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Neevel, Johan G.; van Bommel, M.R.; Lingbeek, Nico; Zwikker, Roelie ; Vellekoop, Marije

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Han Neevel* and Maarten van Bommel
Conservation Research Dept.
Netherlands Institute for Cultural Heritage
PO Box 76709
1070 KA Amsterdam
The Netherlands
Tel.: +31-20 3054 772
E-mail: han.neevel@icn.nl; maarten.van.bommel@icn.nl

Nico Lingbeek
Lingbeek Papierrestauratie
Geertruida Carelsenstraat 32
2032 HL Haarlem
The Netherlands
E-mail: nico@papierrestaurator.nl

Roelie Zwikker and Marije Vellekoop
Prints and Drawings Cabinet
Van Gogh Museum
PO Box 75366
1070 AJ Amsterdam
The Netherlands
Tel.: +31-20 5705 254
E-mail: vellekoop@vangoghmuseum.nl

*Author for correspondence

Abstract

To clarify his working practice, brown and purple inks on 42 drawings, executed by Van Gogh during the period 1878–1890, were identified by applying a non-invasive, portable technique: Fibre-Optics Reflectance Spectrophotometry (FORS). While the shapes of the spectral reflectance curves of the brown inks on the drawings closely matched those of applications on paper of iron gall and chrome logwood ink, the spectral reflectance curve of a purple ink on the drawing *Montmajour* (1888) matched that of crystal violet and of the ink on a contemporary letter written by Van Gogh. HPLC-analysis of the ink extracted from a paper sample, taken from the drawings' edge, indeed showed this to contain crystal violet, in admixture with its de-methylated derivatives.

XRF-analysis of the brown metal-containing inks confirmed the results obtained by FORS. These results indicate that, during his stay in Antwerp (1885), Van Gogh changed from iron gall to chrome logwood ink.

Résumé

Les encres pourpre et marron de 42 dessins exécutés par Van Gogh entre 1878 et 1890 ont fait l'objet d'une identification par l'application d'une technique portable non-invasive: la Spectrophotométrie par Réflectance de Fibres Optiques (FORS), dans l'objectif de clarifier sa pratique de travail. Alors que les formes des courbes de la réflectance spectrale de l'encre marron du dessin correspondent à celles des encres de sulfate de fer et de tannin et des encres de chrome de bois de campêche appliquées sur papier, les courbes de réflectance spectrale de l'encre pourpre du dessin *Montmajour* (1888) correspondent à celles du cristal violet et à l'encre d'une lettre contemporaine écrite par Van Gogh. Les analyses HPLC effectuées sur l'encre extraite d'un échantillon de papier, pris sur le bord des dessins, a vraiment montré qu'elle contenait du cristal violet, en admixtion avec ses dérivatifs déméthylés.

Les analyses XRF des encres marron contenant du métal ont confirmé les résultats obtenus par le FORS. Ces résultats indiquent que Van Gogh est passé de l'encre de sulfate de fer et de tannin à l'encre de chrome de bois de campêche, lors de son séjour à Anvers (1885).

Keywords

Van Gogh, drawings, non-invasive analysis, fibre-optics reflectance spectrophotometry, X-ray fluorescence, HPLC, chrome logwood ink, iron gall ink

Introduction

Since 2005, the Van Gogh Museum, the Shell Research Centre in the Netherlands and the Netherlands Institute for Cultural Heritage are involved in a 5-years' project, called the "Van Gogh's Studio Practice in Context". With the aim to clarify his working practice, art historians, conservators and materials scientists are studying Van Gogh's drawings, letters and paintings in comparison with works of his contemporaries.

