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POSTIMPRESSIONISMUS

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The Use of VIS Spectroscopy in Non Destructive Paint Analysis

Potential and Limits of the Method for 19th and Early-20th-Century Paintings

On the Results of the Investigations of Impressionist and Postimpressionist Paintings in the Collection of the Wallraf-Richartz-Museum & Fondation Corboud Cologne

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VIS Spectroscopy

Method and Apparatus set-up

VIS colour spectrometry measures the reflection of *visible* light (380-730 nm). The surface of the object to be examined is illuminated with visible light and the reflected radiation is measured. In the colour curves, the spectral proportions of the reflected light are plotted against wavelength. Parallel to this, the values of the colours thus measured are determined in the CIELAB colour space. For the identification of colorants, however, only the colour curves are relevant.

For the investigations, an SPM 100 colour spectrometer made by the Gretag company based in Regendorf in Switzerland was used, as it is light (1300 g) and handy. For the measurement, an area of 3 mm diameter is analysed by a extendable measuring-head. The area to be examined is illuminated by a tungsten lamp (2W) for about half a second, and the reflected light is measured. This is refracted by interference filters, the intensities being registered at 4.5 nm intervals and calibrated against an internal reference white. The resolution is converted to 10 nm; the next step is to calculate the curve from these measurements. An external calibration is carried out using a standard white (barium sulphate; DIN 5033). The measuring geometry is 45°/0°, and as a result glare and reflection effects, e.g. from varnished surfaces, do not interfere with the measurement.

The storage of the data and the print-out of the curves is done by a computer program written specially for the device (Robert Fuchs, University of Applied Sciences, Cologne). This program converts the data into a graph; in addition, the first derivative is calculated and represented on the graph as a dotted line. The first derivative represents the inflection points of a curve as highs or lows, making them easier to recognize. This is particularly important in mixtures in which different colour curves are superimposed. It is also important for the interpretation that the graphs be normalized. For this reason all the curves are represented equally clearly and can be compared with the references regardless of intensity differences, e.g. between strong pure colours and pale colours with an admixture of white.

Evaluation

Procedure, Potential and Limits

A series of colorants produce a characteristic colour spectrum which can be identified by comparison with reference measurements. As there are no generally accessible data collections for this purpose, a comprehensive reference collection of one's own is crucial. It should be noted in this connexion that there are numerous historical colorants which are no longer available and must accordingly be reconstructed on the basis of historical sources. The laboratory for non-destructive testing (Cologne Institute of Conservation Science (CICS), University of Applied Sciences, Cologne, which from 1984-1989 was the research centre for the techniques of medieval book illumination at the University of Göttingen) has an extensive collection of historical original reference samples (in particular, pattern books from the 18th-20th centuries) and of reference samples created on the basis of historical recipes. Colorants that were used before the 19th century are available with a fair degree of completeness. The same is true of the most common colorants used in the 19th century.

In the 19th century, the production of numerous paints was switched to large-scale manufacturing processes; in addition, many production processes were changed, giving rise to the appearance of variants of the individual colorants, which can be distinguished not only by their constitution (e.g. degree of hydration, by-products, and in the case of lakes, substrates), but also in hue and spectrum. Furthermore, numerous totally new chemical compounds were discovered.

Many of these colorants did not remain on the market for very long before being replaced by others that were more permanent, cheaper, or easier for painters to use. Of these little-known, forgotten 19th-century colorants, only a few have been researched to date, and consequently the CICS reference collection is incomplete. This is one of the reasons why some of the spectra of the Impressionist paintings are for the time being undetermined or at least doubtful.

As VIS spectroscopy involves only a surface measurement, underlying paint-layers cannot be analysed. The measurement geometry does however allow the measurement of shiny surfaces. Varnishes therefore do not interfere. It is also only in very rare cases, with some blue pigments, that the colour spectrum is influenced by the binding medium. In these cases, reference samples with different binding media must be drawn upon for the analysis.

The unambiguity of the spectra varies according to the colorant in question. Thus the inorganic blue pigments (ultramarine/lapis lazuli, azurite, cobalt blue, cerulean blue, smalt, Prussian blue) each have very characteristic spectra which can be unambiguously distinguished (figs. 1-4). The inorganic red pigments (vermilion, red lead, iron-oxide red, cadmium red, chrome red) by contrast have very similar curves (figs. 8-11). In order to interpret them, the above-mentioned derivative is of importance, as it makes the inflection points of the curves more precise. If the derivative is incorporated into the evaluation of the curves, iron-oxide red, red lead and chrome red can be readily distinguished both from each other and from vermilion and cadmium red, although the two last-named cannot be distinguished from each other. Here a decision can only be made if the painting in question can be shown beyond doubt to have been painted before the invention and marketing of cadmium red (c. 1910).

