NON-INVASIVE INSTRUMENTATION FOR DETECTION AND COLOUR CONTROL OF PAINTINGS AND ART WORKS

MAURO BACCI

Istituto di Fisica Applicata "Nello Carrara" (IFAC-CNR), Firenze, Italy

email: m.bacci@ifac.cnr.it

Abstract

The fact that every work of art is a unique piece emphasises the necessity of working with non-invasive methodologies. In this communication instruments developed at IFAC-CNR, Florence, and their application to actual cases will be presented. Such instrumentation is based on spectroscopic techniques, namely image spectroscopy (IS) and fibre optic reflectance spectroscopy (FORS). Indeed, the combined use of these two techniques constitute a powerful tool for obtaining a large amount of spectroscopic information without any sampling, thus overcoming all the limitations and problems involved in sampling operations. Moreover, the availability of lightweight and compact equipment makes it possible to perform measurements in situ on objects that cannot be removed from their location. Furthermore, due to the fact that these techniques are non-invasive and are thus safe for works of art, it is possible to re-measure the same object after a given time, to monitor the progress of the conservation of the work of art, and also to follow the restoration processes. The methodology also enables the acquisition of a large number of spectra over the entire artefact. This wide sampling operation, the performance of which would be unimaginable with micro-sampling techniques, provides a large amount of data, which can be used for statistical analysis. As regards the application to actual cases, two case studies will be reported: a) a Leonardo da Vinci's painting, where pigments, binding medium, preparatory layer and previous restoration works were identified; b) the monitoring of the colour evolution of a Luca Signorelli's predella over the years during the exhibition to the public, during the restoration intervention and after the restoration. Finally, a brief account of the studies performed at IFAC – CNR on indoor light control will be given and the possible use of a new light dosimeter will be suggested.

KEYWORDS: IMAGE SPECTROSCOPY, FIBRE OPTIC REFLECTANCE SPECTROSCOPY, NON-INVASIVE MEASUREMENTS, COLORIMETRY, PAINTINGS

KULCSSZAVAK: KÉPEK SPEKTROSZKÓPIAI VIZSGÁLATA, SZÁLOPTIKÁS SPEKTROSZKÓPIA, RONCSOLÁSMENTES VIZSGÁLAT, SZÍNVIZSGÁLAT, FESTMÉNYEK

Introduction

The uniqueness of works of art requires analytical techniques that cause as little damage as possible to the work itself. Accordingly, two possibilities are offered to scientists for obtaining knowledge that is as complete as possible regarding an object under study: micro-invasive investigations or non-invasive investigations. Apart from possible damage caused to the object, it is quite evident that micro-invasive techniques, which can supply an accurate characterization of a single specimen, have to be limited to only very few samples, thus providing only partial information. Moreover, if monitoring of conservation state with time is required, analysis cannot be repeated exactly at the same point. It is quite evident that completely non-invasive techniques have to be preferred, even if it is honest to admit that single non-invasive techniques can be exhaustive only in particular cases. However, the combined use of several techniques is an unquestionable advantage. At present, many non-invasive techniques are available, which can give information on elemental composition and molecular or crystal structure. Moreover, many of them, besides the information on a single spot, can give 2D- or 3D-images that can be more easily managed also by non-professional people.

Here the focus will be brought on two techniques, fibre optic reflectance spectroscopy (FORS) and hyper-spectral image spectroscopy (IS). FORS is a point-by-point technique, while IS supplies 2D images. Both techniques require no sampling at all and the instruments can be transported for *in situ* measurements (museums, laboratories, restorer's atelier and so on). This aspect is very important, because many artefacts cannot be moved either for intrinsic (for instance frescoes) or for safety reasons. Moreover, the complete non-invasiveness makes it possible to repeat the measurements time to time to reveal possible alterations of the colour or of the constituting materials.

