

Investigations on the Effect of Metal Ions on the Products Obtained From the Pyrolysis of Cellulose

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Abstract

Investigations on the influence of different metal ions, employed in the form of their chlorides, on the pyrolyzate of microcrystalline cellulose and pulp were performed. Cellulose/metal ion mixtures were pyrolyzed and the volatile reaction products enriched on a cartridge filled with Tenax, followed by GC-MS analysis after thermodesorption of the trapped pyrolysis products. Different metal ions, namely Na⁺, Ca²⁺, Mg²⁺ and Fe³⁺ were tested at levels ranging from 0.18 - 2.2 mM g⁻¹. Evaluation of the GC-MS pyrograms revealed that the distribution of the selected 37 pyrolysis products was significantly influenced by both, the type and the concentration of the metal ion added.

Keywords: pyrolysis, thermodesorption, cellulose, metal ions.

1. Introduction

The characterization of products resulting from the thermolysis or pyrolysis of cellulose and related materials has been the subject of a series of investigations published during a time span covering several decades¹⁻¹⁴. Analytical methods used for the characterization of these reaction products comprise a wide range of different instrumental technologies. Those include methodologies monitoring only a single parameter (e.g. change in weight) like thermogravimetry but also spectroscopic methods, like infrared spectrometry^{8,9}, nuclear magnetic resonance spectroscopy¹¹, chromatographic methods, mainly gas chromatography (GC) or high performance liquid chromatography (HPLC)⁵ and finally hyphenated techniques like GC or HPLC coupled to mass spectrometric [MS] detection.^{3,4,11,15} Particularly the latter methods can provide comprehensive information on the nature and quantity of the products originating from the pyrolysis of the investigated samples.

The addition of metal ions to influence the pyrolysis of cellulose and with it the distribution of volatile and non-volatile products generated by this process has been reported in several publications.¹⁶⁻³⁴ Major driving forces for these investigations come from quite different fields of interest, comprising works dedicated to the general interest in mechanical and kinetical aspects of this pyrolysis reaction^{16,17,19,23,25-30}, experiments focusing on the selective increase in yield for

a specific pyrolysis product after the addition of salts and also phosphoric acid^{18,32,33} but also investigations coming from the fields of fire prevention²². To investigate the effect of these additives on the pyrolysis process, different types of analytical techniques have been employed. Principally two different approaches can be distinguished. First, the direct analysis of the pyrolysis mixture using e.g. thermogravimetry^{17,24}, infrared spectroscopy^{16,17,30} electron spin resonance spectrometry^{32,33} and MS.³⁰ Second, if a more detailed picture is required, the pyrolysis products have to be separated first using chromatographic methods, commonly GC. Consequently the resolved pyrolysis products can be either detected using a simple GC-detector^{18,23,24,32} or further characterized employing a more sophisticated spectroscopic detection method particularly MS.^{22,28,29}

For the presented work we chose an approach using off-line pyrolysis with subsequent trapping of the pyrolysis products on an appropriate sorbent, followed by thermodesorption onto a GC-MS system. By this we wanted to demonstrate that the selected task can be accomplished without dedicated pyrolysis-GC instruments. In this work off-line pyrolysis GC-MS of cellulose and cellulose doped with different metal ions has been performed. The data obtained from these experiments can provide useful information with respect to the products originating from smoldering cellulose and pulp. Thereby valuable findings regarding the manipulation of base-materials used in the production of cigarette paper may be acquired.

2. Experimental

2.1. Instrumentation

For pyrolysis a Pyroprobe 2000 (CDS Instruments, Oxford, PA, USA) was employed. Pyrolysis products were trapped on thermodesorption cartridges filled with Tenax TA (Supelco, Bellefonte, PA, USA). GC analysis was performed with an Agilent Model 6890N gas chromatograph (Agilent Technologies, Palo Alto, USA) equipped with a TDS 2 thermodesorption unit combined with a KAS 4 cold injection system (both Gerstel, Mülheim/Ruhr, Germany). For separation a DB-VRX GC column (J&W Scientific, Folsom, CA, USA) 60 m*0.25 mm I. D., film thickness 1.4 μm was used which was coupled to an Agilent MSD 5973 quadrupole mass spectrometer for detection.

