Use of thermochemolysis-GC-MS for detailed characterization of fractions obtained from HPLC separation of sulphonated lignin

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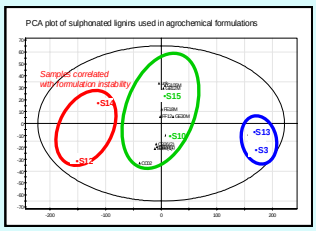
Introduction

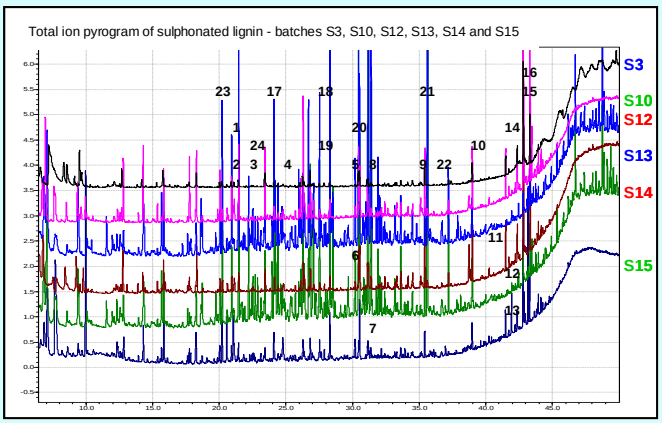
Lignin is a polyphenolic material present in plants. It is formed by the polymerization of coniferyl, sinapyl, and p-coumaryl alcohols. Lignosulfonates (LS) and sulphonated lignins are by-products of pulping processes used in paper manufacturing. They are used as detergents in formulations used for crop protection.

Partial separation of LS is achieved by ion-pair liquid chromatography (IP-LC). The variability in the results was examined by multivariate analysis and the results could be correlated with properties, such as the (in-)stability of agrochemical formulations.

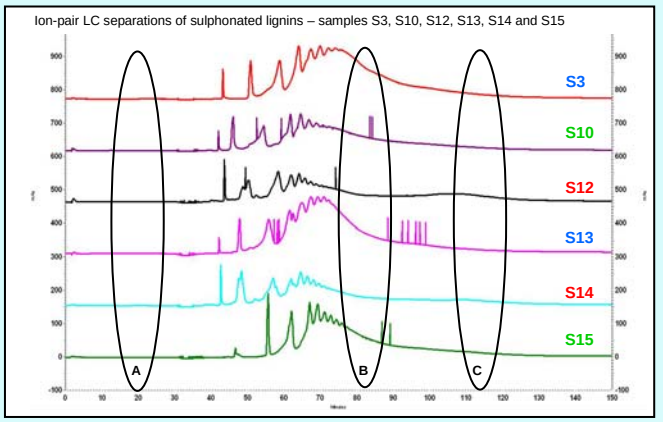


Physical causes of the property variations are currently not fully understood. Thermochemolysis gas chromatography – mass spectrometry (THM-GC-MS, THM=Thermally Assisted Hydrolysis Methylation) can be used to characterize non volatile (*e.g.* high-molecular-weight) materials in terms of the (average) chemical composition. When using state-of-the-art THM-GC-MS, only minute quantities of sample are required and liquid solutions can be injected and processed automatically. For the characterization of sulphonated lignins **pyrolysis-GC-MS** by itself is likely to prove inadequate, due to the very polar (ionic) nature of the fragments. Therefore, a combination of pyrolysis and chemical derivatization ('thermochemolysis') is needed. In this study the structure of sulphonated lignins is investigated by using THM-GC-MS. Furthermore, LC fractions were collected and analysed by THM-GC-MS in order to evaluate the **variations** within individual samples.

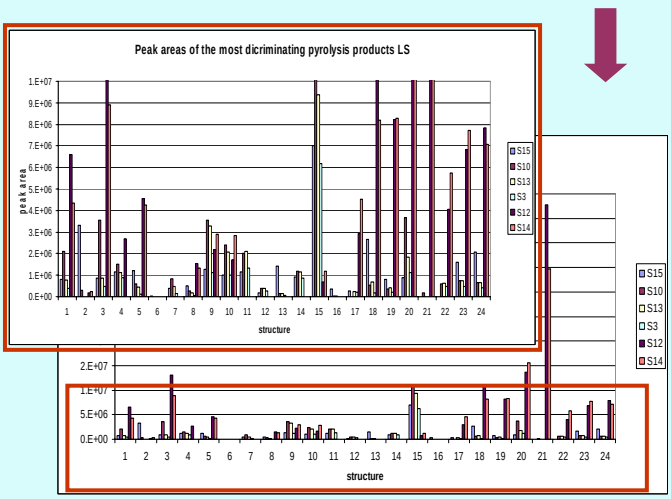
Results



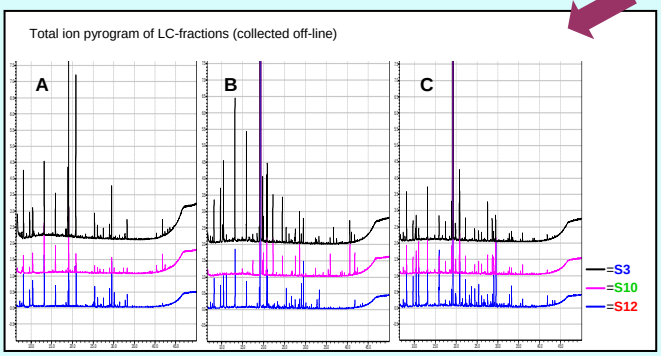
Pyrogram of samples S3, S10, S12, S13, S14 and S15. Distinctly different pyrograms were observed for the samples S12 and S14, which have been incriminated in formulation-instability studies. The most-discriminating peaks are numbered 1-24 and the areas of these are plotted below.



Separations achieved with IP-LC shows clear differences between the batches. Three samples (S3, S10 and S12) were fractionated off-line. The most-interesting fractions (circled above; A, B and C) were further studied using THM-GC-MS. Resulting pyrograms can be seen below.



Comparing samples S12 and S14 with the rest of the samples, additional pyrolysis products are found in higher quantities (peaks 17-24). Some of the pyrolysis products found in S3, S10, S13, and S15 are not found in S12 and S14, indicating that the chemical structure of the entire sample is different.



The fractions of samples S3, S10 and S12 show differences in the pyrograms. The IP-LC chromatogram of fraction A shows no response at the measuring wavelength, suggesting that no analyte is present. The pyrogram of the same fraction is showing the opposite. In fractions B and C more differences can be observed. As noticed earlier, when the whole sample was pyrolysed sample S12 showed different pyrolysis products than those found from S3 and S10. The IP-LC trace of sample S12 shows a hump around 110 min. This peak is not found in the other samples. The pyrograms for the corresponding fraction C shows that additional peaks are found in sample S12.

Conclusions and future work

THM-GC-MS has been shown to be a suitable method for distinguishing between different samples of sulphonated lignins. It was also found that the structures of 'good-batch' and 'bad-batch' lignin-derived surfactants were different. Furthermore, the chosen LC fractions analyzed by THM-GC-MS showed similar results to those found when the whole sample was analyzed. Future work includes coupling LC-THM-GC-MS on-line. It is envisaged that this approach will provide additional details, enabling a more-detailed chemical interpretation of the results.