An investigation of organic red pigments used in paintings by Vincent van Gogh

(November 1885 to February 1888)

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ART MATTERS

Introduction

In 2000 an intensive research program was started to examine paintings by Vincent van Gogh, made in the period November 1885 to February 1888 when he lived in Antwerp and Paris. The main goal of this collaborative project between the Van Gogh Museum, the Netherlands Institute for Cultural Heritage and the Shell Research and Technology Centre in Amsterdam, was to gain knowledge on the artist's working methods in the period, since this had not been well investigated previously. Ninety-three paintings in the collection of the Van Gogh Museum were subject to detailed technical and scientific examination, involving a range of techniques (see description in the appendix). This included all but one of the seven surviving pictures he made during his short stay in Antwerp (from

November 1885 to February 1886), as well as almost half his Paris oeuvre. Bearing in mind that this did not cover his entire production, it provided a representative selection with which to reconstruct his practice. The full results of this research will be presented in the second volume of a new catalogue of paintings by the artist in the collection of the Van Gogh Museum.[1] This paper focuses on the artist's use of organic red pigments in the pictures examined.

Vincent's decision to leave his native Holland for Antwerp, soon moving on to the French capital, stemmed from his ambition to become a professional artist. This aim went hand-in-hand with a desire to improve upon the standard of materials and techniques he employed. The artist's letters reveal that he had felt limited by the quality of paints he had been able to obtain in Holland, hoping to find better colours in Antwerp.[2] Within two weeks of his arrival he had consulted Petrus Johannes Tyck, 'the best' paint manufacturer in the city, for advice on technical aspects.[3] Consequently, he invested in the purchase of fine quality brushes, ready-made canvas supports, and more durable and brilliant colours, including a red lake which he described as follows; 'Carmine' is the red of wine, and it's warm, spirited as wine'.[4]

In Paris, there are very few letters and no paint orders to inform of us where Vincent purchased his art supplies, since he lived with his brother Theo and thus had no need to correspond with him. However, there is evidence for the fact that he gave pictures in exchange for free materials obtained from the informal dealer and paint seller, Julien-François (*père*) Tanguy (active 1874-1894), established at 14, rue Clauzel.[5] Tanguy went on to become a main source of Van Gogh's painting materials from the late Arles period, up to his death in 1890. A price list of Tanguy's materials is kept at the van Gogh Museum, thought to be the one that Vincent's brother Theo used to order colours on his behalf between c. 1888 and 1890.[6] It includes ten varieties of red lake pigment, reflecting the wide choice available to artists at that date. In June 1888 Van Gogh is known to have ordered carmine (*carmin*) from him, complaining however that he had received a dark madder (*garance foncée*) instead.[7] Tanguy's canvases and colours were reputedly of poor quality, but relatively cheap. In fact right up to the end of his life Vincent upheld a charitable view of Tanguy, willing to overlook the shortcomings of his materials in view of their low price, as well as for certain favours received.[8]

Furthermore, original trade stamps and labels left evident on the backsides of Van Gogh's Paris canvases, *cartons* and stretching frames, inform us that they were purchased from at least seven different colour men in the artists' quarters of Montmartre.[9] Though there is no definite proof, it is quite likely that when visiting these shops to buy picture supports, he obtained tubes of paint as well.[10] One of them was Tasset et L'Hôte (active 1887-1910) established at 31, rue Fontaine. Along with Tanguy, Tasset was the other principle source of Van Gogh's paints and canvases from the late Arles period on. In April 1888, he requested six small tubes of *laque geranium*, twelve of *laque ordinaire* and two of *carmin* from the firm, for example.[11] However, the fact that the painter took advantage of a wider range of suppliers than Tasset and Tanguy when living in Montmartre, leaves a high level of uncertainty regarding the provenance of the materials used in his Paris pictures.

The main aim of this study was to identify the organic red pigments that Van Gogh had used in Antwerp and Paris, since so far information on this topic was confined to later periods of his production.[12] Furthermore, we hoped to gain understanding of the aging properties of the different types identified. Often examination of the paintings revealed deteriorated red lake areas, which had been subject to fading, discolouration and fogging, as well as visible changes in surface texture. There was physical and documentary evidence for fading that had occurred since the first decades of the twentieth century, and in one case this process had continued after 1978 (F344, Table 1). Whilst such degradation may have had enormous impact on the way the pictures look now, often this change has not been recognised, let alone taken into account when interpreting the paintings concerned. Such knowledge is essential to art historians for a proper understanding of the artist's developing style and technique in the period. An added concern for the conservator is the physical deterioration of red lake areas, causing possible cracking and flaking of paint, or unusual sensitivity to aqueous or organic solvents used for example, for consolidation or varnish removal. We therefore looked for patterns to establish a link between the organic pigments found (in terms of colorant, substrate and other additives) and the types of deterioration observed on the paintings.

A first step was to find a suitable technique to identify the different types of organic red used. Microscopy of paint sample cross sections often revealed organic red pigments that could readily be distinguished from inor-

ganic ones, but other means were required to identify them. Organic colorants are normally analysed using High Performance Liquid Chromatography (HPLC) coupled to Photo Diode Array (PDA) detection.[13] HPLC-PDA is very convenient for the analysis of dyestuffs extracted from textile samples. Usually a 1 cm long thread, which can be taken from the object without disturbing its integrity, is sufficient for a clear identification. However, paint samples and therefore the amounts of organic colorant they contain are usually much smaller. Furthermore, organic pigments are regularly used in complex mixtures together with other pigments and binding media, so that the organic pigment may be present as only a minor constituent of the sample. An added difficulty is that the organic colorant has to be extracted from both the inorganic substrate and the binding media present in a sample. The yield of extraction may be very low, often below the detection limit of the PDA detector. To overcome this problem the use of fluorescence detection, coupled on-line with HPLC-PDA, was recently introduced by one of the current authors.[14] This exploits the fact that most red organic colorants are known to fluoresce in solution, and that often fluorescence is a more sensitive technique than PDA detection.

Results and discussion

This survey encompassed 52 samples taken from 41 paintings by Van Gogh, analysed using HPLC-PDA-Fluorescence detection, as well as 30 paint cross sections examined with an optical microscope. In addition Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) was used to determine the substrates of the organic red pigments in the cross sections. However, sometimes the very limited sample size meant that it was not possible to perform microscopy and SEM-EDS in addition to HPLC. The combined results of technical examinations of the paintings, with optical microscopy, SEM-EDS and HPLC-PDA-Fluorescence of samples, are tabulated in Table 1. In this table, each type of organic red lake observed in cross section is assigned to a particular organic red dye identified using HPLC. Moreover, any visible deterioration at the sample spots is described. With one exception (F245) the sample material used for HPLC and cross section preparation originated from the same spot on the painting. Table 2, provides a separate overview of the results obtained with HPLC-PDA-fluorescence detection, whereas Table 3 summarizes the substrates found for each organic red pigment using SEM-EDS.

The tabulated data allowed us to look for patterns, linking the analytical results to observations made on the paintings. Though the scale of the project prohibits a detailed discussion of each result here, we will consider some general trends in the findings, and what these mean. Each of the different types of organic red pigment and pigment mixtures found will be discussed in turn. For each red lake sort, case studies will serve to illustrate typical features evident in samples and on the paintings. Also the visual impact of fading and degradation will be considered.

- *Preparation of lakes*

Until the development of mauve by Perkin in 1856, organic colorants were derived only from natural sources, i.e. plants or animals. Most colorants derived from natural sources are soluble in water. When these colorants are used as an organic pigment, they need to be precipitated on substrates. There are numerous recipes for organic pigment preparation. Though a detailed description is beyond the scope of this paper, the basic principles are as follows.[15] Generally, the process begins with extracting the colorant from the plant or animal material, by cutting or grinding and adding water to it. This stage of extraction, usually performed at temperatures of 35-60 °C, can take a couple of hours or even days. If necessary, the solution is filtered to remove residues of the material. Coordination metals, such as aluminium, tin or iron, are added to the solution, which is then neutralised with, for example, calcium or potassium carbonate. As a result, an insoluble metal-organic colorant complex is formed, i.e. the organic pigment, which is filtered and washed several times with water to remove the excess materials. Overall colour will be determined both by the organic colorant, and by the substrate used. For example, cochineal on a tin-containing substrate will give a much brighter red compared to cochineal on an aluminium-containing one.

- *Cochineal*

In numerous samples carminic acid was found. This indicates the presence of cochineal (*Dactylopius coccus* Costa) in the organic red pigment.[16] A synthetic origin of carminic acid is ruled out, since it was not developed before 1991.[17] Cochineal belongs to the well-known insect dyes, often called the coccus species. There are several dye-insects living in Europe and the near-East; such as Kermes (*Kermes vermilio* Planchon), Polish cochineal (*Porphyrophora polonica* L.) or Ararat (*Porphyorophora hameli* Brandt). For centuries these were used to dye textiles red.[18] However, following the discovery of America, cochineal was introduced into

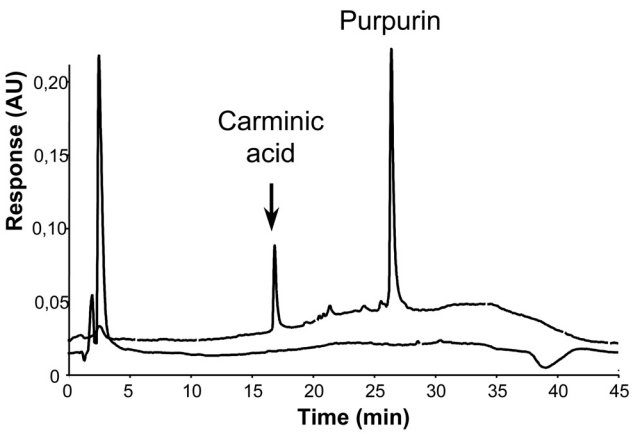


Fig. 1 HPLC-PDA (line below) at 495 nm absorption and fluorescence profile (line above) of a sample from Vincent van Gogh's *The hill of Montmartre with a stone quarry* (F229/3). No components were found with PDA detection, whereas fluorescence detection shows the presence of carminic acid, typical for cochineal, and purpurin

Europe, soon replacing the other insect dyes due to its higher colorant content and better quality. Cochineal lives on cactuses and is native to Central America. The females, wingless and therefore unable to fly, are gathered and dried. The dried insects may be easily crushed, resulting in the excretion of carminic acid, the main organic colorant of cochineal. In addition to carminic acid, often minor compounds were found by PDA and/or fluorescence detection in the samples investigated.

In 33 of the 52 samples analysed, cochineal was identified as the principle organic colorant in the red organic pigment, sometimes combined with other types of red lake (fig. 1). When mixtures of organic colorants were detected in a sample by HPLC, the corresponding cross section revealed that indeed mixtures of organic pigments were present, as opposed to one organic pigment formed by co-precipitation of two organic colorants on a shared substrate.[19] Tin was the usual substrate for the cochineal lake pigment. Alternatively, tin and aluminium, or tin and calcium combinations were found. The cochineal lake pigment showed up as very fine red particles in cross section, which did not fluoresce under UV-light. All the samples examined with a tin-based cochineal lake also included round, blue-fluorescing particles, presumably starch grains. The presence of starch was confirmed by FTIR-analysis of a sample taken from F370, *Agostina Segatori in Le Tambourin*.[20] In each case the diameter of the starch grains measured approximately 4 to 5 µm. One exception however was F244, *Basket of violets on a stool*, in which smaller grains (diameter 4-5 µm) were accompanied by larger ones (diameter c. 10 µm). The addition of starch to cochineal lake paints has similarly been shown by analysis of samples from paintings by Auguste Renoir and Adolphe Monticelli, and from tube paints dating from around the same period.[21] Starch is sometimes known to have served as a substrate for the organic red pigment, or as an inert additive to obtain a lighter shade of red lake.[22] It could also be added as a cheap extender during grinding of the pigment, or already during precipitation of the lake to give the paint more body. All but one of the pictures by Van Gogh in which the tin-based, starch-containing cochineal lake was identified, date from early 1887 on. Only *Portrait of a woman* (F215c), which also contains this particular type of organic red pigment, was painted earlier; in March-early June 1886, soon after the painter arrived in Paris.

