

UV-VIS-NIR REFLECTANCE SPECTROSCOPY OF RED LAKES IN PAINTINGS

Christina Bisulca¹, Marcello Picollo¹, Mauro Bacci¹, Diane Kunzelman²

¹Istituto di Fisica Applicata "Nello Carrara" IFAC-CNR,
Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy

²Opificio delle Pietre Dure, Via Alfani 78, 50123 Firenze, Italy

ABSTRACT

Identification of the natural red dyes and lakes from plants (the madders) and insects (cochineal, lac, and kermes) is typically carried out with destructive methods such as high performance liquid chromatography (HPLC), which can require time consuming and complicated sample preparation and method development. Identification with Fourier transform infrared spectroscopy (FTIR) is usually not possible due to the low concentration of the dye and the presence of the binder, and Raman is generally hindered by fluorescence without a specific instrumental set up. The ability to identify these materials with the non-invasive technique of UV-Vis-NIR fibre optic reflectance spectroscopy (FORS) offers many advantages, as no samples are required and the technique is very sensitive to dyes. There have already been several published studies on the analysis of these red dyes using FORS. While it is sometimes possible to distinguish between these dyes or broadly classify them as of animal or insect in origin, in the analysis of real paintings identification is complicated by the presence of other pigments, the nature of their application, as well as effects of natural ageing. These factors can mask or alter characteristic features in UV-Vis-NIR reflectance spectra. In this study, several of these factors are taken into consideration in order to address the potentiality of UV-Vis-NIR FORS for the analysis of red lakes in paintings. Replicas were prepared using red lakes in several different applications, which were devised to reflect those commonly encountered in tempera painting. The resulting reflectance spectra will be discussed in relation to the different preparations. Lastly, these reference spectra will be compared to those acquired from real tempera paintings.

INTRODUCTION

The red dyes most commonly encountered historically as artists' materials are related compounds based on the anthraquinone structure. These dyes can be derived from insects, such as cochineal (carminic acid), kermes (kermesic acid) and lac dye (the laccaic acids), or can be extracted from plants as is the case with the madder dyes (predominately the compounds alizarin and/or purpurin). Alizarin can now be prepared synthetically, and is still commonly found in artists' paints today. For use as a pigment, these dyes are typically converted to lakes, a process whereby the dyestuff is bound to an insoluble substrate such as aluminium hydrate or calcium sulphate. Furthermore, there are different preparation methods (extraction methods, precipitation procedures and materials), which can produce different shades for the same dye [1, 2].

Identification of these dyes is important for preservation of the artwork as well as historical research. One of the difficulties in analysing these lake dyes is that they are similar compounds, which are often only present in very small quantities in the paint layer. Many methods have been successful for their definitive identification, most of which require that a sample is removed as well as expensive instrumentation. High performance liquid chromatography (HPLC) is one of the more common methods [3, 4]. While this technique is very sensitive (nanogram scale depending on the chromatographic conditions and detection system) and can definitively identify mixtures of anthraquinone-based dyes, it requires time-consuming sample preparation and method development. Raman spectroscopy is another method, but is often limited by strong fluorescence of the anthraquinone dyes as well as the binding media. Recently Surface Enhanced Raman Spectroscopy (SERS) has been used to identify these and other red lakes with high sensitivity [5-7]. Fourier Transform infrared

spectroscopy (FTIR) is another technique, which has been used [8-9] although spectra can be difficult to interpret in real samples where the dye is present at low concentrations and the binder predominates, as well as differences in spectra due to different lake preparations and substrates.

UV-Vis-NIR fibre optic reflectance spectroscopy (FORS) offers a sensitive, non-invasive method for the identification of dyes. To date, there have been several studies on the identification of red lakes with visible transmission spectroscopy [10], FORS for identification of insect dyes [11-12], as well as FORS to monitor fading of red lakes [13-15]. However, in practical paintings analysis, there are limitations to FORS to accurately distinguish between these dyes. To date, to the best of the authors' knowledge, there have been no systematic studies to determine how preparation, ageing, and type of lake affect the reflectance spectra. Many of the absorption features can vary depending on the preparation of the dye into a lake [15] as well as the preparation of the paint, which can entail the use of the raw dyestuff, as is the case in Asian paintings. In some cases characteristic features are less intense or absent altogether, which can cause misleading results in interpretation of spectra. This study was undertaken to determine what effect the preparation of the paint layer has on reflectance spectra using two commercial dyes, one based on carminic acid and the other on alizarin.

