

UV-VIS REFLECTANCE SPECTROMETRY STUDY OF THE DYED SILKS IN A RELIC SHRINE FOUND IN ANTWERP, BELGIUM

Copyright M O R A N A RTD d.o.o.

André Verhecken¹, Patrick Storme² And Olivier Schalm²

FULL PAPER

Abstract

The dye used on the silk textiles in an as yet undated relic shrine in a church in Antwerp was analysed by reflectance UV-Vis spectrometry. The natural dyestuff carthamin from safflower (*Carthamus tinctorius*) was detected; because of its very poor light fastness this does not allow the shrine to be exhibited. Neither does it allow dating of the silk, since safflower has been used over a period of three millennia.

1. Independent researcher, Ed. Arsenstraat 47, 2640, Mortsel, Belgium

2. University of Antwerp, Faculty of Design Sciences, Conservation Studies, Blindestraat 9, 2000 Antwerp, Belgium

corresponding author:
andre.verhecken@telenet.be

1 Introduction

In the stores of the Carolus Borromeus church in Antwerp, a Jesuit church built in 1615-1621, a relic shrine of unusual design was found. According to an accompanying document with the seal of the Antwerp Carmel, written and signed on November 23, 1907 by the prioress of the Carmel and her predecessor, the enclosed relic of Saint Clemens had belonged to the Carmel of Antwerp. The relics owned by that religious order had been dispersed in the aftermath of the French revolution, but this shrine was among the relics recovered afterwards. It is unknown if this is the original pre-1789 shrine, or was purposely made around 1907, or was an older shrine re-employed for the present purpose.

The colour shade of the fabrics suggests that safflower (*Carthamus tinctorius* L.) may have been used, a red plant dye often used historically in pink silk fabrics. In constant strong light, its colour fades in about eleven days.¹ But the excellent condition of the textiles gives no indication that this dye had been used. Hence, identification of the dyes was needed in order to establish if permanent exhibition of this shrine could be allowed.

The shrine shown in Figure 1 was made of wood, with tortoise shell and ivory inlays. Metallic parts such as the columns, decoration, rims, lock and key are made of gilded brass. It has the form of a small house or temple with a slightly overhanging roof. The outer shrine can be closed with lock and key of a type still to be studied. On the inside the wooden parts are covered with a same pink decorated textile that can visually be identified as probably made of silk. The relic bones are placed on a sloping pink cushion in plain silk, enclosed in an all-glass sealed rectangular box, fitting nicely in the shrine. A narrow ribbon, also in pink silk, had been glued to the outside of the glass box for its easy removal from the outer shrine; during the conservation treatment it has now been replaced by a broad white ribbon shown in Figure 1.



Figure 1: The relic shrine studied. The white ribbon is not original, it has been added for easy removal of the glass inner container.

received: 07/08/2014
accepted: 04/10/2014

key words:
relic shrine, silk, dyes, carthamus, reflectance spectrometry

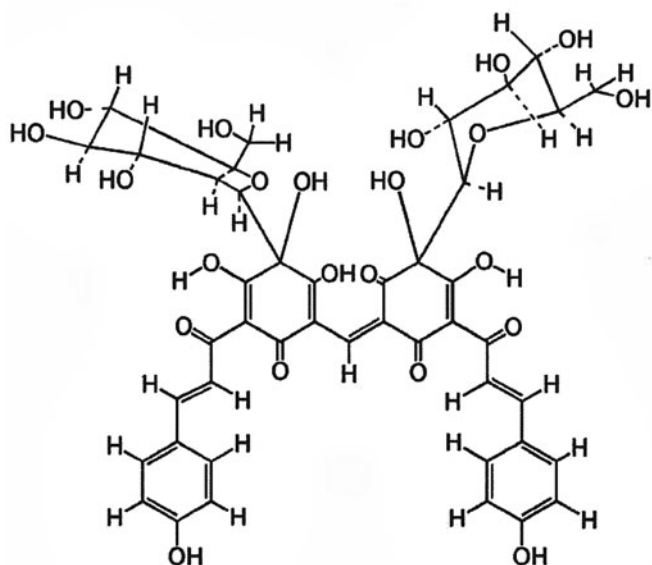


Figure 2: Structural formula of Carthamin (Natural Red 26, C.I. 75140), the red colorant of *Carthamus tinctorius*.

