SYNTHESIS OF CHLORINATED 4-METHYLDIBENZOFURAN AND 4,6-DIMETHYLDIBENZOFURAN - COMPOUNDS FORMED DURING KRAFT PULP BLEACHING

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Up to today about 200 chlorinated compounds formed during bleaching of pulp have been identified. It has been suggested by Buser, Rappe and coworkers that one hitherto unknown group of compounds could be chlorinated and methylated dibenzofurans. We have now synthesized polychlorinated 4-methyldibenzofurans (4-mDF) and 4,6-dimethyldibenzofurans (4,6-dimDF) as reference compounds to be used in subsequent analysis of samples from kraft pulp bleaching.

The results from determination of polychlorinated 4-mDF and 4,6-dimDF in samples taken at different stages in pulp mill bleaching sequences have shown that these compounds can be formed during the first chlorination step.

Analysis of black liquor sample from kraft pulping also indicated the presence of 4-mDF and 4,6-dimDF as possible precursors.

Bleaching of oxygen prebleached pulp using a low chlorine ratio results in a formation of polychlorinated 4-mDF and 4,6-dimDF in very low levels, less than a few ppt in pulp and less than a few ppq in effluent.

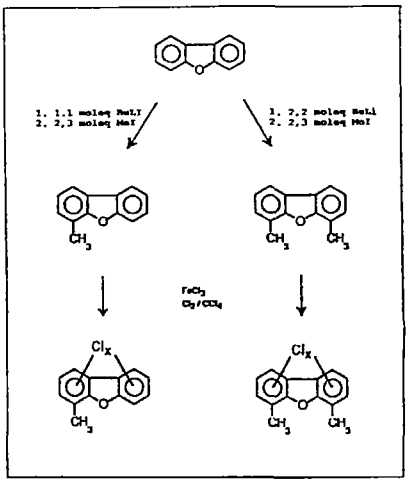

Figure 1. Dibenzofuran were methylated by treatment with butanelithium followed by methyliodide to achieve 4-mDF and 4,6-dimDF. The structure of the products formed were confirmed by ^{1}H and ^{13}C-NMR-spectroscopy and EI-mass spectrometry. The methylated dibenzofurans were chlorinated to give a total of 39 mono- to heptachlorinated 4-mDF and 26 mono- to hexachlorinated 4,6-dimDF.

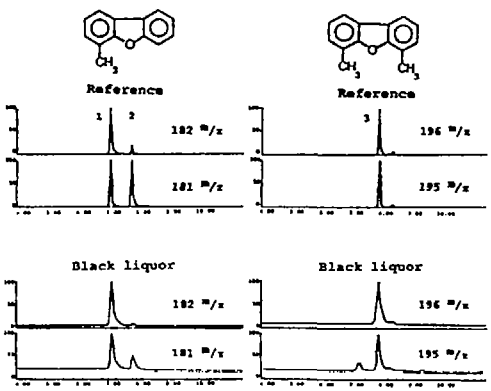

Figure 2. Identification of the precursor compounds in black liquor by analysis of the most abundant ion fragments ,STR-GC/HRMS. Peak 1 refer to 4-mDF, peak 2 to 4,6-dimDF(M $-CH_3^+$ ion) and peak 3 refer to 4,6-dimDF.