EXPERIMENTAL

For this study, one carminic acid based lake (Carminium Pigment, Zecchi colori belle arti e restauro) and one alizarin based lake (Rose Madder, Winsor & Newton) were selected as they represent insect and plant derived dyes, respectively. The identity of the lakes was first confirmed with FTIR.

Tempera medium was prepared according to the following: the yolks and whites were separated and vigorously whisked. They were then combined by mixing 2:1:1 yolk: white: water, with the addition of sorbitol as a preservative. For the preparation of paint the raw pigment was first ground in a mortar and pestle with water. The ground pigment was then combined with the egg medium and thoroughly mixed. Egg medium was added and mixed until the paint could be spread thinly and still appeared glossy. Several sets of samples were prepared for analysis at different concentrations to mimic techniques used in painting. This included red dye glazes over lead white and vermilion, as well as mixtures in different concentrations:

1. Red dye glaze over lead white, one to six coats
2. Red dye glaze over vermilion, one to six coats
3. Red dye mixture with lead white (0.1, 1.0, 25 and 75% by weight)

A commercially prepared canvas board (titanium dioxide, calcium carbonate, gypsum in oil priming) was used for the support.

FORS measurements were performed using two Zeiss spectroanalyzers, an MCS501 model operating in the 200-1000 nm range and an MCS511 NIR 1.7 model operating in the 900-1700 nm range, with a resolution of approximately 0.8 and 6.0 nm/pixel, respectively. An internal tungsten lamp (Zeiss mod. CLH500) for the 350-1700 nm range was used. The 0°/2x45° reflectance configuration was adopted to avoid specular reflectance. A 99% Spectralon diffuse reflectance standard was used for calibration.