1.1 Background

The colour shade of the pink silks resembles well the shades dyed historically with the dye plant safflower (*Carthamus tinctorius* L.), also known as dye thistle, bastard saffron or wild saffron. The plant was already used for dyeing pink in Egypt in the 21st dynasty, around 1000 BCE.² The florets of this plant contain two groups of dyestuffs: the water-soluble safflower yellow (Natural Yellow 5), and the pinkish red carthamin (Natural Red 26, C.I. 75140, structural formula: Figure 2), soluble in an alkaline aqueous medium.³ Carthamin is one of the 18 quinochalcone C-glycosides obtained and identified up to now from that plant.⁴ The natural dye extracted with alkaline solution consists of a rather complex mixture of colored products; the name carthamin is now restricted to the pure red compound shown in Figure 2.

Historically, the yellow dyes were removed first from the dried flower petals by rinsing (often in running water); then the remaining red dye was dissolved in ash lye, and precipitated on to the fibres by acidification, generally with lemon juice or vinegar. The purity of the pink shade obtained depended on the amount of yellow dye still present. A purer pink shade could be obtained by means of a purification step: the pink carthamin was first precipitated on to cotton by acidification, then redissolved in alkaline water, leaving impurities on the cotton, and then dyes the silk. This very attractive pink shade has one important disadvantage: it does not resist the action of light. Its light fastness (ISO R105) is 1, on the blue wool standards series from 1 (minimum) to 8 (maximum).⁵

Other natural dyes that could give a more or less

similar pink shade are the scale insect kermes (*Kermes vermilio*), the Al-complex of which has a light fastness of about 3⁶, and purpurin, a prominent component in some varieties of madder, *Rubia tinctorum*, or that can be enriched in madder extracts; it is also dyed as an Al-complex.

The shrine has not yet been dated, and although the impression given by the inlays used and the craftsmanship techniques is pre-1800, the possibility of a 19th or even early 20th century age cannot be excluded. In the latter period, several synthetic dyes yielding pink shades became available. In general, the light fastness of these early synthetic dyes is not good either. An obvious candidate would be the synthetic dye Safranin O [(Basic Red 2, C.I. 50240: light fastness: 1-2)⁷], the name of which is apparently based on the resemblance of its colour shade to that of bastard saffron (safflower).

2 Material and Methods

2.1 Materials

The bottom, wooden sides and the "roof" of the shrine are covered on the inside with the same decorated silk textile. Parts that have been exposed to light, including the downside parts of the protruding roof, are partly discoloured (Figure 1). Also parts of the cushion not covered by the relic bones are strongly discoloured. Reflectance measurements were taken on the least discoloured parts of the textiles of bottom, side and roof of the shrine, of the cushion and the pink ribbon.

2.2 Methods

The visual and tactile impression that the textiles consist of silk was confirmed by non-invasive digital microscopy, using a Carson zOrb digital viewer MMO-480, with the measuring head directly on the textile (Sorber, pers. comm.).

The three different textiles in the shrine – the decorated and plain silk, and the pink ribbon – are in excellent condition: there are no important holes or loose ends of yarn. The decision whether or not sampling can be tolerated must be taken by the owner and/or the conservator of the work of art. In the present case it was decided to take no samples. Hence, non-destructive

Fibre	Mordant	Dye	Colour Index	Light fastness	Reference Spectrum
Cotton, raw	-	-			Fig. 5
Wool	-	-			Fig. 5
Silk, raw	-	-			Fig. 5
Silk, degummed	-	-			Fig. 5
Silk, degummed	-	Carthamus	Natural Red 26, C.I. 75140	1	Fig. 7
Silk, degummed	Alum/tartar	Kermes	Natural Red 3, C.I. 75460	3	Fig. 7
Wool	Alum	Purpurin	Natural Red 16, 8; C.I. 58205		Fig. 7
Silk, degummed	-	Safranin O	Basic Red 2, C.I. 50240	1-2	Fig. 8
Silk, degummed	-	Rhodamine B	Acid Violet 10, C.I. 45170	2	Fig. 8
Silk, degummed	-	Phloxine B	Acid Red 92, C.I. 45410	1	Fig. 9
Silk, degummed	-	Rose Bengal B	Acid Red 94, C.I. 45440		Fig. 9