2.2. Materials and Reagents

Water was purified using a Milli-Q (Millipore, Bedford, MA, USA) system. The following metal salts were used: NaCl, $\text{CaCl}_2 \times 2 \text{H}_2\text{O}$, $\text{MgCl}_2 \times 6 \text{H}_2\text{O}$, FeCl_3 (all Merck, Darmstadt, Germany). Microcrystalline cellulose (ALPHA CEL BH300[®]) was obtained from International Fiber Cooperation (New York, USA) and Lapponia pine pulp was from StoraEnso (Finland). He 4.6 (Linde, Stadl Paura, Austria) was used as carrier gas for GC experiments as well as for pyrolysis.

2.3. Procedures

Pyrolysis experiments were performed by introducing 100 μg – 150 μg of the cellulose into a quartz tube which was subsequently plugged using glass wool. The quartz tube was introduced into the pyrolysis unit and heated to 500°C for 10 s employing a heating rate of 20 °C s⁻¹. During the pyrolysis procedure a stream of helium gas was applied, transferring the volatile pyrolysis products onto a thermodesorption cartridge filled with Tenax TA, which was connected to the pyrolysis unit using a Swagelock union. The loaded cartridge was introduced into the thermodesorption unit, desorbed at 300 °C and the analytes trapped in the cold injection system (KAS) at -100°C. Finally they were transferred to the GC column employing a heating rate of 12°C s⁻¹ and a final injector temperature of

260 °C that was maintained for 10 min. GC separation was performed using a start temperature of 35 °C and a ramp of 5 °C min⁻¹ up to a final temperature of 260 °C that was maintained for 20 min. He 4.6 was used as carrier gas at flow rate of 1.4 mL min⁻¹. The MS instrument was operated in the positive ion mode (EI ionization at 70 eV) and full scans from 15 – 420 mass units were acquired.

Cellulose/metal ion mixtures were prepared by combining 200 – 250 mg of cellulose with 1 mL of the appropriate salt solution, containing 2 – 20 mg L⁻¹ of the metal ion in Milli-Q purified water, in a vial. Subsequently, another 0.5 mL of water was added and the mixture placed into an ultrasonic bath for 2 min. Finally the vial was placed into a drying cabinet and maintained at 80 °C for 16 hours. After 12 hours the sample was removed temporarily and homogenized using an agate mortar. In the case of pulp a somewhat modified method had to be used. To 5 mg of pulp 100 μL of the aqueous salt solution were added whereby the whole solution was absorbed by the pulp. Drying was performed at 90 °C for 6 hours.

3. Results and Discussion

3.1 Pyrolysis of microcrystalline cellulose and pulp

Firstly untreated microcrystalline cellulose was pyrolyzed and subsequently analyzed by GC-MS to optimize the experimental parameters and to identify the resulting pyrolysis products. To ensure the suitability of the selected procedure (in particular with respect to the trapping efficiency and capacity of the selected Tenax cartridges) a series of experiments was performed employing different amounts of cellulose for pyrolysis. These experiments were finally used to obtain the set of parameters given in section 2.3. Figure 1 shows a pyrogram obtained for such a sample, using these optimized conditions. The pyrogram obtained for Lapponia pulp was almost identical. As can be seen from this figure an acceptable separation of the different pyrolysis products could be achieved and the identification of 36 different pyrolysis products (listed in Table 1) was possible, using the NIST database of the GC-MS system and information taken from the

