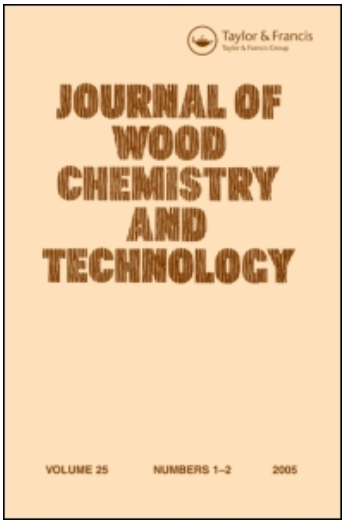

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The Valence State of Chromium in Treated Wood, Studied by Magnetic Susceptibility

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THE VALENCE STATE OF CHROMIUM IN TREATED WOOD, STUDIED BY MAGNETIC SUSCEPTIBILITY

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ABSTRACT

Adducts were prepared by reacting wood cell wall polysaccharide, lignin and model compounds of these polymers with chromium(vi) ions. Magnetic susceptibilities of these adducts were measured using a Gouy balance. It was shown that under the reaction conditions used, (polysaccharide, lignin, etc. in molar excess), the adducts were paramagnetic. This implies that the chromium in the adducts is in the tervalent state.

INTRODUCTION

It has been shown by several workers that hexavalent chromium compounds (dichromates of alkali metals and chromium trioxide) will react with wood[1,2,3,4,5,6]. Wood modified by such reactions exhibits some interesting properties; eg. water repellency, enhanced weathering properties[1]. Use of the process commercially is limited by the health hazard associated with chromium in the hexavalent state[7]. Over the past few years several workers have demonstrated that during reaction with wood the chromium is reduced to its tervalent form[5,6,8]. It is suggested however, that

some of the chromium, probably associated with the polysaccharide part of the cell wall may remain hexavalent[6]. Reactions have been conducted between wood cell wall polymers (and their corresponding monomeric models) and hexavalent chromium compounds. The valence state of the chromium in the products was then determined by the magnetic susceptibility technique.

EXPERIMENTAL

The following substances were used in the reaction studies.

1) o. methoxy phenol (guaiacol)
2) softwood lignin (prepared by the acid dioxane method[9])
3) methyl glucoside
4) wood holocellulose (prepared by the chlorite method[10])

The reactions were carried out by refluxing for 30 minutes a 4 fold molar excess of substances 1 - 4 above with chromium trioxide in aqueous solution (substances 1; 3 and 4) and with potassium dichromate in dimethyl sulphoxide solution (substance '2' - softwood lignin). The solid products from the reactions with substances 1, 2 and 4 were washed with water and dehydrated with ethanol prior to the magnetic susceptibility determination. The methyl glucoside product was very water soluble. It was isolated by evaporation until precipitation occured. This product was re-precipitated and dehydrated with ethanol. Melting point/ solubility properties confirmed that it was an adduct and not simply a mixture of the starting reagents.

RESULTS AND DISCUSSION

Magnetic susceptibilities of the products together with that of the Cr(iii) hydrated cation [chromium(iii) chloride hexahydrate] were determined using a Gouy magnetic balance.

The method is based on the principle that ions, atoms or molecules with unpaired electrons are generally paramagnetic, whereas those with all paired electrons have diamagnetic properties only. The technique is a well established one and is described in many advanced inorganic chemistry texts[11]. From the magnetic susceptibility measurements, 'spin moments' in units of Bohr magnetons were calculated. These are cited in Table 1 below.

TABLE 1

Experimental Spin Moments

Product	Spin Moment (Bohr magnetons)
Cr(iii) hydrated cation	3.88
Cr/o. methoxy phenol	3.39
Cr/lignin	3.82
Cr/methyl glucoside	3.08
Cr/holocellulose	3.83

These spin moments confirm that the products are paramagnetic and therefore that they contain chromium in the tervalent state. Furthermore, the spin moment values correspond quite closely to that of the pure hydrated Cr(iii) cation and to those cited for several pure tervalent chromium complexes[12,13,14]. This suggests that all the chromium in our adducts is in its tervalent state.

Hence our data suggest strongly that hexavalent chromium ions are able to react with both polysaccharide and lignin components of the wood cell wall. Furthermore, provided that the hexavalent chromium is not applied in molar excess relative to lignin (phenyl propane) and polysaccharide units the chromium is tervalent in the adducts formed. This is in agreement with and lends confirmation to the work of Feist[8] and Williams & Feist[7] based on ESCA studies.

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