Considering the rich colour palette he used in the paintings, made during his 4-years' stay in France (1886–1890), it is tempting to think that he also applied differently coloured inks on his drawings. However, although there are some multicoloured drawings, which were partly executed in crayon, most ink drawings now only show different shades of brown. With some drawings there is proof that exposure to light has caused the inks to fade and change colour. For example, with the drawing "Montmajour", shown in Figure 1, the lines at the edges still show bright purple shades, while, more to the centre of the drawing, they have faded to a light chocolate-brown shade. Mounts with windows of different sizes have protected the edges of the drawing during exhibition, resulting in various degrees of fading of the purple ink at the edges. A black-and-white reproduction of this drawing (see Figure 2), published in a catalogue in 1928, indicates that, at that time, the contrast was much higher. The cooperative research project on his drawings was set up in order to determine whether Van Gogh used more than one ink on the same drawing, which ink or inks he applied, whether there is a relation between the inks used and the period of production of a specific drawing, how and how fast the colorants in the inks deteriorate and whether it is feasible to reconstruct the original colours of a faded drawing.

Synopsis

Para aclarar sus prácticas de trabajo, se identificaron tintes marrones y morados en 42 dibujos realizados por Van Gogh durante el periodo de 1878–1890, aplicando una técnica portátil no invasiva: Espectrofotometría Reflectante de Fibra Óptica (FORS). Mientras la forma de las curvas de la reflectancia espectral de los tintes marrones de los dibujos coincidía mucho con aquellas de las aplicaciones sobre papel de tinta de bellota de hierro y campeche de cromo, la curva reflectante espectral de una tinta morada en el dibujo *Montmajour* (1888) coincidía con la de violeta cristal y de la tinta sobre una carta contemporánea escrita por Van Gogh. El análisis-HPLC de la tinta extraída de una muestra de papel, tomada del margen de los dibujos, mostraba de hecho que esta contenía violeta cristal, en mezcla con sus derivados desmetilados.

El análisis-XRF de los tintes marrones con contenido metálico confirmó los resultados obtenidos mediante FORS. Estos resultados indican que, durante su estancia en Antwerp (1885), Van Gogh cambió el uso de tinta de bellota de hierro a tinta de campeche de cromo.

Figure 1. "Montmajour" (Arles 1888 – Van Gogh Museum)

For the ICN, this project was a test-case to evaluate the possibilities of identifying drawing inks with two newly acquired non-invasive analytical instrumental techniques: Fibre Optics Reflectance Spectrophotometry (FORS) and portable X-Ray Fluorescence spectrometry (XRF). During the European InkCor Project, the FORS already had proven its usefulness for ink identification (Neevel 2006). In 2005, on the occasion of an exhibition of some of Van Gogh's drawings at the Metropolitan Museum of Art in New York, several drawings were investigated by XRF and Raman Spectrometry, resulting in the identification of three types of ink used: iron gall, chrome logwood and triarylmethane (Shelley and Centeno 2005). The metal-containing inks were distinguished by XRF-elemental analysis, showing the presence of chromium and the absence of iron in the second ink. Due to fluorescence, overruling the Raman signal, this technique did not produce conclusive results. Raman Spectrometry, however, was more successful with the third type, the purple ink of the *Montmajour* drawing (Figure 1), showing it to be of the triarylmethane type (e.g. Methyl Violet). This research will and already has lead to the publication of new catalogues and results are and will be shown at special exhibitions (Van Heugten, Vellekoop and Zwikker (1996–2007).

Materials and methods

FORS was used for obtaining spectral reflectance curves of ink applications on 42 drawings, covering each period of his life as a painter (1878–1890), as well as on some of his letters. While for the purple inks spectra were obtained in the wavelength range 300–850 nm, for the brown-to-black inks a range between 350 and 1000 nm was chosen. Previous experiments had demonstrated that brown-to-black inks, e.g. sepia, soot, iron gall and bistre ink, could, to a certain degree, be distinguished by the different shapes of their spectral reflectance curves in the NIR-range (650–1000 nm) (Neevel 2006). These spectra were compared to those of applications on paper of iron gall, and chrome logwood ink, for the brown-to-black inks, and of aqueous solutions of crystal violet and ParaRosAniline, for the purple inks. The latter two dyes had been chosen as representatives of the triarylmethane dyes, found by our colleagues of the Metropolitan on the drawing *Montmajour* (Shelley and Centeno 2005).