Table 1: Undyed and dyed fibre references used.

methods are needed for identifying the fibre and the dyestuff(s). Therefore, chromatographic techniques could not be used. Even Raman dispersive micro-spectroscopy using a laser of 1064 nm wavelength could not be used, not only because of possible bleaching in the focal spot of the laser but also because of intense fluorescence caused by some organic dyes.⁸

An analysis method in agreement with the non-invasive demand is UV-Vis reflectance spectroscopy. It is non-destructive for the sampled textile and dye, and allows measuring through the closed glass box. Complications concerned with the two different methods of reflectance spectroscopy (by specular and by diffuse reflection) are summarized by Kortüm.⁹ The Kubelka-Munk theory is used for quantitative treatments¹⁰; qualitative work in transmission is generally based on the Lambert-Beer law. Results of the latter type of measurements are often presented as Vis-reflectance spectra¹¹, or UV-Vis reflectance spectra (as in Figure 3), but this is not easily compared to the UV-Vis absorbance curves in general use in chemistry, therefore the use of UV-Vis absorbance curves is preferred here. Reflectance spectra were recorded with an optical spectrum analyser Avaspec 2048 instrument (Avantes B.V., Apeldoorn, The Netherlands) between 200 and 1000 nm with a spectral resolution of 0.5 nm. The integration time for each spectrum was 900 ms and the final spectrum is the average of 10 acquisitions. The Avalight DH-S-BAL light source has two lamps: a 30-W deuterium lamp for the UV region (emitting between 190 nm and 400 nm) and a 20-W halogen lamp for the VIS-NIR (emitting between 350 and 1000 nm) region. The light is guided from the sources towards the sample by means of an optical fibre bundle. The beam is directed to the measured surface at an angle of 8° at a measuring area of 5 mm diameter. The diffusive reflected light is transmitted to the optical analyser by means of a fibre bundle. For calibration, at each wavelength, the incident intensity was measured by collecting a spectrum from a white tile. The background noise is taken with the lamp shut off. The reflectance from a sample was calculated by dividing the measured intensity at a specific wavelength by the incident intensity at that wavelength. From this, the absorbance spectra are calculated using the software AvaSoft 7.7 for USB2.

Spectra were recorded in reflectance and absorbance mode, by measuring in direct contact of the integrating sphere with the samples. Only the cushion was by necessity measured through the closed glass box, shielded off from all external light sources.

Identification of the dye was done using the fingerprint method. First, reference spectra were collected from different textile fibres and from the same fibres dyed with a set of dyes that might have been used to colour the fabric (Table1).

The measurement of dyed silk yields a spectrum consisting of the superposition of the reflectances or absorbances of the silk material and those of the dyestuff. Since the spectrum of undyed silk was also measured, a subtraction of these two spectra should give the spectrum of the dyestuff(s).

In a study published after our measurements were finished, Clementi *et al.*, partly with equipment similar to ours, obtained non-invasive absorption curves

expressed in Kubelka-Munk K/S values, and also fluorescence emission data of carthamus-dyed silk.¹⁴

3 Results

3.1 The Fibre References

Reflectance spectrometry measures not only the colour of the dye, but also the underlying substrate (e. g. the textile fibres), particularly in the UV region. Therefore it is possible to distinguish if a white textile consists of animal fibres (wool; silk) or of plant fibre (cellulose).¹²