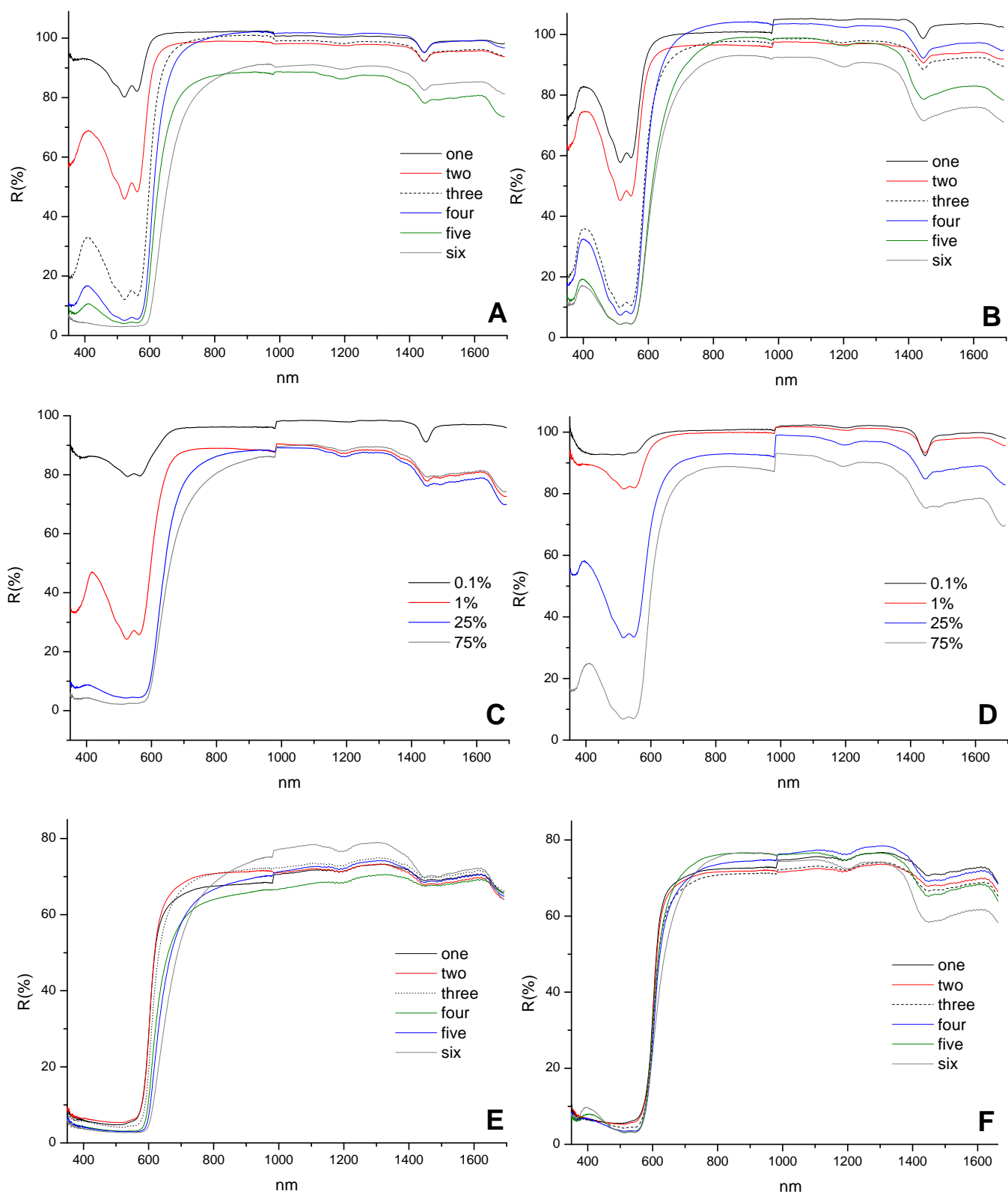


Figure 1: Carminium glazes on lead white, One through six refer to the number of coats (A), Rose Madder glazes on lead white (B), Carminium and lead white mixture, numbers refer to % wt, of dye in lead white (C), Rose Madder lead white mixture (D). Carminium glazes on vermilion (E), Rose Madder glazes on vermilion (F).

RESULTS AND DISCUSSION

Reflectance spectra of the red lake preparations are reported in Figure 1. Both dyes show characteristic patterns in the visible region, which includes a strong absorption band (which is usually structured into two main sub-bands) from 500-560 nm, a shoulder at 480-500nm, a peak of reflectance at about 420 nm, and a sharp increase in reflectance at about 600 nm into the NIR. The absorption behaviour in the visible region of these anthraquinone based dyes is principally due to $n \rightarrow \pi^*$ transitions of the carbonyl groups. Another intense absorption band due to a $\pi \rightarrow \pi^*$ transition occurs in the UV region (below 350 nm). Accordingly, between these absorption bands a reflectance peak can appear at around 400 nm. Based on spectroscopic studies on anthraquinones in solution, the wavelength position of these bands was found to depend on many factors, including the nature and number of other functional groups in the anthraquinone, their relative positions, the overall inter and intra-molecular structure, as well as the local environment [16-18].

In the analysis of the red lakes with lead white preparation, the dye characterisation is found to be optimal at low concentrations (Fig. 1A-D). This demonstrates the sensitivity of FORS, where the absorption bands of the two red lakes were readily observed even as dilute mixtures of 0.1% by weight or as thin translucent layers. However, at higher concentrations the absorption intensity becomes so strong that only a strong absorbance in the visible region is observed instead of the characteristic two absorption sub-bands in the 500-560 nm range. For the two red lakes painted over vermilion, many features in the visible region are masked as vermilion has an intense absorption below approximately 590 nm. In this case identification of the red lake was only possible with thicker layers (Fig. 1E-F).

