



## Comparison of three methods for the analysis of lignin in soils and sediments: CuO oxidation, thermochemolysis and Derivatization Followed by Reductive Cleavage method.

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Lignin monomers are among the most effective biomarkers for woody material because they provide an unambiguous fingerprint for vascular plants. Much of the work examining lignin in soils and sediments has been conducted using CuO oxidation [1] or tetramethylammonium hydroxide (TMAH) thermochemolysis [2]. Because they differ in the mechanism of degradation [3], each method results in a different suite of lignin products and compound ratios. On the other hand, Derivatization Followed by Reductive Cleavage (DFRC) is highly efficient for cleaving lignin  $\alpha$ - and  $\beta$ -aryl ethers. Commonly used in wood chemistry, it is therefore suitable for lignocellulose materials [4] but also for lignite [5]. The purpose of this study was to compare lignin analysis by CuO oxidation, TMAH thermochemolysis and DFRC procedures on a set of samples of soil and sediments. These methods were applied to three samples: (1) a sandy acid forest soil sample collected from the upper layer (0-30 cm) of a plot located in a maritime pine (*Pinus pinaster*) forest (Cestas, Landes de Gascogne, France), (2) a peat sample from a wooded Sphagnum-dominated mire (Frasne, Jura Mountains, France) and (3) a low rank coal lignite sample (Hodonín, Moravia, Czech Republic).

Different mechanisms are involved in each process: oxidation and hydrolysis with CuO, hydrolysis and methylation with TMAH, acetylation-bromination followed by reductive cleavage with zinc dust for the DFRC method. Lignin monomers obtained after CuO oxidation and TMAH thermochemolysis procedures were similar to those described in the literature [1,2]. Compounds with guaiacyl units were predominantly identified while components with a syringyl or p-hydroxyphenyl structures were less abundant. The DFRC method released monolignols (trans coniferyl diacetate and trans sinapyl diacetate) that arose from  $\beta$ -ether cleavage and minor components with predominantly guaiacyl units originating from other structures. Total lignin yields, reported as  $\Lambda$ , were calculated as the sum of the concentrations of all lignin-derived compounds normalized to 100 mg of organic carbon in the sample. For the three samples, results showed that  $\Lambda$ CuO is higher than  $\Lambda$ TMAH (between twice and four times) and  $\Lambda$ DFRC (between twenty and one hundred times).

Because the three methods do not react with the same lignin pools (differences could be due to chemical and/or physical arrangements), direct comparisons should be made carefully but could be viewed rather than complementary methods for a fine characterization of lignin in soils and sediments.

### References

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