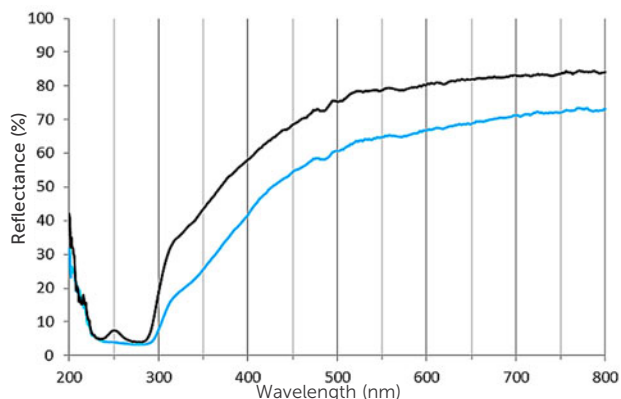


Figure 3: UV-Vis reflectance spectra of silk: raw (blue) and degummed (black). Abscissa: wavelength in nm; ordinate: percentage reflectance (R).

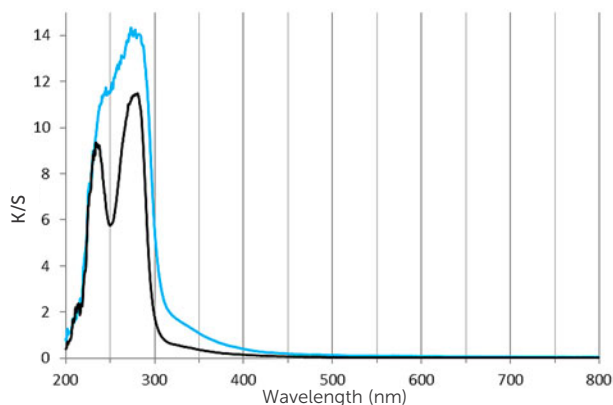


Figure 4: Kubelka-Munk K/S values of raw silk (blue) and degummed silk (black), in function of wavelength. Abscissa: wavelength in nm; ordinate: K/S.

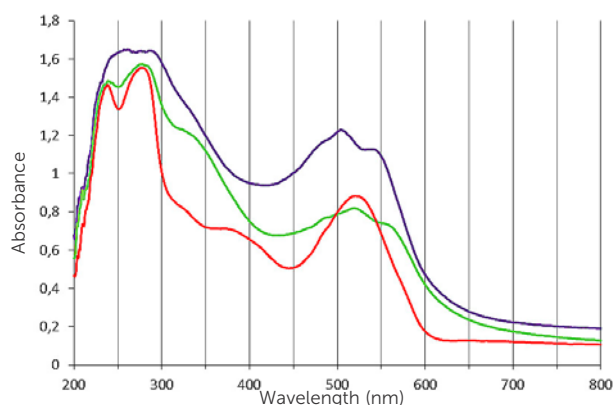


Figure 5: UV-Vis Absorbance spectra of (a) raw silk (blue), (b) degummed silk (black), (c) wool (green) and raw cotton (red). Abscissa: wavelength in nm; ordinate: absorbance.

Spectra based on the Kubelka-Munk remission function:

$$F(R)_{\infty} = K/S = (1-R)^2/2R$$

allow qualitative comparison with conventional UV-Vis absorption spectra.¹² This is indeed confirmed in Figure 4, where the form of the K/S curve (calculated from Figure 3) and the peak wavelengths agree well with those in the absorbance curves (Figure 5) of raw and degummed silk. Thus it shows that for qualitative work absorbance spectra can be used instead of Kubelka-Munk data.

The undyed fibres can be identified based on the form of their absorbance peak(s) in the region between 200-300 nm. Degummed silk has in that region two peak maxima, whereas raw silk has only one broad peak (Figure 5).

3.2 The Dye References

It must be taken into consideration that the absorbance peaks of a compound in solution may vary slightly according to the solvent used for the measurement: e.g. carthamin in ethanol has peaks at 515, 377 and 244 nm¹³; in methanol 519, 403 (sh.) and 373 nm¹⁴, whereas for pure carthamin peaks at 520, 373 and 245 nm (Figure 6) in 90/10 methanol/aqueous