To better define the position of these absorption bands and the inflection point of the steep increase in reflectance in the red region of the visible (IP), it was decided to calculate the first derivative of each spectrum (Fig. 2A-D). Averages of the positions of the two absorption sub-bands for each paint sample preparation are listed in Table 1. There are variations in the location of absorption features, and from the table it is evident that carmine lake presents slight difference in behaviour depending on preparation. Some of these variations can be accounted for by inhomogenities in the paint surface. Additionally, when absorption features are strong, in some instances it is difficult to define a local maximum. However, in both carmine samples on lead white and mixed with lead white there is a shift to lower wavelengths as the concentration increases. This could be explained by the fact that the two sub-bands tend to merge into one broad and intense band with higher concentration, and hence greater absorption. In lead white preparation the IP shows a shift towards higher wavelengths along with a decrease in slope. This trend is clearly seen in the graph of first derivative (Fig. 2 A-B). For the carmine preparation on vermilion, the shift in the absorption bands was in the opposite direction, toward longer wavelengths. This is likely because there is a greater contribution to absorption from vermilion with thin transparent layers of red lake. With vermilion samples, the IP presents a similar trend as lead white preparations (Fig. 2C-D).

With Rose Madder preparations the variation in the absorption sub-band positions was not as great. The shift to greater wavelengths is observed with the vermilion preparation, but no decrease in band position occurred for lead white preparations. The shift in the IP toward the NIR was only seen with lead white preparations, and not with the vermilion. It should be stressed however that these trends do necessarily reflect the behaviour of all the different types and preparations of madder or insect dye lakes.