The FORS uses a low-energy halogen lamp to illuminate a small area of the sample (less than 1 mm^2) through an optical fibre, perpendicular to the surface. The reflected light is collected into a second fibre, which makes an angle of 45° with the reflecting surface to block directly reflected light. Figure 3 shows the equipment. The fibres are locked into their position by a transparent PMMA block, in order to allow visual control of the illuminated area on the original. To exclude disturbing stray light, the block is covered with black tape, except for a small window. The reflected light is guided by the detection fibre to a spectrophotometer (Avantes AvaSpec-2048 Fibre Optic Spectrometer), connected to a laptop computer. Software, delivered with the spectrophotometer, converts the signal of the Photo Diode Array detector (PDA) to a spectral reflectance curve, shown on the screen. Reflectance data can be saved in a MicroSoft® Office Excel Worksheet. This software also can convert the spectral data into CIE L*a*b colour space data (CIE – Commission International d'Éclairage) (McDonald 1997). To compare the colour of the measured surface with that of a reference application, ΔE can be calculated. When ΔE is less than 1.5, colour differences are not visually perceptible (Derbyshire, 1999).

These reference applications were prepared by plotting liquid inks of the expected types, e.g. iron gall, chrome logwood and triarylmethane onto modern drawing paper (Van Gelder and Zonen, 150 g/m^2, lignin-free, sized). The triarylmethane dyes ParaRosAniline (PRA, Acros p.a.) and Crystal Violet (CV, Acros p.a.) were chosen, as these are pure compounds, contrary to Methyl Violet (MV), which already is a mixture. Ink applications were made onto drawing paper with a computer-guided refillable plotter pen (HP 7475 Plotter).

The ink on a small paper sample, which we were allowed to take from the drawing's edge in the least faded purple-ink application was analysed by High Performance Liquid Chromatography with detection by Photodiode Array Detector (water/methanol/HCl-extract of paper sample, heated 10 min. at 100 °C, dissolved in dimethyl formamide, eluted with methanol – phosphoric acid).

Moreover, 39 other drawings, executed in inks, which now appear to be brown, were investigated by FORS. They cover Van Gogh's whole active period as a painter (1878–1890). This time, the wavelength region was extended to 1000 nm, as the inked areas on some of the Near-Infrared Images of the drawings showed differences in transparency in this spectral range. As these were the two types of metal-containing brown ink, identified by our colleagues of the Metropolitan on several Van Gogh drawings, the spectral reflectance curves were compared to those measured on laboratory-prepared and artificially aged applications of iron gall ink and chrome logwood ink, Artificial ageing was carried out in a programmable oven at 90 °C and RH, cycling each 3 hours between 80 and 35%. By using X-ray Fluorescence Analysis, our colleagues of the Metropolitan Museum of Art in New York had detected chromium in brown inks of several other contemporary drawings, made by Van Gogh. The presence of chrome logwood ink was therefore suspected.

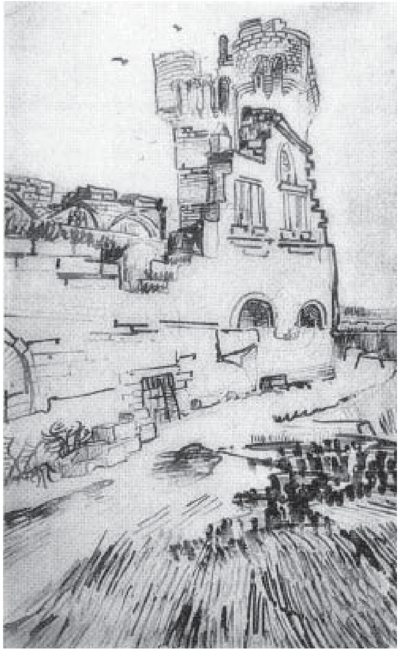


Figure 2. B-W reproduction, published in 1928, of "Montmajour" (De la Faille 1928)

