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Regular Article

Non-destructive monitoring of molecular modifications in the restoration of works of art on paper*

Application of theoretical and experimental optical spectroscopy

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Abstract. The discoloration of paper, due to the development of oxidized groups acting as chromophores in its chief component, cellulose, is responsible for severe visual degradation of works of art on paper. By adopting a diagnostic method based on *in situ* non-invasive optical reflectance spectroscopy and time-dependent density functional theory *ab initio* calculations, it is possible to describe and quantify the chromophores in cellulose fibers in a non-destructive way. In order to recover the absorption coefficient of cellulose fibers from reflectance measurements a specific approach based on the Kubelka-Munk theory was applied. The concentrations of carbonyl groups acting as chromophores were obtained by fitting the experimental optical absorption spectra to those simulated by using *ab initio* calculations. This method was applied for monitoring the restoration interventions of two great format engravings *Le Nozze di Psiche* and *Gesù Cristo e l'adultera* by Diana Scultori (1547–1612), as well as a contemporary artwork by Renato Guttuso, *Bozzetto per Crocifissione* (dated 1940). All artefacts were affected by chromatic deterioration due to a strong oxidation of the paper. Results quantified the decreasing of chromophores concentration after washing and reducing treatments evidencing the different behavior of the carbonyl groups as a function of the specific protocol performed.

1 Introduction

Yellowing is the most evident sign of paper aging and degradation [1]. It appears with different intensities, from a ligth discoloration up to brown hue, and with different shapes, from localized spots —known as foxing— to widespread discoloration [2].

Ancient paper made in Western countries was obtained from cellulose fibers from hemp, flax or cotton rags [3]. Cellulose is an unbranched polymer whose polymeric unit is β-D-glucopyranose. The units are bonded by β-$(1,4)$-glycosidic linkages forming long polymeric chains of the order of thousands of monomers (fig. 1) [4]. Yellowing of ancient paper can be mainly attributed to the development of ultraviolet-visible (UV-Vis) active oxidized groups — called chromophores— in the degradation products of paper components. Modern soft or hardwood paper is instead constituted of several components and may include lignin, which is the main responsible of yellowing of the sheets [1].

Cellulose oxidation is a consequence of aging, for which the causes and influencing factors are manifold: exposure to light and radiation, thermal stress, pollutants, humidity and humidity changes, or simply long-term exposure to standard ambient atmosphere [5]. Cellulose oxidation runs through the radical mechanism initiated by active oxygen species and follows complex routes with many possible reactions still to be clarified [6,7]. However, even if the causes of oxidation are diverse their primary effect is simple because cellulosic hydroxyl groups are converted either to carbonyl structures (keto groups at C-2 or C-3 and aldehyde groups at C-6) or carboxyl moieties (only possible at C-6 and at the few reducing end groups) (fig. 1) [8].

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