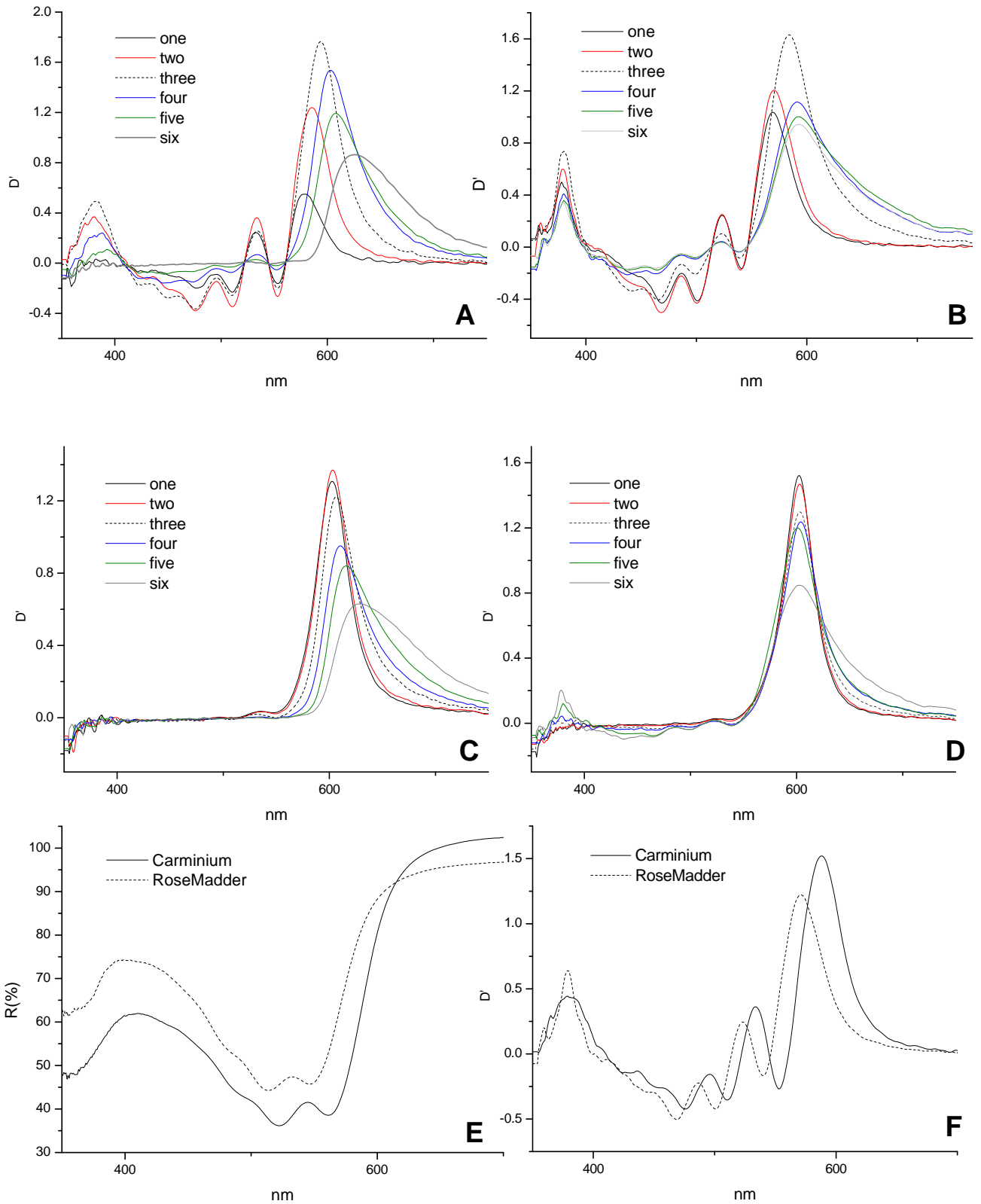


Figure 2: First derivative spectra of Carminium on lead white (A), Rose Madder on lead white (B), Carminium on vermilion (C), and Rose Madder on vermilion (D). Visible region of reflectance spectra of red lake glazes on lead white, two coats (E) and first derivative of spectra (F).

Carminium on lead white									Carminium on vermilion							
Cts	Sh	ME	A-1	ME	A-2	ME	IP	ME	Sh	ME	A-1	ME	A-2	ME	IP	ME
1	495.2	0.4	521.4	0.2	560.2	0.1	579.4	0.9	nd	-	nd	-	nd	-	602.7	0.1
2	495.6	0.3	522.1	0.1	560.7	0.6	586.4	1.7	nd	-	516.8	1.3	550.1	-	603.6	0.4
3	495.9	0.2	522.8	0.8	561.4	0.1	595.1	1.3	nd	-	517.2	0.5	552.4	1.0	608.0	1.4
4	495.9	0.6	521.8	0.1	560.3	0.3	603.0	0.1	nd	-	522.1	0.9	554.2	2.8	610.0	0.6
5	495.3	2.2	520.2	0.3	560.0	0.2	607.3	0.6	nd	-	521.5	-	553.2	-	613.9	3.5
6	nd	-	514.3	0.8	552.5	0.0	626.3	3.4	nd	-	521.6	-	555.5	-	633.3	4.0
ave	495.6	1.9	520.5	7.0	559.2	6.7	598.5	51.2*	nd	-	519.0	3.8	553.2	3.8	614.3	41.5*
Rose Madder on lead white									Rose Madder on vermilion							
Cts	Sh	ME	A-1	ME	A-2	ME	IP	ME	Sh	ME	A-1	ME	A-2	ME	IP	ME
1	486.6	0.1	514.1	0.1	546.6	0.1	568.9	0.3	nd	-	505.6	4.2	nd	-	602.5	0.3
2	486.0	0.6	513.8	0.3	546.2	0.1	571.9	1.5	nd	-	506.9	1.5	nd	-	603.0	0.1
3	486.2	0.3	513.4	0.2	545.8	0.3	579.9	1.8	488.6	1.7	513.2	0.3	543.7	0.9	602.7	0.8
4	486.3	0.2	513.4	0.1	545.9	0.2	583.7	0.6	484.5	2.3	514.0	0.9	544.4	0.4	603.7	0.2
5	486.3	0.4	513.8	0.1	545.8	0.2	591.5	0.4	486.0	0.9	513.9	1.1	544.8	0.6	603.0	1.9
6	486.4	0.5	513.4	0.3	546.0	0.1	592.2	0.6	486.6	2.7	513.5	0.5	545.3	0.1	602.9	0.5
ave	486.3	0.6	513.7	0.6	546.0	0.6	581.4	23.8*	486.0	3.7	511.1	9.7	544.4	1.3	602.9	3.7*
Carminium and lead white mixture									Rose Madder and lead white mixture							
Cts	Sh	ME	A-1	ME	A2	ME	IP	ME	Sh	ME	A-1	ME	A2	ME	IP	ME
0.1%	494.5	2.0	526.7	0.4	562.7	1.3	584.9	1.0	480.6	0.4	513.9	0.8	544.1	-	569.2	4.3
1%	497.2	0.6	524.0	0.3	561.6	0.3	595.1	1.0	486.2	0.7	516.9	0.1	548.6	0.1	573.3	1.2
25%	495.0	1.5	519.9	0.9	558.3	1.4	619.9	1.4	487.6	0.2	515.0	0.2	546.3	0.1	575.3	2.0
75%	492.5	1.8	508.8	1.0	551.6	0.1	622.0	1.6	486.6	0.8	514.8	0.1	546.2	0.2	588.5	0.9
ave	494.8	3.4	519.9	11.6	558.6	7.1	609.4	39.7*	485.4	5.3	515.1	2.0	546.3	4.7	573.3	18.3*