In three samples (F229/3, F248a/2 and F28/0) aluminium and calcium were identified rather than tin, though the very low intensity of these peaks in the EDS-spectra made it hard to identify the substrate with certainty. Moreover in the case of *Kingfisher at the waters edge* (F28), the calcium peak might partly be accounted for by the fact that chalk seems present in the sample, rather than by the substrate itself. This survey suggested that the use of the aluminium/calcium-based lake was not confined to a narrow period. Though *The hill of Montmartre with stone quarry* (F229) and *Vase with gladioli and Chinese asters* (F248a) were painted quite close to each other, in the early summer to autumn of 1886, *Kingfisher at the waters edge* (F28) is dated a whole year later, to the summer of 1887. In fact the sample analysed from *Kingfisher at the waters edge* was taken from the red painted border on the tacking margins, thought to have been added retrospectively by the artist when the picture was exhibited without a frame (figs. 2- 4). In all of these examples the cochineal lake was found to be mixed with a small amount of vermilion (as is often the case for other types of red lake too). Striking is that, contrary to the tin-based cochineals, the samples with a calcium/aluminium-based cochineal lake do not contain any starch. Both types of cochineal lake, the aluminium/calcium-based and the tin/aluminium- based variety, have previously been identified in a series of Orchard tree paintings by Van Gogh, made in Arles in the spring of 1888.[23]

Fig. 2 Vincent van Gogh, *Kingfisher at the waters edge*, F28, August 1887, oil on canvas, 26.5 x 19.0 cm, Van Gogh Museum (Vincent van Gogh Foundation) Amsterdam

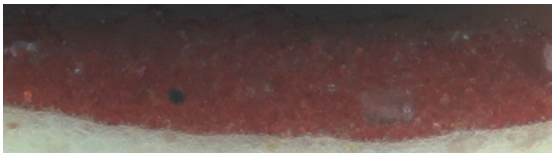
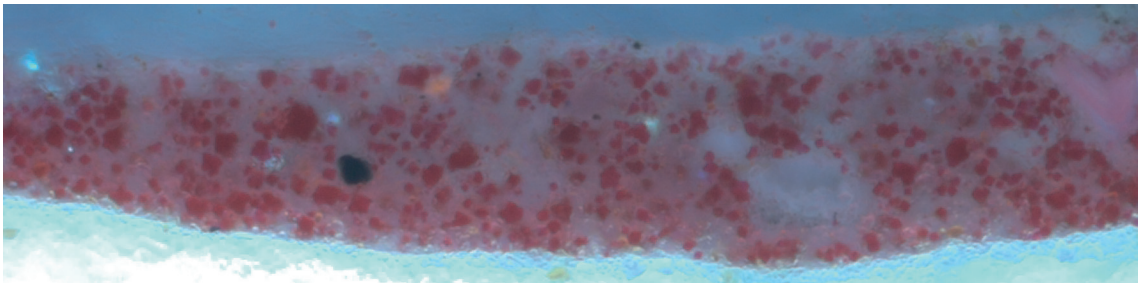


Fig. 3 Microscope magnification: 500x. Bright field illumination

Fig. 4 Microscope magnification: 1000x. UV-fluorescence. Paint cross section of a sample taken from the red painted tacking margin. The red paint contains aluminium/calcium based cochineal lake and little zinc white, lead white, vermilion, barium sulphate and possibly chalk



An important difference is that the calcium/aluminium-based cochineals appear to be much more stable than the tin-based ones. Though this was to be expected on the basis of published literature, it was very clearly demonstrated by the pictures examined.[24] Besides the influence of the tin, it seems likely that the added starch has adversely affected the permanence of the tin-based cochineals. On the pictures, the calcium/aluminium-based cochineals might exhibit slight dulling or darkening of surface colour, but no perceptible fading. The tin-based cochineal lakes however, showed dramatic change. Fading was most marked where the lake had been mixed with lead and/or zinc white, a well known phenomenon. This was the case in violet passages, where the cochineal lake was combined with white, blue and other pigments, to achieve the appropriate hue. Often these faded colours cover substantial areas, as in the backgrounds of *Basket with violets on a stool* (F244) and *Red cabbages and onions* (F374), or in the clothing of *Portrait of Etienne-Lucien Martin* (F289). Some evidence for the original violet shade is given by spots of colour preserved along the edges of the three paintings, which have been covered by paper tape since lining treatment in 1932 (F244) (figs. 5-7) or by the rebate of a frame (F289 and F374) (figs. 15-16). Where exposed, the mixed violet has now altered to an insipid greenish-grey however, due to fading of the tin-based cochineal it contains. Further evidence for fading is given by sample cross sections from the paintings, evident in the uppermost part of the layer. Bearing in mind that the tin-based lakes would originally have provided the brightest colours, this change has had tremendous impact on how the paintings look today.

In *Basket with violets on a stool*, originally the violet background would have formed a strong opponent to the complementary yellow of the flowers, demonstrating the forceful colour contrasts employed by May 1887 when the painting was made. Where used as a pure glaze

Table 1. Results of technical examination, optical microscopy, SEM-EDS, HPLC-PDA and fluorescence analysis

Title **Date** **Sample no**	**Sample spot** **Co-ordinates in cm.** **Description**	**Visible deterioration**	**Microscopic examination** **Incident light**	**UV-fl.?**	**Elements present in substrate**	**HPLC result**	**Mixture with**
Head of an old woman, Antwerp, mid December 1885- mid January 1886. F174/1+2	Sample 174/1, exposed paint; 19.2↓, 0.5←. Sample 174/2 adjacent, underneath tape; 19.2↓, 0←. Background.	The background preserves a dark purplish-grey colour where it has been protected by paper tape covering the edges of the painting since it was lined in 1929. Elsewhere it has faded to a light bluish-grey however. Thick strokes of pure red lake glaze used in the portrait (not sampled) show deep cracks and raised spots, some in the form of open pustules.	Red particles No discoloration observed in the Cs.	No	(Al)/(Ca) [2]	Alizarin[3] Purpurin[4] Brasilein[4]	Zinc white, lead white, chrome orange, ultramarine, chalk, organic brown-black.
Idem F174/3	↑3.7, ←0. Dark, bluish-black dress.	None.	Red-brown particles	No	Al/Sn	Trace Purpurin[4] Brasilein[4]	Zinc white, lead white, chrome orange, ochre. organic brown-black.
Portrait of a woman, March-June 1886. F215c/2	↓0.5,← 0.4 Reddish background.	Darkened.	Fine red particles	No	Sn	Carminic acid	Starch (ø ~ 4 µm), red ochre, vermilion, viridian, ultramarine, lead white, barium sulphate and black particles.
			Coarse red particles	Orange	**Al**, S, (P), (K)	Purpurin[5]	
The hill of Montmartre with a stone quarry, June- mid July 1886. F229/3	→1.3, ↑0. Streak of red paint below the signature.	None.	Red particles	Orange	**Al**, S, K, (P)	Trace Purpurin[4]	Zinc white, viridian, vermilion, possibly ultramarine and lead dryer?[6]
			Fine red particles	No	(Al)/(Ca)	Carminic acid[4]	
Glass with yellow roses, late June-mid July 1886. F218/1 Cs F218/1 and 2	↑12, →0. Taped edge of background. Sample includes both dark underlayer and bright red glaze on top.	The top red glaze in background shows spotting, concentrated in certain areas. The colour is well preserved, except where swept thinly over the light colours of the still-life, where it has become slightly more transparent and brown. Some thick brushstrokes in the vase (not sampled) have turned brown and show marked surface degradation, comparable to F243a.	Large red particles	Orange	**Al**, S, P, (K)	Purpurin[5]	Underlying layer: Vermilion, red ochre, lead white, zinc white, ultramarine, brown pigment, presumably starch grains (ø ~ 15 µm) and possibly Prussian blue. Glaze: zinc dryer?[6]
			Purple particles	Blue	No response	4 purple components = Methyl violet[3]	
			Red (at the edges of the presumed starch grains)	No	Not performed	Brasilein[4]	
						2 unknown yellow components[3]	
Idem F218/4 Cs F218/2	↓6.6, 2.1 →. Background, bright red glaze only.	As for 218/1	Red glaze	Orange	**Al**, S, P, (K)	Purpurin[5]	Zinc dryer?[6]
						Ellagic acid	
Flame nettle in a flowerpot, late June- mid July 1886. F281/3	→13, ↑0.2. Bright red brush stroke at taped edge of table.	'Spotting' of red glazes in the leaves. The colour is well preserved.	Not performed			Purpurin[5-7]	
Carnations, (Stedelijk Museum, Amsterdam) Summer 1886 F245/2 Cs F245/3	←10.4, ↓16.6. Red stroke in flower. (Cs ← 15.9, ↓ 13.5)	None	Large red particles	Orange	**Al**, S, P, (K)	Purpurin[5]	Ultramarine, vermilion, zinc dryer?[6].

Table 1. Results of technical examination, optical microscopy, SEM-EDS, HPLC-PDA and fluorescence analysis

Title **Date** **Sample no**	**Sample spot** **Co-ordinates in cm.** **Description**	**Visible deterioration**	**Microscopic examination**		**Elements present in substrate**	**HPLC result**	**Mixture with**
			Incident light	**UV-fl.?**			
Idem F245/4 Cs F245/1	→33.5, ↑23.2. Red stroke in flower. (Cs →13.8, ↓ 0.2 Top edge of background)	Turned brownish.	Large red particles	Orange	Al, S, P, (K)	Purpurin[5] Brasilein[4]	Red ochre, vermilion, Prussian blue, bone black, presumably starch grains (ø - 15 µm), zinc dryer?[6].
Small bottle with peonies and blue delphiniums, late June - mid July 1886. F243a/4, Cs F243a/2	↑11.2, →0. Red paint stroke in flower. (Cs ↑6.2, →0.7 red paint stroke in table top)	The red stroke has turned brownish. Where thicker touches are applied elsewhere, these have severely degraded to a yellowish crust.	Red particles (many)	No	Sn	Brasilein[4] Type C component[3, 8]	Starch grains (ø - 15 µm)
			Red particles (very few)	Orange	Not identified	Trace Purpurin[4]	
Vase with Chinese asters and gladioli, August-mid September 1886. F234/5 Cs F234/1	↑12.95, →0.2. Dark blackish-red shadow on the table.	The dark glaze exhibits drying cracks, with underlying colours migrating up through them. Sharp stress cracks have also formed in places.	Red particles (few)	Orange	**Al**, P, S, (Na)	Trace of purpurin[4] Unknown red component[4], eosin?	Red ironoxide, ultramarine and black pigment.
Idem F234/6 Cs F234/3	↑40.3, ←0. Ridge of bright red paint at right edge of background.	None	Red glaze	Orange	**Al**, P, S, (K)	Purpurin[5?]	Lead and zinc dryers?[6]
Idem F234/9 Cs F234/8	↑12.1, →0.5. Dark blackish-red shadow on the table.	As for F234/1 & 5.	Not performed			No response	
Vase with gladioli and Chinese asters, August-mid September 1886. F248a/4 Cs F248a/2	↑5.3, ←0. Bright red flower.	None	Red particles	Orange	**Al**, S, P, (K)	Purpurin[4]	Vermilion, zinc and lead dryers?[6]
			Fine dark red particles	No	(Ca) or (Al)/(Ca)	Carminic acid[5] 2 Carminic acid-like components[4]	
Portrait of Agostina Segatori, January-February 1887. F215b/1	←2.5 cm, 0↑. Thin red underlayer for grey dress, extending onto the tacking margin.	The red glaze is well preserved at the sample spot, which is covered by the frame and the dark paint of the costume. There is suspected fading and increased transparency of red lake in the lips and warm flesh tints however (not sampled).	Fine red particles (many)	No	Sn	Carminic acid[5] 2 Carminic acid-like components[4]	Starch grains (ø - 4 µm), barium sulphate, little bone black, clay, blue pigment, possibly little vermilion and zinc and lead dryers?[6]
			Red particles (very few)	Orange	Not identified	Purpurin[4]	
In the café; Agostina Segatori in Le Tambourin, January-February 1887. F370/5 Cs F370/3	→3.7, ↑0.4. Red stroke on dark grey underlayer in tambourine table.	The red paint has turned brownish. Elsewhere, where the red paint is thickly applied, it shows deep cracks with a rough surface that looks pinkish due to fading/and or scattering of light. The paint readily bleeds in mild organic solvents and in water, and has required past consolidation.	Fine red particles In the top half of the c. 25 µm layer the organic red has discoloured.	No	Sn	Carminic acid[5] 2 Carminic acid-like components[5] Carminic acid-like component[3]	Starch grains [9] (ø - 4 µm), little Schweinfurt green, ultramarine, cadmium yellow, vermilion, lead and zinc dryers?[6]. Binding medium: linseed oil .[10]
Dish with citrus fruit, February-March 1887. F338/7 Cs 338/ 2 & 6	↓5.2, →0. End of thin red brush stroke in the background.	The red retains a brighter colour where it has been protected under the frame rebate. Elsewhere it has turned brownish.	Red particles	No	Sn or Sn/Ca	Carminic acid[4]	Lead white, vermilion, ultramarine, barium sulphate and a few starch grains (ø - 4 µm).
Carafe and dish with citrus fruit, February-March 1887. F340/2	↑16, → 5.25. Light orange-red colour in the left orange.	A bright, mixed orange-red colour is preserved at the sample spot. Where the lake is used as a pure red glaze elsewhere, it appears to have faded however (not sampled).	Red particles (many)	Orange	**Al**, S, P	Purpurin[4]	Cadmium yellow, vermilion, cobalt violet and chrome yellow/orange.
			Red particles (few)	No	No response	Trace Carminic acid[4]	

Table 1. Results of technical examination, optical microscopy, SEM-EDS, HPLC-PDA and fluorescence analysis