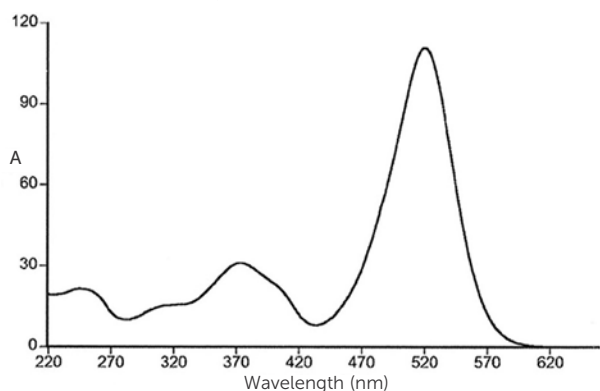


Figure 6: Spectrum of pure carthamin in solution. "Republished with permission of Maney Publishing, *Markers for the identification of faded Safflower (Carthamus tinctorius L.) colorants by HPLC-PDA-MS*, Wouters, Grzywacz & Claro, *Studies in conservation*, vol. 55, 2010, p. 193; permission conveyed through Copyright Clearance Center, Inc." Copyright Maney Publishing 2010.

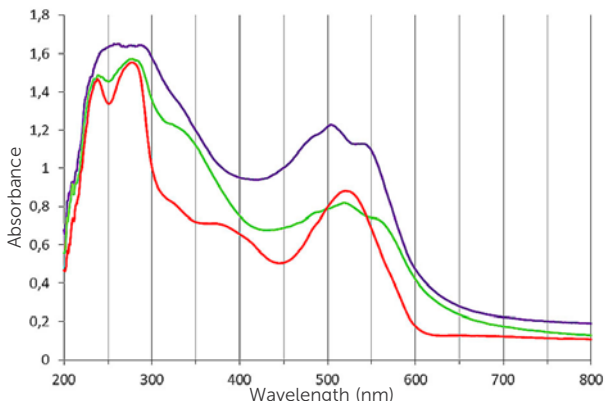


Figure 7: UV-Vis absorbance spectra of (a) carthamin on degummed silk (red), (b) kermes on alum/tartar mordanted silk (green) and (c) purpurin on alum-mordanted wool (purple). Abscissa: wavelength in nm; ordinate: absorbance.

formic acid HPLC eluent were found.¹⁵ Almost identical absorption curves are given by these authors. Therefore slight differences can exist between published ϵ -max values in solution, and those measured in reflectance.

The mordant dyes purpurin and kermes in the reference samples are present as the Al-complexes with the fibre, therefore their spectra must not be compared to those of the pure (unmordanted) dyes. Purpurin mordanted on wool has a spectrum easily distinguishable from that of carthamin; kermes mordanted on silk has an absorbance maximum at 520 nm, but also a strong shoulder at 560 nm (Figure 7).

3.3 The Silks in the Shrine

The decorated pink silks of the shrine all yield essentially the same absorbance spectra with the same Vis absorption maximum at 520 nm (Figure 10). The measurement of the cushion through the glass yields a differently shaped curve, possibly also due to dust or other contaminants on the glass, but the maximum peak at 520 nm is the same. Further in this paper, the spectrum of the silk at the bottom inside the shrine is used as representing the decorated shrine silks. Their UV peak between 200-300 nm suggests non-degummed silk, in contrast to the pink silk ribbon where the two peaks are indicative of degummed silk. However, the influence of the degree of degumming on the separation of the UV absorbance peaks in that

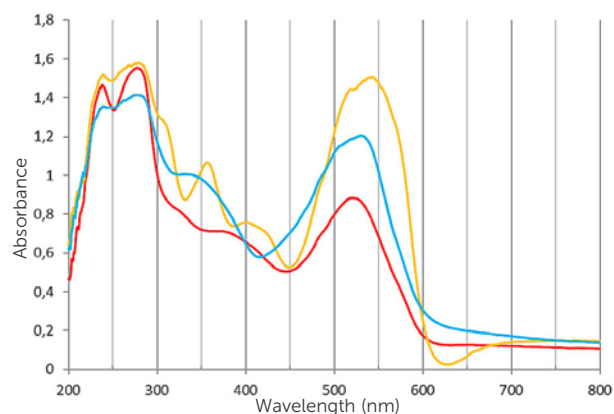


Figure 8: UV-Vis absorbance spectra of the silks dyed with (a) carthamin (red) or with early synthetic dyes: (b) Safranin O (blue) and (c) Rhodamine B (yellow). Abscissa: wavelength in nm; ordinate: absorbance.