These examples relate to pure, unmixed colours. If we are dealing with mixtures, the colour curve of one colorant may be overlaid by the spectrum of the other. This is true in particular when materials of similar hue are mixed. Many colorants can however also be identified in mixtures. Here too a derivative is useful, as the characteristics of some colorants are more clearly visible in the derivative than in the main curve. Thus for example cobalt blue and viridian evince typical peculiarities not encountered with other colorants, and these can still be recognized in mixtures (fig. 3a). As pure colours provide results which are less ambiguous, however, on principle an attempt should be made, by means of a precise preliminary macroscopic inspection, to select the measuring points in such a way that the results are clouded as little as possible by mixtures or by the structure of the paint-layer. If this is not possible, the macroscopic finding should be noted in the description as an aid to interpretation. Even in the 19th century, however, one should be prepared for industrially produced mixtures created by extremely find grinding; in such cases grains of pigment can only be seen at great magnifications, and consequently the identification of several components with the binocular is more difficult, if not impossible. This is true in particular of greens created by mixing Prussian blue with some yellow pigment.

White and black colorants, which, respectively, totally reflect or totally absorb visible light, can only be distinguished by this method up to a point. As the program generates a normalized curve, they generally do not cause a problem in mixtures, except that when the proportion of white is very high, the representation of reflection intensities may be inadequate, which may make the interpretation of the spectrum more difficult.

The only 19th-century white to show a characteristic reflection, between 380 and 400 nm, is zinc white, which allows us to recognize this pigment in 19th and early-20th-century paintings when it is present in larger proportions (fig. 5). As small proportions of zinc white are however often submerged beneath the reflection curves of other colorants, the absence of the typical zinc-white reflection is not necessarily a sign that what we have is lead white. The reflection spectrum of titanium white is only slightly different from that of zinc white, so that zinc white in paintings dating from after about 1920, or whose authenticity is questionable, can no longer be analysed by VIS spectrometry.

The pigments

Blue pigments

In the 19th century, when most of the paintings under investigation were painted, the only permanent blue pigments available for painting in oils were inorganic. Indigo was less suitable, not being lightfast, and its use was not noted in any of the pictures investigated. Organic blue pigments suitable for painting were only developed in the 20th century; they have to be considered for the few paintings in the investigation that date from after the turn of the century.

The inorganic pigments known in the 19th century, namely azurite, Prussian blue, cobalt blue, cerulean blue, smalt and ultramarine generate very different VIS spectra. When used alone, therefore, they can be easily distinguished. On the other hand it is more difficult, if not impossible, to identify minor additions of one blue pigment to another (e.g. to create colour nuances).

Azurite

Azurite (basic copper carbonate) occurs naturally as a mineral, but was also produced artificially by precipitation. The spectrum is fairly characteristic, but, with very high admixtures of white, can become badly blurred, in which case it can be difficult to tell apart from Prussian blue. In our investigations, no azurite was identified, nor are there any doubtful cases with a high proportion of white. This finding is not surprising, as reported investigations of 19th-century paintings only rarely identified any azurite.

Cobalt blue

Cobalt blue (cobalt aluminium oxide) was first manufactured as a pigment by Thénard in 1802. It was an important pigment for painters in the 19th and 20th centuries; among the paintings investigated, it is by far the most important blue pigment.

Cobalt blue has a very characteristic curve (fig. 1), which differs unmistakably from the spectra of other blue pigments, including the other two with a cobalt component, namely cerulean blue (fig. 2a) and smalt. The shape of the curve can be influenced by the binding medium: the spectra of cobalt blues used when freshly bound with oils or oil/resin mixtures show a much broader minimum in comparison with reference samples bound with glue, egg tempera or gum arabic. In the paintings investigated, the curve largely corresponds to the non-oil-bound reference samples, although we can be certain that the binding medium was oil in all cases. Whether this is a result of the paints being prepared beforehand, or of aging, is still to be investigated.

The characteristic bands of the derivative are often still clearly recognizable in mixtures (fig. 3a), except that when there is a high proportion of ultramarine, or when mixed with red lakes, the characteristics of the cobalt-blue spectrum can be covered to the extent that no identification, or at least no unambiguous identification, is possible. Conversely, the curve of cobalt blue largely obscures the characteristics of Prussian blue; the latter can therefore, when mixed with cobalt blue, often only be identified with any certainty when the proportion of cobalt blue is very small (fig. 3a).

Some of the curves measured in the paintings under investigation evince a shift in the maximum relative to the reference samples. Whether this is a secure indication of an admixture of Prussian blue or ultramarine, we have not yet been able to determine. It would be conceivable that what we have here are variants of cobalt blue for which we have no reference samples.

Cerulean blue (Coeruleum)

Cerulean blue (cobalt(II) stannate), which has something of a greenish cast, likewise known since the beginning of the 19th century, was far less commonly found in the investigated pictures than cobalt blue (fig. 2). The colour curve resembles that of cobalt blue; maxima, minima and inflection points are however characteristically shifted by 10-20 nm (fig. 2a). It is therefore always possible to distinguish the two pigments unambiguously, even in mixtures with other colorants. Cerulean blue also differs unmistakably from smalt and other blue pigments. Like cobalt blue, cerulean blue is usually easily identifiable above all by the characteristic bands of the derivative, even in mixtures (provided its proportion is not too small).

Smalt

Smalt (ground glass coloured with cobalt) is the oldest cobalt-based pigment and has been used in European painting since the 15th century. The colour spectrum differs characteristically from the other blue cobalt pigments and from other blue pigments. No smalt was found in the pictures under investigation.