Title Date Sample no	Sample spot Co-ordinates in cm. Description	Visible deterioration	Microscopic examination Incident light	 UV-fl.?	Elements present in substrate	HPLC result	Mixture with
Boulevard de Clichy, March-April 1887. F292/1	→9.85, ↓0.4. Red paint along edge of composition, possibly transferred from an original coloured frame.	Turned brownish.	Not performed			Carminic acid[5] 2 Carminic acid-like components[5] Purpurin[5]	
Idem F292/2	↑12.1,→ 0. End of a red brush-stroke in the build-ing.	Turned brownish. Very thinly applied.	Not performed			Trace Carminic acid[4]	
Idem F292/3	↑12.26, ←0. End of purple brush stroke in pavement.	None, though very thinly applied.	Not performed			Trace Carminic acid[4]	
Idem F292/4	↑28.9, ←0. End of purple brush stroke in tree.	None, though very thinly applied.	No organic red pigment present			Trace Carminic acid[4] Indigotin[3]	Lead white, zinc white, cobalt violet, possibly little red lead and cobalt blue.
Montmartre; mills and vegetable gardens, March-mid April 1887. F346/2	→20.3, ↑0.1. Dash of thinly applied red paint below red post in the foreground, underneath tape.	A bright red colour is preserved under the taped edges of the painting, which has faded within the main pic-ture area however. Mixed purple strokes have become bluer where they are not covered by the frame.	Not performed			Carminic acid[5]	
Impasse des deux frères and Moulin de Poivre, March-mid April 1887. F347/2	↑0, ←6.9. Light pink stroke in the foreground sand path.	No deterioration is evident at the sample spot. However, a non-fluorescent organic red pigment (not sampled), used in more concentrated form in the fig-ures and small mill, has faded significantly and turned brown.	Red particles	Orange	**Al,** S, P, (K)	Purpurin[4]	Few black and red particles and zinc dryer?[e].
Portrait of Léonie Rose Charbuy-Davy, March-April 1887. F369/2	→20, ↓13.2. Thick red paint stroke in her hair.	Where thinly applied, the organic red paint has faded and turned brownish.	Red glaze	Orange	**Al,** P, (S)	Purpurin[4] Two unknown red components[4]	Little ultramarine, viridian and Schweinfurt green, lead and zinc dryers?[e].
Self-portrait, March-June 1887. F356/2	→28.5, ↑0. From deep brown-purple stroke pre-served under the frame at the top edge of the background.	A photograph of c. 1905 shows that the background was originally laid in with a very thin, sketchy layer. This is still evident along the edges of the picture, under the frame, where it retains a brownish-purple colour. Since this date, the thin layer has severely faded within the main picture area however, becoming virtu-ally transparent. Some thicker brushstrokes of more concentrated lake (not sampled) retain a crimson colour in the costume and portrait, showing bright orange fluorescence in contrast to the non-fluorescent, faded background layer.	Not performed			Trace Carminic acid[4] Trace Purpurin[4]	
Basket of violets on a stool, May 1887. F244/1	→19.3, ↑0.1. Taped edge of back-ground.	The background paint retains a deep purple colour where it has been protected by paper tape covering the edges of the painting since 1932. Elsewhere it has faded to a light bluish-grey however.	Red particles. Discoloration of the organic red visible in the uppermost c. 20 µm of the c. 100 µm thick layer.	No	Sn	Carminic acid[4] Purpurin[4] Unknown red component[4]	Schweinfurt green, ultramarine, vermilion, lead white, zinc white and barium sulphate and a few starch grains (ø - 5 µm and ø - 10 µm)
Idem F244/3	↑14.25,←0. Idem	As for 244/1	Red particles	No	Sn	Carminic acid[5] Purpurin[4] 2 Carminic acid-like components[4]	Schweinfurt green, ultramarine, vermilion, lead white, zinc white, barium sulphate and starch grains (ø - 5 µm and ø - 10 µm).

Table 1. Results of technical examination, optical microscopy, SEM-EDS, HPLC-PDA and fluorescence analysis

Title **Date** **Sample no**	**Sample spot** **Co-ordinates in cm.** **Description**	**Visible deterioration**	**Microscopic examination** **Incident light**	**UV-fl.?**	**Elements present in substrate**	**HPLC result**	**Mixture with**
Courting couples in a park in Asnières, mid-late May 1887. F314/2	→33.4 , ↑ 12.5. Red brush stroke in the lady's skirt.	None	Not performed			Carminic acid[5] Carminic acid-like component[5] Purpurin[5] 2 Carminic acid-like components[4] Unknown red component[4]	
Along the Seine, May-June 1887. F299/3	→28.7,↑0.7. Foreground, light pink brush stroke.	Where organic red pigment has been used in concentrated form in the picture, it has faded and become more transparent.	Not performed			Trace Carminic acid[4] Purpurin[4]	
The bridge of Courbevoie, June-July 1887. F304/2	→23.5, ↑11.6. Red stroke in arm of left figure in the boat.	Brittle and cracked paint, with rough surface that looks whitish due to fading and/or scattering of light.	Not performed			Carminic acid[5] 2 Carminic acid-like components[4]	
Woodland view, May-July 1887. F307/3	→19.5, ↑0. Red brush stroke in foreground, over blue.	None	Not performed			Trace Purpurin[4]	
Woodland view, May-July 1887. F309a/2	→49.8, ↑0. Dab of red paint in foreground, over blue.	Cracked, with matt surface.	Not performed			Carminic acid[5] 3 Carminic acid-like components[4] Purpurin[4]	
Undergrowth, July 1887. F308/15	↑21.2, ←0. Dark red brush stroke run over onto unprimed edge of canvas. Very small sample.	None	Not performed			Trace Carminic acid[4]	
Kingfisher at the waters edge, July-August 1887. F28/0	Pre-existing flake from red painted tacking margin. Exact spot unknown.	Dulling of surface colour, evident where brighter colour has been preserved under former tack heads. Possible slight increase in transparency of thinly applied paint.	Fine red particles	No	Al/Ca[3]	Carminic acid[5] 2 Carminic acid-like components[5, 11] 2 Carminic acid-like components[3]	Little zinc white, lead white, vermilion, barium sulphate and possibly chalk.
Self portrait, mid July-August 1887. F77v-1	↓7.8 , →0.3. Background, wet-in-wet mixture of bright red and blue.	Localised wide cracks, often in circular formation, with some flaking loss.	Not performed			Carminic acid[5] 2 Carminic acid-like components[5] Purpurin[4]	
Montmartre; behind Moulin de la Galette, August- mid September 1887. F316/1	↓45, →0.1. End of thin red brush stroke in the foliage that was once covered by paper tape.	Browned.	Fine red particles (many)	No	Sn/Ca	Carminic acid[5] 2 Carminic acid-like components[4] Carminic acid-like component[3]	Starch grains (ø - 4 µm), little vermilion, chrome orange and lead dryer?[6].
			Red particles (few)	Orange	**Al,** S, (P)	Purpurin[4]	
Idem F316/4	↑11.1, ←0.3. Deep pinkish-red brush stroke at taped edge of fence.	Spotted appearance. No obvious colour change.	Red glaze	Orange	**Al,** S, P, (K), (Na)	Purpurin[1, 7]	Little cobalt blue, cerulean blue and lead dryer?[6]. Binding medium: linseed or walnut oil and possibly animal glue[10]
Two dried sunflowers, mid August- mid September 1887. F377/3	→12.8, ↓ 5.5. Red stroke on yellow sunflower.	Dulling of surface colour noted during sampling.	Not performed			Carminic acid[5] Trace Purpurin[4]	

Table 1. Results of technical examination, optical microscopy, SEM-EDS, HPLC-PDA and fluorescence analysis

Title **Date** **Sample no**	**Sample spot** **Co-ordinates in cm.** **Description**	**Visible deterioration**	**Microscopic examination** **Incident light**	**UV-fl.?**	**Elements present in substrate**	**HPLC result**	**Mixture with**
Self portrait, August-September 1887. F469/3	→78, ↑0.5. End of purple stroke in costume at the bottom edge, under the frame, where a brownish-purple colour is preserved.	A photograph of c. 1908 shows that the background was laid in with a very thin, sketchy layer, with more solid strokes detailing folds in the artist's smock too. Since that date, the mixed purple paint has severely faded however, becoming totally transparent in the background area. Some more concentrated strokes of a bright crimson lake that fluoresce orange in UV light, were used in the portrait (not sampled). These have faded and become more transparent. There are transferred remnants of chrome yellow paint from an original frame painted by the artist, which would have provided complementary contrast to the purple background and smock.				No response	
Self portrait, September-October 1887. F524/4	→23.5, ↑21.3. Red stem of pipe.	The red paint looks brittle, with fine cracks traversing some thicker strokes. Damage reveals that the colour has darkened at the surface.	Red particles (many) Red particles (very few)	No Orange	Sn **Al,** P, possibly S and K (obscured by other peaks)	No response	Starch grains (ø - 5 µm), vermilion, little barium sulphate, one particle Schweinfurt green and lead dryer?[6].
Quinces, lemons, pears and grapes, September-October 1887. F383/1	→2.6, ↓30.4. Transparent red stroke on light blue one in the table.	None	Not performed			Carminic acid[5]	
Grapes, September-October 1887. F603/2 , Cs F603/1	↓14.8, →0.1. Red stalk of grapes, underneath tape.	There is some evidence for fading of the pink grapes at bottom edge, since a brighter colour is preserved under the paper tape applied in 1932.	Red glaze	Orange	**Al,** S, (K)	Purpurin[5] Unknown red component[4]	Little Schweinfurt green
Self portrait, September-October 1887. F344/2	←5.2, ↓0. Purple brush stroke in background continuing over tacking margin.	A purple hue is preserved where blue strokes around the edges of the painting have been shielded from light by the frame rebate. A colour transparency of the painting made in 1978 shows an even deeper purple colour preserved at the edges. Removal of a small filling that overlapped original paint, applied during treatment in 1978, revealed a brighter purple colour underneath it. This suggests that the background has continued to fade since this date. Thicker strokes of concentrated red lake show deep cracks with a fogged surface, due to fading and/or scattering of light.	Not performed			Carminic acid[5] 2 Carminic acid-like components[4]	
The flowering plum tree (after Hiroshige), October-November 1887. F371/3	→18.75,↓16.15. Bright crimson-red stroke in branch of tree.	Thinly glazed red and purple paint areas show increased transparency. Thicker areas of red lake show a dense network of deep cracks with cupping. A brighter colour is evident in the depth of cracks viewed with the stereo-microscope.	Not performed			Carminic acid[5] 2 Carminic acid-like components[4] Carminic acid-like component[3]	
The bridge in the rain (after Hiroshige), October-November 1887. F372/3	→1.7 , ↑2.5. Overlap of warm red on green borders to the composition.	None	Not performed			Carminic acid[5] Carminic acid-like component[4] Purpurin[5]	
The courtesan (after Eisen), October-November 1887. F373/1	→10.9, ↓0. End of red brush-stroke on painted border.	Red lake paint areas appear brittle, with a cracked and sometimes cupped surface, which looks foggy due to fading and/or scattering of light.	Fine red particles Red particles (few)	No orange	Sn/Ca **Al,** S	Carminic acid[5] Unknown orange-red component[3] Two unknown red components[3] Unknown red component[4]	Starch grains (ø - 5 µm), little vermilion, Schweinfurt green and lead dryer?[6].

Table 1. Results of technical examination, optical microscopy, SEM-EDS, HPLC-PDA and fluorescence analysis

Title **Date** **Sample no**	**Sample spot** **Co-ordinates in cm.** **Description**	**Visible deterioration**	**Microscopic examination** **Incident light**	**UV-fl.?**	**Elements present in substrate**	**HPLC result**	**Mixture with**
Red cabbages and onions, November 1887-February 1888. F374/9	↓6.5, →0. Edge of background.	At the sample spot the background retains a light purple colour, where it has been shielded from light. Elsewhere the colour is changed to light blue due to fading of the red lake ingredient.	Fine purplish red particles	No	Sn/Al	Carminic acid[5]	Lead white, cobalt blue, little viridian and a few starch grains (ø - 4 µm)
Study for 'Romans Parisiens', October-November 1887. F358/1	From glaze in shadow of tablecloth at bottom edge, exact co-ordinates unknown	Areas of pure crimson glaze for the shadows in the tablecloth have patchily faded. A brighter colour is kept towards the bottom edge, especially where the lower border has been covered by paper tape since 1932. Mixed light pink strokes in the tablecloth (not sampled) retain a brighter colour where they have been protected under the right frame rebate. Neither paint fluoresces in UV light.				Trace Carminic acid[4]	
Idem F358/4 Cs F358/5	↑0.3, ←1.5. Bright crimson colour preserved under paper tape covering the bottom edge.	As for F358/1	Not performed			Carminic acid[4] Purpurin[4]	
Portrait of Etienne-Lucien Martin, November 1887. F289/1 Cs F289/2	→ 23.7, ↑0. Edge of jacket.	The jacket retains a warm purple colour at the sample spot, which has been shielded from light by the frame rebate. Elsewhere it has changed to a light bluish-grey, due to fading of the red lake ingredient.	Red particles Discoloration of the organic red visible in the uppermost c. 15 µm of the c. 120 µm thick layer.	No	Sn	Carminic acid[5] Trace Purpurin[4] Indigotin[3]	Lead white, zinc white, ultramarine, little clay, Schweinfurt green, vermilion, orange ochre and starch grains (ø - 5 µm).
Self portrait as a painter, December 1887- February 1888. F522/6	→19.4, ↑8.5. Transparent red colour on his palette.	The samples patch of red lake shows deep cracks with a fogged surface, due to fading and/or scattering of light.	Red particles The organic red has discoloured in the uppermost c. 20 µm of the c. 75 µm thick layer.	No	Sn	Carminic acid[5] 2 Carminic acid-like components[5] Carminic acid-like component[3] Kermesic acid[4]	Starch grains (ø - 5 µm) and little vermilion.