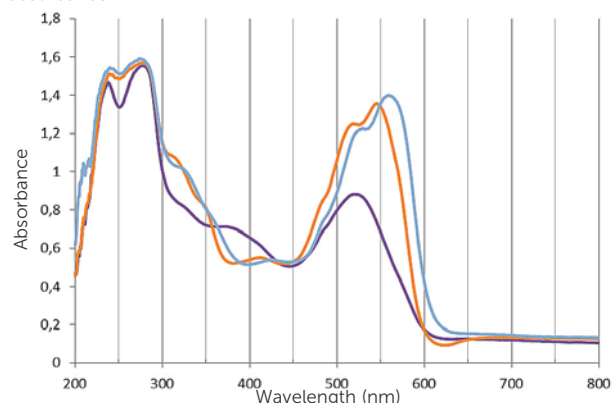


Figure 9: UV-Vis absorbance spectra of the silks dyed with (a) carthamin (red) or with early synthetic dyes: (b) Phloxine B (blue) and (c) Rose Bengale B (orange). Abscissa: wavelength in nm; ordinate: absorbance.

region has not yet been studied. Hence it cannot be concluded that these silks are either completely raw or completely degummed.

A spectrum with a shape similar to that of carthamin and with peaks at 244-248 nm, 323 and 383 with a shoulder at 408, and 520 nm, is obtained by subtraction of the silk absorbance spectrum from that of the reference silk sample dyed with safflower red [Figure 11 (a)]. That subtracted spectrum has the main peak also at 520 nm, in fact in the region 360-570 nm it is almost identical to that of pure carthamin, shown in Figure 6. Possibly some safflower yellow dye absorbing until 450 nm remained because of insufficient washing of the safflower petals. Also Clementi *et al.* detected

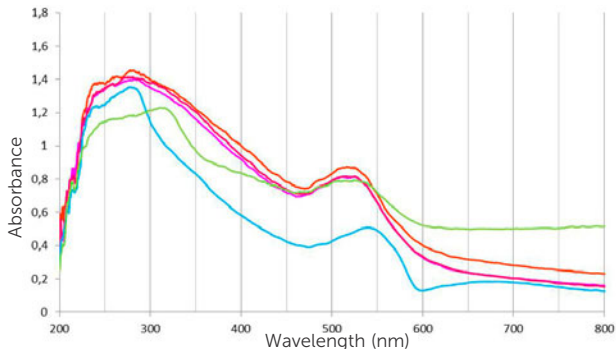


Figure 10: UV-Vis Absorbance spectra of the different silks in the shrine. (a-c) decorated silk bottom, sides and inside of 'roof' (reddish); (d) plain silk cushion, measured through the glass (green); (e) pink silk ribbon (blue). Abscissa: wavelength in nm; ordinate: absorbance.

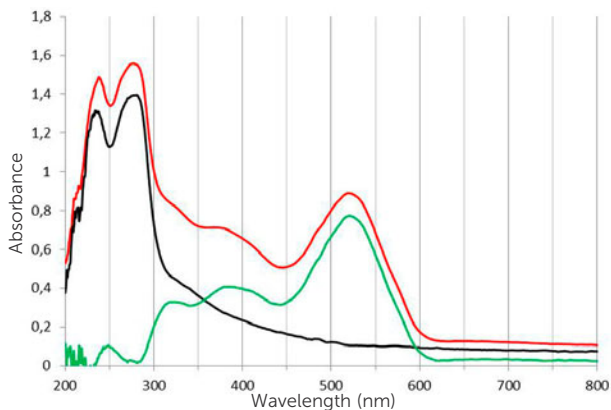


Figure 11: (a) Curve (green) obtained by subtraction of degummed silk spectrum [Figure 5(b)] (black) from the spectrum of the reference carthamin on degummed silk [Figure 7(a)] (red). Abscissa: wavelength in nm; ordinate: absorbance.