Prussian blue

Prussian blue (iron(III) hexacyanoferrate(II), also ferric ferrocyanide) was discovered by Diesbach in about 1706. From the mid 18th century it was one of the most important blue pigments. In the pictures under investigation, it was often found with the help of VIS spectroscopy.

When making identifications, it should be remembered that depending on the production process, varieties of Prussian blue can be produced that vary in their chemical composition, physical properties and exact hue (Berrie 1997). The different types of Prussian blue also vary sometimes in their VIS spectra; while these are similar in the shape of the curves, the position of the maximum and the inflection points may be shifted. In principle, the colour curves of pure, unmixed Prussian blue varieties differ unmistakably from those of most other blue pigments (fig. 3). When mixed with white, however, the spectrum is less clear, and with high proportions of white, Prussian blue is no longer distinguishable from azurite. Similarly, when mixed with other blue pigments, especially cobalt blue and ultramarine, the characteristic features of the Prussian blue spectrum are largely concealed, so that the pigment can only be identified with certainty when it is the dominant component of the mixture (fig. 3a). This explains the large number of dubious findings. In addition, it cannot be excluded that Prussian blue occurs in more of the investigated paintings as an addition to other blue pigments.

Ultramarine

Natural ultramarine comes from the mineral lapis lazuli, which is very rare, and in good pigment quality only found in Afghanistan. Processes for synthesizing it were developed by Guimet and Gmelin in 1828, and industrial production began not long after. Artificial ultramarine, like lapis lazuli, is a sulphur-containing sodium aluminium silicate, whose composition can vary considerably depending on the proportions of the ingredients and the manufacturing process [Plesters 1993].

The colour curves of synthetic ultramarines also show a certain degree of fluctuation, especially in the position of the maximum; in oily binding media there may be a significant broadening of the minimum, depending on the type and the way it is prepared as a paint. The latter is also true of the natural pigment made from lapis lazuli, whose spectra are otherwise more constant. The colour curve typical of the mineral colorant is also found in some of the synthetic pigments, so VIS spectroscopy cannot provide an unambiguous identification of natural lapis lazuli. In the analyses, therefore, the term “ultramarine” has been used to cover both the natural and the synthetic pigment, although the presumption is that if only for reasons of price, only the latter was used.

In spite of the variants mentioned, the spectra for ultramarine/lapis lazuli can be unambiguously distinguished from other blue pigments used in the 19th century (fig. 4). By contrast, the colour curves of a few synthetic organic 20th-century pigments are very similar to those of ultramarine. These include Victoria blue, which was produced shortly after 1900. In paintings dating from shortly after the turn of the century, therefore, even pure ultramarine can no longer always be identified beyond doubt by the use of VIS spectroscopy, and this is all the more true of mixtures. To the extent that the date of origin or the macroscopic findings (clear pigmentation) do not allow any confusion with organic colorants, ultramarine is usually very easy to recognize in mixtures with Prussian blue; in mixtures with cobalt blue, however, superimposition of the curves can make identification more difficult.

Violet pigments

In the second half of the 19th century there were three violet pigments commercially available: cobalt violet, ultramarine violet and manganese violet. They differ very clearly in their colour spectra; in the paintings which have been investigated, it is cobalt violet that has most often been identified. Ultramarine violet was only found once, and even this finding was uncertain, while manganese violet was not identified at all.

Ultramarine violet

Ultramarine varieties were first produced in 1877 [Kühn 1984]. The colour spectrum of ultramarine violet differs markedly from those of the cobalt violet pigments and of manganese violet. As a pure pigment it can thus be easily identified. In mixtures with cobalt violet, ultramarine blue or cobalt blue, by contrast, there are superimpositions, which complicate any unambiguous identification. Sometimes the pigment cannot be distinguished from ultramarine blue at all. Accordingly, there is only one questionable finding, in the painting by Rysselberghe.

Cobalt violet

The name cobalt violet is applied to various violet compounds of cobalt: depending on manufacturer, either cobalt arsenates or cobalt phosphates. The latter were traded in three variants, whose hue fluctuated between pink and violet. The structure of different cobalt-violet pigments from the 1920s, 1960s, 1970s and 1990s has recently been explained by Corbeil et al. Among the older pigments, there was one magnesium cobalt arsenate ($Mg_2Co(AsO_4)_2$) and one cobalt phosphate ($Co_3(PO_4)_2$). The most recent samples were in some cases mixtures of the salts cobalt phosphate and ammonium cobalt phosphate (NH_4CoPO_4) or lithium cobalt phosphate ($LiCoPO_4$). Colour differences can, in addition, result from different states of hydration, especially with the phosphates. According to older descriptions of the manufacturing process, in which no magnesium supplier is named, one must reckon also with the existence of pure cobalt arsenate ($Co_3(AsO_4)_2$) as a pigment, as well as with possibly other mixed salts [Corbeil et al. 2002].

Cobalt arsenate was named as a familiar pigment in England as early as 1855. In the late 19th century, the manufacture of magnesium cobalt compounds was also described, not necessarily arsenates, however. Cobalt phosphate was discovered by Salvétat in 1859. Ammonium cobalt phosphate was first described in 1864, and mentioned as a colorant by the 1890s at the latest. Lithium cobalt phosphate has only been in production since 1965 [Corbeil et al. 2002].

