

Trace analysis of lignin-phenols in speleothems by UHPLC-ESI-HRMS: Comparison of two lignin degradation methods

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Secondary mineral deposits in caves like stalagmites, stalactites, or flowstones are valuable paleoclimate archives. Advantages of organic trace analysis in such deposits are stable conditions in a cave, protecting compounds from external influences, as well as the possibility to precisely date samples up to 600,000 years using the uranium/thorium method.[1]

Lignin, a biopolymer, is one of the main constituents of higher plants and consists of three monomeric units: sinapyl-, coniferyl-, and coumaryl alcohol. Lignin can be degraded into its monomeric units by alkaline CuO-oxidation. The oxidized monomer units can be analysed by UHPLC-ESI-HRMS with limits of quantification in the ng/g range.[2] By determination of the ratios among different oxidation products in a speleothem, conclusions can be drawn on the type of vegetation above the cave.

To date, lignin degradation was conducted by a microwave-assisted alkaline digestion using copper(II)-oxide catalyst as a catalyst. [3] The insolubility of copper(II)-oxide can lead to inhomogeneous distribution in the reaction solution and thus to losses or over-oxidation of the lignin-phenols. A recently developed degradation method of Yan and Kaiser [4] includes the usage of copper-sulphate as a catalyst and was suitable for low sample volumes. In the herein presented project this method was adapted to the specific matrix of speleothems and compared to the existing CuO-oxidation method. The more efficient method was then applied to samples of a flowstone from a cave of the Dolomites in Southern Tyrol.

[1] D. Scholz, D. Hoffmann, *Quat. Sci. J.* 57 (2008) 52–76. [2] C.N. Jex, G.H. et.al. *Quat. Sci. Rev.* 87 (2014) 46–59. [3] M.A. Goñi, S. Montgomery, *Anal. Chem.* 72 (2000) 3116–3121. [4] G. Yan, K. Kaiser, *Anal. Chem.* 90 (2018) 9289–9295.