The samples are numbered in sequence, using F. nos. that refer to the identifying number of the painting listed in the oeuvre catalogue of J.-B. de la Faille, *The works of Vincent van Gogh; his paintings and drawings* (Amsterdam, 1970, first edition 1928). Cs = nos. of paint cross-sections made. Given titles and dates of works follow those published in L. van Tilborgh and E. Hendriks, *Vincent van Gogh, Paintings, Antwerp and Paris 1885-1888*, volume 2, Van Gogh Museum (Amsterdam and Zwolle, 2005).

1. Elements identified with SEM-EDS, **X** = main component, X = minor component, (X) = trace component
2. The low signal of calcium found can also be attributed to the presumed presence of chalk
3. Detected by PDA only
4. Detected by fluorescence detection only
5. Detected by both PDA and fluorescence detection
6. Small amounts of lead and/or zinc have been identified in the layer with SEM-EDS, but no separate lead- or zinc-containing pigment particles could be observed under the microscope (see text).
7. The purpurin peak had a fronting peak shape, see discussion
8. This (UV absorbing) component is a typical minor component for redwoods (see redwood section)
9. The presence of starch in the paint layer was confirmed by FTIR-analysis
10. The linseed or walnut oil was identified by GCMS-analysis and the animal glue by HPLC-analysis. The presence of animal glue in the sample is perhaps a contamination since the sample spot has been covered by paper tape.
11. Carminic acid-like components are components with similar UV-VIS spectra as carminic acid but eluting at different retention times. These components are typical for the *Dactolopius coccus* species and indicates a natural source for the organic pigment

Fig. 5 Vincent van Gogh, *Basket with pansies on a stool*, F244, May 1887, oil on canvas, 46.0 x 55.0 cm, Van Gogh Museum (Vincent van Gogh Foundation) Amsterdam

Fig. 6 Detail of fig. 5 where paper tape covering the bottom edge of the painting since 1932 is removed, revealing a strip of violet preserved underneath

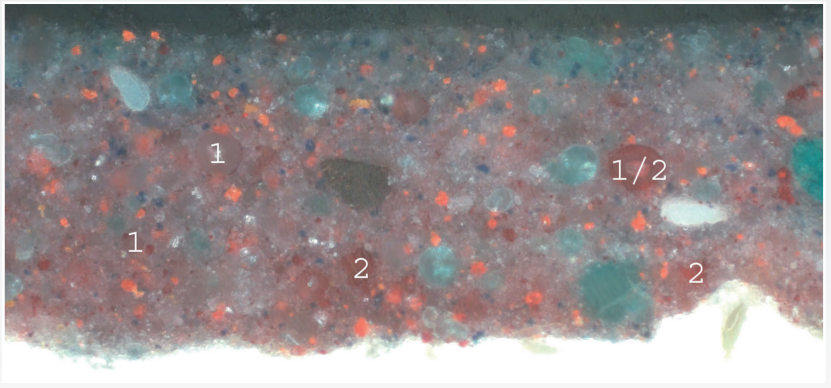


Fig. 7 Paint cross section of a sample taken from the purple background that was covered by tape, showing the fading of the tin-cochineal lake before application of the tape in 1932. The c. 100 µm layer contains Schweinfurt green, ultramarine, vermilion, lead white, zinc white, barium sulphate and starch grains (examples indicated by 1) in addition to the lake (examples indicated by 2).
Microscope magnification: 500x.
Bright field illumination

in the violet petals, the lake has also faded and become more transparent, revealing part of an exuberant underdrawing for the still life. In the later *Red cabbages and onions* (F374), the original saturated purple would have asserted itself against the complementary yellow part of the background, as well as yellow streaks of colour in the still life, contributing to the highly stylised, planar design of the picture. HPLC of a sample from the slightly earlier *Self-portrait* (F344), has identified the use of cochineal in the deep blue background and clothing, discoloured from a violet colour that is still evident around the edges of the painting. Again the dramatic colour shift points to the use of the highly fugitive, tin-based and starch-containing variety of cochineal, though the substrate has not been confirmed.

In the paintings examined, the tin-based cochineal with starch has also been used as a pure (rather than mixed) colour, as confirmed by the virtual absence of other inorganic pigments present in sample cross sections. In *The Courtesan (after Eisen)* (F373), the characteristically dense yet fluid body of the starch-containing paint left raised tracks along the periphery of textured brush strokes, translating the flat example of the Japanese

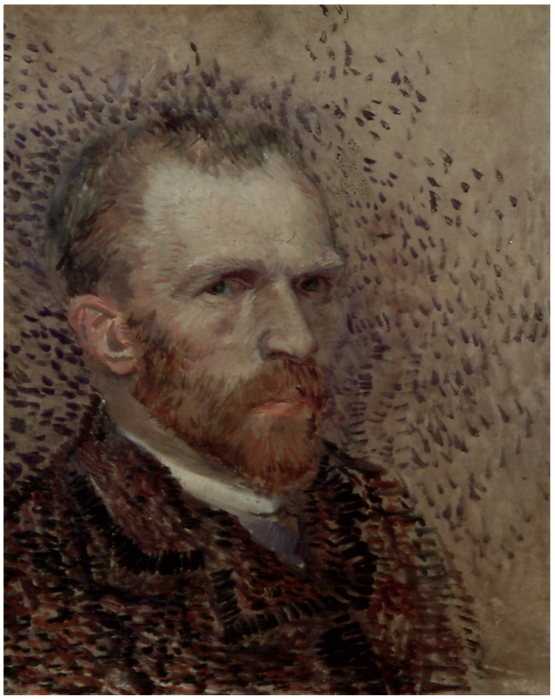


Fig. 8 Vincent van Gogh, *Self-portrait*, F356, March-June 1887, oil on carton, 41.0 x 33.0 cm, Van Gogh Museum (Vincent van Gogh Foundation) Amsterdam. Compare the faced cochineal glaze in the background to how the painting looked around 1905 (see fig. 9)

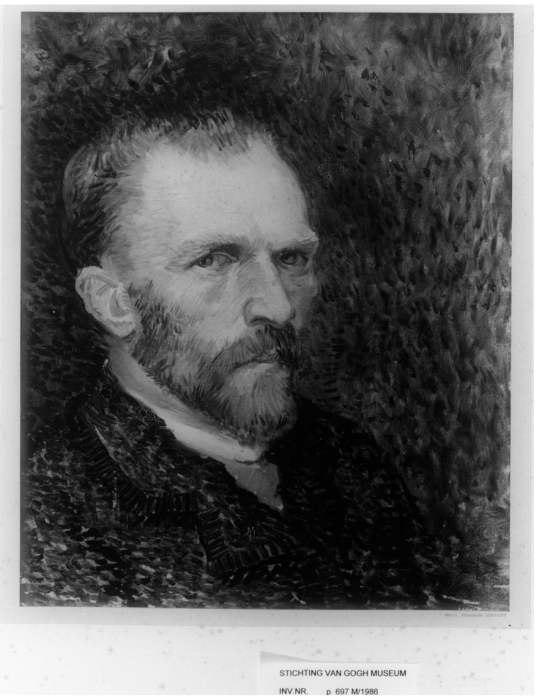


Fig. 9 Black-and-white photograph, c. 1905, Vincent van Gogh, *Self-portrait*, F356, March-June 1887, oil on carton, 41.0 x 33.0 cm, Van Gogh Museum (Vincent van Gogh Foundation) Amsterdam. Compare to the current appearance of the painting after substantial fading of the background (fig. 8)

print into the painterly qualities of the artist's copy (fig. 10). These same working properties of the paint were exploited for fine relieved outlines of features made with a pointed brush, as in *In the café; Agostina Segatori in Le Tambourin* (F370), and *Self portrait as a painter* (F522) for example (figs. 11-12). The patch of organic red paint depicted on the palette in the latter work was also shown to consist of the same tin-cochineal pigment, though Van Gogh did not mention it as one of the colours he used for this portrait (figs. 13-14).[25] In all these examples, the cochineal lake has now faded to a pinkish colour, though the original saturated crimson hue may still be witnessed in cracks viewed with the stereo-microscope. Besides fading, 'fogging' caused by scattering of light from the roughened paint surface, also seems to contribute to the evident loss of colour. Often deep cracks may have formed, with possible cupping and crumbling of paint. Characteristically the colour has required repeated consolidation, with the complication that it has proven to be readily affected by mild organic solvents and even water.[26] In fact the signs of physical degradation are so characteristic, that one may assert that the cochineal used in *The bridge of Courbevoie* (F304) and in *The flowering plum tree (after Hiroshige)* (F372) is likely to be of the same tin-based and starch-containing type, though limited sample material meant that no microscopy and SEM-EDS could be performed to confirm this fact.

In pictures where the tin-cochineal was glazed more thinly over a pale surface, it may even have faded to the extent that it is no longer visible. One striking example seems to be *Study for 'Romans Parisiens'* (F358), though the lake substrate not been confirmed by analysis. In this picture, the bright crimson colour of the cochineal glaze, applied directly on the light ground, is still evident towards the bottom edge of the painting that has been taped over since it was lined in 1932. The glaze has patchily faded in the tablecloth however, disrupting the more solid planes of colour intended. Originally the still life would have been more in keeping with the flat decorative style of painting that Vincent's direct colleagues, Emile Bernard and Louis Anquetin were developing at

Organic pigment	sample	Ratio mixtures
Cochineal	F28/0	
	F292/2	
	F292/3	
	F292/4	
	F304/2	
	F308/15	
	F338/7	
	F344/2	
	F346/2	
	F358/1	
	F370/5	
	F371/3	
	F374/9	
	F383/1	
	F522/6	
Kopp's purpurin	F218/4	
	F234/6	
	F245/2	
	F281/3	
	F307/3	
	F316/4	
	F347/2	
	F369/2	
Cochineal and Kopp's purpurin	F77/1	C ▸▸ P
	F215b/1	C ▸ P
	F215c/2	C ≈ P
	F229/3	C ≈ P
	F244/1	C ◂ P
	F244/3	C ▸ P
	F248a/4	C ▸▸ P
	F289/1	C ▸▸ P
	F292/1	C ▸▸ P
	F299/3	C ≈ P
	F309a/2	C ▸ P
	F314/2	C ▸▸ P
	F316/1	C ▸▸ P
	F340/2	C ◂ P
	F356/2	C ≈ P
	F358/4	C ▸ P
	F372/3	C ▸ P
	F377/3	C ▸ P
Madder and redwood	F174/1+2	M ≈ R
	F174/3	
Kopp's purpurin and redwood	F218/1	P ≈ R
	F243a/4	P ≈ R
	F245/4	P ▸ R
Kopp's purpurin and unknown(s)	F234/5	P ≈ U
	F603/2	P ▸▸ A
Cochineal and unknowns	F373/1	C ≈ U
No response	F234/8+9	
	F468/3	
	F524/4	

Table 2 Overview of the HPLC-PDA-Fluorescence results showing the relative ratios of mixtures organic pigments. C = cochineal, P = purpurin, M = madder, R = redwood, U = unknown. (ratio more or less the same, C > P, more cochineal then purpurin, C >> P much more cochineal then purpurin. C < P less cochineal then purpurin, C << P much less cochineal then purpurin.

Colorant	Substrate	Fluorescence	Sample
Cochineal	Sn	No	F215c/2
			F215b/1
			F370/5
			F338/7
			F244/1
			F244/3
			F289/1
			F522/6
	Sn/Ca	No	F316/1
			F373/1
	Al/Ca	No	F229/3
			F248a/4
			F28/0
	Al/Sn	No	F374/9
Madder	Al/Ca	No	F174/1+2
Kopp's Purpurin	Al, S, P, K	Orange	F215c/2
			F229/3
			F234a/4
			F218/1
			F218/4
			F245/3
			F234/5
			F234/6
			F248a/4
			F347/2
			F340/2
			F369/2
			F316/1
			F316/4
			F603/2
Redwood	Al/Sn	No	F174/3
	Sn	no	F234a/4
Methylviolet	No response	Blue	F218/1

Table 3 Overview of the substrates found for each organic pigment.

Time (min)	%A (10 % methanol/water, v/v)	%B (100 % Methanol)	%C (5 % Phosphoric acid ,w/v)
0	74	16	10
15	0	90	10
20	0	90	10
23	0	100	0
27	0	100	0
30	74	16	10
45	74	16	10

Table 4 HPLC gradient, all changes are linear.

the time (that later became known as *Cloisonism*). Two self-portraits on light primed *carton* (F344 and F356) also provide examples where the thin, cochineal-based glazes in the background areas have faded to an extreme degree. Black-and-white photographs of the portraits from the first decade of the twentieth century give some idea of how the backgrounds looked earlier on, comprehensively blocked in with a thin, sketchy layer (figs. 8-9). Except under the frame rebates, the mixed purple glazes are almost entirely faded now however, exposing the light primed surfaces of the *carton* supports throughout the background areas. Consequently, scattered brushstrokes on top of the glaze that retain a blue colour seem to 'float' on the pale grounds. The resultant loose sketchy patterning of the background lends the portraits an unintended, almost unfinished look today. Examination of *Self portrait* (F524) also revealed remnants of chrome yellow paint, thought to have been transferred to the edges of the painting from the rebate of an original frame painted by the artist. Together with the straw hat, the yellow frame would have provided a striking contrast to the complementary purple of the background and the artist's smock.