The VIS spectra published by Corbeil et al. reveal clear differences between the various cobalt-violet pigments. As the different presentations of the curves does not allow a perfect comparison of the spectra with our own measurements, and in addition the calculation of the first derivative as an aid to interpretation is absent, the reference samples at CICS (and the measurements made on the paintings in the WRM-FC) cannot be unambiguously matched with the compounds characterized by Corbeil et al. For the reference sample from Wagner 1928, cobalt and arsenic were determined using EDX (Sandra Uckermann), so it is presumably a cobalt arsenate (fig. 5). The two other reference samples (Schallfarben, cobalt violet pale (fig. 6) and Kremer, cobalt violet pale (fig. 7)) evince certain similarities with spectra of cobalt phosphates published by Corbeil et al. The Kremer pigment is described as cobalt ammonium phosphate; an exact characterization of the Schallfarben reference sample still has to be carried out, however.

In the paintings which were examined, the predominant spectra were those of the Wagner reference sample type. Accordingly, one might presume that the most frequent violet colorant was a cobalt arsenate. The spectra of this cobalt violet are only slightly concealed in mixtures, only red lakes and ultramarine or ultramarine violet having the capacity to prevent the unambiguous identification of the pigment.

The type represented by the Schallfarben reference can only be safely proved twice (Morisot, *Child among Hollyhocks* (fig. 6) and Caillebotte, *Garden in Trouville*), the type represented by the Kremer reference samples only once (Luce, *Saint-Tropez* (fig. 7)), in both cases as pure colours. When mixed with cobalt blue, ultramarine or red lakes, there may be superimposed spectra, which complicates identification of these cobalt violet pigments.

Red- and orange pigments

In the 19th and early 20th centuries, painters had a really quite broad spectrum of red, red-brown and orange-red paints at their disposal. For orange or orange-red, they could use red lead as well as orange chrome and cadmium yellows, more strongly red were vermilion, chrome and cadmium red, and for dark red to brownish red they had various iron oxides. The colour spectra of these pigments are quite similar, but can in some cases, at least when they occur unmixed, be fairly well distinguished by the position of the inflection point (clearly recognizable as the maximum in the derivative) (figs. 8-11). In mixtures, however, it is difficult, if not impossible, to distinguish between red lead and orange chrome yellow, and above all between vermilion, cadmium red and chrome red. Vermilion and cadmium red can hardly be distinguished even as pure colours, while the organic red pigments produced after 1900 as vermilion substitutes likewise have in some cases identical spectra. Only when it can be dated to pre-1900, therefore, can vermilion be positively identified by VIS spectrometry, unambiguously when pure, and quite well in mixtures (fig. 13a).

Cadmium orange/cadmium red

Cadmium yellow (cadmium sulphide) can be produced in various shades between lemon yellow and pale orange. The hue is dependent on the size of the particles and the crystal structure. Cadmium red pigments (cadmium sulphoselenide) are orange red to vermilion red; here the proportion of selenium determines the hue [Fiedler, Bayard 1986].

As an artists' paint, cadmium yellow was available from at least the mid 19th century. Cadmium red was probably not manufactured as a pigment until about 1910 [Kühn 1984].

The colour spectrum can unambiguously distinguish orange cadmium yellow from red lead, and somewhat less clearly from orange chrome yellow. In mixtures, cadmium and chrome yellow can no longer be distinguished.

When it contains selenium, cadmium orange has a very characteristic spectrum, but cannot always be distinguished beyond doubt from mixtures of chrome yellow and chrome red. However, before 1900 the use of cadmium pigments containing selenium is unlikely.

The date of a painting is also an important criterion for distinguishing cadmium red and vermilion, as the colour spectra of the two pigments are almost identical. Only with a dating after about 1910 (maybe a little earlier) is cadmium red also conceivable, although it cannot be proved beyond doubt by VIS spectroscopy.

Chrome orange/chrome red

Chrome yellow, chrome orange and chrome red are lead chromates of varying composition and crystal form. The hues vary between lemon yellow, orange and dark red. Yellow, orange and red chrome pigments have been produced since the early 19th century [Kühn, Curran 1986].

The variously coloured lead chromates also differ in their colour spectra. However the spectra of the yellow chrome-yellow types are very similar to those of the yellow cadmium-yellow types (fig. 15) and of different variants of arylamide (Hansa) yellow. VIS spectroscopy can therefore not unambiguously identify chrome yellow; in 19th-century paintings, cadmium yellow is always a possibility, and in the 20th century, arylamide yellow too.

The orange chrome-yellow types differ somewhat more clearly from other pigments of the same general hue, namely orange cadmium yellow and red lead.

This is however only true of pure colours; in mixtures, the pale variants can hardly be distinguished from cadmium yellow, nor the strong ones from red lead.
The colour spectrum of chrome red, while resembling that of vermilion and cadmium red, is not quite identical in the shape of its curve or the derivative (fig. 8). Accordingly, the pure pigment can also be identified with some degree of probability by VIS spectroscopy. In mixtures, by contrast, it can no longer be adequately distinguished from vermilion, iron-oxide red or cadmium red.