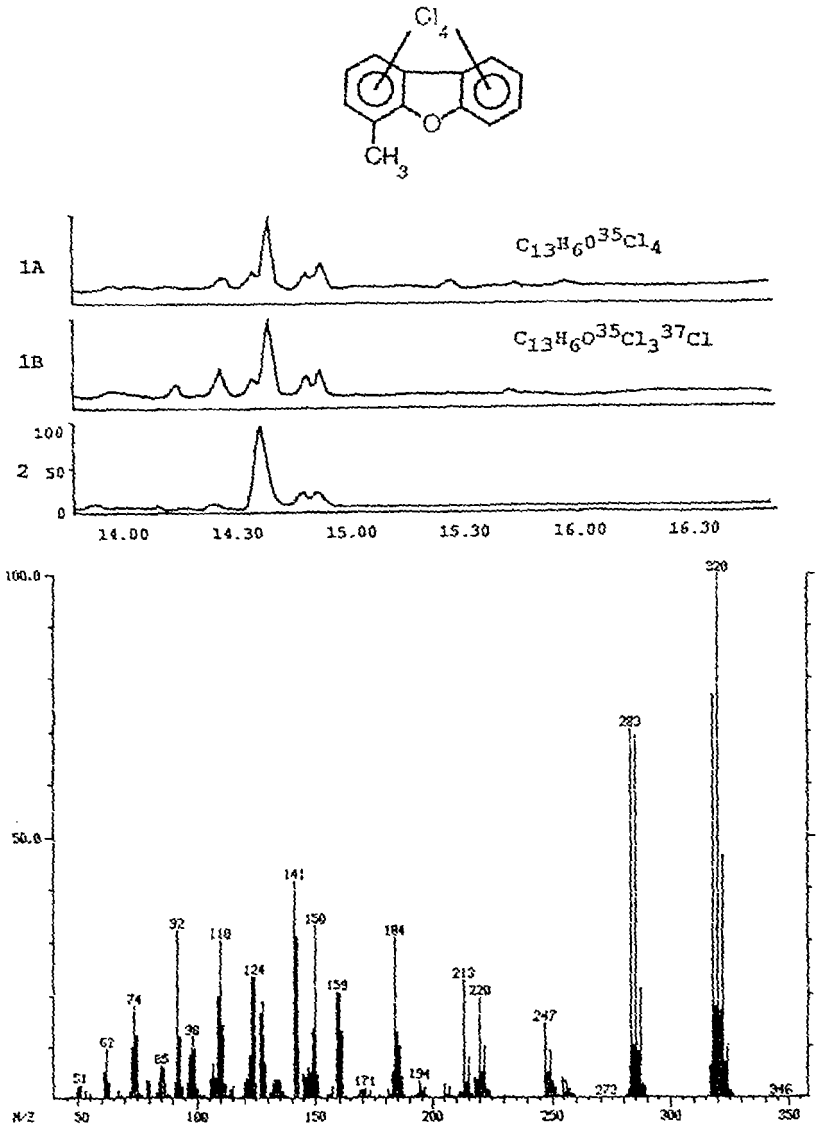

Figure 3. Ion chromatogram of tetrachlorinated 4-mDF in effluent from first chlorination stage (1A and 1B) and tetrachlorinated 4-mDF in the reference mixture (2). The masspectrum refer to the major isomer in reference mixture.

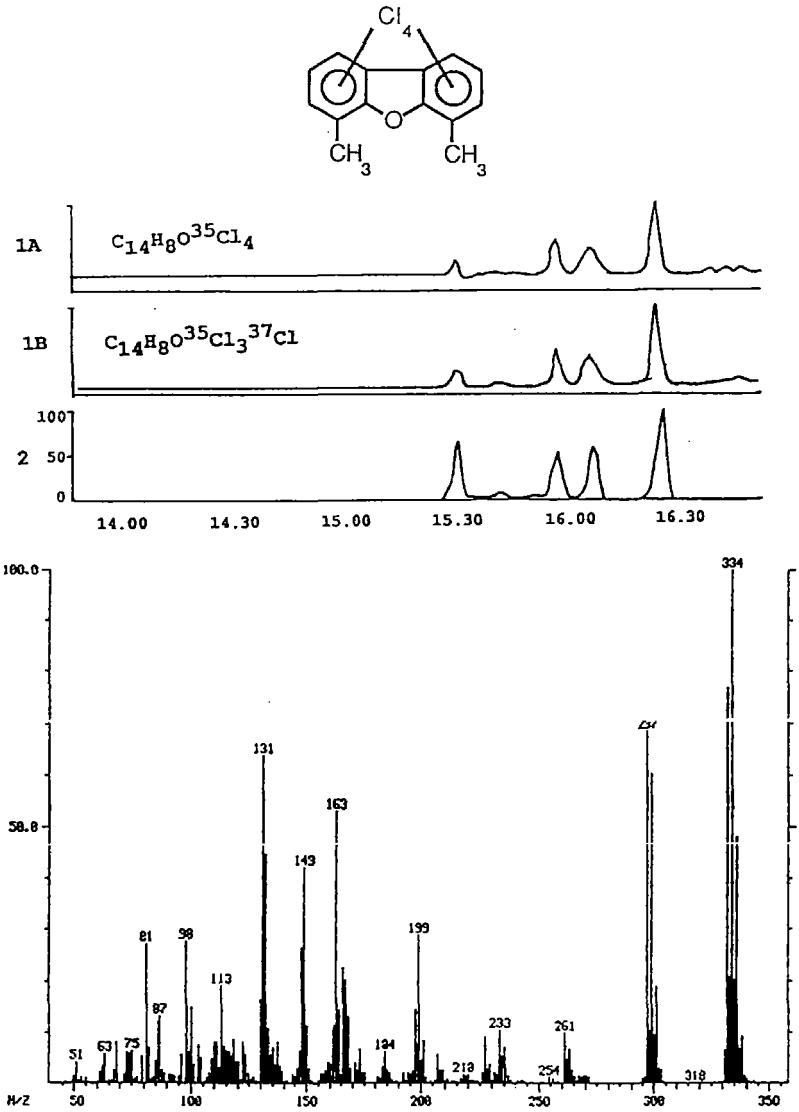

Figure 4. Ion chromatogram of tetrachlorinated 4,6-dimDF in effluent from first chlorination stage (1A and 1B) and tetrachlorinated 4,6-dimDF in the reference mixture (2). The masspectrum refer to the major isomer in reference mixture.