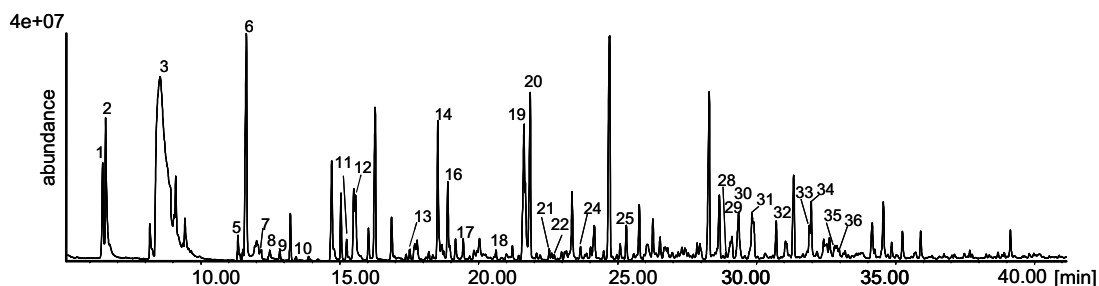


Figure 1. GC-MS pyrogram for microcrystalline cellulose. Experimental conditions: see section 2.3. Peaks: see Table 1.

literature.² These 36 identified pyrolysis products were subsequently used as markers to judge the influence of different metal ions on the pyrolysis behavior of the investigated cellulose. For quantitative analysis and comparisons all peak areas obtained were normalized with respect to the amount of cellulose employed.

3.2. Pyrolysis of microcrystalline cellulose and pulp with metal ions

To investigate the effect of different amounts of metal ions added to the cellulose on the qualitative and quantitative composition of the pyrolyzate a series of samples containing microcrystalline cellulose and metal salts were prepared. The salts employed included alkaline metals (Na^+), alkaline earth metals (Ca^{2+} and Mg^{2+}) as well as a trivalent species (Fe^{3+}) all used in the form of their chlorides. Mixtures were prepared containing between 0.18 mM g^{-1} and 4.4 mM g^{-1} of the metal ion, employing the procedure described in section 2.3. In Figure 2 pyrograms of pure cellulose and cellulose/metal salt mixtures at metal ion levels of around 1 mM g^{-1} are compared. A discussion of the observed effects is given in the following paragraphs.

Table 1. Analytes identified from the pyrolysis of cellulose

Nr. Analyte	Retention time	Quantitation (m/z)
1 2-Butanone	6.47	TIC ¹
2 Formic acid	5.56	46
3 Hydroxyacetaldehyde + Acetic acid	8.40	31
4 2,3-Butandione	9.09	43
5 Crotonaldehyde	11.38	41
6 Hydroxyacetone	11.63	TIC
7 Propenic acid	12.16	72
8 Ethanediol	12.41	31
9 2,3-Pentandione	12.83	TIC
10 2,5-Dimethylfuran	13.41	TIC
11 Methylfuran	15.23	TIC
12 1-Hydroxybutanone	15.56	57
13 3-Furfurale	17.51	TIC
14 2-Furfurale	18.52	TIC
15 2-Cyclopentenone	18.56	82
16 2-Furanemethanol	18.87	98
17 1-Acetyloxy-2-propanone	19.43	TIC
18 Cyclopenten-1,3-dione	20.61	96
19 2-Furanone	21.60	55
20 2-Hydroxy-2-cyclopentene-1-one	21.83	98
21 3-Methyl-2,5-furandione	22.51	TIC
22 5-Methyl-2-furanone	22.69	55
23 Phenole	23.37	94
24 5-Methylfurfurale	23.64	TIC
25 2-Hydroxy-3-methyl-2-cyclopentene-1-one	25.75	112
26 o-Cresol	26.29	108

Continued

27 m-,p-Cresol	26.95	108
28 Levoglucosenone	28.86	68
29 2-Hydroxy-3-methyl-4-pyranone	29.02	126
30 Dihydro-4-hydroxy-2-furanone	29.32	TIC
31 Benzoic acid	29.84	105
32 1,2-Dihydroxybenzene	28.84	105
33 1,4:3,6 Dianhydro- α -glucopyranose	31.85	TIC
34 5-Hydroxymethyl-2-furfurale	31.92	TIC
35 Hydrochinone	32.75	110
36 1,2-Dihydroxy-3-methylbenzene	32.93	124

