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Determination of carbohydrate- and lignin-derived components in complex effluents from cellulose processing by capillary electrophoresis with electrospray ionization-mass spectrometric detection

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ABSTRACT

Degradation products from lignocellulosic materials receive increasing attention due to the continuously growing interest in their utilization. The inherent structural variance of lignocellulosics combined with the intricacy of lignocellulosic processing (e.g. pulping of wood and bleaching of cellulosic pulps) and the complexity of degradation processes occurring therein result in rather complex mixtures in the process streams and effluents that contain a large quantity of structurally different degradation products. This is true for most processing steps, but also for degradation reactions occurring during aging of lignocellulosic materials, such as paper, cellulosic tissue or textiles. In order to render such mixtures better analytically accessible than hitherto possible a CE-ESI-MS method was established for the simultaneous determination of aliphatic carboxylic acids from the degradation of (hemi)celluloses and aromatic compounds from lignin degradation. CE and ESI-MS parameters have been optimized towards sensitivity and good reproducibility. The method was tested in two real-world scenarios: the determination of major components in effluents from bleaching stages in the pulp and paper industry, and the analysis of degradation products in extracts of naturally aged papers. The advantages and drawbacks of this approach are critically discussed.

1. Introduction

The analysis of lignocellulose degradation and identification of the products formed from these materials are still posing analytical challenges, especially due to the complexity of the reaction mixtures. This applies to nearly all byproduct streams in lignocellulose processing, no matter whether related to "classical" pulp and paper processing or to more recent biorefinery scenarios. The degradation products in industrial effluents after different steps of pulp bleaching have large similarities to the products found in extracts of aged paper. The mixtures of degradation products of low-molecular weight carbohydrates under strongly alkaline, alkaline-oxidative or acidic-oxidative conditions are complex, being formed by superposition of multiple fragmentation, rearrangement, and condensation reactions. These carbohydrate-derived products come along with fragmentation products of (residual) lignin. In the pulp and paper industries, such degradation products contribute significantly to the spent liquor streams, and hence also to the corresponding organic effluent load (total organic carbon). Degradation reactions similar to those enforced during the pulp bleaching stages by drastic reaction environments are proceeding also under ambient conditions over longer times upon natural or artificially accelerated paper aging. Also here, carbohydrates and lignins are fragmented and degraded into very complex compound mixtures. Degradation processes in paper are determined by numerous factors including the material of the paper (fiber type, sizing, fillers, etc.) as well as storage conditions (temperature, relative humidity, acids, pollutants, etc.). As a result of such degradation, mechanical and optical properties of paper can suffer dramatically [1]. More detailed information on the

Abbreviations: CE, capillary electrophoresis; ESI-MS, electrospray ionization-mass spectrometry; GC–MS, gas chromatography–mass spectrometry; BGE, background electrolyte; LMM, low molecular mass; MT, migration time; PA, peak area.

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degradation mechanisms and the reaction products formed is of great significance for a suitable conservation treatment of paper and in summary for the general understanding of lignocellulose degradation.

For the separation of degradation products of (hemi)celluloses, an analytical methodology is required which shows high sensitivity and robustness as well as the ability to simultaneously determine degradation products of both carbohydrates and lignin. The task is rendered even more complicated by the complexity in case of effluent mixtures, the matrix and the rather low concentrations of its individual components. Gas chromatography/mass spectrometry (GC–MS) is often applied for the analysis of such complex mixtures. This method requires preliminary sample derivatization to produce volatile analytes, e.g. by esterification, etherification, silylation, etc. [2–4]. This is not only a time-consuming procedure, but might effect losses during sample preparation, and cause discrimination effects [5–7].

In the recent years capillary electrophoresis (CE) has been established as a fast and suitable method for both the analysis of carbohydrates, their degradation products (aliphatic carboxylic acids) and the determination of phenolic and aromatic compounds. It provides short analysis times and, at the same time, high separation efficiencies without a preliminary derivatization step. In most cases UV-detection is applied after separation by CE [8–11]. This method was used to study effluents of pulping woody biomass [12–14], which offers complex matrices.

Hyphenation to MS provides more information on the actual structures of the analytes. CE-MS was applied for the analysis of low molecular mass carboxylic acids in atmospheric particles [7], beverages [5,15], biological fluids [16,17], urban atmosphere and vehicle emissions [6]. CE-MS was used further for the analysis of phenolic compounds (with similar structures to the lignin-derived compounds) in biomass pyrolysis and burning [18], virgin olive oil [19,20], walnut [21] and atmospheric aerosols [22]. Pulp bleaching effluents and celluloses aging extracts have been studied by CE much less extensively, since due to dilution effects of the process the overall concentrations – at similarly complex compositions – are significantly lower.

