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Quantitative analysis of lignins based on permanganate oxidation (Version 2)

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Two methods (Method "quadratic" and Method "linear") for the calculation of the compositions of lignins based on degradation by permanganate are described. Method "quadratic" is presumably the most reliable one but model experiments are not completely unequivocal (Erickson, M., Larsson, S. and Miksche, G.E. Acta Chem. Scand. 27 (1973) 127-140) and Method "linear" is therefore of some interest. Furthermore we think the two modes of calculations may be applicable to other types of lignin degradations.

Method "quadratic"(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).

Miksche and co-workers (1) have estimated the composition of spruce lignin (representative of softwood lignins) based on the yields of esters **I-VII** (Fig. 1) obtained from methylation/permanganate oxidation experiments (additional esters amounted to 3-5% of the weight of esters **I-VII**). Assuming that the weight of the lignin sample examined is 100 mg and that the average lignin unit weights are 157 (*p*-hydroxyphenylpropane), 187 (guaiacylpropane) and 217 (syringylpropane) the yield factor (F) can be calculated from the following equation:

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/ F^2 + **VII** (mg) x 2 x 187 / 390.39/ F^2 + carbohydrates (mg) + total amount of units in trace constituents (mg) = 100

Using the yields of esters reported by Miksche and co-workers (1) (see Table 1 in Worksheet 1) and assuming the presence of 1 mg carbohydrates and 4 mg trace constituents (approximation based on the proportion of esters attributed to trace constituents) the factor F becomes 0.55 (see Worksheet 1).
The total amount of lignin units in the sample (mmol) corresponding to **I-VII** (U_S) can be calculated when F is known:

I (mg) / 166.18/ F + **II** (mg) / 196.20/ F + **III** (mg) / 226.23/ F + **IV** (mg) / 254.24/ F^2 + **V** (mg) / 254.24/ F^2 + **VI** (mg) x 2 / 376.37/ F^2 + **VII** (mg) x 2 / 390.39/ F^2= U_S

The composition of the carbohydrate free portion of the sample (trace constituents neglected) with respect to “uncondensed” and “condensed” units [esters **IV**, **V**, **VI** (one of the nuclei) and **VII** correspond to "condensed" units] can then be calculated:
I (mg) / 166.18/ F x 100/U_S= percentage of *p*-hydroxyphenylpropane units etc. (the results are given in Table 2 in Worksheet 1).
The results differ somewhat from those reported by Miksche and co-workers (1). This is because the calculations made by Miksche and co-workers (1,2) involve certain approximations.

The composition of birch lignin (representative of hardwood lignins) can be calculated in a similar manner based on the yields of esters **II-IX** (Fig. 1) obtained from a 100 mg sample on methylation/permanganate oxidation using data given by Larsson and Miksche (2) (see Table 1 in Worksheet 2) and assuming a carbohydrate content of 7.5 % and that the trace constituents amounts to 4% (the results are given in Table 2 in Worksheet 2).

The results of the calculations are given in Worksheets 1 and 2. These worksheets 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] in other lignin samples by replacing the yields of esters given in Table 1 in Worksheets 1 or 2 by the data valid for the lignin sample concerned and adjustment of carbohydrate content and amount of trace constituents to those present in this sample. Calculated data for this latter sample will then appear when you press "Enter".

A method for the determination of the phenolic units in lignins based on permanganate oxidation (Worksheet 3)

Assume that the phenol content in the lignin moiety of a particular spruce lignin sample is 0.26 phenol group per lignin unit (this phenol content has been reported for spruce MWL, cf. Ref. 1). If the amounts (mg) of esters **I-VII** obtained on methylation/permanganate oxidation of 100 mg of this lignin sample are known, the yield factor (F) for phenolic units can be calculated

from the following equation (as an approximation the average weight of the phenolic units is assumed to be the same as that of the other units):

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, mg) + 0.26 x trace constituents (total amount in the sample, mg) = 0.26 x 100.

The factor F obtained can then be used for the determination of the phenolic units (and distribution of different types of phenolic units) in lignin samples (the carbohydrate free portion) of the same type as the one used for the determination of the factor F (Tables 2 and 3). Data from the lignin sample selected for the determination of F are consistently used as examples in the discussion of calculations below (and in Worksheet 3).
Insertion of the calculated factor F in the above equation gives the proportion of phenolic units in the sample examined (= 0.26 in Worksheet 3 since data from the lignin with known lignin phenol (0.26) selected for the determination of F are consistently used in the examples in Worksheet 3).
The total amount of phenolic lignin units (mmol) in the sample corresponding to **I**-**VII** and trace constituents (U_{Ph}) can be calculated when F is known (trace constituents are calculated as a 1:1 mixture of guaiacylpropane units and *p*-hydroxyphenylpropane units (cf. Ref. 1) and are assumed to be phenolic to the same extent as the rest of the lignin):

I (mg) / 166.18/ F + **II** (mg) / 196.20/ F + **III** (mg) / 226.23/ F + **IV** (mg) / 254.24/ F^2 + **V** (mg) / 254.24/ F^2 + **VI** (mg) x 2 / 376.37/2/ F^2 + **VII** (mg) x 2 / 390.39/ F^2 + 0.26 x 4/187= U_{Ph}

The relative frequency of different types of phenolic units can be calculated as follows:
I (mg) / 166.18/ F x 100/U_{Ph}= percentage of phenolic *p*-hydroxyphenylpropane units etc. (the results are given in Table 3 in Worksheet 3).