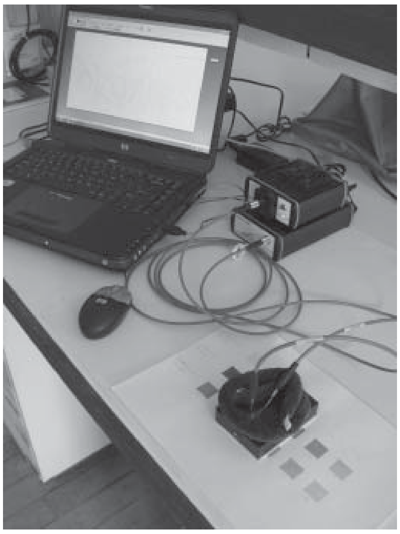


Figure 3. FORS-equipment, with fibre holder, fibres, spectrophotometer, halogen lamp and laptop computer

These black inks are prepared by mixing an extract of logwood (*Haematoxylon campechianum*), with a solution of potassium chromate. They were introduced in 1847 by the German chemist Runge as a non-corrosive alternative for iron gall ink. One of his recipes was used to prepare the ink used for our investigations: "If solid extract of logwood be used, 15 parts are dissolved in 1000 parts of water and 1 part of potassium chromate added" (*Runge's Chrome Ink*, Ainsworth Mitchell and Hepwort 1916). Upon oxidation, a purplish black 2:1 polynuclear complex of chromium (III) and haematein is formed (Puchtler, Meloan and Waldrop 1986). As can be seen in Figure 4, the spectral reflectance curve of a chrome logwood ink distinguishes itself from that of an iron gall ink by its inflection point at about 650 nm, where the curves of two visually identical applications of chrome logwood and iron gall ink are shown, as indicated by their, almost completely overlapping, curves in the visible wavelength range between 400 and 650 nm. Between 660 and 900 nm, the slope of the chrome logwood curve decreases, while the slope of the iron gall ink curve keeps on increasing.

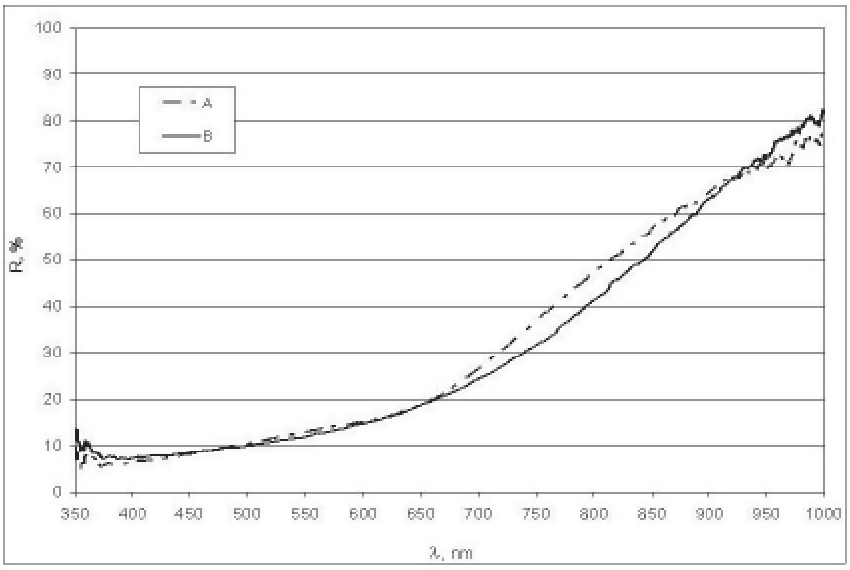


Figure 4. Spectral reflectance curves of two visually identical, artificially-aged applications of a chromium-logwood (A) and an iron gall ink (B)

In addition to the FORS-measurements, we also obtained X-ray Fluorescence spectra from the same ink locations at each drawing. Analysis was carried out with a portable instrument (Bruker Key Master TRACer III-V) in the storage room of the Van Gogh Museum.