Cts: coats of glaze applied; Sh: shoulder peak; A-1: absorption sub-band 1; A-2: absorption sub-band 2; ME: maximum error; nd: not detected, * for the average IP, the full range is given instead of the maximum error

Table 1: Peak locations and IP for red lake preparations

With the two red lakes assessed, it is possible to distinguish between the insect and vegetable dyes based on the position of their absorption sub-bands (see figure 2 E-F) in cases where the dye is not highly concentrated. If the behaviour of all samples is considered, absorption bands averaged 520 ± 5 nm and 557 ± 4 nm for Carminium, and 514 ± 2 nm and 546 ± 1 nm for Rose Madder. In some cases in these analysis, the variation was enough to cause misleading results or to prevent a confident designation. This is a noteworthy point, particularly as the difference between madder and insect lakes is 10 nm shift or less.

When FORS is applied to the study of real paintings identification of a red lake is not usually straight forward. As case studies, the reflectance spectra of red areas from Albrecht Durer's *Adoration of the Magi*, 1504 and Mariotto di Cristofano's *Resurrection of Christ*, 1445-47 are shown in figure 3A-B, along with the first derivative of spectra (fig. 3C-D). In all the reported spectra except sample D15, samples show the characteristic absorption sub-bands of anthraquinoid lakes, but their position does not precisely match either the alizarin or carminic based lakes. However, as the bands are shifted to the longer wavelength, they are probably due to an insect dye. Based on historical use of these dyes, Kermes is most likely the pigment used. Kermes is a dye derived from insects indigenous to the Middle East and Eastern Europe, and the colorant is kermesic acid, which is very similar to carminic acid. The shape of the reflectance spectrum does deviate from those obtained in this study. This can be due to a number of factors, including the properties of the paint layer, the source and processing of the lake, and natural ageing. For spectrum D15, no features of a red lake are observed, however the investigated area is likely an organic red based on its colour and an IP of 610.5 nm. The colorant material could not be identified in this case, although may be an anthraquinone lake, or another organic red that does not show the same patterns in the visible [9].