Iron-oxide red/iron-oxide brown

Red and brown iron oxides occur frequently in nature as red and brown ochres, or else can be obtained by burning yellow ochre. Since the early 19th century, iron-oxide pigments have also been produced synthetically. VIS spectroscopy cannot distinguish the natural and artificial colorants, as they are chemically identical and thus give rise to the same curves. “Iron-oxide red”/“iron-oxide brown” are thus superordinate terms covering both the natural and the synthetic pigments.
In mixtures, it is sometimes impossible to distinguish the colour-curve of pure anhydrous iron-oxide red from those of dark chrome orange or chrome red. However, yellow and brown iron oxides, with their water of crystallization, have very typical spectra, which are clearly different from those of other yellow and brown pigments (fig. 9).

Red lead

Red lead (lead tetroxide) has been much used as an orange-red or light red pigment since classical times. The colour spectrum differs characteristically from that of vermilion, chrome red, cadmium red and dark chrome orange. On the other hand it is fairly similar to that of pale chrome orange (chrome yellow). In pure form, however, the two can be distinguished quite easily, as the shape of the curve and the derivative are not quite identical, although in mixtures an unambiguous identification is often no longer possible. In the 20th century, organic pigments were produced as a substitute for red lead: their colour spectra are identical with that of red lead. For the pictures under investigation, however, this is irrelevant, as the few paintings in which a red-lead spectrum was measured were painted no later than 1900 (fig. 10).

Vermilion

The red mercuric sulphide vermilion can be obtained from the mineral cinnabar, but since the Middle Ages has been predominantly artificially produced. VIS spectroscopy can distinguish it unambiguously from red lead and iron-oxide red, and to a large degree also from chrome red, although here the parallels in the colour curves can complicate identification in mixtures. By contrast, the spectra of cadmium red and of some organic vermilion substitutes (e.g. some eosin lakes) is identical with that of vermilion. These colorants became commercially available from about 1900-1910. Accordingly, the interpretation of the measured curves must take account of the date of the painting in question. If it pre-dates 1900, vermilion can be identified with a fair degree of confidence using VIS spectroscopy (fig. 11), and in higher concentrations alongside red lakes also in mixtures (fig. 13a). Where the picture was painted later, this method alone cannot prove the presence of vermilion, and of course the same is true where the dating of a work is dubious or uncertain.

Red lakes

The spectra of red lakes measured in the paintings under investigation belong to various groups. Two of these types can be confidently assigned to the madders or to genuine carmine obtained from cochineal. Natural colorants or pre-industrial lakes extracted from animal or vegetable sources usually evince a spectrum typical of the respective source material, irrespective of the hue or the precise method of production; problems with the precise attribution only result when different red lakes have been mixed. Thus the "refinement" of madder with cochineal was very popular until well into the 19th century. The industrial madder lakes, by contrast, evince a broader variation in their colour spectra, above all by dint of the use of different substrates. In addition, madder could, by the late 19th century, be replaced by pure (synthetic) alizarin. From about 1900, furthermore, numerous synthetic red lakes were produced as artists' pigments. Their spectra sometimes resemble those of natural red lakes, so that from 1900 the identification of red lakes by VIS spectroscopy becomes increasingly difficult. However, given the date when most our pictures were painted, with the exception of the alizarin lakes we can overwhelmingly expect natural red lakes.

As the substrate or as an addition to both natural and synthetic red lakes, we sometimes encounter red lead or vermilion. They can rarely be identified with absolute confidence by VIS spectroscopy, as their curves are largely covered by those of the lakes, and occasionally blur the characteristics of the latter. Mixtures with red pigments, and in particular mixtures of different red lakes, often complicate the identification of the individual components, which is one reason for the large number of spectra which cannot be interpreted, or cannot be interpreted with confidence.

Madder lakes/alizarin lakes

Madder has been used as a colorant since classical times. Regardless of the hue, the spectra of the older aluminium lakes are largely identical. While the shape of their curves resembles the spectra of colorants derived from scale insects (kermes, cochineal, lac dye), the minima, maxima and inflection points typically differ by 5-15 nm in each case (as can be clearly seen above all in the derivatives) (figs. 12, 13). As a result, pure madder lakes can be confidently distinguished from pure carmine. Madder was, however, "refined" by the less lightfast but more intense carmine. In this case the two spectra are superimposed, so that the two components cannot be identified with confidence.

In the 19th century, further substrates were introduced for the production of madder lakes. While natural madder contains various colorants, in particular purpurin as well as alizarin, it was only from 1868 that pure alizarin lakes could also be produced from alizarin that had been obtained synthetically. The colour spectra of some of these 19th and 20th-century madder lakes are different in places from those of the older types. On the other hand, depending on the production method, alizarin lakes may also show the same spectrum as natural madder lakes. The designation "rose madder" in the interpretation of the measurements does not therefore necessarily exclude the use of a synthetic alizarin lake.

Cochineal/genuine carmine

Genuine carmine had been produced from cochineal from the 16th century. The colour spectra (fig. 13), while resembling those of rose madder (fig. 12), are not identical to it, allowing pure carmine to be distinguished from rose madder with a fair degree of confidence. In the cases of mixtures of the two red colorants with one another or with blue pigments, above all cobalt blue, identification is, by contrast, difficult (cf. above, rose madder).