The observed impermanence of the tin-cochineal lakes in Van Gogh's paintings, entirely agrees with nineteenth-century expectation. In his 'Chromatography' treatise of 1835, George Field remarked that cochineal lakes were impermanent in tint with lead white and 'in glazing are soon discoloured and destroyed by the action of light'. In the 1869 edition of the treatise revised by Thomas W. Salter however, it was suggested that 'when well-made, pure, employed alone and in body', cochineals might retain their colour for some years.[27] Although unclear whether the cochineal lakes referred to by these authors are the same tin-starch variety of cochineal lake employed by Van Gogh at a rather later date, these observations on how the way the paint is applied affects the permanence of the colour do agree with what we see on his paintings today. Often the impact of fading in areas of pure tin-cochineal has been mitigated by the thickness of the paint layer. From his letters it emerges that Van Gogh considered a solid application of paint without added oil necessary to provide lasting colour, so this may have been a conscious feature of his technique.[28] Equally however, the inherent body of the starch-containing paint must intuitively have appealed to van Gogh, who utilised impasto brushwork as an inevitable feature of his style.

• *Madder and Kopp's purpurin*

Madder (*Rubia tinctorum* L.) is a well known source for textile dyeing and as organic colorant in red organic pigments. It was already used by the Egyptians, the Greeks and the Romans and was distributed throughout Europe, North Africa and parts of Asia. In Europe, madder was cultivated on a large scale until it was finally replaced by the synthetic dyes at the end of the 19th century. The roots of the plant were used to provide the colorant. The amount of dyestuff extracted depended upon the age of the plant. In Holland, where madder was cultivated on a large scale, the dyestuffs were usually extracted from three year old plants. However, allowing the plant to grow for as long as eight years, as was done in the Orient, increased the amount of colorant and therefore the quality of the dye.[29]

The main colorants present in madder are alizarin and pseudo purpurin. However, when pre-treating a sample in preparation for HPLC analysis (hydrochloric acid extraction), the pseudo purpurin is converted into purpurin. Other analytical procedures are required to extract pseudo purpurin from the sample without this conversion taking place. The ratio of alizarin to purpurin may vary somewhat, depending upon the exact species and age of the plant, where it was grown and the methods used for extracting the dyestuffs from the raw material. However, alizarin is usually found in abundance when *Rubia tinctorum* L. was used. Only one of the samples investigated, taken from the painting *Head of an old woman* (F172/1+2), contained alizarin and purpurin in a ratio which indicates the use of madder. This is also the only picture with red lake analysed that dates from Vincent's stay in Antwerp, before he moved on to the French capital. Since the madder was found together with brasilein, it will be discussed under the section Redwood.

In 31 of the 52 samples analysed using HPLC, purpurin but no alizarin was found. For the cases where the purpurin was only picked up by the fluorescence detector (but not by PDA), one needs to take the much higher detection limit for alizarin into account. Under the HPLC conditions used, purpurin would show a strong fluorescence whereas alizarin would not, making it possible to miss the alizarin component. However, in 12 samples taken from 10 different paintings, purpurin was detected by PDA in addition to fluorescence, indicating without a doubt that purpurin was the main organic colorant in the pigment. Based on the high purpurin content and the absence of alizarin, the red lake was

Fig. 10 Detail of the toad depicted in Vincent van Gogh, *The Courtesan (after Eisen),* F373, October-November 1887, oil on canvas, 100.7 x 60.7 cm, Van Gogh Museum (Vincent van Gogh Foundation) Amsterdam. The red tin-cochineal paint shows characteristic degradation, with pronounced cracks, fading and a blanched surface

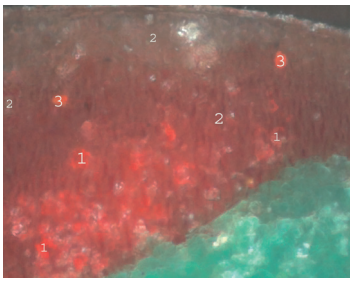


Fig. 13 Paint cross section of a sample taken from the tin-cochineal lake on top of emerald green paint on the palette. Fading of the tin-cochineal lake is clearly visible in the top part of the layer (examples of lake particles are indicated by 1), which contains starch grains (examples indicated by 2) and little vermilion (3) in addition.
Microscope magnification: 500x. Bright field illumination

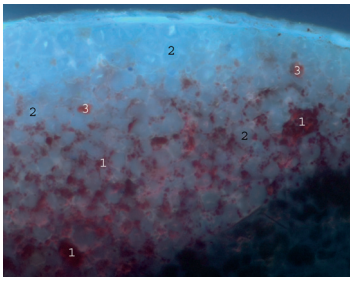


Fig. 14 Microscope magnification: 1000x. UV-fluorescence

Fig. 11 Vincent van Gogh, *Self-portrait as a painter*, F522, December 1887-February 1888, oil on canvas, 65.0 x 50.0 cm, Van Gogh Museum (Vincent van Gogh Foundation) Amsterdam

v

clearly not a madder, which would contain an abundance of alizarin. Instead it is thought that Kopp's purpurin could be present, a red lake that possesses fifty to fifty-five times the tinting strength of madder.[30]

As for madder, the madder root was used for the preparation of Kopp's purpurin. However, rather than dissolving the colorants in warm water, they were extracted over a period of a day using dilute sulphurous acid. Next the solution was filtered, and concentrated sulphuric acid was added in a ratio of 2% by volume. Subsequently the solution was heated to 55 °C, so that precipitation occurred. The precipitate was filtered and washed with water, until sulphuric acid was no longer detected in the filtrate. Next, the precipitate was treated with an alum solution at 70° C until the precipitates dissolve. The organic pigment was obtained by neutralisation with a solution of potassium or calcium carbonate.[31] There are several other recipes known where Kopp's purpurin is prepared in a similar way. As a result, the pigment mainly contains pseudo purpurin. Aluminium was identified as the main element in the Kopp's purpurin lake pigment, with sulphur, phosphorus and potassium present in addition (fig. 17). In general, the EDS-peak for sulphur was higher than the peaks for phosphorus and potassium. The same four elements were recently identified in a similar Kopp's purpurin lake paint used by Odilon Redon [32] and a high sulphur content was identified in a number of Kopp's purpurin lakes found in Georges Seurat's paintings.[33] The sulphur is presumably part of the substrate; its presence might

Fig. 12 Detail of fig. 11 showing fine red contours around the artist's hand and palette dippers, made with a tin-cochineal lake

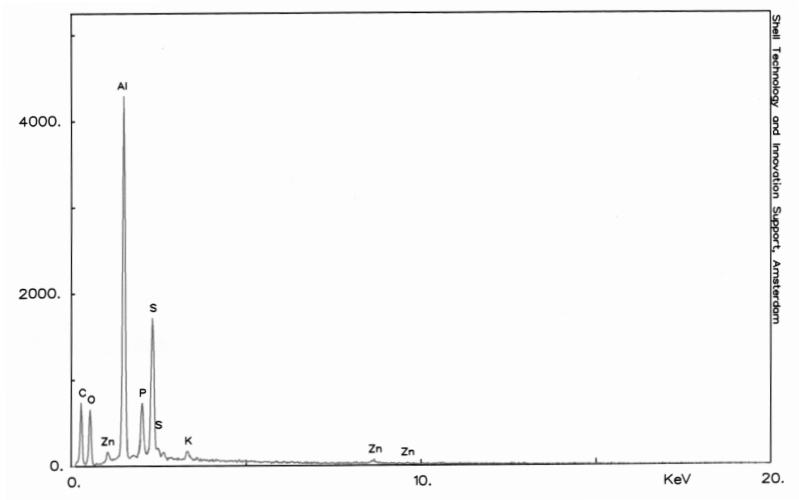


Fig. 15 Vincent van Gogh, *Red cabbages and onions*, F374, November 1887-February 1888, oil on canvas, 50.0 x 64.3 cm, Van Gogh Museum (Vincent van Gogh Foundation) Amsterdam

Fig. 16 Detail of fig. 15, revealing a strip of violet preserved down the right edge where it has been shielded by the frame rebate

Fig. 17 Typical EDS-spectrum for the Kopp's purpurin lake pigment. Aluminium, phosphorus, sulphur and potassium are presumably part of the substrate of the lake. The presence of zinc possibly indicates the addition of a zinc drier to the paint

be explained by incomplete reaction of potash alum (aluminium potassium sulphate) with alkali during preparation of the red lake pigment.[34] This would result in a substrate containing basic aluminium sulphate, which was known for its better filtering and washing properties compared to hydrated alumina.[35] The high phosphorus content in the Kopp's purpurin lake might be explained by the precipitation of the lake pigment with phosphate rather than carbonate.[36]

Kopp's purpurin was observed in 19 of the 30 paint cross sections examined, evident as translucent red particles that are often quite large, or alternatively, as a continuous red glaze layer. In all cases the Kopp's purpurin pigment shows a strong orange fluorescence under UV-light in paint cross sections. This readily distinguishes it from the other types of organic red that Van Gogh used in Paris, since none of these fluoresce. Kopp's Purpurin lake was also observed to fluoresce bright orange on the paintings themselves, when used as a pure glaze (F218, F 234, F281, F316 and F369).[37] The pattern of orange fluorescence clarified the careful later addition of a red glaze around the still life *Glass with yellow roses* (F218), skirting slightly over it in places, as well as final touches added to detail petals and accentuate the silhouette of the bouquet in *Carnations* (F245, Stedelijk Museum, Amsterdam) for example. Van Gogh's exploitation of the intense hue of Kopp's purpurin glazes to create the warm-toned backgrounds in these floral still lifes is though to imitate a similar effect in flower-pieces by the recently deceased painter, Adolphe Joseph Monticelli (1824-1886), whose work Van Gogh greatly admired.[38]

In some instances the characteristic fluorescence of Kopp's purpurin was a useful feature to help distinguish between various types of red lake used for different parts

of the same painting, as in *Montmartre; behind the Moulin Galette* (F316). Here the bright orange fluorescence of the Kopp's purpurin lake present in thick pinkish-red brushstrokes in the foreground fences (sample 316/4) contrasts the non-fluorescent lake used in translucent brownish-red strokes in the willowy foliage and tufted vegetation that were shown to contain chiefly cochineal (sample 316/1). However it should be noted that fluorescence of the Kopp's purpurin pigment might be quenched when it is incorporated in a light (F 347/2) or dark (F 234/5) paint mixture, or combined with other types of red lake (redwood or cochineal). Hence the absence of fluorescence on a painting need not imply that Kopp's Purpurin was not used.

Van Gogh seems to have used the aluminium-based Kopp's purpurin lake throughout his stay in Paris, since it was found in paintings that date from the spring of 1886 to autumn 1887. However, only eight of these paintings showed the use of Kopp's purpurin lake alone. In eighteen paintings it was mixed with cochineal that was usually present as the major ingredient, and in three paintings with redwood, as discussed under the appropriate sections. When used pure the Kopp's purpurin lake has generally proven to be relatively stable, agreeing with the fact that, contrary to purpurin lakes, pseudo-purpurin lakes are known to be very lightfast.[39] There was no evidence for fading of the pure Kopp's purpurin lake in any of the relevant paint cross sections and only limited signs of degradation on the paintings examined, depending on how it had been applied. Generally, where the lake was thickly applied as a pure glaze, it has kept its colour well. Striking examples are the flame patterning of the leaves in *Flame nettle in a flowerpot* (F281), or the liquid touches detailing petals in *Carnations* (F245). In *Glass with yellow roses* (F218) the good preservation of the Kopp's purpurin glaze across the background may be attributed to its solid application, but also to the fact that it lies on top of a blackish layer that offered low light reflectance (fig. 18). Where the glaze was swept out more thinly however, slightly overlapping the lighter colours of the still life, there is some evidence that its colour has browned and become more transparent. A similar effect is evident in a picture made in the spring of 1887, at which time Van Gogh adopted a thinner painting technique reminiscent of watercolour, applying thin washes and graphic touches of colour on luminous pale grounds. One example is the red strokes of Kopp's purpurin used for the hair of *Leonie Rose Charbuy-Davy* (F369), which show brown discolouration and fading in the thinnest parts. Another characteristic feature of the Kopp's purpurin applied as a glaze, was its spotted structure, witnessed in three of the paintings examined (F218, F281 and F316) (fig. 19). Stereomicroscopy revealed agglomerations of brighter red discs of colour, distributed in an amorphous pattern that seemed independent of the structure of underlying paint layers. So far this effect seems peculiar to Kopp's purpurin and was not witnessed for the other types of red lake examined.

- *Redwood*

Brasilein was identified in four of the paintings investigated. In *Bottle with peonies and blue delphiniums* (F243a) it was found together with a UV-absorbing component, which we will label as 'Type C' in keeping with the results of Nowik's thorough investigation of the soluble blue and redwoods.[40] Type C is typical for redwood species, but has no impact on the overall colour of the lake. Interestingly, it is much more stable to light than brasilein. Hence in historical samples that have severely faded, the type C component can still be found whereas the brasilein has completely vanished.[41] Both brasilein and the Type C component indicate a dye from a redwood species was used in the organic pigment. Redwood species are among the most frequently used red organic colorants, together with insect species and madder.[42] Redwoods are not native to Europe, but were imported from Asia since the middle ages and from Central America straight after it was discovered. There are several species of different origin. The two most common species were *Caesalpina sappan* L (also known as sappanwood) that was derived from the Far East, and *Caesalpina Brasiliensis* L. (otherwise known as Brazilwood), which is native to Brazil. The amount of dyestuff in Brazilwood is usually lower than in sappanwood. Redwood was imported as large blocks that were then cut into smaller pieces (usually by prison inmates). The main component to be extracted from the wood pieces is the colourless brasilin. Subsequently brasilin is oxidised to brasilein, the actual colouring matter. Redwoods were frequently used for textile dyeing, though their relatively poor light-fastness was known.