Figure 5. The drawing "The Sower" (Arles, 1888), location of FORS-measurement indicated by arrow

Results and discussion

(i) Drawings in brown ink

With 24 of the 39 investigated drawings, executed in brown-to-black ink, the spectral curves closely matched those of visually and colourimetrically comparable applications of *Runge's Chrome Ink*.

Figure 6 shows an example of the results, obtained by FORS, for the drawings *The Kingfisher* (Nuenen, 1884) and *The Sower* (Arles 1888). An image of the drawing is shown in Figure 5. As the spectral reflectance curve of the ink on this drawing has an inflection point at 660 nm, it resembles that of a chrome logwood ink. The spectral reflectance curve of the ink in the drawing *The Kingfisher*, on the contrary, lacks this inflection point and the curve resembles that of the iron gall ink. Therefore, it is likely that this drawing has been executed in iron gall ink.

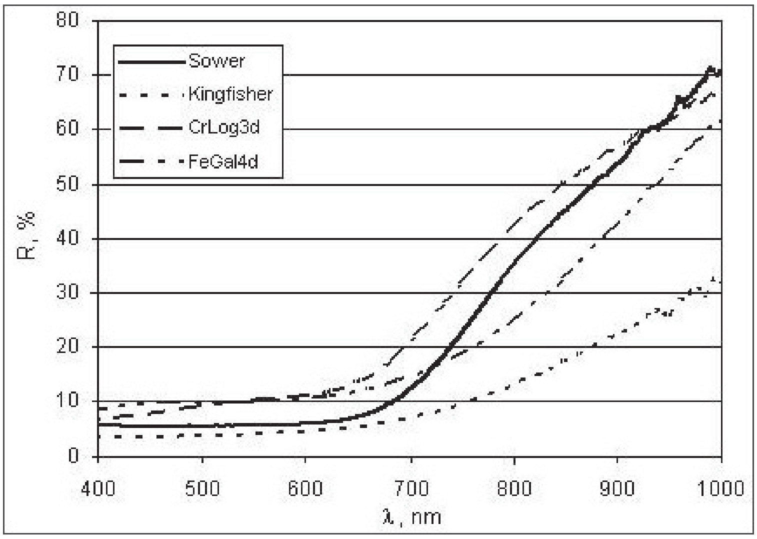


Figure 6. Spectral reflectance curves of ink locations on the drawings "The Kingfisher" (Nuenen, 1884) and "The Sower" (Arles, 1888,) compared to those measured on reference applications of iron gall ink and chrome logwood ink

The drawing *The Sower* has also been analysed by XRF-spectrometry. In order to be able to separate the background signal from the ink signal, the paper has been analysed separately. In Figure 7, the ink and paper spectra are shown superimposed. Compared to the paper spectrum, the ink spectrum has an additional peak at around 5.5 keV, which can be attributed to the K_α – emission of chromium. This, together with the absence of the iron peak at 6.5 keV, indicates that Van Gogh has applied a chromium-containing ink and, judging from the results of the FORS-analysis of this spot, most probably, a chrome logwood ink.

By XRF-analysis of the brown ink at the drawing *Kingfisher* only the presence of iron could be proven, indicating that this ink was of the iron gall ink type.

Until now, the earliest drawing, where a chrome logwood ink could be detected, was the one executed by Van Gogh in 1885 of the Antwerp town castle *Het Steen*, nowadays the Maritime Museum. The change from iron gall ink to chrome logwood also could be observed with his letters. FORS-analysis showed that the last letter from Nuenen, just before leaving for