The 20th century saw the invention of a few synthetic organic red colorants whose spectrum is almost or completely identical with that of genuine carmine. This is true for example of the anthraquinone derivative Helio fast pink, which came on to the market no later than about 1928 [Wagner 1928]. For the paintings investigated however this colorant is excluded by date.

Synthetic red lakes

Since the mid 19th century, synthetic organic red colorants (aniline dyes) had also been produced, initially for dyeing textiles. However, most durable synthetic lakes did not appear, probably, until the early 20th century [Kühn 1984]. Particularly in the field of red colours, there exist very many dyes, lakes and pigments. VIS spectrometry cannot identify these with any confidence, as in many case different compounds have identical or very similar spectra.

Yellow pigments

For the identification of 19th and 20th-century yellow pigments, the usefulness of VIS spectroscopy is very limited. Unambiguous spectra are produced only by iron-oxide yellow/yellow ochre. Also relatively easy to distinguish from other yellow pigments are barium chromate (barium yellow) and Naples yellow, but only if we are talking about pure colours. However, yellow pigments were also sold as industrial mixtures, which is not always clear from the trade name. Chrome yellow, cadmium yellow and arylamide yellow can be produced in different hues. The respective spectra of lemon-yellow and dark chrome yellow, cadmium yellow and arylamide yellow are so similar that no unambiguous distinction is possible.

Barium chromate

Barium chromate was commercially available as baryta yellow or ultramarine yellow from the mid 19th century [Kühn, Curran 1986]. Its spectrum is markedly different from those of other yellow pigments, so that when unmixed it is relatively easy to identify. In the paintings under investigation, however, it only occurs twice (fig. 14).

Cadmium yellow

Cadmium yellow (cadmium sulphide) can be produced in various hues ranging from lemon yellow to pale orange, the exact hue being dependent on the size of the particles and the crystalline structure. The spectra also differ according to hue. However, the colour curves match those of similarly coloured types of chrome yellow and arylamide yellow (fig. 15). For this reason cadmium yellow cannot be confidently identified by VIS spectroscopy (cf. also above cadmium orange/cadmium red).

Chrome yellow

Chrome yellow, chrome orange and chrome red are lead chromates of varying composition and crystalline structure. The hues vary between lemon yellow, orange and dark red. Yellow, orange and red chrome pigments have been produced since the early 19th century [Kühn, Curran 1986].

The differently coloured lead chromates also differ in their colour spectra, the spectra of the yellow chrome-yellow types being very similar to those of the yellow cadmium-yellow types and of various kinds of arylamide yellow. VIS spectroscopy cannot therefore identify chrome yellow unambiguously; in the case of 19th-century paintings, cadmium yellow is always another possibility (fig. 15), while in the 20th century, so is arylamide yellow.

In the case of greens produced by mixing Prussian blue with a yellow pigment, we may presume that chrome yellow was preferred to cadmium yellow if only because it was cheaper. As an industrial mixture, this green was traded under names including “chrome green”.

Iron-oxide yellow

Yellow and brownish-yellow iron oxides are widespread in nature as yellow ochre. Since the early 19th century, iron-oxide pigments have also been produced synthetically. VIS spectroscopy cannot distinguish between the natural and synthetic colorants, as they are chemically identical and thus produce the same curves. “Iron-oxide yellow” must therefore always be understood as the superordinate term covering both the natural and the artificial pigment.

The spectra of iron-oxide yellow vary according to hue (yellow or brownish), but are always clearly distinguishable from those of other yellow and brown pigments (fig. 16). In mixtures too, iron-oxide yellow can usually be identified with some confidence.

Arylamide yellow (Hansa yellow)

The azo dye sold under the trade-name Hansa yellow came on to the market in about 1909. It could be produced in hues varying from lemon yellow to yellow ochre [Fritsch 2006].

The differently coloured arylamide-yellow lakes also differ in their colour spectra, while resembling very closely the corresponding types of chrome and cadmium yellow. For this reason, VIS spectroscopy cannot identify them with certainty. For most of the paintings investigated, however, arylamide yellow is irrelevant, as they were painted before it was invented.

Naples yellow

Naples yellow (lead antimonate) has been used as a pigment since the 16th century. The colour spectrum is markedly different from that of other yellow pigments as a result of its shallow gradient and the position of the inflection point. In its pure form, the pigment can thus be identified by VIS spectrometry with considerable confidence. In mixtures, especially with other yellow pigments but also with blue or green, these characteristics are however easily overlaid by the other curves, so that it becomes difficult or impossible to distinguish it from other yellow pigments.

Zinc yellow

Zinc yellow (zinc potassium chromate) was commercially available as a pigment from the mid 19th century [Kühn, Curran 1986]. The colour spectrum differs from those of pale chrome yellow and cadmium yellow varieties and from those of other yellow pigments. For this reason, zinc yellow can be identified when pure by VIS spectroscopy with a fair degree of confidence. It is much more difficult to identify in mixtures. Zinc yellow was mixed primarily with Prussian blue to obtain zinc green. Here, though, it is not easy to distinguish from other yellow pigments, e.g. barium yellow, Naples yellow and above all chrome yellow, which was also mixed with Prussian blue to create “chrome green”. Similarly, zinc yellow used to impart a yellow tinge to viridian cannot be identified with any degree of certainty.