¹ Total Ion Current

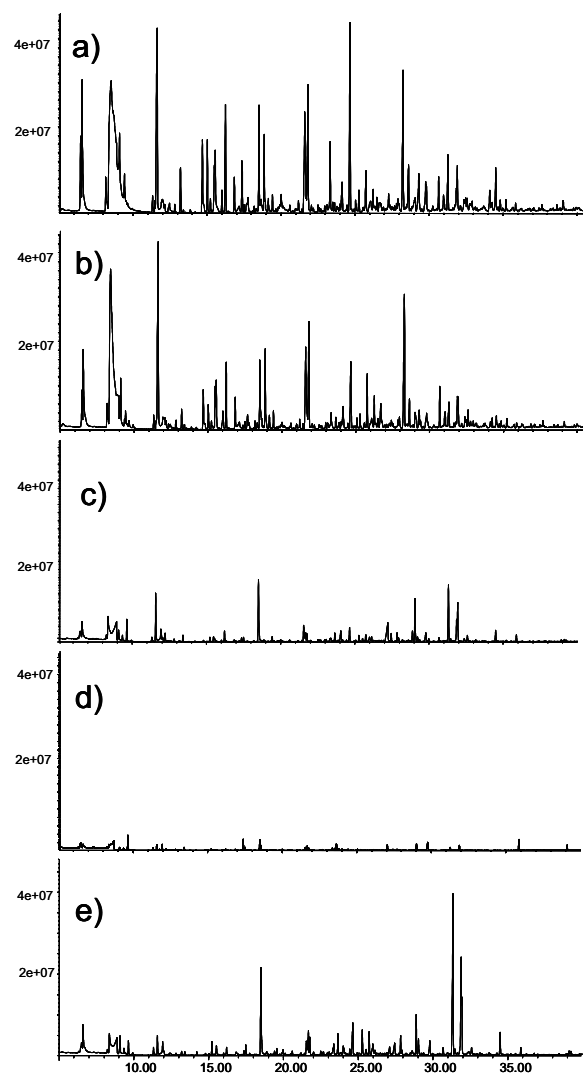


Figure 2. GC-MS pyrogram for microcrystalline cellulose (a), containing $2.2 \text{ mM g}^{-1} \text{ Na}^+$ (b), $1.25 \text{ mM g}^{-1} \text{ Ca}^{2+}$ (c), $1.25 \text{ mM g}^{-1} \text{ Mg}^{2+}$ (d) and $0.9 \text{ mM g}^{-1} \text{ Fe}^{3+}$ (e). Experimental conditions: see section 2.3.

3.2.1. Cellulose/pulp Na⁺ mixtures

First mixtures of cellulose and Na⁺ were tested at different metal levels ranging from 0.44 mM g⁻¹ – 4.4 mM g⁻¹ Na⁺. As can be seen from Figure 2b no significant changes between the patterns obtained for pure cellulose and the Na⁺ treated cellulose could be observed even at a level of 2.2 mM g⁻¹ Na⁺.

In depth analysis of the individual pyrolysis products revealed that the first impression, originating from the visual evaluation of the chromatographic pattern, was correct. Changes in concentration were insignificant for most analytes. Exceptions were hydroxyacetone, 2,3-pentandione, 1-acetyloxy-2-propanone, 2-furanmethanol and 5-methylfurfural, where a slight increase in concentration could be observed and 2,3-butandione, 2,5-dimethylfuran, 2-hydroxy-3-methyl-2-cyclopentene-1-one, 1,2-dihydroxybenzene and the cresol isomers with a more pronounced trend in the same direction. Reduction in concentration, compared to the untreated cellulose was found for benzoic acid and dihydro-4-hydroxy-2-furanone. With respect to the amount of Na⁺ employed no significant influence of the metal ion concentration on the obtained signal areas could be observed.