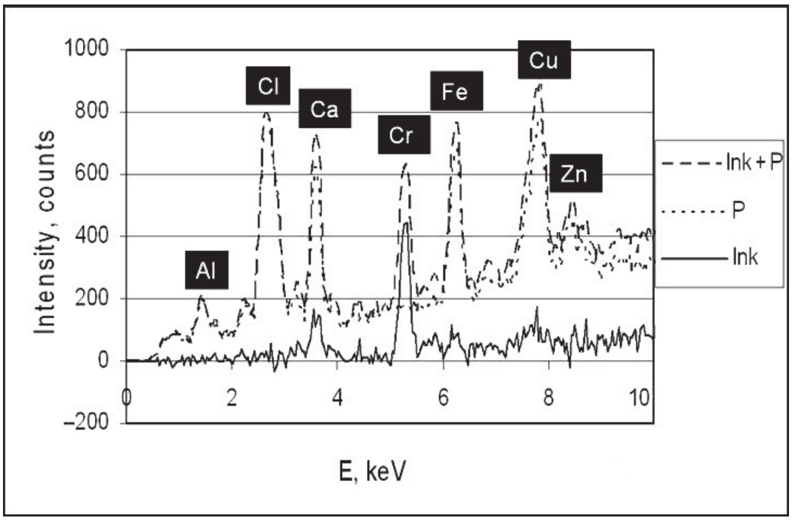


Figure 7. XRF-spectra, showing elemental composition of a brown ink and the Paper(P) of "The Sower" (Arles 1888)

Antwerp, had been written with an iron gall ink. With the same technique, the first two letters from Antwerp were shown to be written with a chrome logwood ink.

(ii) Drawings and letter in purple ink

Two drawings in purple ink and one letter, all from the French period (Arles) were investigated:

Montmajour (Arles 1888, see Figure 1), *Avenue in park at Arles* (Arles 1889) and a letter, sent from Arles to his brother Theo in Paris, dated August 9, 1888. In Figure 8 the spectral reflectance curves of the ink in the letter, the ink on the drawing *Montmajour*, and applications of the triarylmethane dyes ParaRosAniline (PRA) and Crystal Violet (CV) on paper are compared. As can be seen from this Figure, the curve of CV closely matches those of both, the ink on the letter and on the drawing. The curve of PRA does not match at all. Therefore, the ink on the drawing might well be the same as the ink on the letter and consist mainly of CV.

HPLC-analysis, of a small paper sample, taken from the edge of the drawing *Montmajour*, demonstrated the ink to contain a mixture of PRA and the mono-, di-, tri-, tetra-, penta- and hexamethylated forms of PRA, the latter structure being that of CV. The basic structure of PRA and its methylated substitutes is shown in Figure 8. In a recent paper on the photocatalytic degradation of crystal violet, dissolved in TiO_2-dispersion, proof is given that this process leads to a stepwise demethylation of CV, to end up with PRA (Li, Liu and Zhao 1999). A much older paper states that one of the products of the photodegradation of CV is Michler's ketone (4,4'-bis(dimethylamino)-benzophenone) (Kuramoto 1982). This structure can be derived from the structure, given in *Scheme 1*, by substituting the upper aromatic ring with a carbonyl-oxygen. Michler's ketone is a photo-initiator for free-radical polymerisation (Cottart, Loucheux and Lablache-Combier 1981). Upon exposure to near-ultraviolet or violet radiation (λ_{max} = 380 nm), it will react with oxygen and produce oxy-radicals and peroxides, which will degrade dyes and other organic substances present, leading to photo-oxidative dye fading and paper yellowing, as demonstrated by the drawing *Montmajour* in Figure 1. However, a photo-reductive fading process has also been suggested for triarylmethane dyes (Allen 1987).

The drawing *Avenue in Park at Arles*, is mostly executed in watercolour. However, the bench has been drawn with a blue-purple ink. The spectral reflectance curve (not shown here) of this ink did not match that of a triarylmethane dye. By XRF-analysis, it was demonstrated that the ink contained copper. The spectral reflectance curve matched that of reference sample on paper of a copper-aluminium logwood ink, prepared according to a recipe given by Böttger (Ainsworth Mitchell 1916).

Conclusions

(i) Drawings and letters in brown ink

During his life as a painter, Van Gogh has used iron gall ink and chrome logwood ink, both for drawing and writing. According to our results, it does not appear that he has used both inks on the same object. As far as our results obtained up to now are concerned, it seems that during his stay in Antwerp, in the winter of 1885, he started using chrome logwood ink, both, for drawing, and for writing his letters. The earliest drawing, where a chrome logwood ink could be detected was that of the Antwerp town castle *Het Steen*. As to a reason why he would have changed the type of ink: he might have known or observed that iron gall ink is corrosive to the paper and therefore changed to the non-corrosive chrome logwood ink. In Antwerp, being an important harbour city, he might have had a more easy access to this type of ink than in Nuenen, which is a small village in Brabant.