Green pigments

For greens as for yellows, VIS spectroscopy is only of limited usefulness. Only the spectra of chromic oxide green and its hydrous form known as viridian are so striking that they can always (largely, even, in mixtures) be identified with certainty. However, also widespread in painting were blue-and-yellow mixtures, with Prussian blue as the blue pigment and in particular chrome or zinc yellow as the yellow component. These two mixtures are not easy to distinguish by VIS spectroscopy. Also problematic is the distinction between these blue-and-yellow mixtures and green copper-based pigments with a heavy admixture of white or yellow. Finally, the green copper-based pigments cannot be distinguished from each other using VIS spectroscopy.

Viridian (hydrous chromic oxide green)/chromic oxide green

Chromic oxide green (Cr_2O_3) and its hydrous form ($Cr_2O_3 \cdot H_2O$), known as viridian, had been commercially available as pigments since the second quarter of the 19th century and about 1860 respectively [Kühn 1984]. Both have very characteristic colour spectra, which not only allows them to be distinguished from other green pigments, but also from each other. Particularly in the derivative, some typical bands of viridian are also very easily visible even in mixtures, so that even relatively small proportions of the pigment are still identifiable (fig. 17). On the other hand, the spectrum superimposes itself very strongly on the curves of other colorants, so that these are often no longer identifiable. This is true in particular of yellow pigments, which, according to the sources, were often mixed with viridian [e.g. Wagner 1928], while being recognizable with difficulty, if at all, in the spectra.

These pigments must not be confused with "chrome green", which was used as a trade name for (usually) industrially produced mixtures of chrome yellow and Prussian blue. While the colour spectra allow the individual components to be distinguished, they do not reveal whether the artist used a pre-mixed product or mixed blue and yellow on the palette him or herself (fig. 18). When the colorants are listed in the picture documentation, the expression "chrome green" is accordingly not used, the findings for green mixtures being listed separately for the individual pigments.

Copper-based green pigments

Copper-based green pigments continued to be much used in the 19th and 20th centuries. In particular emerald green (copper(II) aceto-arsenite, also known among other things as Paris green and Schweinfurt green), produced on a factory scale since 1814 is mentioned in the literature and in the sources time and again. In addition, however, other copper compounds were also on the market, e.g. other copper arsenites, basic copper chloride and copper sulphates. The colour spectra of the various green copper compounds do not differ significantly enough to be identifiable using this method. However, the spectra of copper-based green pigments to which no, or very little, yellow pigment has been added, deviate quite markedly from those of greens produced by mixing Prussian blue with yellow pigments, so that copper-based green pigments in this case can be identified at least as a group by the use of VIS spectrometry.

Green mixtures

Alongside genuine green pigments, green mixtures consisting of Prussian blue and a yellow pigment were much used in the 19th and 20th century; the mixture with chrome yellow was known as chrome green, while that with zinc yellow was known as zinc green. The spectra of the green mixtures generally differ quite considerably from those of the copper-based greens, but when the proportion of white is greater, or when the copper-based green is mixed with a yellow pigment, it is no longer possible to tell apart the two groups unambiguously.

The yellow pigments used in the mixed greens are not at all easy to identify by spectroscopy. When the proportion of yellow is high, zinc yellow is the easiest to recognize, while chrome yellow can often be presumed (fig. 18), as the sources tell us that cadmium yellow (which has a similar spectrum) was too expensive to use in mixtures of this kind. This is of course not proof positive. Nor can other yellow pigments be excluded with a sufficient degree of certainty.

Summary

VIS spectroscopy is a non-destructive method for measuring all the colours used in a painting. This makes it an excellent choice for preliminary investigations, on the basis of which further, possibly invasive, methods might be considered. Some colorants can be determined with confidence, or at least with a high degree of probability, by the use of VIS spectroscopy alone. Confining ourselves to the pigments used in the 19th century, these are: cobalt blue, cerulean blue, smalt, ultramarine, cobalt violet (various types), iron-oxide yellow, chromic oxide green and viridian. In addition, the following pigments can be identified with a fair degree of confidence when used in pure, unmixed form: ultramarine violet, Prussian blue, red lead, vermilion, iron-oxide red, rose madder and genuine carmine. The development of new (in particular, synthetic organic) colorants means that in 20th-century paintings vermilion, red lead, rose madder and carmine, and sometimes also ultramarine, can no longer be identified with confidence. By contrast, it is precisely the organic colorants in older (pre-19th century) paintings which can often be identified more certainly by VIS spectroscopy than by invasive methods. For yellow pigments and, with the exception of chromic oxide, green pigments too, VIS spectroscopy is only appropriate for a preliminary rough classification.

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- **Wagner 1928**
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- **Schallfarben**
  Lothar Schall (1924-73), produced colorant of artitsts. Samples in the collection of CICS

- **Kremerpigmente**
  Kremerpigmente, Aichstetten

Brief Biography by Doris Oltrogge

Studied art history and archaeology in Göttingen and Bonn.

Took her doctorate with a dissertation entitled “Illustrationszyklen der Histoire ancienne, 1250-1400”.

From 1987 to 1992 research assistant at the Forschungsstelle für Technik mittelalterlicher Buchmalerei (Centre for research into techniques of medieval book illumination) in Göttingen.