3.2.2. Cellulose/pulp Ca²⁺ and Mg²⁺ mixtures

Three different mixtures of cellulose and Ca²⁺ were prepared at levels of 0.25, 0.75 and 1.25 mM g⁻¹ of Ca²⁺. As can be seen from Figure 2c the intensities of a series of analytes were substantially decreased at the 1.25 mM g⁻¹ level. Detailed evaluation of the individual pyrograms revealed several different trends. First, for most substances a significant influence of the metal ion concentration could be observed, with higher concentrations leading to decreased peak areas. Exceptions were benzoic acid, 2-hydroxy-3-methyl-4-pyranone, 2-butanone and 2,5-dimethylfuran where no impact of the Ca²⁺ concentration could be found. Second, the addition of Ca²⁺ led to an increase in concentration (compared to the untreated cellulose) for the following substances: propenic acid (only at the 0.25, 0.75 mM g⁻¹ level), 2,5 dimethylfuran, all furfurals, 3-methyl-2,5-furanedione (only at the 0.25 mM g⁻¹ level), 2-hydroxy-3-methyl-4-pyranone, 5-methyl-2-furanone, levoglucosenone and 1,4:3,6 dianhydro- α -glucopyranose, whereas the concentrations obtained for phenol and cresols remained almost unchanged. All other analytes showed a more or less pronounced decrease in peak areas upon the addition of Ca²⁺. The effects observed after the addition of Mg²⁺ (0.42, 1.25 and 2.01 mM g⁻¹) were similar to those described for Ca²⁺. In general Mg²⁺ led to an even more pronounced reduction in signal area than Ca²⁺. The sample containing 2 mM g⁻¹ Mg²⁺ provided the least signal areas for all samples investigated in this study.

3.2.3. Cellulose/pulp Fe³⁺ mixtures

The cellulose/Fe³⁺ mixtures showed an interesting behavior with respect to the increase and decrease of signal intensities upon the addition of the metal salt. As can be seen from Figure 2e most signals were significantly suppressed when a cellulose sample containing 0.9 mM g⁻¹ Fe³⁺ was pyrolyzed. Nevertheless the formation of some substances was greatly enhanced. In particular levoglucosenone, 1,4:3,6 dianhydro- α -glucopyranose and the furfurals were present in much higher concentrations compared to the untreated cellulose sample. Figure 3 depicts the changes in the chromatographic pattern induced by increasing the Fe³⁺ concentration. Detailed inspection of the investigated analytes shows that, similar as in the case of Ca²⁺, reduced signal intensities are obtained with increasing concentration of the metal ion. Pyrolysis products that are not affected by the Fe³⁺ concentration are formic acid, the furanone derivatives, 2-cyclopentenone, benzoic acid and hydroquinone. In a few cases higher concentrations of Fe³⁺ led to increased signal intensities. Examples for this type of behavior are phenol and the cresols.

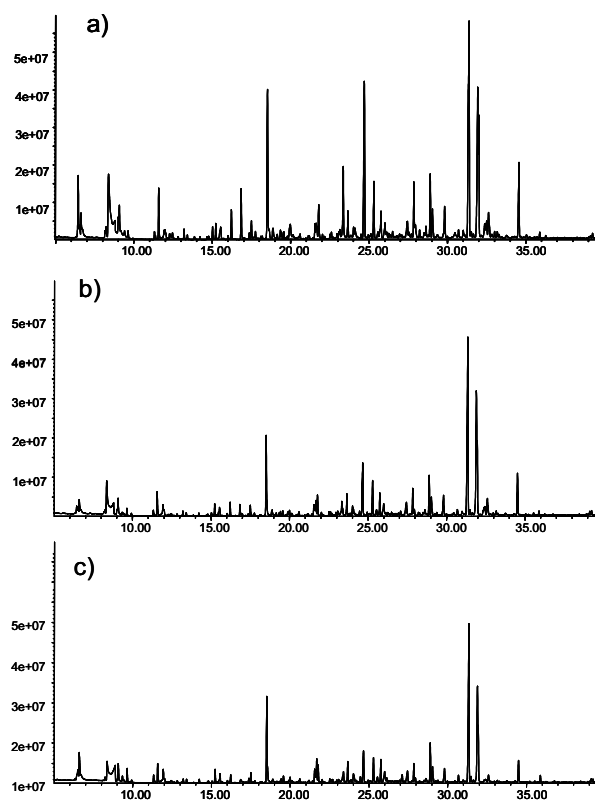


Figure 3. GC-MS pyrogram for microcrystalline cellulose containing 0.18 mM g⁻¹ of Fe³⁺ (a), 0.54 mM g⁻¹ of Fe³⁺ (b) and 0.9 mM g⁻¹ Fe³⁺ (c). Experimental conditions: see section 2.3.