(ii) Drawings and letter in purple ink

In 1887, in Paris Van Gogh seems to have started using triarylmethane-based purple ink, as shown by the results of the FORS analysis of the drawing *Menu*. This type of ink sporadically reappears in his later drawings, e.g. *Montmajour*, from the Arles period (1888). As these inks are very light-sensitive, drawings, containing them, should only be exhibited during a limited time period and at low light intensities (50 lux). Further research, using the newly-developed micro-destructive light-fastness tester to asses light fastness on the object itself, will lead to a better prediction of the behaviour of the material during light exposure (Neevel 2007).

Besides the triarylmethane-based purple ink, Van Gogh occasionally used a copper-containing logwood ink, which also has a purple colour.

Future research (natural science aspects)

As demonstrated by the drawing *Montmajour* (Figure 1), overexposure to light during several exhibitions dramatically changes the appearance of the drawing. In another project, called "ì-Fado", a method is developed to assess light-fastness data by carrying-out micro-destructive fading tests on the object itself (Neevel 2008). Future research will apply this technique to assess the light

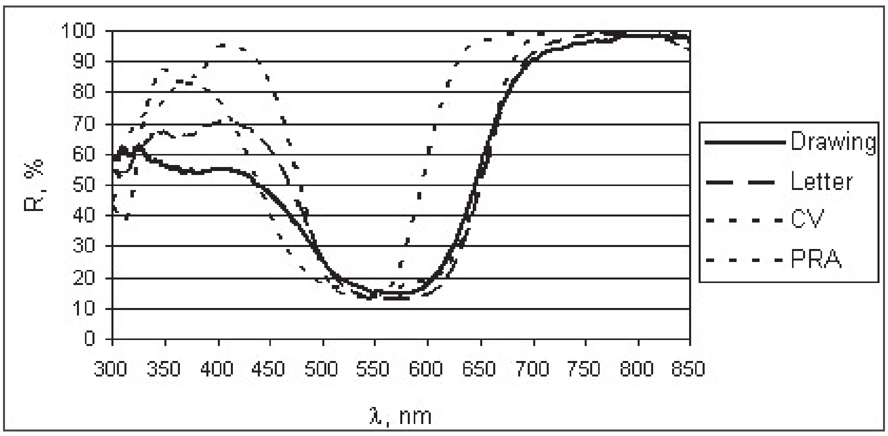
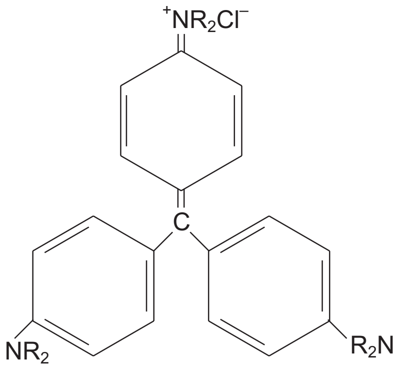


Figure 8. Spectral reflectance curves of the purple ink of a contemporary letter, compared to that of the ink on the edge of the drawing Montmajour (Arles 1888) and to those of applications on paper of Crystal Violet (CV) and ParaRosAniline (PRA)



Scheme 1. Basic structure of PRA and its methylated substitutes, if R = *methyl, the structure is that of CV*

fastness of the purple inks, used in the drawings with the aim of predicting more accurately their behaviour during light exposure when exhibited. Also, the fading mechanism of CV will be studied in order to see which products are formed and whether they speed up further degradation (e.g. Michler's ketone).

The chemistry of chrome logwood inks is not very clear. Further research will focus on the elucidation of the structure of the actual complex (or complexes), present in the ink in order to better understand the observed colour changes during thermal ageing.

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