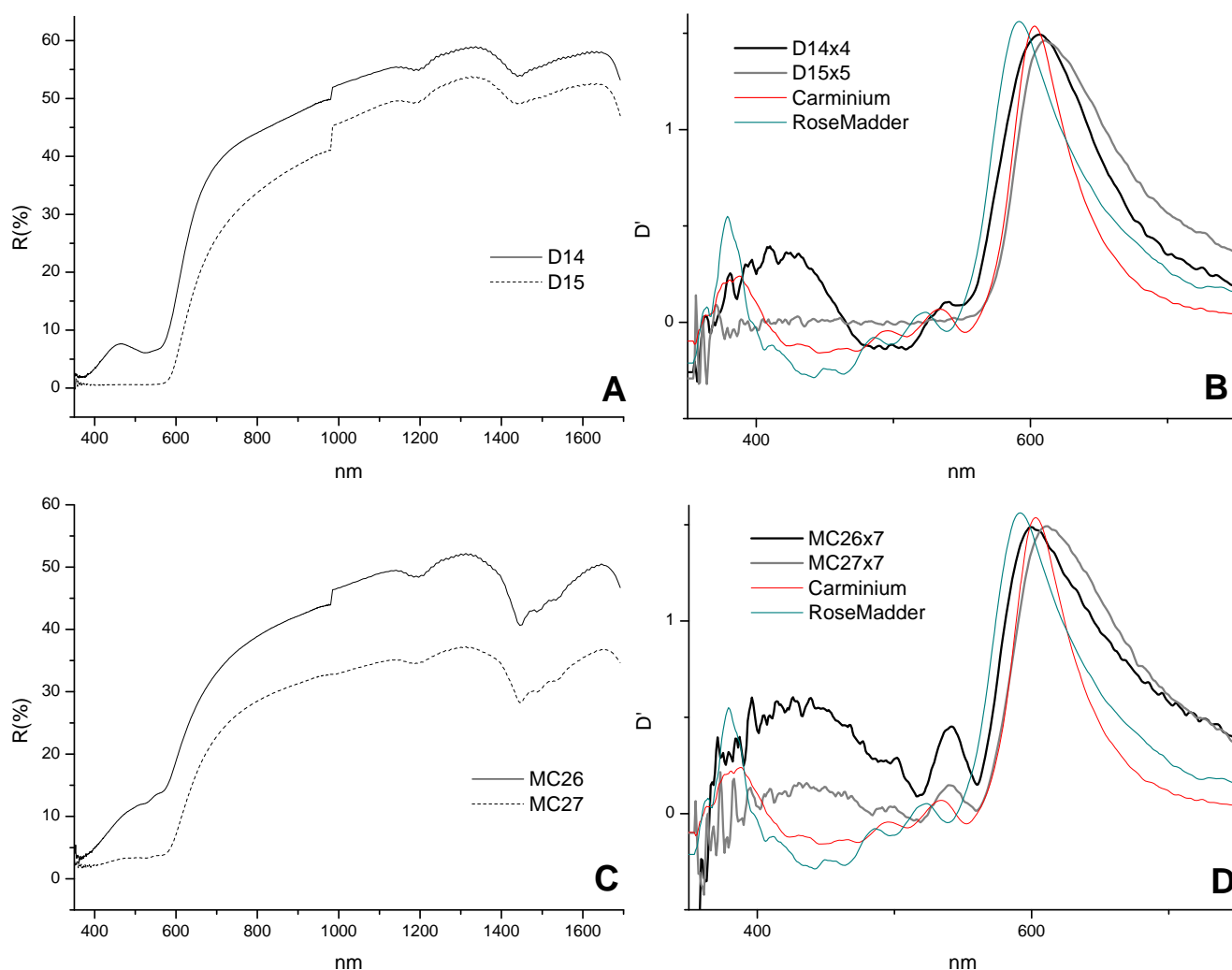


Figure 3: A. Two reflectance spectra taken on red areas in Durer's Adoration of the Magi (A), Mariotto di Cristofano's Resurrection of Christ (C), and first derivatives of spectra (B and D, respectively) with Carminium and Rose Madder references (preparation is four coats of red lake on lead white)

CONCLUSION

FORS is a sensitive method which can be used to determine the presence of the anthraquinone based red lakes in paintings, and in some cases identify the class of lake (*i.e.* insect vs. plant) by the positions of characteristic absorption sub-bands in the visible region. However, FORS analysis may not be sufficient for their identification, particularly when the dye is concentrated or applied with a highly absorbing pigment. In this study three preparations were tested using only two commercial lakes. Further investigation is needed to determine how other paint preparations, other classes and manufacture of lakes, as well as the effect of ageing affect reflectance spectra before definitive conclusions can be drawn from FORS spectra.