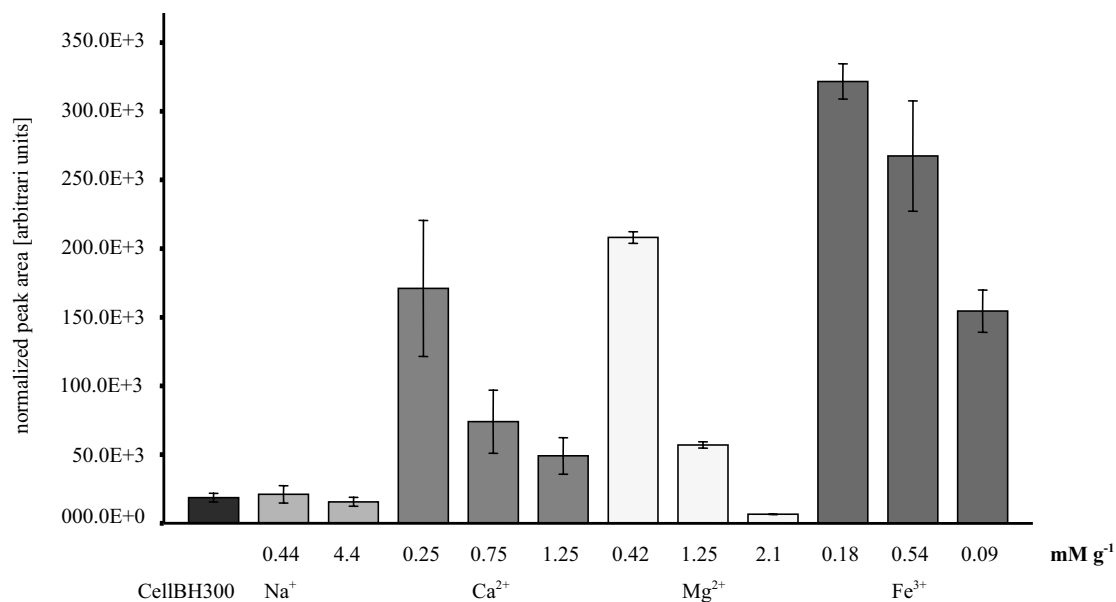


Figure 4. Dependence of the levoglucosenone concentration (data are mean values from three determinations) upon the type and amount of metal ion added.

3.3. Comparison of the effects generated by different metal ions on the pyrolysis products of microcrystalline cellulose

Moving from Na⁺ to Ca²⁺ and finally Mg²⁺ a general trend, namely an increase in influence leading to decreased peak areas for most of the selected analytes can be observed. This is also clearly apparent from Figure 2, where the addition of Mg²⁺ led to the most significant reduction in intensities. Additionally it can be seen that Ca²⁺ and Mg²⁺ induce a significant decrease in peak areas for most of the analytes included in this study. The trivalent Fe³⁺ ion behaves somewhat different. Although (comparing the lowest concentration level of each metal ion) Fe³⁺ provides the minimum signal intensities for the majority of substances, increasing the metal concentration had a less pronounced effect than in the case of Mg²⁺. For this reason, focusing on the highest metal ion level, Mg²⁺ provided the most significant reduction in signal intensities.

Focusing on the increased formation of levoglucosenone and 1,4:3,6 dianhydro- α -glucopyranose upon the addition of metal ions, it can be seen that the most pronounced effect is generated by Fe³⁺ followed by Mg²⁺, Ca²⁺ and finally Na⁺. A graphical description of this behavior can be seen in Figure 4.