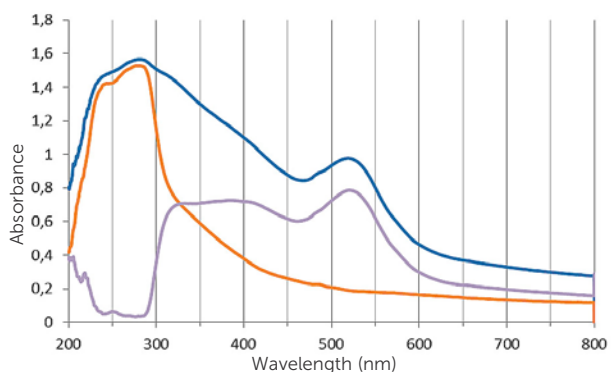


Figure 12: (a) Curve (green) obtained by subtraction of raw silk spectrum [Figure 5(a)] (black) from the spectrum of the shrine bottom silk [Figure 10(a)] (red). Abscissa: wavelength in nm; ordinate: absorbance.

residual yellow component around 390-410 nm in carthamus-dyed textiles.

The precision of the subtraction may suffer from non-linearity of the measured high absorption peaks of the textile fibres in the range 180-270 nm, but this does not influence the interpretation of the curves in the visible region needed to determine the dye present.

A similar subtraction of the raw silk absorbance spectrum from that of the decorated shrine silk must yield a spectrum with the peaks of the unknown dye used in the shrine [Figure 12 (a)]. It has the main peak of carthamin at 520 nm, but also an amount of what are probably some of the many impurities and safflower yellows absorbing between 280 and about 450 nm.

The pink ribbon gives a different spectrum with an absorbance peak near 550 nm, and a small dip near 600 nm [Figure 10 (e)] might point to a fluorescent dye or impurity in the dye. This fluorescence is also visible when the ribbon is placed under the UV-lamp at 254 and 365 nm. The absorbance peak might be referred to the xanthene dyes Phloxine B, discovered in 1882, or to Rhodamine B, dating from 1887.¹⁶ The former has an absorption maximum at 548 nm in 50% ethanol; the shoulder in the absorption curve near 510 nm (Figure 9) is also present in the spectrum of the Aldrich certified quality of the dyestuff.¹⁷ Rhodamine B has its maximum at 543 nm in methanol, and a very weak shoulder near 510 nm.¹⁸ Both cited dyes are fluorescent. A further identification has not been attempted.

4 Discussion

The difference between the subtraction spectra in Figure 11 (reference sample of safflower) and Figure 12 (sample of the shrine) can be explained by the presence in the latter of impurities or light-induced decomposition products. Reflectance measurements do not directly indicate if the measured surface was coloured with a single colorant or with a mixture.

Carthamin from safflower (*Carthamus tinctorius*) is identified on the silks in the shrine, except on the pink ribbon. Safflower red has been used for three millennia, till the early 20th century. Before the discovery of aniline dyes, safflower was often used for the dyeing of silk, wool and even cotton.¹⁹ Even in the 20th century the proverbial 'red tape' used to bind official documents in England was still dyed with safflower.²⁰ Hence it would be premature to think that safflower was no longer used in the 19th century; and dating the shrine based on the presence of that dye is not possible.

Based on the spectra in Figs. 5 and 10, the narrow pink ribbon may consist of a silk more degummed than the other silks of the shrine. It is not dyed with safflower, but apparently with a synthetic dye of the xanthene class, first synthesized in 1882 or 1887. But this is of only minor importance here, since the ribbon may have been added to the shrine long after its construction, even possibly during the last visitation in 1907.

5 Conclusions

The analyses reported here show that UV-Vis reflection spectrometry allows characterisation of dyes and of the type of fibres used in textiles of historical importance.

They also show that the silk textiles in the relic shrine studied, except for the narrow pink ribbon, are dyed with safflower. Because of the notably poor light fastness of that natural dye this implies that the relic shrine cannot be exhibited without damage to the shrine textiles.

