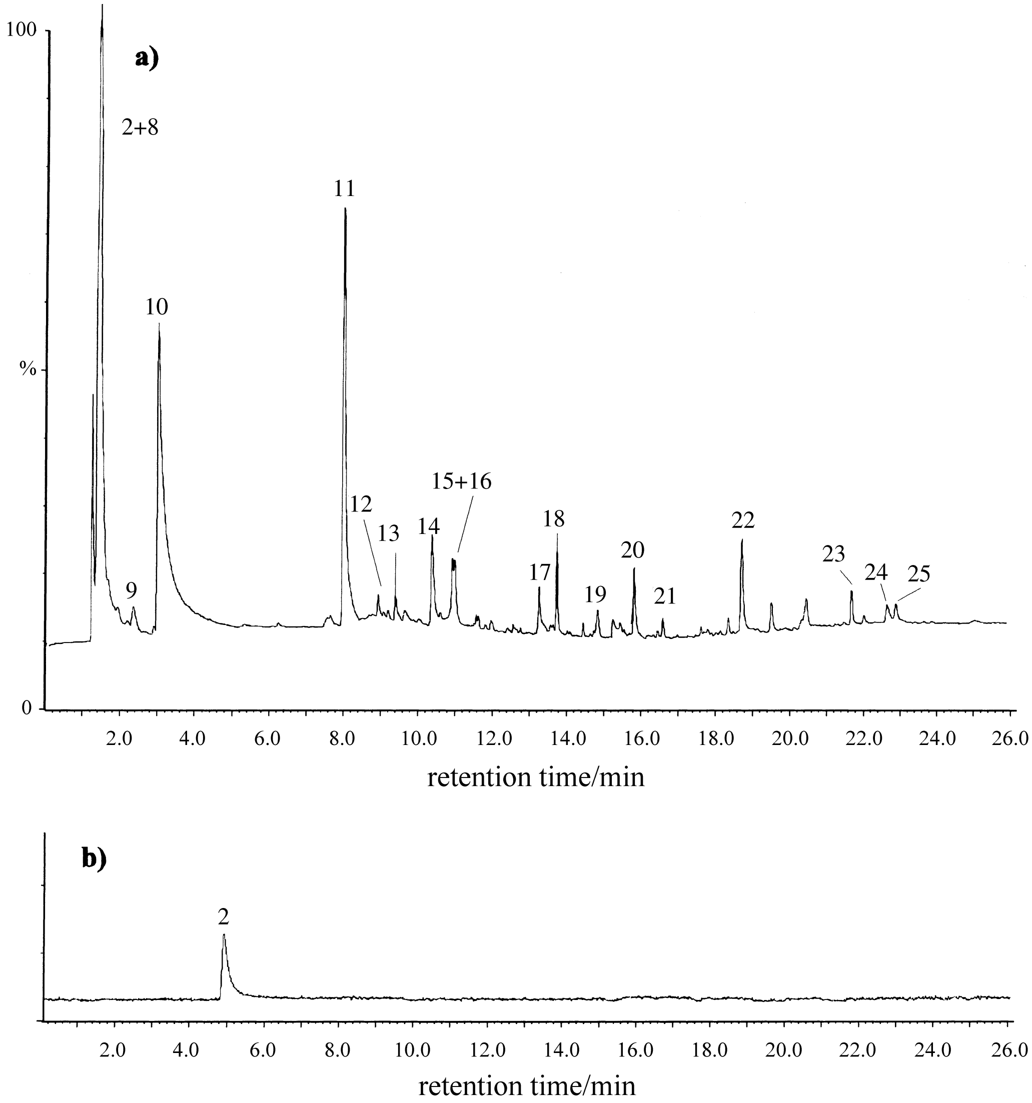


Fig. 1. Pyrogram of cationic cotton; a) mass spectrometric detector, b) nitrogen selective detector; peak numbers in the chromatogram refer to compounds listed in Table 1

Table 3. Comparison of the nitrogen contents in $g(N) \cdot kg(cotton)^{-1}$ and their standard deviations obtained by *Kjeldahl*, elemental analysis, and pyrolysis–GC/NPD

No.	*Kjeldahl*	Elemental analysis	Pyrolysis–GC/NPD
1	1.62	1.1	1.73
2	1.61	0.7	1.69
3	1.58	0.9	1.83
4	1.60	1.0	1.63
5	1.58	0.7	
6		0.8	
Mean value	1.60	0.87	1.72
Standard deviation	0.018	0.163	0.084

still visible results from trimethylamine and can easily be measured. Different retention times for the trimethylamine peak result from different carrier gas velocities, which are due to the fact that the column ends are in vacuum on the mass spectrometer side and at ambient pressure on the NPD side. The nitrogen content of the cotton fibers can be calculated according to Eq. (1) (*A*: peak area, *m*: mass in μg, *M*: molecular weight in $g \cdot mol^{-1}$, *N*: nitrogen, *GTMAC*: glycidyltrimethylammonium chloride).

$$\frac{g(N)}{kg(cotton)} = \frac{A(cotton) \cdot m(GTMAC) \cdot M(N) \cdot 1000}{m(cotton) \cdot A(GTMAC) \cdot M(GTMAC)} \tag{1}$$

The areas of the trimethylamine peaks are listed in Table 2 together with a mean value, the deviation, and the resulting nitrogen content. The rather strong deviation of the values for cotton is probably due to the not homogeneously distributed cationization reagent.