Instrumentation

As regards fibre optic reflectance spectroscopy (FORS), at present exist optical fibres that allow investigation of a wide range of the electromagnetic spectrum (from about 250 nm up to about 11,000 nm). Special quartz fibres can cover the UV, visible and near IR range, while chalcogenide glass fibres are suitable for the mid-IR region except the small range 2250 – 2050 cm^{-1}, where the absorption due to Se-H stretching mode can mask possible absorptions occurring in this range. Two commercial instruments, Zeiss MCS 501 and MCS 511 spectro-analysers, are used for the UV-visible and near IR regions, respectively. Different probe heads were realised in our laboratory to meet the requirements of the objects under investigation. The most used probe consists of a hemisphere, in dome of which 3 fibre optic bundles are connected with 45°/0°/45°geometry. The hemisphere is gently placed upon the surface of the object, which is illuminated by the light coming from the two bundles at 45°, while the reflected light is gathered by the bundle perpendicular to the surface. Such a device is particularly suitable for colour measurement, because specularly reflected light, which could desaturate the colour, is avoided. Usually, these probe heads are used for paintings or textiles, but they were also profitably used for 3D dimensional artefacts such as statues or archaeological objects. The mid-IR region is investigated by means of a Nicolet Protégé 460 FT-IR spectrophotometer equipped with the above mentioned chalcogenide glass fibres: in this case the geometry is approximately 0°/180°, *i.e.* the fibres, which send and receive radiation, are practically collinear. This fact can lead to a distortion of the absorption band shape, so that particular care is necessary in the interpretation of the spectra.

As regards image spectroscopy (IS), two different instruments were realised in our laboratory. From a historical point of view, the former instrument consisted of a video camera visible-near IR working in the 400 nm – 2000 nm range, in front of which a rotating wheel containing interferential filters of different width was placed. Software allowed the rotation of the wheel in a way to record the image at a given wavelength. The camera was located in front of the object, which was illuminated by two halogen lamps at 45°. By using this procedure a sequence of multi-spectral near-monochromatic images was collected and stored for successive retrieval. Then, the images could be processed using multivariate analysis techniques in order to extract most of the information they contain. Finally, the reflectance spectrum related to each pixel could be obtained. The instrumentation was built up with modular items so that it could be easily transported for *in situ* measurements. However, in spite of its advantages (transportability, friendly use) the instrument had some limits as regards sensitivity and resolution. So, a new instrument was developed in our laboratory, which is characterised by high spatial and spectral resolution, 0.1 mm and 1 nm, respectively, and by fast acquisition time (an area of about 1 m^2 requires less than 4 hours). Further details of this hyper-spectral IS scanner can be found elsewhere (Casini et al. 2005). At the present the working range is 400 nm – 900 nm, but it can be extended up to 1700 nm or even above, depending on the availability of the suitable detectors. The only drawback is its size. However studies for miniaturizing the equipment are in course.

Applications to actual cases

a) Investigation of a Leonardo da Vinci's painting

To show the potentiality of the combination of the abovementioned two techniques, here will be outlined an application to a Leonardo's painting, one of the several versions of the *Madonna of Yarn winders*. As a first approach some trials were made by FORS throughout the painting to identify the constituting materials (Bacci et al. 2005a). Information was obtained regarding pigments, preparatory layer, binding medium and previous restoration works. The experimental data reveal an oil painting with a simultaneous presence of kaolin and gypsum in the preparatory layer. Different pigments were detected such as iron oxides (probably Sienna or umber earth), vermilion and copper based green pigments (verdigris or copper resinate) by comparison with our own database of spectral data of pigments. The blue areas constituted an interesting and intriguing aspect, because, besides lapis lazuli, Thénard's blue, with its characteristic three sub-bands due to the Jahn-Teller effect, was detected in some areas (**Fig. 1**). Since this latter pigment was introduced in the artists' palette only in the XIXth century, its presence is attributed to recent restoring. Therefore, detecting where the restoration was made is for us of extreme interest. The above described IS hyper-scanner resulted to be particularly suitable for solving the problem. The images were processed by means of Principal Component Analysis, but similar results could be obtained, in this particular case, looking at the band shapes of the two pigments in the range of 450 nm – 600 nm. In fact, parabolas could fit the curves, and their radius (for each pixel) was normalized and *projected* in grey levels on the 2D image (**Fig. 2**), so that the retouched areas appeared straightforwardly evident.

b) Colour monitoring and colour control

Investigating the reflectance in the visible region allows obtaining information also about colour and its possible alterations with time (Johnston-Feller 2001).

