Visible Reflectance Spectroscopy for Monitoring Damage to Paint-Based Dosimeters

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Summary

Visible reflectance spectroscopy using fiber optics (FORS) is a non-invasive technique. Currently it is being used in the European Commission supported project, Microclimate Indoor Monitoring in Cultural Heritage Preservation, MIMIC, contract no. EVKV-CT-2000-00040. for analyzing color variations induced by the atmospheric pollutant (NO_2) in paint-based dosimeters (**Fig. 3**). These dosimeters were prepared to using egg tempera paint on Melinex support as described elsewhere [1]. Previously the effect of various dosage levels of accelerated light ageing and a single exposure to pollutants (NO_x,SO_2) was measured and compared to that of natural ageing [2,3]. In this paper the effect of various dosage levels of NO_2 are measured. The objective was to evaluate the damage caused to works of art by indoor environment, in particular indoor pollutants. Different specific pigments and dyes were selected based on the experience in the previous study to create these dosimeters that were first cured in the dark and subsequently exposed in ageing chambers to low/medium dosage of atmospheric pollutant (NO_2). A large Pyrex vessel closed with a removable leak-proof cap in which airflow, relative humidity, temperature and gas concentration can be controlled, was used for the ageing tests. A pump attached to the ageing chamber created a steady airflow through the vessel up to 10 l/min. A fan placed at the top of the vessel ensured good circulation of air within the chamber. The effect of exposure of the dosimeters was monitored evaluating the colour and/or spectral variations of the dosimeters by the acquisition of their visible reflectance spectra recorded before and after ageing. Moreover, a few dosimeters were placed in museums and galleries for a natural ageing trial.

Fibre Optics Reflectance Spectroscopy (FORS)

The reflectance spectra were recorded with a Zeiss MCS501 spectrophotometer (**Fig. 1**) in the 350-1000 nm (0.8 nm/pixel resolution) range on small areas of about 6 mm diameter. The spectrophotometer is a portable device with its own internal light source (a voltage-stabilized 20Watt tungsten-halogen lamp, Model CLH500). Calibration was performed by means of 99% Spectralon® diffuse reflectance standard. Each acquired spectrum was the average of 3 acquisitions. The colorimetric data were calculated from the reflectance spectra following the CIE (Commission Internationale de l'Eclairage) 1964 and CIELab76 recommendations (**Fig. 6**) under D_{65} CIE standard illuminant [4,5]. The probe-head, which was made at the IFAC laboratory, was a dark hemisphere of 3 cm in diameter terminating with a flat base and with three apertures on the dome. One aperture was at the top of the dome and was used for receiving the back-scattered light from the sample. The other two were placed at 45°, symmetrically with respect to the first, for illuminating the investigated area of the sample. This set-up (45°/0°/45° probe configuration) made it possible to work in diffuse reflectance by collecting the light scattered at 45° with respect to the incident light, thus avoiding specular reflected light.

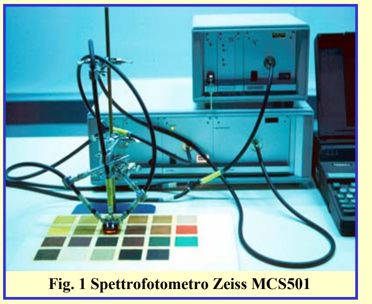

Fig. 1 Spettrofotometro Zeiss MCS501

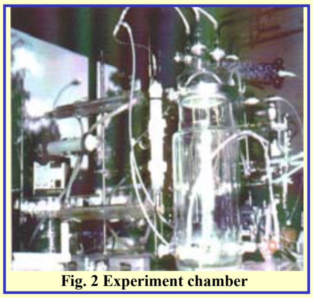

Fig. 2 Experiment chamber

Ageing in the laboratory

The apparatus that was used for the laboratory ageing consisted of:
1. An exposure chamber constructed of inert materials and of sufficient capacity to accommodate six dosimeters simultaneously. 2. A system for generating and delivering a known concentration of the pollutant under test to the exposure chamber.
3. Provisions for systematically measuring, controlling and varying the rate of air flow through the chamber and the concentration, temperature and relative humidity of the test atmosphere. A reference method was used to verify the concentration of the generated standard atmosphere of the pollutant under investigation. All the experimental work described in this paper was carried out in the vessel shown in **Figure 2.** NO2 permeation tubes were prepared using stainless steel tubes sealed at one end and capped at the other by a membrane. At constant temperature NO2 leaks out through the membrane at a stable rate. Nitric acid was removed by using a diffusion denuder so that the effect of NO2 alone could be determined. Clean air was irradiated with UV light to convert oxygen to ozone.

Fig. 3 Dosimeter exposed at the Uffizi Gallery

Fig. 4 Reflectance spectra of smalt paint strips

Table I. Colour variations of four selected paint strips

	Uffizi – Natural ageing From 15/04/2002 to 25/11/2002				O_3 – Artificial ageing 11 ppm x 10 hours				NO_2 – Artificial ageing 25 ppm x 12 hours			
	ΔL*	Δa*	Δb*	ΔE*	ΔL*	Δa*	Δb*	ΔE*	ΔL*	Δa*	Δb*	ΔE*
Lead white	-0.2	0.7	-2.2	2.3	0.4	-0.5	-0.1	0.7	0.3	-0.0	2.6	2.6
Lead chromate	-1.9	-1.0	-1.9	2.9	-0.4	-0.2	3.0	3.0	0.8	0.1	0.4	0.9
Alizarin	0.0	-0.9	0.1	0.9	2.8	-0.3	-1.9	3.4	0.5	2.1	0.9	2.3
Smalt	-0.3	0.1	0.9	0.9	1.0	0.3	-0.8	1.3	0.8	-0.1	-0.3	0.9

Artificial ageing performed without environmental light, at room temperature and relative humidity. The artificial ageing is equivalent to a dose (concentration multiplied for duration of exposure) approximately corresponding to one year.

Fig. 5 Dosimeter in the Pollaiolo Room, Uffizi Gallery

The results of the reported spectra (**Fig. 4**) and the colorimetric data (**table I**) stress that both the artificial tests induced different levels of variation in the paint dosimeters. Nevertheless, the comparison of these data with those obtained from the dosimeters aged naturally at the Uffizi Gallery (**Fig. 5**) showed different behaviour in the spectral evolution. This is because in the natural environment, a combination of various factors could have produced a synergistic effect. Among these factors, light certainly plays a fundamental role.

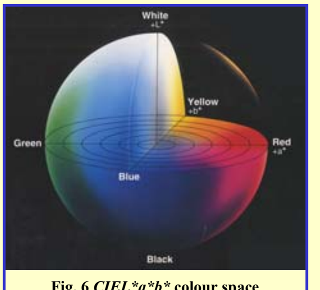

Fig. 6 *CIEL*a*b colour space**

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