Worksheet 3 shows calculations based on ester yields reported by Miksche and co-workers (1) for spruce MWL (Table 1 in Worksheet 3) and assuming the presence of 1 mg carbohydrates and 4 mg trace constituents. The phenol content of this sample is known and this makes it possible to calculate the yield factor. The phenol content in another lignin

sample of the same type can then be calculated by replacing the data in Table 2 in Worksheet 3 by those valid for this latter sample. The distribution of phenolic groups will appear in Table 3 in Worksheet 3 when you press "Enter".

The principles of the calculations above are generally applicable to different types lignins but modifications of the formulas may be required. 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. If isolated, modified lignins (e.g. kraft lignin) are examined the appropriate unit weights should be filled in in Table 1 in Worksheets 1-3. Method "quadratic " was presented at Eighth European Workshop on Lignocellulosics and Pulp (3).

References

1. Erickson, M., Larsson, S. and Miksche, G.E. Acta Chem. Scand. **27** (1973) 903-914.
2. Larsson, S. and Miksche, G.E. Acta Chem. Scand. **25** (1971) 647-662.
3. Parkås, J., Lundquist , K. and Brunow, G. Proceedings of Eighth European Workshop on Lignocellulosics and Pulp, Riga/Latvia, August 22-25. (2004) pp 271-274.

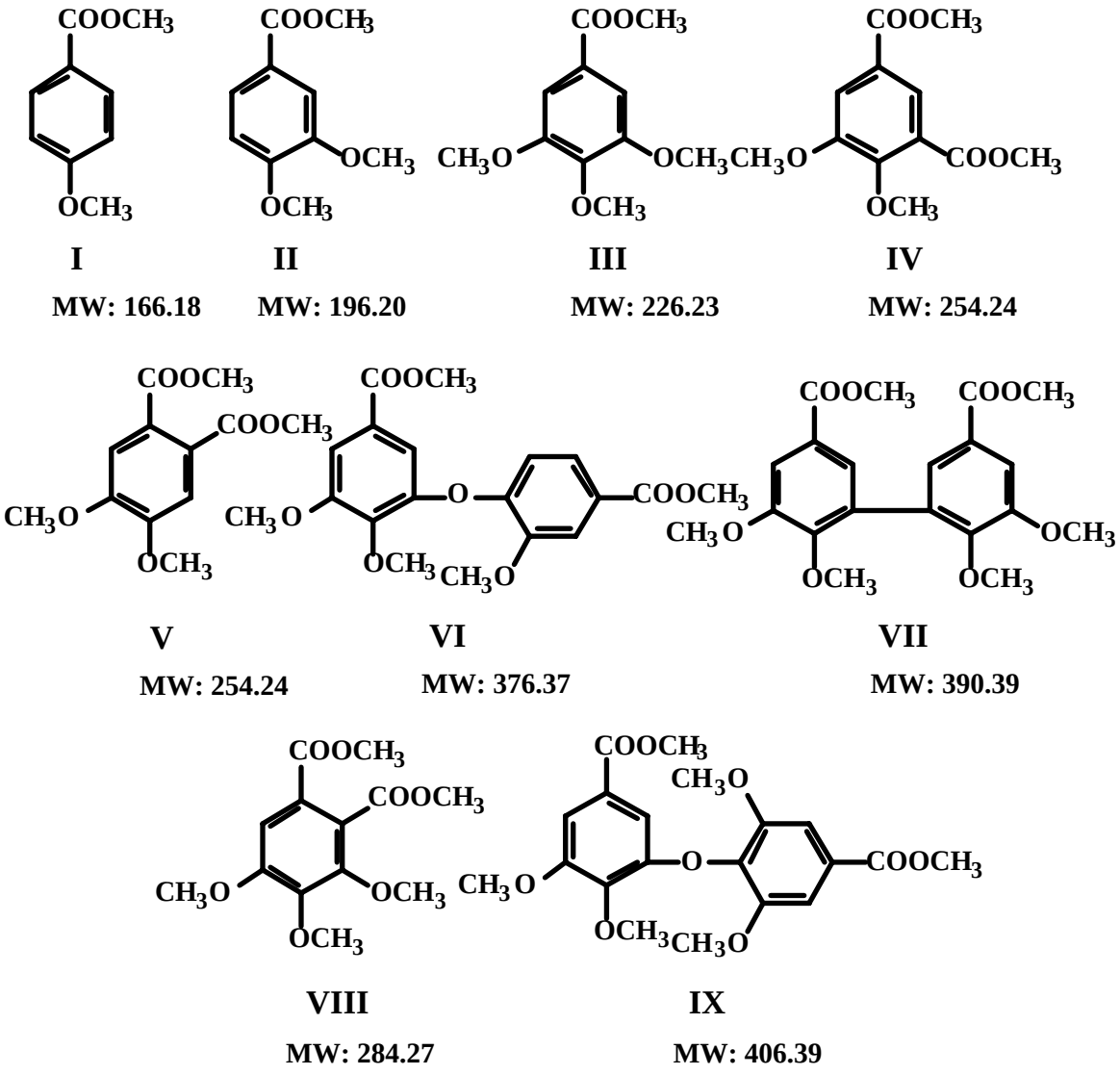

Fig. 1. Methyl esters of acids obtained from lignins on methylation/permanganate oxidation.

An Excel-file designed for these calculations is available for download here:

Permanganateoxidation"quadratic".xls

Method "linear" (based on the assumption that the structural elements in lignin corresponding to esters I-IX are converted to these esters to the same extent)

The description of Method "linear" differ in principle from that of Method "quadratic" (see above) only in the respect that F^2 in the equations and elsewhere is replaced by F.

An Excel-file designed for "linear" calculations is available for download here:

Permanganateoxidation"linear".xls