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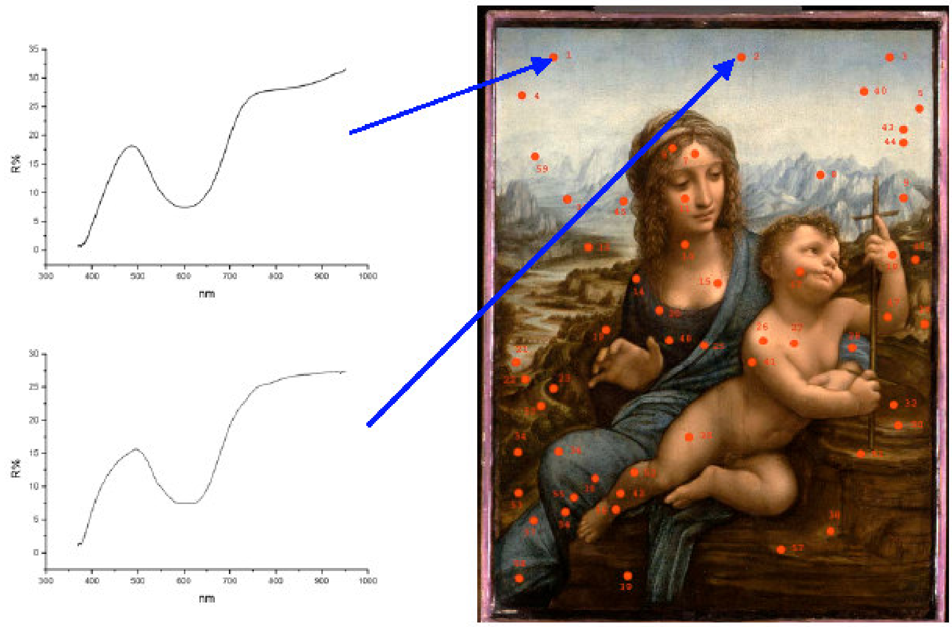

Figure 1.

The Madonna of Yarn winders. Red spots correspond to the areas investigated by FORS. The reflectance spectra of two different blue pigments, lapis lazuli (top) and Thénard's blue (bottom), are also displayed.

At this point it is worth recalling the importance of colour control both for conservation and restoration purposes. Actually, light, pollutants and other environmental factors can alter the colour of an artefact limiting the *reading* of the work or even distorting the original idea of the artist.

However, other points to be taken into account are the control of the colour during restoration works (varnish removal, colour integration, re-varnishing) and, when the restoration is terminated and the object is displayed again to the public, the monitoring of the colour evolution, which can supply useful information about environmental conditions.

Just to stress the importance of these studies for a correct conservation policy, here the experimental results of an investigation, which was done during several years, are shortly described, while a more detailed report can be found elsewhere (Bacci et al. 2005b). The work of art investigated is a *Predella* painted by Luca Signorelli in the early years of the XVIth century, which is on display in the Uffizi Gallery, Florence. The investigation cover three stages: 1) the painting was initially monitored *in situ* over a five-year period (1990 – 1995), when it was exhibited in the Leonardo's room of the Uffizi Gallery; 2) monitored during the cleaning work in the conservator atelier (2000 – 2001); 3) monitored during the new period of display to the public (2001-2004) in the museum, after the restoration and re-varnishing. The stage (1) revealed that, in spite of air conditioning and environmental control made inside the exhibition room, important colour changes occurred (Bacci et al. 1997), mainly due to the varnish layer. In stage (2) 62 points throughout the painting were investigated in February 2000 just before the restoration, in May 2000, when the old varnish was removed, and, finally, in June 2001 after the new re-varnishing with mastic resin from Chios. The latter date was the starting time ($t=t_0$) of stage (3), when a sub-set of the above points (23 points) of the painting was again examined after 18 months ($t=t_1$) and 30 months ($t=t_2$) during the new exhibition to the public. The amount of points investigated in stage (3) was reduced owing to time constraints, because the measurements could be made only when the Gallery was closed to the public. The 23 points considered were still representative of the artist's palette.

