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Quantitative analysis of lignins based on permanganate oxidation (Version 3)

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An Excel-file including **Worksheets 1-4** is available for download here:
Permanganateoxidation"phenolic".xls

Introduction

A previous version (**Version 2**) describes two methods (Method "quadratic" and Method "linear") for the calculation of the compositions of lignins based on degradation by permanganate. Method "quadratic" is presumably the most reliable one but model experiments are not completely unequivocal (Erickson et al., 1973a). Method "quadratic" was presented at the Eighth European Workshop on Lignocellulosics and Pulp (Parkås et al., 2004). **Version 3** describes a modification of Method "quadratic". The new method is denoted Method "phenolic". It requires knowledge of the phenol content of the lignin sample examined (an estimate of the phenol content may be satisfactory in several instances). In Method "phenolic" it is taken into consideration that it is solely the phenolic fraction of the lignin samples examined that gives rise to the products analysed (**I-IX**, Fig. 1) (cf. Bose et al., 1998). Method "phenolic" (and also Method "quadratic") is based on the assumption that all the individual types of carbon atoms susceptible to permanganate oxidation, that are attached to aromatic nuclei, are converted to carboxyl groups to the same extent.

Method "phenolic" applied to softwood lignin (Worksheets 1 and 2)

Calculation of the yield factor (F)

To exemplify the calculations in Worksheets 1 and 2 we have used data reported by Miksche and co-workers (Erickson et al., 1973b) for milled wood lignin from spruce and its methylation/permanganate oxidation/esterification products **I-VII** (Fig. 1); additional esters amounted to 3-5% of the weight of esters **I-VII**. Phenol content: 0.26/phenylpropane unit. Trace constituents are assumed to consist of equal amounts *p*-hydroxyphenylpropane units and

guaiacylpropane units and are supposed to be phenolic to the same extent as the rest of the units. The weight of the lignin sample examined is 100 mg [trace constituents, 4 mg (approximation based on the proportion of esters attributed to trace constituents); carbohydrates 1 mg, assumed value]. The assumed average lignin unit weights are 157 (*p*-hydroxyphenylpropane), 187 (guaiacylpropane) and 217 (syringylpropane) (as an approximation the average weight of the phenolic units is assumed to be the same as those of the non-phenolic units). Based on the data given above the yield factor (**F**) can be calculated from the following equation (for molecular weights of esters **I**-**VII**, see Fig. 1):

I (mg) x 157 /166.18/ F + **II** (mg) x 187 /196.20/ F + **III** (mg) x 217 /226.23/ F + **IV** (mg) x 187 / 254.24/ F^2 + **V** (mg) x 187 /254.24/ F^2 + **VI** (mg) x 2 x 187 /376.37/ 2/ F^2 + **VII** (mg) x 2 x 187 /390.39/ F^2 + 0.26 x carbohydrates (total amount in the sample, 1 mg) + 0.26 x trace constituents (total amount in the sample, 4 mg) = 0.26 x 100.

See A (Table 1) in Worksheets 1 and 2!

Calculation of the composition of softwood lignin samples (known phenol content) (Worksheet 1)

It is assumed that the proportions of different types of units are the same in the phenolic and the non-phenolic fractions of the lignin samples investigated. In Worksheet 1 data for milled wood lignin is used as an example. It is obvious that there is a considerable uncertainty in the calculation of the composition of the total lignin in this case, since the fraction of phenolic units in milled wood lignin is rather small. The reliability of the calculated data obtained increases with the magnitude of the phenolic fraction. The composition of the lignin sample investigated can be calculated based on the determined yield factor (**F, See A (Table 1) in Worksheet 1**). Cleavage of ether bonds (e.g. during alkaline pulping) results in ring-opening of phenylcoumarans (β-5 structures). Therefore there are two options for the calculation of the distribution of the lignin units:

1) The ester **IV** is considered to originate from β-5 substituted units: **B (Table 2) in Worksheet 1**.
2) The ester **IV** is considered to originate from monoetherified biphenyls: **C (Table 3) in Worksheet 1**.

Calculation of phenol content and the distribution of phenolic units in softwood lignin (Worksheet 2)

The basis for the determination of the yield factor **F** (**A (Table 1) in Worksheet 2**) appear in the section **Calculation of the yield factor (F)**.

The calculated yield factor **F** can be applied to the determination of the phenolic units in lignin samples (the carbohydrate-free portion) of the same type as the one used for the determination of the factor **F** (**B (Table 2) in Worksheet 2**). Simultaneously the distribution of different types of phenolic units in the lignin samples is calculated (**C (Table 3) in Worksheet 2**). Note: If data for the same sample are introduced in both Table 1 and Table 2, the distribution of phenolic units in this sample will appear in Table 3.

Method "phenolic" applied to hardwood lignins (Worksheets 3 and 4)

The composition of hardwood lignins (example, birch lignin) and their phenol content can be calculated from permanganate oxidation products by a method analogous to the one applied to softwood lignins (see above). To exemplify the calculations in Worksheets 3 and 4 we have used data reported by Larsson and Miksche (1971) for milled wood lignin from birch and its methylation/permanganate oxidation/esterification products **II-IX** (Fig. 1). Amount of sample: 100 mg (7.5 mg carbohydrates; 4 mg trace constituents assumed to consist of equal amounts of guaiacylpropane units and syringylpropane units). Phenol content: 0.20/phenylpropane unit.