3.4. Pyrolysis of levoglucosane in the presence of Mg²⁺

Levoglucosane is an intermediate generated during the pyrolysis of cellulose.³⁵ According to the literature, further reactions of this substance during the pyrolysis process lead to the formation of a substantial number of components detected in the final pyrolyzate.^{7,35} Therefore experiments were

performed to investigate the behavior of this important pyrolysis intermediate upon the addition of metal ions in particular Mg²⁺. Results from these investigations revealed that for levoglucosane a similar trend was observed in the presence of Mg²⁺ (1.25 mM g⁻¹) as in the case of cellulose and pulp. Figure 5 depicts a pyrogram of levoglucosane and one of a levoglucosane/Mg²⁺ (1.25 mM g⁻¹) mixture.

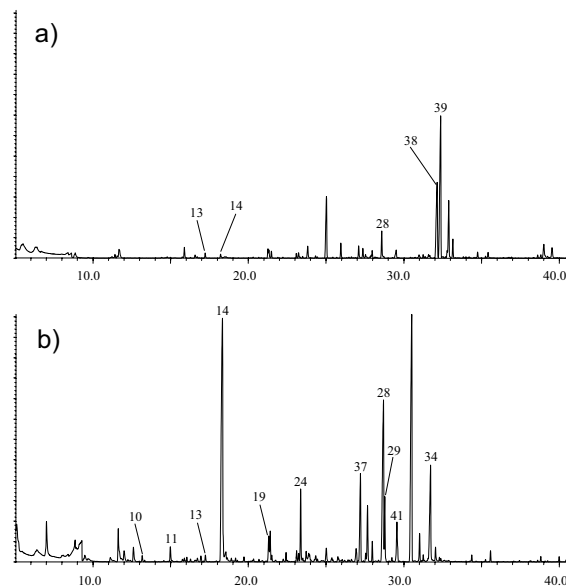


Figure 5. Pyrogram of levoglucosane (a) and a levoglucosane/Mg²⁺ (1.25 mM g⁻¹) mixture (b). Peak assignment see Table 1 except for: 37 = 2,5-furandicarboxaldehyde; 38 = 1,6:3,4-dianhydro- β -d-galactopyranose; 39 = 1,6:2,3-dianhydro- β -d-mannopyranose.

Particularly furane-, furfurale- and pyranone-derivatives as well as levoglucosone and 1,4:3,6 dianhydro- α -glucopyranose showed increased signal intensities when the levoglucosane was treated with Mg^{2+} . These findings can be taken as an evidence that in the pyrolytic decomposition of cellulose the presence of Mg^{2+} also plays an important role with respect to the reactions following the intermediate production of levoglucosane.

4. Conclusions

The presented investigations revealed that the addition of metal ions strongly influences the distribution of products resulting from the pyrolysis of cellulose and pulp. A strong decrease in concentration for the majority of the analyzed pyrolysis products was observed upon the addition of Ca^{2+} , Mg^{2+} and Fe^{3+} , whereas Na^+ did not significantly influence the chromatographic pattern of the pyrolyzate. In contrast to this behavior the yield of some compounds in particular levoglucosone, 1,4:3,6 dianhydro- α -glucopyranose, furfurals and some pyrane and furane derivatives was enhanced when metal ion doped cellulose was pyrolyzed. These findings can help to develop strategies for the selective manipulation of the amount of certain classes of compounds produced during the pyrolysis of cellulose and pulp, which can be seen as an important issue in the manufacturing of cigarette paper.

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Povzetek

Opravili smo raziskave vpliva različnih kovinskih ionov v obliki kloridov na nastajanje pirolizata mikrokristalinične celuloze in vlaknine. Mešanice celuloza/kovinski ioni smo pirolizirali in hlapne razgradne produkte koncentrirali z uporabo kolonic, napolnjenih s Tenaxom. Termodesorpciji je sledila analiza z uporabo GC-MS.

Ione Na^+ , Ca^{2+} , Mg^{2+} in Fe^{3+} smo nanegli v intervalu vsebnosti 0,18 – 2,2 mM mg^{-1} . Analiza kromatogramov je pokazala, da je produkcija 37 produktov pirolize, ki smo jih opazovali, zelo odvisna od dodatka kovinskih ionov.