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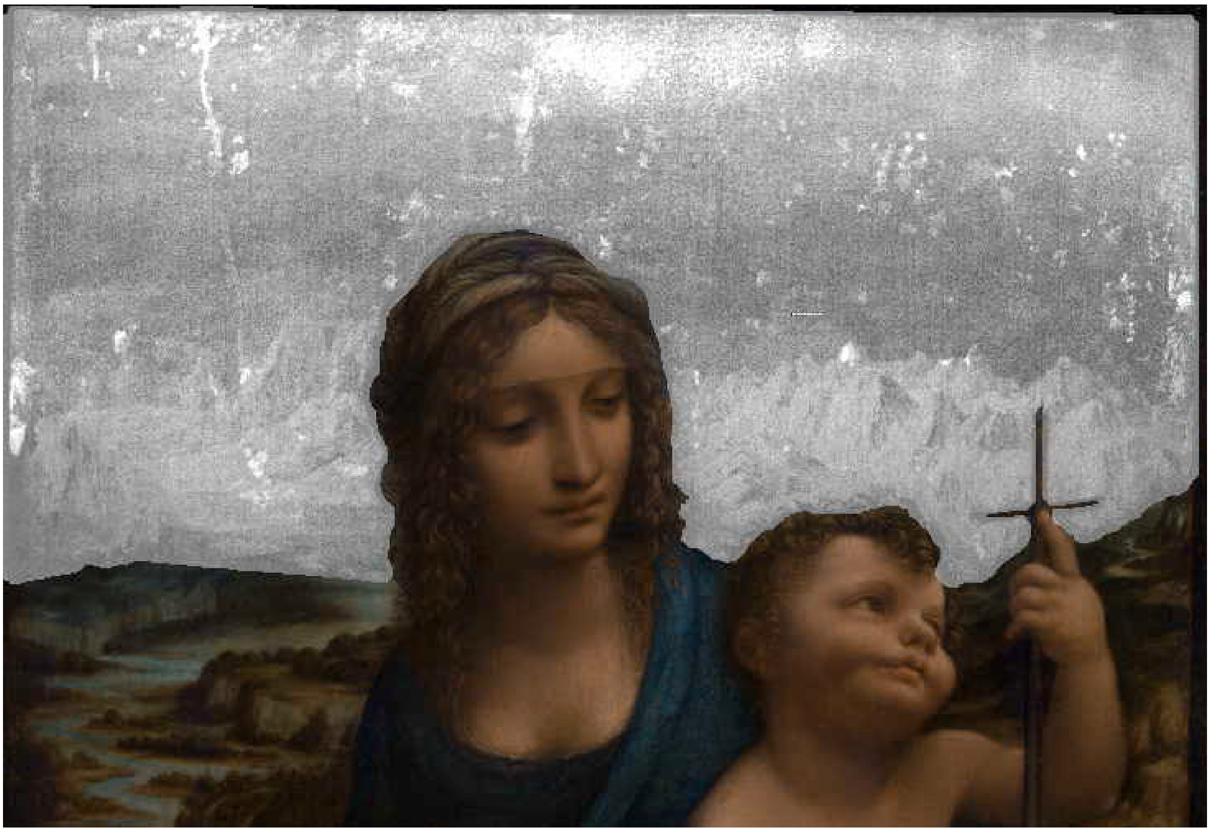

Figure 2.

Particular of the Madonna of Yarn winders. The blue areas are displayed in grey tones. Thénard's blue retouching corresponds to the whitish portions.

The removal of the varnish produced, as expected, a general desaturation of the colour and a decrease of the yellow hue, while the new varnish induced higher colour saturation (**Fig. 3**). As regards the period 2001 – 2004, a constant increase of the colour change ΔE was observed, which reached values detectable by the human eye after 30 months of exhibition to the public (Bacci et al. 2005b).

The main contribution to ΔE is given by lightness (L*), which, in general, tends to increase with time (**Fig. 4**).

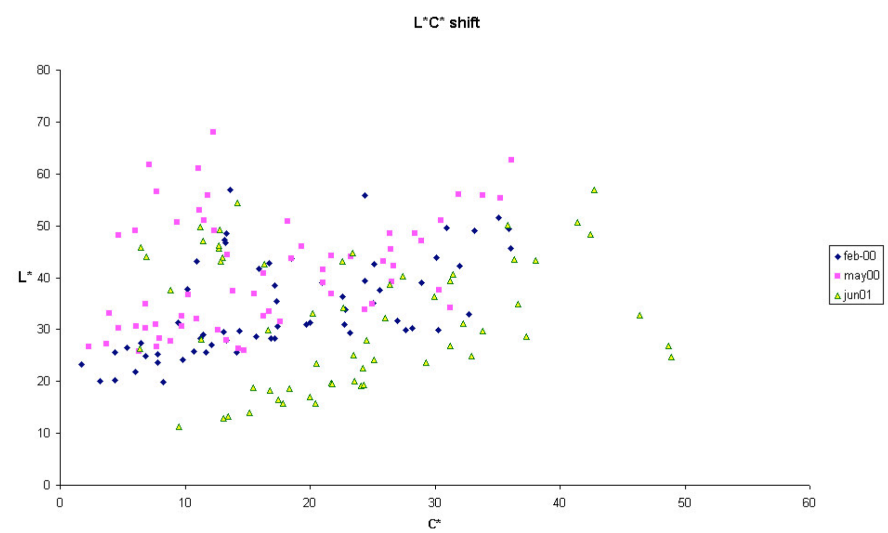

Figure 3.