Comments

General

Fill in your data in the applicable Table 1 in Worksheet 1, 2, 3 or 4 and in Table 2 in Worksheet 2 or 4 in case of phenolic group analysis! Calculated data will now appear when you press Enter!

Alternative derivatives and unit weights

The principles of the calculations in Worksheets 1-4 are generally applicable to different types of lignins but modifications of the formulas may be required. If isolated, modified lignins (e.g. kraft lignin) are examined the appropriate unit weights should be filled in Table 1 in the Worksheets. If the benzoic acids are analysed as other types of derivatives than those used here, it is possible to

calculate the corresponding yields of **I**-**IX** and then use the worksheets. It is alternatively possible to replace the molecular weights in the tables with those of other derivatives.

"Condensed" and "Uncondensed" units

Results obtained in Worksheets 1 and 3 can be used for the calculation of the proportions of "condensed" and "uncondensed" units [esters **IV**, **V**, **VI** (one of the nuclei), **VII**, **VIII** and **IX** (one of the nuclei) correspond to "condensed" units (Fig. 1)] in the lignin samples examined. Trace constituents could be neglected in estimates of the proportions of "condensed" and "uncondensed" units (i.e. the proportions of "condensed" and "uncondensed" units in "trace constituents" is assumed to be the same as in the rest of the lignin sample).

References

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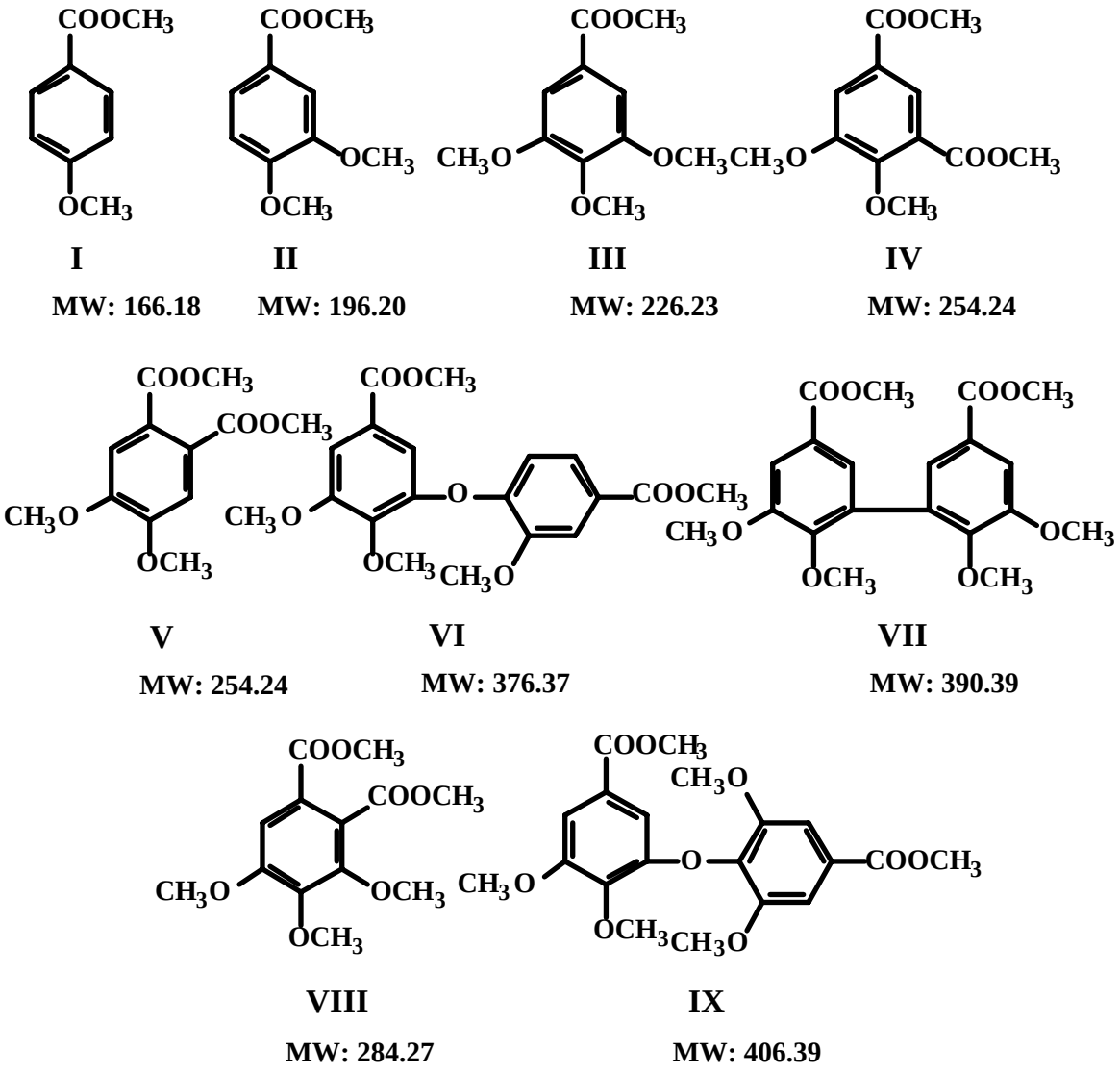

Fig. 1. Methyl esters of acids obtained from lignins on methylation/permanganate oxidation/esterification.