A comparison of the results obtained from analytical pyrolysis with the results of elemental and *Kjeldahl* analyses (Table 3) reveals that it gives the highest nitrogen content of all methods but is in the magnitude of the *Kjeldahl* analysis, which so far is considered to be the most reliable one. Elemental analysis does not only have the highest mean variation, but also a nitrogen content which is only about one half of the value found by the other methods.

Conclusions

Whereas the results from elemental analysis are much to low, *Kjeldahl* and analytical pyrolysis give comparable results. One of the biggest benefits of analytical pyrolysis is that the amount of sample required is very low. In case of an inhomogeneous sample, however, this may result in a certain deviation from the mean value. The same holds for elemental analysis. For *Kjeldahl* analysis, a rather high amount of sample (1 g) was used, and therefore any errors due to inhomogenities should be eliminated.

Analytical pyrolysis seems to be the method of choice, especially if the task is to compare the degree of substitution of fibers of the same class. In this respect, the advantages of the fast and easy to handle method are outrageous. Another field of use could be the characterization of stable heterocyles, like triazines, attached to cellulose, where elemental analysis as well as *Kjeldahl* are known to give wrong results. The most challenging part in the quantification with analytical pyrolysis is to find a suitable reference compound to build up a calibration table and to weigh the compound in a μg range with as little error as possible.

Experimental

Chemicals

Glycidyltrimethylammonium chloride and 3-chloro-2-hydroxypropyltrimethylammonium chloride (*CHPT*) were purchased from Fluka and cotton from Testfabrics, Inc. (type 405 W). The compounds were weighed on a Mettler Toledo UMT 2 micro balance.

Preparation of the cationic cotton fabric

17 g of dry cotton are treated with $500\,cm^3$ of NaOH ($0.4\,mol \cdot l^{-1}$) at room temperature for 20 min. After padding the fabric with a pad mangle it is inserted into $500\,cm^3$ of an aqueous *CHPT* solution ($0.2\,mol \cdot dm^{-3}$) for further 20 min and padded again. The reaction is accomplished at 100°C for 10 min. Finally, the fabric is washed with 0.1 *N* HCl acid and hot H_2O.

Analytical pyrolysis

Pyrolysis experiments were carried out using a CDS Pyroprobe 2000 pyrolysis unit coupled to a Fisons GC 8000 *via* a CDS 1500 interface. From the split/splitless injector of the GC, a short fused silica precolumn was connected *via* a 'Y'–connector to two identical analytical columns leading to a Fisons MD 800 mass spectrometer on the one side and a nitrogen-phosphorus detector (NPD) on the other side. Pyrolysis products were separated on J&W Scientific CAM columns (30 m, ID 0.32 mm, 0.25 μm film thickness) with He 4.6 (40 kPa) as carrier gas and identified through comparison of their EI mass spectra with NIST 98, Wiley, and NBS electronic libraries as well as literature data [12, 13]. The GC was operated in the split mode with a split of $15\,cm^3 \cdot min^{-1}$ and programmed as follows: 60°C for 5 min and raised to 220°C at a rate of $10°C \cdot min^{-1}$ where it was held for 5 min. The pyrolysis interface, injector block, and the GC/MS interface were all heated to 220°C, and the NPD was operated at 300°C. For the NPD the following conditions were used: make-up gas: He 4.6 (50 kPa), H_2 5.0 (25 kPa), and synthetic air (35 kPa). The mass spectrometer was operated in EI mode (70 eV) with a source temperature of 200°C.

About 250 μg of each cotton sample were weight to the tenth of a microgram, placed in a quartz tube, and subsequently pyrolyzed for 10 s at 400°C. To enable quantification, an exactly weighed amount of glycidyltrimethylammonium chloride was transferred to a cotton fiber (100 μg) and pyrolyzed immediately under the same conditions as described above.

All samples were analyzed at least in triplicate to ensure reproducibility and to exclude statistical errors.

Kjeldahl analysis

About 1 g of the fabric was digested with H_2SO_4 and a catalyst containing 2.8% TiO_2, 3.0% $CuSO_4 \cdot 5H_2O$, and 94.2% K_2SO_4. The residue was treated with NaOH to liberate NH_3 which was subsequently absorbed in boric acid and titrated with HCl.

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