The Predella by Luca Signorelli. Shift of the representative points of the areas investigated in the plane L*C*, after the varnish removal and the new re-varnishing.

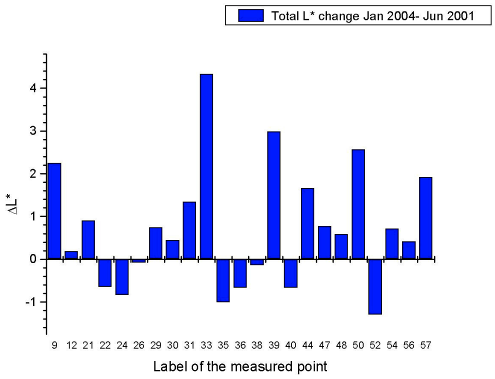

Figure 4.

The Predella by Luca Signorelli. Variation of the lightness L* for the different points that were investigated after 30 months since the new re-varnishing.

To conclude this brief survey on the scientific activity of our laboratory in the field of cultural properties, few words about monitoring lighting conditions in museums. In fact, this topic is closely related to the colour of the exhibited objects, because light is one of the most important factors in affecting colour.

References

BACCI, M., Picollo, M., Porcinai, S. & Radicati, B. (1997): Non-destructive Spectrophotometry and Colour Measurements Applied to the Study of Works of Art. *Techne* **5**: 28-33.

BACCI, M., Cucci, C., Dupont, A. L., Lavédrine, B., Picollo, M. & Porcinai, S. (2003): Disposable indicators for monitoring lighting conditions in museums. *Environ. Science & Technolog.* **37**: 5687-5694.

BACCI, M., Bellucci, R., Cucci, C., Frosinini, C., Picollo, M., Porcinai, S. & Radicati, B. (2005a): Fiber Optics Reflectance Spectroscopy in the Entire VIS-IR Range: a Powerful Tool for the Non-invasive Characterization of Paintings. *Mat. Res. Soc. Symp. Proc.* **852:** OO.2.4.1 - OO.2.4.6.

BACCI, M., Cucci, C., Picollo, M., Porcinai, S., Pretzel, B. & Radicati, B. (2005b): Control of the Colour Evolution with Time of a Luca Signorelli Painting. *Proceedings of the 10th Congress of the*

The problem is: how can an efficient indoor light monitoring be arranged? What are the characteristics of an ideal light sensor? Surely, it has to be easily controlled also by non-trained personnel, it has to be aesthetically acceptable and, last, but not the least, its cost has to be moderate. To meet all these requirements, indicators were developed within a EC project under the Fifth Framework Program (Bacci et al. 2003; Bacci et al. 2005c). Small strips that change their colour when illuminated constitute these indicators. The comparison of the colour with a calibrated card, in a way quite similar to the pH indicator paper, allows a semi-quantitative estimate of the total luminous exposure.

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International Colour Association, Granada: 623-626.

BACCI, M., Cucci, C., Dupont, A.L., Lavedrin, B., Loisel, C., Gerlach, S., Roemich, H. and Martin, G. (2005c): LightCheck®, new disposable indicators for monitoring lighting conditions in museums. *Preprints of the 14th Triennial ICOM Meeting*, The Hague: 569 – 573.

CASINI, A., Bacci, M., Cucci, C., Lotti, F., Porcinai, S., Picollo, M., Radicati, B., Poggesi, M. & Stefani, L. (2005): Fiber optic reflectance spectroscopy and hyper-spectral image spectroscopy: two integrated techniques for the study of the Madonna dei Fusi. *Proceedings SPIE* **5857**: 58570M1-58570M8.

JOHNSTON-FELLER, R. (2001): Color Science in the Examination of Museum Objects. The Getty Conservation Institute, Los Angeles, 363 pp.

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