Three of the four pictures in which redwood was identified were floral still lifes painted in the summer of 1886, as exercises in the use of bright and opposing colours (F218, F243a and F245). Redwood was a particularly cheap type of organic red, often added as an adulterant to reduce the cost of manufacturing other types of lake pigment. Economy is certainly likely to have played a role in Van Gogh's choice of painting materials at the

time, when lack of money to hire a portrait model had driven him to painting flowers instead.[43] Rather than saleable pieces, all three pictures in which redwood was identified have the character of small informal studies. Two of them (*Glass with yellow roses* F218 and *Bottle with peonies and blue delphiniums* F243a) were painted on *carton* supports, considered a cheap substitute for canvas and suited for learning purposes. On the other hand, no redwood was found in two large ambitious canvases that crowned the summer series; namely, the signed *Vase with Chinese asters and gladioli* (F234), and *Vase with gladioli and Chinese asters* (F248a).

In three of the sampled paintings with redwood, it was found together with purpurin, though mixed in different proportions in each case. Paint cross sections showed that the redwood lake was associated with many rounded, transparent particles, presumably starch grains.[44] The starch grains are much bigger (measuring c. 15 µm across) than those found in the tin-based cochineal lakes however. A sample from, *Bottle with peonies and blue delphiniums* (F243a) contained almost exclusively redwood lake pigment, on a substrate with tin (fig. 23, 24, 25 and 26). Samples from F218 and F245 however, showed both Kopp's purpurin present alone, or mixed with a little redwood (fig. 20, 21 and 22)[45], depending on the exact sample spot. A possible explanation is that Van Gogh mixed the redwood with the Kopp's purpurin himself, blending different tube colours on the palette, explaining the different proportions found in the different spots analysed. The particular ratio of the two red lake types would have affected the stability of the colour, Kopp's purpurin being much more stable than redwood. This seems borne out by observations on the paintings. Thus whilst the pure Kopp's purpurin glaze in the background of *Glass with yellow roses* (F218) appears well preserved, a thickly applied stroke of organic red in the bottle depicted in *Bottle with peonies and blue delphiniums* (F243a), found to chiefly contain redwood mixed with starch, has severely deteriorated to a crusty yellow lump. As for the starch-containing cochineals, it seems likely that the added starch has contributed to the marked physical degradation of the redwood paint evident on these paintings

Exceptionally, in *Head of an old woman* (F174), the only Antwerp period picture sampled, an organic red-brown pigment is present that contains alizarin, purpurin and brasilein (figs. 27-29). The pigment has an aluminium and tin containing substrate, and does not fluoresce in UV-light. Since only one type of organic red lake is observed in cross section, it is possible that the lake pigment used is a co-precipitate of madder and redwood. More likely however, is that the two types of red lake are present as a mixture, each dye with its own corresponding aluminium, or tin-containing substrate. Probably the redwood was added to madder as a cheap adulterant, during manufacture of the colour.[46] Though Van Gogh only mentioned the use of 'carmine' in his Antwerp correspondence (see page 112), rather than the madder and redwood found, he may have used the term in a more general descriptive sense.[47] Removal of a tiny piece of the paper tape that had covered the edges of *Head of a woman* since lining in 1929, provided evidence for a dramatic shift in colour of the background area, attributed to deterioration of the fugitive redwood component.[48] Clearly the original dark, purplish-grey hue (rather than the pale bluish-grey now evident) would have brought the background more in line with the dark backdrops of his Nuenen character studies of peasant heads, than with the brighter and more spacious handling he developed in subsequent Antwerp portraits.

- *Other organic pigments*

When performing HPLC analysis of mixed paint samples to identify the red lakes, some other organic pigments were encountered, as summarised below. Two unknown yellow, presumably flavonoid, ingredients, as well as methyl violet, were found mixed into dark underpaint in the background of *Glass with yellow roses* (F218) (fig. 22). Methyl violet is a synthetic colorant that was brought on the market in 1866, consisting of a mixture of tetra, penta and hexa methylated pararosaniline.[49] Some quite large (c. 15 - 20 µm across) purplish organic particles were observed in the corresponding layer of the paint cross section (F218/2, figs. 20-21), possibly to be identified with this methyl violet containing pigment. Indigotin was found in two paintings, *Boulevard de Clichy* (F292) and *Portrait of Etienne-Lucien Martin* (F289), indicating the use of blue indigo as a pigment. In both cases the indigo was found in conjunction with cochineal (as well as other pigments), presumably added to modify the colour of the lake[50], though this was not confirmed by paint cross sections. Indigotin is the main ingredient of both natural (*Indigofera tinctoria*) and synthetic indigo, making them hard to differentiate by analysis.[51] However, the synthetic variety may be excluded in this case, since it became commercially available only from 1897, after a modified protocol was developed by Heumann in 1890.[52] Finally, several unknown red components were detected, usually present in low concentration, which suggests that these were minor components such as those often found in natural organic colorants.

Fig. 18 Vincent van Gogh, *Glass with yellow roses*, F218, late June-mid July 1886, oil on carton, 35.0 x 27.0 cm, Van Gogh Museum (Vincent van Gogh Foundation) Amsterdam

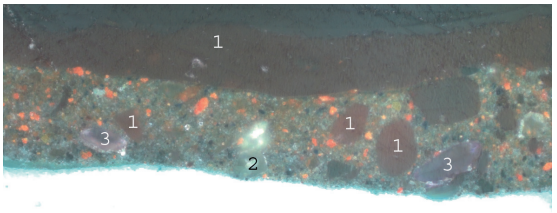


Fig. 20 Paint cross section of a sample taken from the background, showing the dark underlayer and the red glaze on top, both containing Kopp's purpurin lake (indicated by 1). In the dark underlayer redwood lake is also present as is indicated by the big starch grain (2, ø ~ 15 µm) visible in the centre at the bottom of the layer. The dark paint contains vermilion, zinc white, lead white, red ochre, ultramarine, brown pigment and possibly Prussian blue in addition. Furthermore methyl violet was identified in the dark paint by HPLC-analysis, possibly corresponding with the purple particles indicated by 3. Microscope magnification: 500x. Bright field illumination

• *Admixtures of inorganic pigments*

Several samples taken from a pure Kopp's purpurin glaze contained the red lake alone, or mixed with only very little inorganic pigment. Usually however, the different types of red lake were found in more complex mixtures; most commonly with lead white, zinc white, barium sulphate, vermilion, ultramarine, emerald green and viridian.

Fig. 19 Detail of fig. 18 showing the Kopp's purpurin glaze in the background with characteristic 'spotting'

All but one of the cochineal samples examined showed the red lake mixed with vermilion, usually present in small quantities.[53] Combinations of vermilion and carmine were made intentionally, but also as a consequence of using vermilion to adulterate carmine. A mixture of red lake tinted by vermilion was known as scarlet lake, similarly encountered in paintings by Georges Seurat for example.[54] Several pictures dating to 1886 also showed small quantities of red ochre added instead, either by the artist or the paint manufacturer; mixed with a cochineal-based lake (F215c), or with Kopp's purpurin (F218, F234 and F245).

Ultramarine and green pigment (emerald green and/or viridian) were commonly added to deepen the shade of the bright red lake. Occasional traces of carbon black pigment might also be present where a particularly dark red was required; as in the background of *Portrait of a woman* (F215c), and in the shadow on the table in *Vase with Chinese asters and gladioli* (F234). An especially elaborate range of 7 inorganic and 4 organic pigments was found in a blackish underlayer for the background of *Glass with yellow roses* (F218) (fig. 20 and 21), including Kopp's purpurin and redwood lakes. The thick layer of dark paint served to cover up part of an abandoned design, at the same time providing a base coat for the pure glaze of Kopp's purpurin subsequently applied on top.

In several samples the red lake was used as part of a mixed violet, combined with white and various blue pigments. French ultramarine was used most often; mixed with madder (F174), Kopp's purpurin (F244), or cochineal with Kopp's purpurin (F289). Alternatively, cobalt blue (F374), or cobalt and cerulean blue (F316), were found mixed with cochineal. Often it is hard to

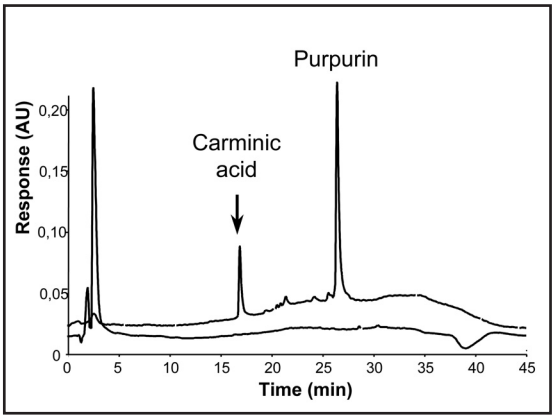


Fig. 22 HPLC-PDA (line below) at 535 nm absorption and fluorescence profile (line above) of a sample from the dark underlayer. With the use of PDA purpurin and three components were found indicating the use of methyl violet, a synthetic colorant. In addition, fluorescence detection points to the presence of brasilein, derived from a redwood

Fig. 21 Microscope magnification: 500x. UV-fluorescence.

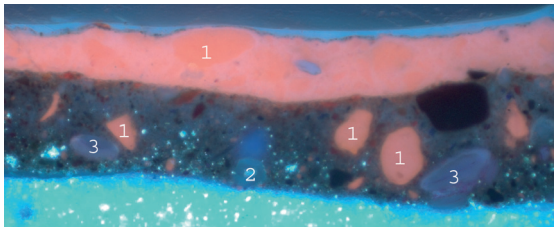
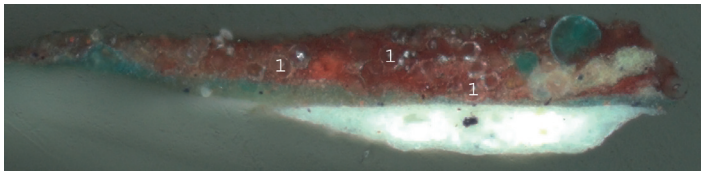


Fig. 23 Vincent van Gogh, *Bottle with peonies and blue delphiniums*, F243a, late June- mid July 1886, oil on carton, 35.0 x 27.0 cm, Van Gogh Museum (Vincent van Gogh Foundation) Amsterdam

Fig. 24 Detail of fig. 23, showing degraded paint stroke that contains chiefly redwood (with starch) and a trace of Kopp's purpurin. The red streaks of paint have turned yellowish-brown and crumbled



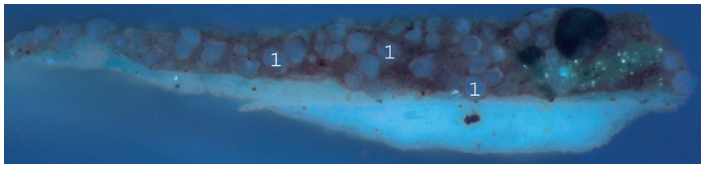


Fig. 25 Paint cross section of a sample taken from a browned red brush stroke in the table top. The cross section shows the lead white containing ground layer of the picture, a greenish-blue paint layer and the top red paint layer. The red layer contains chiefly redwood lake and the presence of big starch grains (examples indicated by 1, ø ~ 15 μm) in the paint is clearly visible. Two big particles of emerald green and a dot of yellow paint are visible on the right hand side.
Microscope magnification: 200x. Bright field illumination

Fig. 26 Microscope magnification: 200x. UV-fluorescence

estimate how the original shade of mixed violet would have looked, since fading of the organic red component has caused an unknown shift towards the blue end of the spectrum. Purple brushstrokes in *Boulevard de Clichy* (F292) with a fugitive mix of carminic acid and indigotin retain a surprisingly intense colour, despite the fact that they have been very thinly applied on the light ground. This must be due to the added presence of relatively stable pigments; cobalt violet, and an inorganic red-blue combination in the form of red lead and cobalt blue. A broader survey of Van Gogh's paintings in the collection has indicated the use of cobalt violet for several other pictures executed in a similar style in the period January to April 1887.[55]

Yellow pigment was found less often mixed with red lake paints in the samples examined. Uniquely, a sample from the orange fruit in *Carafe and dish with citrus fruit* (F340) showed Kopp's purpurin present as the main component, but very intimately mixed with cadmium sulphide, so that it was impossible to distinguish individual particles of either pigment under the research microscope. This might suggest that the cadmium yellow was mixed with the Kopp's purpurin during manufacture of the colour. Traces of cadmium yellow were also found in a sample of red colour from the contemporary, *In the café; Agostina Segatori in Le Tambourin* (F370), though combined with a tin-cochineal lake rather than Kopp's purpurin.

