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Laser-induced Fluorescence in Cellulose

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Summary The laser-induced fluorescence of cellulosic materials is attributed to trace amounts of transition-metal ions remaining after normal preparation procedures.

THE occurrence of laser-induced fluorescence† has been described in a number of reports concerning the application of Raman spectroscopy to investigation of polymers.[1] Recently, laser-induced fluorescence has been encountered in Raman spectral investigations of inorganic materials,[2] and attributed to surface-adsorbed impurities arising from the decomposition of hydrocarbon vacuum greases. We have observed fluorescence in our investigations of the Raman spectra of celluloses, and believe that, in this instance, the fluorescence is due to trace amounts of transition-metal ions remaining in the cellulose after normal preparation procedures.

The levels of fluorescence of the samples were monitored in a Raman spectrometer system (Spex) using the 5145 Å line of an argon ion laser (Coherent Radiation 52 Å) as an exciting source. Exposure in the laser beam usually leads to decay of the fluorescing species at a rate which is related to the power level at which the laser is operated. The decay of fluorescence was monitored at $\Delta\nu$ 1650 cm^{-1} as this is near the peak of the fluorescence curve, and the spectrum of cellulose does not include any bands at this frequency.

Our investigations have focused on cotton-derived samples of cellulose. Among the other constituents of the cotton fibre, the ones most likely to have fluorescent residues are the proteins, which occur primarily in the lumen, and which are therefore more resistant to the usual extraction and cleansing procedures.[3a] The first efforts to reduce or eliminate fluorescence were thus based on procedures known to reduce the content of protein in the cotton fibre. These included extended extractions with organic solvents and with strong caustic solutions, followed by bleaching in chlorine dioxide solution.[3b] The levels of fluorescence were found to be unchanged after all of these treatments.

The possibility that trace amounts of transition-metal ions which absorb the green light are responsible for the fluorescence was considered. A number of treatments which might be expected to reduce the level of such ions were tested. In previous experience at the Institute[4] EDTA has been shown capable of removing metal ions from cellulosic tissue. Treatment with EDTA resulted in a measurable reduction of the level of fluorescence; the effectiveness of treatment depending on concentration of the reagent and the period of treatment. Washing in 8% nitric acid also reduced the level of fluorescence, although it was not as effective as EDTA for equal treatment intervals. By far the most effective procedure, however, was exposure to carbon monoxide in either organic or aqueous media. Such treatments, which presumably result in formation of the carbonyls of the particular metal ions responsible, can reduce the level of fluorescence to half that of the untreated control samples. There are indications that both EDTA and carbon monoxide may act by inhibiting or quenching the fluorescence rather than by removal of the metal ions.

Emission spectrographic analysis of a typical sample showed it to contain the following transition metals, at the levels indicated in p.p.m.: chromium 0·060, copper **0·011,**

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† It is not implied that coherence of the exciting radiation is a factor, but rather that the levels are such that they have been more frequently encountered at the energy concentrations possible with laser excitation.

iron 0·40, manganese 0·047, molybdenum 0·29, nickel 0·080, titanium 0·064. Since these levels are low, and the ions of a number of these elements absorb the green light, it is difficult to identify the ion or ions responsible for the fluorescence. In a recent monograph,[5] photochemical reactions were described for co-ordination compounds of most of the metals listed above.

Our experience with other polysaccharides indicates that the same types of fluorescing impurities are present, to varying degrees, in all of them. Monosaccharides and disaccharides, in many cases, also contain enough of the metallic impurities to fluoresce.

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