In this study, we would like to communicate our efforts towards a CE-MS-based analytical technique for the simultaneous determination of carbohydrate-derived reaction products, such as aliphatic mono- and di-carboxylic acids and hydroxy-acids, as well as phenolic lignin-fragments in effluents of pulp bleaching and extracts of aged paper artifacts. Together with our parallel study on (hemi)cellulose and lignin degradation products in artificially aged papers [23], this is the first report on a MS-hyphenated method for direct analysis of the complex pulp bleaching effluents and aged paper extracts.

2. Materials and methods

2.1. Chemicals

All chemicals were of the highest purity available and were used without further purification. Ultrahigh quality water (HPLC grade, Sigma–Aldrich) was used for all aqueous solutions.

The chemicals were obtained from the following suppliers: ammonium formate (97%), ammonium hydroxide solution (≥25% in water) and sodium hydroxide (≥98%) from Sigma–Aldrich–Fluka (Schnelldorf, Germany), 2-propanol (99.9%) from Fisher Scientific (Germany). All the model compounds (either as the free acids or as their sodium salts) were obtained from Sigma–Aldrich–Fluka, at a purity of 97% or better except lactic acid (90%). Stock solutions of each model compound with a concentration of 1 g/l were prepared in deionized water and stored at 4 °C. Solid phase extraction cartridges Supel™-Select HLB SPE 1 g/20 ml were purchased from Supelco (Bellefonte, PA, USA). Phenex polytetrafluoroethylene (PTFE) syringe filters with pore size of 0.2 and 0.45 μm and various diameters were supplied by Phenomenex (Aschaffenburg, Germany).

2.2. Sample preparation

2.2.1. Pulp bleaching effluents

The pulp bleaching effluent sample was obtained from combined effluents of a totally chlorine free (TCF) bleaching of hardwood sulfite pulp, prior to the biological effluent treatment, from Lenzing AG, Lenzing, Austria. The sample was stored at 4 °C and was warmed to room temperature before sample preparation, which started with vacuum filtration through 0.4 μm membrane filters. As the concentration of analytes was too low for the direct analysis, effluent samples were concentrated by solid-phase extraction (SPE) according the following procedure [24]: the SPE cartridge was conditioned with 10 ml methanol and 10 ml of deionized water, 200 ml of sample was loaded with 1 drop per second. Salts are not retained on the SPE cartridge, which thus allows the separation of organic analytes from salts in the loading step. Carboxylic acids were eluted from the cartridge with a methanol/acetonitrile mixture (v/v = 1:1). The organic solvent was removed in vacuum under exclusion of oxygen, and the sample was redissolved in deionized water. This removes long-chain carboxylic acids in amounts according to their solubility in water [25]: acids with up to 10–12 carbon atoms are still in the sample, larger ones are completely removed. This step is necessary to protect the separation capillary from clogging. Evaporation of the organic solvent did not cause changes in the analyte composition which was proved by GC–MS analyses of silylated samples before and after the treatment (recovery above 90%). Prior to injection, the sample was filtered through a 0.2 μm membrane filter.

2.2.2. Aged paper extracts

Aqueous extracts from an old book and aged papers were prepared as follows: 17 g of air dry book paper were extracted in 230 ml of deionized water containing 10% methanol for 45 h. The extract was brought to a volume of about 25 ml by freeze-drying and was filtered through a 0.2 μm membrane filter prior to injection.

Characteristics of the book paper: publication year 1924, brittle paper, double fold number: 2. The weighted average molecular weight (Mw) of the cellulose as determined by GPC in DMAc/LiCl [26] was between 100 and 120 kg/mol.

2.3. CE-ESI-MS

CE-MS analysis was performed on a G1600 Agilent capillary electrophoresis system (Agilent Technologies, Waldbronn, Germany) in combination with an Agilent 6320 series ion trap mass spectrometer equipped with an Agilent CE-ESI-MS sprayer (Agilent Technologies). For separation, a fused-silica capillary (Agilent Technologies) with a total length of 60 cm and an inner diameter of 50 μm was used. For maintaining constant performance over time, the capillary was flushed daily with 0.1 M sodium hydroxide for 10 min, water for 10 min and background electrolyte (BGE) for 5 min. Between the actual runs, the capillary was preconditioned by flushing 5 min with water and 5 min with BGE. BGE and samples were filtered through 0.2 μm membranes. Hydrodynamic injection was used at 50 mbar for 10 s followed by injection of buffer at 50 mbar for 5 s. The separation voltage was 20 kV, the resulting current was 20 μA. The capillary was thermostated at 25 °C.

The sheath liquid was delivered by an Agilent 1200 series isocratic pump equipped with a 1:100 splitter. System control, data