• *Oil medium and added driers*

In several cases lead and/or zinc were identified by SEM-EDS in a layer with cochineal lake, but with no microscopic evidence for the presence of lead- or zinc-containing pigments. Presumably a lead and/or zinc salt had been added as a drier to the paint. This supposition is supported by FTIR-analysis carried out on a sample of almost pure cochineal lake (F370), in which zinc carboxylate was identified, along with starch and oil. Zinc carboxylate can form by the reaction of a zinc salt with the oil medium. Since no zinc-containing pigments are evident in the layer, it seems that the zinc salt was added as a drier instead, perhaps in the form of zinc sulphate that was often used for this purpose. In every case, the samples with a Kopp's purpurin lake glaze were similarly found to contain small amounts of lead and/or zinc, again perhaps indicating the use of driers in the oil paint (*vide supra*). In a sample taken from the right edge of *Montmartre; behind Moulin de la Galette* (F316), the binding medium was confirmed to be linseed or walnut oil.[56]

Conclusion

From this study it emerged that, in the Antwerp and Paris period investigated, Van Gogh used almost exclusively organic red pigments derived from natural sources. The only exception was the synthetic pigment, methyl violet, identified in an underlayer for the background of *Glass with yellow roses* (F218). None of the works investigated showed the use of the synthetic aluminium lake of eosine, known as Geranium lake, which Van Gogh is known to have used from the spring of 1888 onwards. Essentially, four different organic red lakes were used in the Paris period. The characteristic appearance and fluorescence of these different lake pigments viewed in paint cross sections, coupled to knowledge of the substrate, went far towards indicating the types that had been used.

The first type was an aluminium-based Kopp's purpurin lake, seen under the microscope as relatively large, translucent particles, or as a continuous glaze. It is the only one of the four types of red lake encountered to show strong fluorescence under UV-light. Furthermore, the lake has a characteristic EDS-spectrum, with peaks for aluminium, sulphur, phosphorus, and often potassium. Two types of cochineal lake were also encountered; with either a tin-based, or an aluminium- and calcium-based substrate respectively. Both appear as fine red to dark red particles under the research microscope, but the tin-based cochineal lake may be distinguished by the added presence of starch grains, which are absent from the aluminium/calcium variety. The fourth red lake type used by Van Gogh in Paris was a redwood lake on a tin-containing substrate. The redwood lake paint also contains starch grains, but these are much larger than for the tin-cochineal lakes, having roughly three times the diameter (15 µm as opposed to 5 µm for the cochineal).

However, HPLC was required to identify the organic pigments with certainty. The strong suitability of HPLC-PDA-Fluorescence detection for the analysis of organic red pigments in paint samples was well demonstrated by this survey. From the results listed in appendix 1, it emerged that much more information was obtained with complementary fluorescence detection compared to the use of PDA detection alone. For the investigated red organic pigments, the fluorescence detector gave a higher response and detected several components that were missed by the PDA detector. However, the PDA detector identified other components than those picked up by the fluorescence detector, including indigotin, methyl

violet and several yellow and orange components. In summary, it appears that that the combination of both techniques offers the most information.

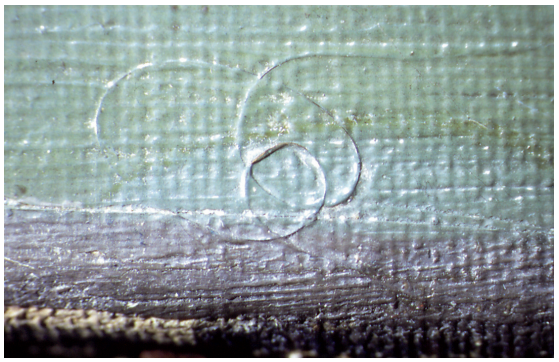
Bearing in mind that this survey covered only roughly half of the painter's Paris production, the following chronological pattern in his use of red lake pigments emerged. In the single Antwerp picture analysed, uniquely a mixture of madder and redwood was found. In a small group of floral still lifes painted in the summer of 1886, Kopp's purpurin was identified, used as a pure glaze, or mixed with minor to major quantities of redwood. Van Gogh made very occasional use of a calcium/aluminium-based cochineal, from June 1886 in the pictures examined. The tin-based cochineal was employed much more often however, almost exclusively from early 1887 on. Both types of cochineal were often found combined with traces of aluminium-based Kopp's purpurin, a lake type that was also used as a pure glaze. Van Gogh used Kopp's purpurin lake throughout his stay in Paris, in works dating from the spring of 1886 to the autumn of 1887. Microscopic analysis suggested that mixtures of organic pigments were used, rather than pigments made by co-precipitating two organic colorants onto a shared substrate. Besides these mixtures of organic pigments, combinations of organic and inorganic pigments were also encountered. Some of these are thought to be manufacturer's tube paint recipes, such as the combination of cochineal lake and vermilion. It was not possible to link these different mixtures to a particular supplier of Van Gogh's tube paints in the period however. In other cases, especially when the red lake pigment was found together with many other pigments, it seems more likely that the mixtures were made by the artist himself.

Coupling analytical findings to observations made on the paintings identified characteristic features for each type of red lake found. In the Paris pictures, Kopp's purpurin was the only lake sort to show bright orange fluorescence when examined with a UV-lamp, when applied alone as a pure glaze. In general the purpurin glazes have kept their colour well, though a distinctive 'spotting' may be evident when viewed with the stereomicroscope. However, areas containing redwood (with starch) as the main or exclusive ingredient have been subject to marked fading and brown discolouration. Especially the thicker strokes have severely crumbled, leaving only a yellowish crust behind. Similarly, the tin-based cochineal paints (with starch) often show pronounced deterioration. Where the pure crimson colour was thickly applied, it has developed marked cracks traversing brushstrokes, with possible cupping. A weathered surface contributes to the faded appearance by the scattering of incident light. Where the tin-cochineal was applied as a thin glaze however, its colour has faded almost entirely, and when the lake was mixed with white in a violet area, fading has been exacerbated to a high degree. By comparison, in the few examples where calcium/aluminium-based cochineals have been used instead, the red lake areas of paint seem well preserved. Based on these joint findings from the technical examination and analysis of Van Gogh's paintings, an experimental project has been set up to investigate these aspects of deterioration in a more systematic way using artificially aged paint reconstructions.[57]

Van Gogh's preference for the fugitive cochineal-based lakes ran counter to general nineteenth-century recommendations to substitute them with more permanent madders instead.[58] Madders were very expensive however, and the painter's use of other low grade materials point to his need to economise. Examples of inferior redwood, madder adulterated with redwood, as well as redwood and tin-cochineal paints with starch added as a cheap ingredient, were found in the pictures examined. Besides issues of cost however, like other painters Van Gogh may also have been won over by the physical appeal of the cochineal paints, despite their known drawbacks. Wisely, Sir Arthur Herbert Church, in his 'The Chemistry of Paints and Painting' published in 1890, concluded that 'Beautiful and rich as are the colours prepared from cochineal, not one of them should ever find a place upon the palette of an artist…No artist who cares for his work and hopes for permanency should employ them'.[59]

Fig. 27 Vincent van Gogh, *Head of an old woman*, F174, Antwerp, mid December 1885-mid January 1886, oil on canvas, 50.5 x 39.7 cm, Van Gogh Museum (Vincent van Gogh Foundation) Amsterdam

Fig. 28 Detail of fig. 27 where paper tape covering the right edge since 1929 is removed, revealing a strip of violet colour preserved underneath. A small spot of the yellowed varnish has been removed from the left, discoloured part of the background. Note too the coiled hair embedded in the paint



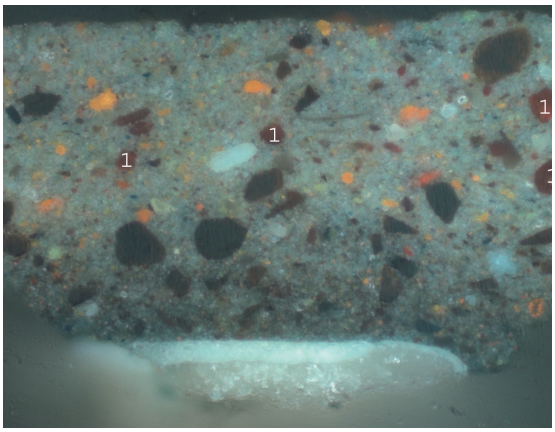
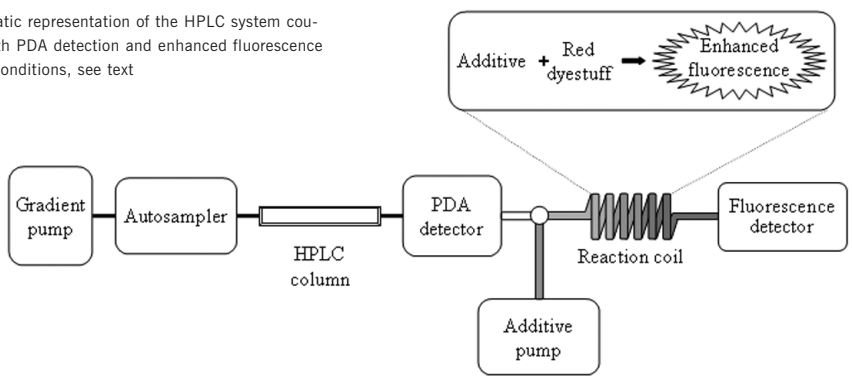


Fig. 29 Paint cross section of a sample taken from the dark purplish-grey background paint, where it has been covered by tape. The top paint layer contains a mixture or co-precipitate of madder and redwood lake (examples indicated by 1) in addition to zinc white, lead white, chrome orange, ultramarine, chalk and large lumps of an organic brown pigment.
Microscope magnification: 500x. Bright field illumination

Fig. 30 Schematic representation of the HPLC system coupled on-line with PDA detection and enhanced fluorescence detection. For conditions, see text



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APPENDIX
Methods of examination and analysis

Technical and scientific examination
Each picture was examined out of its frame, with the naked eye in normal and in raking light, and under the stereo-microscope. Often tiny sections of tape covering the edges of the paintings were removed to look for evidence of colour change caused by faded organic red pigments. Since the date when the tape was applied is documented, this presents us with a known time frame for the changes that have occurred. The fluorescence characteristics of the organic red containing paint areas were examined in UV light, and relevant detail photographs and photomicrographs were made. Finally, paint samples were taken, selecting appropriate spots under the stereomicroscope. Most samples originated from the edges of pictures (which often have been shielded from light), or occasionally from the edges of a damaged area. Besides confirmation of the organic red pigment used, often fading or other signs of degradation were of interest at the sampled sites.

Some of these samples were prepared as paint cross sections, to determine the composition and build-up of layers. Inorganic constituents were identified using optical microscopy and Scanning Electron Microscopy with Energy Dispersive X-ray spectroscopy (SEM-EDS). Other samples were used for binding medium analysis by Fourier Transform Infrared Spectrometry (FTIR) and Gas Chromatography-Mass Spectrometry (GC-MS), or for analysis of the organic pigments using HPLC- PDA-Fluorescence. A more detailed description of the scientific techniques employed follows.

- *Optical Microscopy*

The samples were embedded in polyester resin and ground with SiC-paper. The resultant cross sections were examined under a Zeiss Axioplan 2 microscope both with incident polarised light and incident UV-light (from a Xenon-lamp and a mercury short arc photo optic lamp HBO, respectively). The filter set 'UV H365' used for examination in UV-light consists of the following filters: excitation BP 365/12, beam splitter FT 395 and emission LP 397.

- *Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS):*

SEM-EDS analyses were carried out by Kees Mensch at Shell Research and Technology Centre, Amsterdam, using a JEOL JSM 5900 LV scanning electron microscope and a Noran Vantage EDS-system with pioneer Norvar detector. The primary electron beam energy was 25 KeV. Some samples were coated with carbon and examined in the high vacuum mode; others were examined without coating using the low vacuum mode.

- *Extraction of the organic colorant from organic pigments*

The size of samples available for HPLC analysis varied, but could be as small as 50 µm x 50 µm. These small samples are difficult to handle, particularly if they have to be transferred from one vial to the other. Therefore, when possible the samples were transferred directly from the painting to small insert vials (250 µl vials from Waters Chromatography BV, Etten-Leur, The Netherlands). The samples were introduced carefully into the conical tip of the vials. Prior to analysis, the organic colorants had to be dissolved in an HPLC compatible solvent. Hydrochloric acid was used to hydrolyse the samples, destroying the binding media and thereby breaking the bond between organic colorant and substrate and causing the organic colorants to dissolve. For this purpose 50 µl hydrochloric acid: water : methanol (2:1:1, v/v/v) solution was added to the sample, and heated at 100 °C in a water bath for 10 minutes. The samples were then evaporated to dryness under a nitrogen flow, dissolved in 20 µl dimethyl formamide, and centrifuged at 6000 rpm for 2 minutes. All these steps (hydrolysis, followed by evaporation, dissolution in dimethyl formamide and centrifugation) could be performed in the same vial, which could subsequently be used for direct injection of the sample into the HPLC system. 10 µl of the sample solution was injected into the HPLC system by means of the auto-sampler.

- *HPLC-PDA-Fluorescence*

In figure 30, the system is schematically represented. Separation of the organic colorants was performed on a Luna C_{18} HPLC column (100 mm x 2 mm i.d.) from Phenomenex (Torrance, CA, USA). The column was protected by a Luna C_{18} guard of 4 mm x 2 mm i.d. A gradient, given in table 4, of water, methanol and phosphoric acid was used to separate the compounds of interest. The flow rate was 0.2 ml/minute.
Table 4: HPLC gradient, all changes are linear.