The presence of this natural dye does not give a reliable indication of the period when this silk was dyed. The pink ribbon, with an unclear relation to the rest of the shrine, was dyed with a synthetic dye of the xanthene class, indicating for the dyeing of that ribbon a *post quem* age after 1882 or 1887. Due to the high light sensitivity of the dyes, we recommended to the collection keepers that the shrine cannot be exposed for any extended period of time.

6 Acknowledgments

Sincere thanks are due to Nora Andries, Godelieve Vroom and the Church Council of the Carolus Borromeus church, Antwerp, for allowing analysis of this artwork; to Frieda Sorber (Fashion Museum, Antwerp) for digital microscopy data; to Gianluca Poldi (Segrate, Italy) and Han Neevel (Cultural Heritage Agency of the Netherlands, Amsterdam) for helpful information, and to Chris Cooksey (Watford, UK) for checking the English language of this paper.

7 References

1. E. Chevreul, *Recherches chimiques sur la teinture. Onzième Mémoire*. Institut Impérial de France, Didot, Paris, 1861, 180-193.
2. R. Germer, *Die Textilfärberei und die Verwendung gefärbter Textilien im alten Ägypten*, Harrassowitz, Wiesbaden, 1992, 95.
3. Colour Index, second edition, The Society of Dyers and Colourists, Bradford, and The American Association of Textile Chemists and Colorists, Lowell, 1956, **3**, 3577.
4. S. Yue, S., Y. Tang, et al., *Chemical and biological properties of quinochalcone C-glycosides from the florets of Carthamus tinctorius*. *Molecules*, 2013, **18**, 15220-15254.
5. <http://cameo.mfa.org/wiki/Safflower>, accessed 2014.04.08.
6. T. Padfield, S. Landi, *The light-fastness of the natural dyes*. *Studies in Conservation*, 1966, **11**, 181-196.
7. <http://www.worlddyevariety.com/basic-dyes/basic-red-2.html>, accessed 2014.04.08.
8. C. Schmidt, K. Trentelman, *1064 nm dispersive Raman micro-spectroscopy for the in-situ identification of organic red colorants*. *e-Preservation Science*, 2009, **6**, 10-21.
9. G. Kortüm, *Reflectance spectroscopy. Principles, Methods, Applications*. (transl. J. E. Lohr). Springer, New York, 1969, Preface.
10. G. Dupuis, M. Menu, *Quantitative characterization of pigment mixtures used in art by fibre-optics diffuse-reflectance spectroscopy*. *Applied Physics A*, 2006, **83**, 469-474.
11. F. Pozzi, G. Poldi, et al., *Multi-technique characterisation of dyes in ancient Kaitag textiles from Caucasus*. *Archaeological and Anthropological Sciences*, 2012, **4**, 185-197.
12. K. Millington, *Diffuse reflectance spectroscopy of wool and fibrous proteins*. *Amino Acids*, 2012, **43**, 1277-1285.

13. K. Kazuma, T. Takahashi, et al., *Quinochalcones and flavonoids from fresh florets in different cultivars of Carthamus tinctorius L.* *Bioscience, Biotechnology, and Biochemistry*, 2000, **64**, 1588-1599.

14. C. Clementi, G. Basconi, et al., *Carthamus tinctorius L.: a photo-physical study of the main coloured species for artwork diagnostic purposes*, *Dyes and Pigments*, 2014, **103**, 137-147.

15. J. Wouters, C. Grzywacz, et al., *Markers for identification of faded safflower (Carthamus tinctorius L.) colorants by HPLC-PDA-MS*. *Studies in Conservation*, 2010, **55**, 186-203.

16. *Ibit ref.* 3, 3384, 3391.

17. F. Green, *The Sigma-Aldrich Handbook of Stains, Dyes and Indicators*, Aldrich Chemical company Inc., Milwaukee, 1991, 577.

18. *Ibit ref.* 17, 628.

19. P. Schützenberger, *Traité des matières colorantes*, Masson, Paris, 1867, **2**, 411.

20. D. Cardon, *Natural Dyes. Sources, Tradition, Technology and Science*, Archetype Publications, London, 2007, 58.