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REFERENCES

1. Schewppe, H. and Winter, J. 'Madder and alizarin', *Artists' Pigments: A Handbook of Their History and Characteristics* Vol. 3, ed. R. L. Feller National Gallery of Art, Washington DC (1997) 109-142.
2. Schewppe, H., and Roosen-Runge, Heinz. 'Carmine – Cochineal Carmine and Kermese Camine', in *Artists' Pigments: A Handbook of Their History and Characteristics*, Vol. 1, ed. R. L. Feller, National Gallery of Art, Washington DC (1986) 255-283.
3. Wouters, J. 'High performance liquid chromatography of anthraquinones: analysis of plant and insect extracts and dyed textiles', *Studies in Conservation*, 30 (1985) 119-128.
4. Novotna, P, Pacakova, V., Bosakova, Z., Stulik, K. 'High-performance liquid chromatographic determination of some anthraquinone and naphthoquinone dyes occurring in historical textiles', *Journal of Chromatography A* 863 (1999) 235–241.
5. Leona, M., Stenger, J., Ferloni, E. 'Application of surface-enhanced Raman scattering techniques to the ultrasensitive identification of natural dyes in works of art', *Journal of Raman Spectroscopy* 37 (2006) 981–992.
6. Chen, K., Vo-Dinh, K., Yan, F., Wabuyele, M. B., Vo-Dinh, T., 'Direct identification of alizarin and lac dye on painting fragments using surface-enhanced Raman scattering', *Analytica Chimica Acta* 569 (2006) 234–237.
7. Whitney, A V., Van Duyne, R. P., Casadio, F. 'An innovative surface-enhanced Raman spectroscopy (SERS) method for the identification of six historical red lakes and dyestuffs', *Journal of Raman Spectroscopy* 37 (2006) 993–1002.
8. Higgit, C. 'Red lake pigments in Old Master Paintings: what can FTIR spectroscopy tell us?' Preprints of the 7th International IRUG Conference, Museum of Modern Art, New York (2006) 77-79.
9. Masschelein-Kleiner, L. and Heylen, J. B. 'Analyse des Laques Rouges Anciennes', *Studies in Conservation* 13 (1968) 87-97.
10. Kirby, Jo. A spectrophotometric method for the identification of lake pigment dyestuffs. *National Gallery Technical Bulletin* 14 (1977) 35-44.
11. Giaccai J. and Winter, J., 'Chinese painting colors: history and reality', *Scientific Research on the Pictorial Arts of Asia: Proceedings of the Second Forbes Symposium at the Freer Gallery of Art, London: Archetype Publications* (2005) 99-108.
12. Leona, M. and Winter, J. 'Fiber Optics Reflectance Spectroscopy: A Unique tool for the investigation of paintings', *Studies in Conservation* 46 (2001) 153-162.
13. Salmon, L. G., and Cass, G. R. 'The fading of artists' colorants by exposure to atmospheric nitric acid', *Studies in Conservation* 38 (1993) 73-91.
14. Burnstock, A. 'The fading of the Virgin's robe in Lorenzo Monaco's 'Coronation of the Virgin'', *National Gallery Technical Bulletin* 8 (1988) 58-65.
15. Bacci, M. Orlando, A., Picollo, M. Radicati, B., Lanterna, G. Colour analysis of historical red lakes using non-destructive reflectance spectroscopy. *Compatible Materials for the Protection of Cultural Heritage*, in PACT 58 (2000) 21-35.
16. Fabian, J., and Hartmann, H. *Light Absorption of Organic Colorants: Theoretical Treatment and Empirical Rules*. Springer-Verlag, New York (1980).
17. Reta, M. R., Cattana, R., Anunziata, J.D., Silber, J.J. 'Solvatachromism of anthraquinone and symmetrical dihydroxy derivatives. Local Interactions', *Spectrochimica Acta* 49A (1993) 903-912.
18. Yoshida, Z., and Takabayashi, F. 'Electronic spectra of mono-substituted anthraquinones and solvent effects', *Tetrahedron* 24 (1968) 933-943.