All the HPLC equipment used was from Waters Chromatography BV (Etten-Leur, The Netherlands). A 616 LC pump, controlled by a 600S controller delivered the HPLC effluent. An on-line degasser was connected to the pump to degas all the effluents used. Samples were injected by a 717 autosampler. After separation, analytes were detected by a 996 PDA detector, scanning from 200 to 700 nm at a scan rate of 1 scan/second and with a resolution of 4.8 nm. The 996 PDA detector was equipped with a 10 µl detector cell. After PDA detection, 100 mM aluminium chloride in methanol-water (80:20, v/v) was added via a mixing union by a 6000A pump at a flow rate of 0.2 ml/minute. Complexation of aluminium with the red colorants was performed in a 100 µl knitted reaction coil (250 µm i.d.) to ensure sufficient mixing and avoid peak broadening. Fluorescence detection was performed with a 474 fluorescence detector at an excitation wavelength of 510 nm and an emission wavelength of 580 nm (40 nm slit). Control of the HPLC system and data acquisition was done by Millennium[32] software. Fluorescence detection was performed by connecting the outlet of the PDA detector to the inlet of the fluorescence detector. The system was tested with several anthraquinones, such as carminic acid, alizarin and purpurin and one neoflavanoid, i.e. brasilein. Although most model compounds used show fluorescence, the improvement of the sensitivity of the system was rather low. Therefore, fluorescence enhancement was performed by adding aluminium chloride via a mixing union directly after PDA detection prior to fluorescence detection. Aluminium forms strong fluorescent complexes with the organic colorants.[60] A knitted reaction coil was used to allow complexation without peak broadening. With the use of aluminium chloride as additive, detection limits were improved by a factor of 16 to 50, compared to PDA detection. As a result, sample size could be reduced by at least a factor 16. Unfortunately, alizarin shows only a factor 2 improvement due to a lower quantum yield. Analytical data of the new developed fluorescent enhancement system coupled to HPLC-PDA is published elsewhere.[61]

Notes

1 L. van Tilborgh and E. Hendriks, *Van Gogh Paintings, Antwerp and Paris 1885-1888*, vol. 2, Van Gogh Museum, (Amsterdam and Zwolle, 2005). See especially introductory essays by Hendriks, 'Van Gogh's materials and techniques' and 'Developing technique and style'.

2 Letter 535/424, c. 25-29 September 1885, and letter 545/434, 17 November 1885.

3 Letter 550/439, 14 December 1885. Tyck was established as '*Marchand de couleurs pour peintres-artistes*' at Rubensstraat 8, Antwerp. Information kindly provided by Hans Luijten, Van Gogh Museum.

4 Letters 550/439, 14 December 1885, 552/441, c. 21 December 1885, and 553/442, c. 25 December 1885.

5 Letter 574/461, c. 17-19 July 1887. The painter A.S. Hartrick later recalled; 'Tanguy used, I believe, to let him have colours sometimes in exchange'; see, A.S. Hartrick, *A Painter's Pilgrimage through Fifty Years*, (Cambridge, 1939), 49.

6 Document B 1445 v/1973, Vincent van Gogh Foundation. The approximate date of 1888-90 is supported by the mention of cobalt green on the list of colours for sale. The earliest known listing of this colour in tube oil paint occurs in the 1889 catalogue of Winsor and Newton. See L. Carlyle, *The Artists' Assistant. Oil painting instruction manuals and handbooks in Britain 1800-1900 with references to selected eighteenth-century sources*, (London, 2001), 534.

7 Letter 637/503, c. 28 June 1888.

8 Letters 631/501, c. 31 June 1888, and 894/642, 17 June 1890.

9 An overview is provided in E. Hendriks and M. Geldof, 'Van Gogh's Antwerp and Paris picture supports (1885-1888); reconstructing choices', *Art Matters*, 2 (2005), 39-74, Table 2, compiled in collaboration with Stéphanie Constantin, Paris.

10 One of the other shops Van Gogh visited, namely maison vallé/Hofer Frères (active 1770-1890), established at Grands-Augustins 3, was especially listed in the Paris edition of *Didot-Bottin, Annuaire-Almanach du Commerce, de l'Industrie, de la Magistrature et de l'Administration* for the period 1886 to 1888 as being a representative for Michael Huber, manufacturer of carmine and geranium lakes at Haidhausen.

11 Letter 595/475, c. 5 April 1888.

12 C. Peres et al., *A Closer Look. Technical and Art-Historical Studies on Works by Van Gogh and Gauguin, Cahier Vincent 3*, (Zwolle, 1991). See especially the contributions by M.M. Bang, 'Van Gogh's Palette', 57-60, and J.H. Hofenk de Graaff et al., 'Scientific Investigation', 75-85. J-P. Rioux, 'The Discoloration of Pinks and Purples in Van Gogh's Paintings from Auvers', in A. Distel and S.A. Stein, *Cézanne to Van Gogh. The Collection of Doctor Gachet*, [exh. cat.] (New York, 1999), 104-113. J.-P. Rioux, 'Charactérisation de pigments décolorés dans des tableaux de Van Gogh peints à Auvers-sur-oise', *ICOM-CC Lyon pre-prints*, vol. 1, (1999), 403-08. E. Hendriks and L. van Tilborgh, 'Van Gogh's 'Garden of the Asylum'; genuine or fake?', *The Burlington Magazine*, March (2001), 145-156.

13 J. Wouters and N. Rosario-Chirinos, 'Dye Analysis of pre-columbian Peruvian Textiles with High-Performance Liquid Chromatography and Diode-Array Detection', *Journal of the American Institute of Conservation*, 31 (1992), 237-255; R. Hofmann-de Keijzer and M.R. van Bommel, 'TLC and HPLC analysis on red and violet cotton yarns of Indonesian textiles', *Dyes in History and Archaeology*, 20 (2001), 70-79.

14 M. R. van Bommel, 'The analysis of dyes with HPLC coupled to Photo Diode Array and Fluorescence Detection', *Dyes in History and Archaeology*, 20 (2001), 30–38.

15 Personal communication with Jo Kirby (National Gallery, London) and Arie Wallert (Rijksmuseum Amsterdam).

16 Colour Index name: natural red 4. Colour index number: 75470.

17 P. Allevi et al., *Synthesis of carminic acid, the colorant principle of cochineal*, J. Chem. Soc., Perkin Trans. 1 (1998), 575-582.

18 H. Schweppe, *Handbuch der Naturfarbstoffe*, (Landsberg, 1992), 254-281, H. Böhmer, *Koekboya, Natural dyes and textiles. A Colour Journey from Turkey to India and Beyond*, (Weppert, 2002), 203-214.

19 This observation applies for all the mixtures of organic pigments found, with the exception of the mixture of madder and redwood identified in *Head of an old Woman* (F174); see under redwood.

20 The FTIR-analysis was performed by Suzan de Groot at ICN. Besides starch, also zinc carboxylate and possibly oil were identified in the red paint.

21 See the article in this volume by A. Burnstock et.al., 'Painting techniques of Pierre-Auguste Renoir: 1868-1919', *ArtMatters*, 3 (2005). E.Hermens et.al., 'A travel experience: the Corot painting box, Matthijs Maris and 19th century tube paints', *ArtMatters*, 1 (2002), 117. Jo Kirby at the National Gallery in London personally informed us that analysis of red lakes used in four pictures dated between c. 1870 and 1882 by Adolphe Monticelli (inventory numbers, NG 5010, 5013, 5014 and 5015) revealed that, in each case, cochineal, with tin in the substrate and a starch extender, was found. Starch was also added to the zinc yellow tube colour used by Georges Seurat, see J. Kirby et al., 'Seurat's Painting Practice: Theory, Development and Technology', *National Gallery Technical Bulletin*, 24 (2003), 24-25.

22 H. Schweppe and H. Roosen-Runge, 'Carmine – Cochineal Carmine and Kermes Carmine', in R.L. Feller ed., *Artists' Pigments, A Handbook of their History and Characteristics*, I, (National gallery of Art, Washington DC, 1986), 263 and 272.

23 J.H. Hofenk de Graaff et al. 1991, 77. In this earlier study, analytical findings were correlated to the red lakes mentioned in his paint orders from Tasset et L'Hôte in the period, tentatively identifying the aluminium lake of carminic acid as *laque ordinaire*, and the tin/aluminium lake of carminic acid as *carmin*.

24 D. Saunders and J. Kirby, 'Light-induced Colour Changes in Red and Yellow Lake Pigments', *National Gallery Technical Bulletin*, 15 (London, 1994), 88.

25 Letter to Wil, 633/W4, 16-20 June 1888. Van Gogh described a palette with lemon yellow, vermilion, Veronese green and cobalt blue. All these pigments were identified by analysis of samples from the colours on the palette, if one takes the lemon yellow to correspond to zinc yellow and the Veronese green to emerald green. However, besides the tin-based cochineal with starch, also red lead, cadmium orange, cadmium yellow, zinc white and lead white pigments were identified in addition to those mentioned in Vincent's letter.

26 The presence of zinc soaps in the cochineal lake paint in *Agostina Segatori in Le Tambourin* (F370) might well contribute to the observed sensitivity of the paint to water and organic solvents. SEM-EDS analysis of the cochineal lake paints used in other paintings indicated that these paints similarly contained zinc and/or lead soaps as well (see Table 1).

27 For both Field and Salter, see Carlyle 2001, 507.

28 Letter 541/430, c. 2 November 1885.

29 J.H. Hofenk de Graaff, *The colourful past, origins, chemistry and identification of natural dyestuffs*, (London, 2004).

30 H. Schweppe and J. Winter, 'Madder and Alizarin', in E. West Fitzhugh ed., *Artists' Pigments, A Handbook of their History and Characteristics*, 3, (Oxford, 1997), 122.

31 Personal communication with Jo Kirby.

32 O.Redon, *L'arbre rouge*, Van Gogh Museum, S464. The analysis were performed at the ICN (project no. 2004-062).

33 Kirby et. al. 2003, 26.

34 Kirby, 'Late 19th century lake pigments and their preparation: Introduction to the workshop held at ICN', 7-9 April 2003.

35 Kirby et. al. 2003, 34.

36 Kirby workshop paper 2003, see note 34.

37 The fluorescence of the Kopp's Purpurin lake showed up regardless of fluorescent, old natural resin varnish layers present on top.

38 Letter 591/471, c. 28 March 1888, expressed his strong praise of Monticelli's *Vase of flowers* c. 1875 for example, a picture known to him in Theo's collection, which is now in the collection of the Van Gogh Museum (Vincent van Gogh Foundation), Amsterdam, S251 v/1960.

39 Schweppe and Winter 1997, 114.

40 W. Nowik, 'The possibility of differentiation and identification of red and blue 'soluble' dyewoods', *Dyes in History and Archaeology*, 16/17 (1997/1998), 129-144.

41 Personal communication with Judith Hofenk de Graaff

42 Hofenk de Graaff 2004, 141-158.

43 Letter 572/459a to H. M. Livens, September or October 1886.

44 The presence of starch grains

was indicated by their appearance under the microscope only (see fig. 25 and 26). No further analyses were performed to confirm this assumption.

45 It is not possible to calculate the exact ratio between purpurin and brasilein found with HPLC, due to the fact that brasilein is not very stable during sample pretreatment (hydrochloric acid hydrolysis). This inherent instability also means that, if brasilein is present in a small amount, it could remain undetected.
The presence of redwood was indicated by the observation of large starch grains in the cross sections.

46 Madders were exacting to prepare, and particularly expensive due to their bright and stable colour, so that they were especially prone to adulteration; see Carlyle 2001, 509.

47 In the nineteenth century, the term 'carmine' was commonly used to denote any lake sort that resembled cochineal in terms of colour and texture; see Carlyle 2001, 506.

48 Although the discolouration was obvious on the painting, surprisingly no difference could be seen between cross sections made from paint samples taken from a covered spot, or an exposed spot that had faded.

49 According to the Colour Index it is called basic violet 1, Colour index number 42535. See also K-J. van den Berg and M.de Keijzer, 'Onderzoek naar rode lakken, de rode lakken van Vincent van Gogh en de overgang van natuurlijke naar synthetische kleurstoffen', KM, 12 (2003), 14-17.

50 Carlyle 2001, 503.

51 C.I. name: vat blue 1, C.I. number 73000

52 Personal communication with Matthijs de Keijzer.

53 The only sample that did not contain vermilion was taken from *Still life with cabbages and onions* (F374), but this could be explained by the fact that the amount of red lake contained in this sample is rather low.

54 Carlyle 2001, 507. Kirby et al. 2003, 23.

55 Cobalt violet was similarly identified in samples from the pictures F216g, F216h, F337 and F340 for example.

56 Py-TMAH-GCMS-analysis was performed at the ICN by Henk van Keulen. A palmitate/stearate (C16 : C18) ratio of 2.1 was obtained, indicating the use of linseed or walnut oil or, alternatively, a mixture of linseed oil with walnut or poppy oil.

57 The interdisciplinary project involves collaboration between the following institutions; the Van Gogh Museum (Vincent van Gogh Foundation), the Netherlands Institute for Cultural Heritage, the De Mayerne Program (subsidized by the Dutch organisation for Scientific Research), and the Shell Research and Technology Centre in Amsterdam, as well as the Courtauld Institute, Department of Art and Technology , and the National Gallery in London. For some published results, see; A. Burnstock et al., 'A comparison of the fading and surface deterioration of red lake pigments in six paintings by Vincent van Gogh with artificially aged paint reconstructions', ICOM -CC, *The Hague pre-prints* (The Hague, 2005).

58 Carlyle 2001, 507.

59 Carlyle, 2001, 507.

60 Van Bommel 2001, 35

61 Van Bommel 2001, 30-38