Trace analysis of levoglucosan and lignin-phenols in speleothems by HILIC-UHPLC-ESI-HRMS: A new method

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Motivation

Speleothems are valuable paleoclimate archives and organic trace analysis in speleothems offers a great variety of information and can be used to complement and correct well-established inorganic proxies like $\delta^{18}O$ and $\delta^{13}C$.

Lignin, a biopolymer, is one of the main constituents of higher plants. When degraded, the ratios among the different groups of oxidized monomer units (LOPs) allow to draw conclusions on the type of vegetation it originated from.

Levoglucosan, an anhydrosugar, naturally only originates from the combustion of cellulose and can thus be used as a biomass burning marker. Analysis of levoglucosan in sediments shows good correlation with traditional burning markers like black charcoal. Correlation of levoglucosan in speleothems with $\delta^{18}O$ and $\delta^{13}C$ could help prevent misinterpretation of the latter due to fire events.

As Levoglucosan is a highly polar molecule, extraction and analysis with traditional reversed phase systems proved difficult. An optimized sample preparation to access both lignin and levoglucosan in speleothems was developed. Furthermore, a HILIC-UHPLC-ESI-HRMS method was developed.

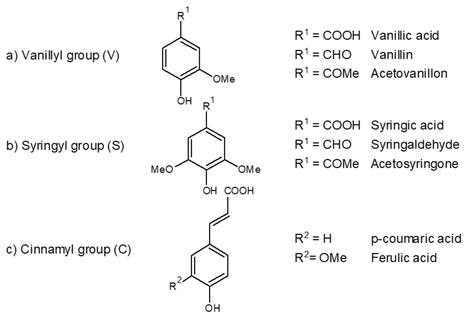


Fig. 1: Structures of the three LOP groups [1].

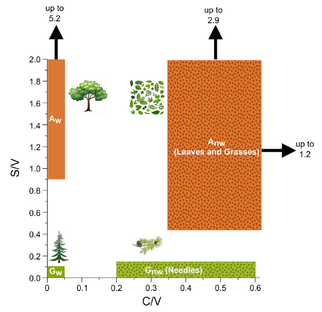


Fig. 2: Scatter plot of the LOP ratios [2].

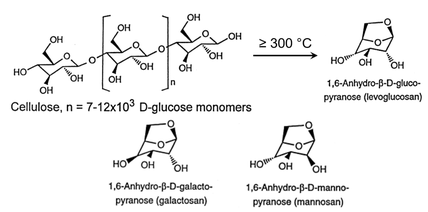
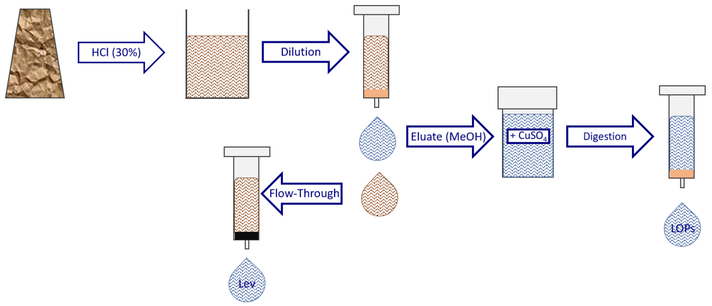


Fig. 3: Structure of the analysed anhydrosugars [3].

Sample preparation

- Alkaline $CuSO_4$-oxidation to produce LOPs
- Anhydrosugars have to be separated beforehand to avoid disintegration



- Separation of the analytes on first SPE
- Enrichment on second SPE, respectively

Instrumental setup

- HILIC (*hydrophilic interaction liquid chromatography*) allows separation of very polar analytes
- Various retardation mechanisms take place

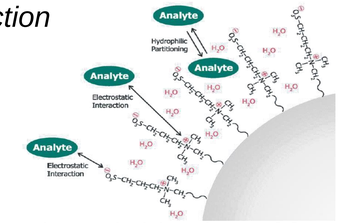
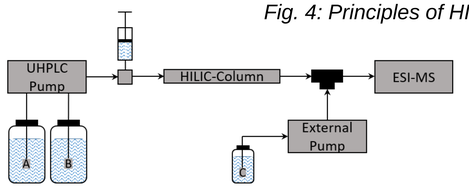


Fig. 4: Principles of HILIC [4].



- Addition of NH_4OH after the column to improve ionisation

Results

- Separation of all isobaric compounds

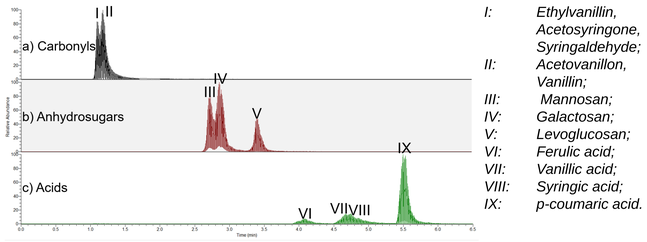


Fig. 5: Chromatogram of the optimised HILIC-ESI-HRMS method.

- Successfull calibration and validation of the developed HILIC-UHPLC-ESI-HRMS method
- Application to flowstone CO-54 from the Conturines cave in South Tyrol proved effective

Ref.: [1] Jex et al. *Quaternary Science Reviews* **2014,** *87*, 46–59
[2] Hedges, Mann *Geochimica et Cosmochimica Acta* **1979,** *43* (11), 1803–1807
[3] Elias et al. *Geochimica et Cosmochimica Acta* **2001,** *65* (2), 267–272
[4] Vogel, www.analytik-news.de, 2012