Since 1992 has worked in the laboratory for non-destructive analysis / restoration and conservation of written materials, graphic art and book illumination at the Cologne Institute for Conservation Science (CICS) at the University of Applied Science in Cologne. She conducts research into the techniques of medieval book illumination, and the history, manufacture and non-invasive investigation of colorants, while building up an internet database of art-technological sources of the Middle Ages and the early modern period.

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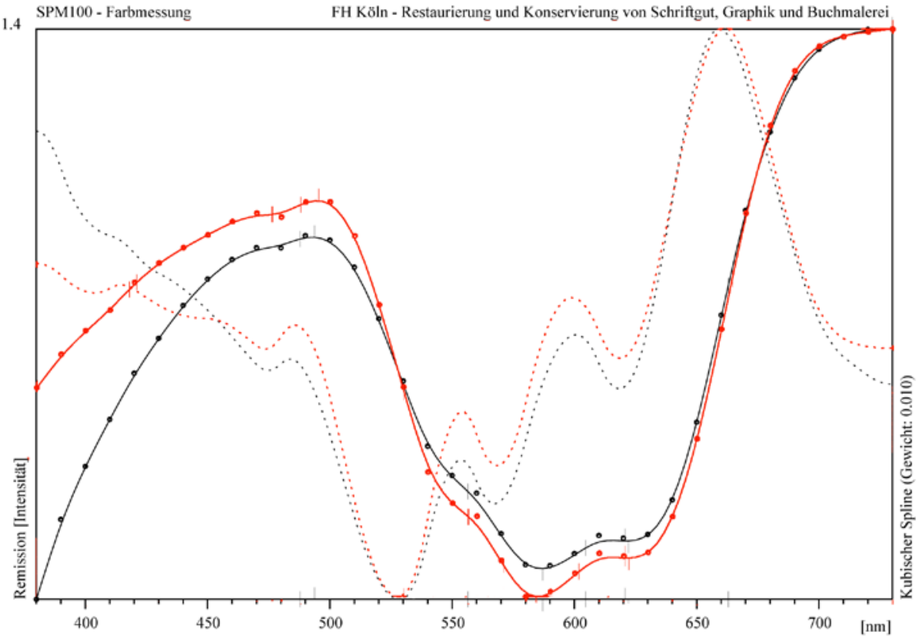


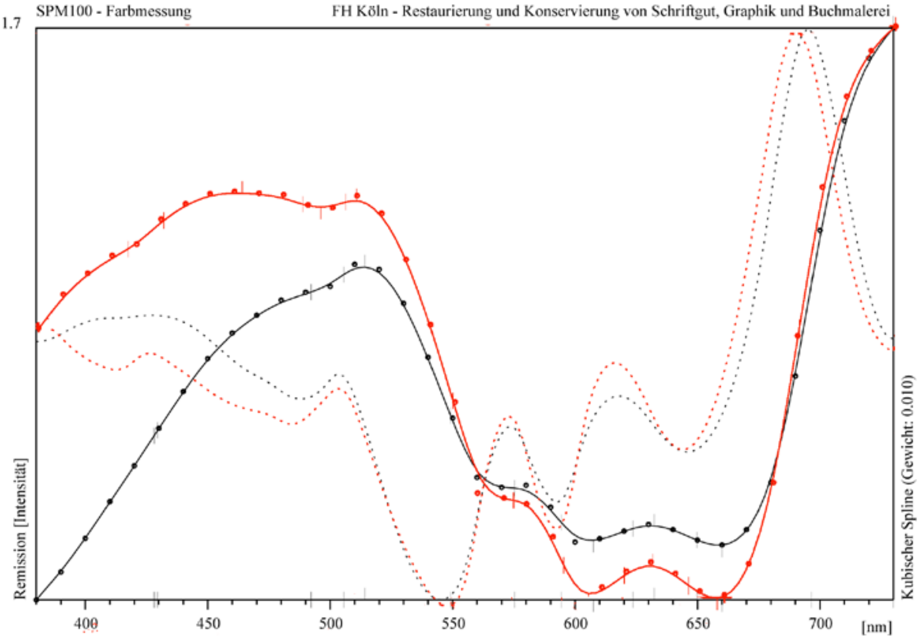
[BL2.MAB] MANET SPARGEL DEP.318 BL2 BLAU IN SPARGELKOEPFEN MUG 8.8VR 17.8VU

Lab-Werte (gemessen am: 14.6.2006)
L = 31.272, a = -4.155, b = -11.680

Fig. 1

Manet
Still-Life with Asparagus
1880, WRM Dep. 318

Blue in the asparagus heads. The measured curve (black) matches the reference spectrum (red) of cobalt blue (cobalt aluminate) almost exactly.



[BL1.MOG] MORISOT ENFANT AU JARDIN DEP. FC 614 BL1 VS BLAUGRUEN IM ZAUN 38.0VU 23.5VL

Lab-Werte (gemessen am: 17.7.2006)
L = 22.674, a = -11.832, b = -3.690

Fig. 2

Morisot
Child among Hollyhocks
1881, WRM Dep. FC 614

Blue-green in the fence. The measured curve (black) differs from the reference spectrum (red) of cerulean blue only in the somewhat steeper gradient. This could be caused by a trivially different composition of the mixture of cobalt and stannic oxide.

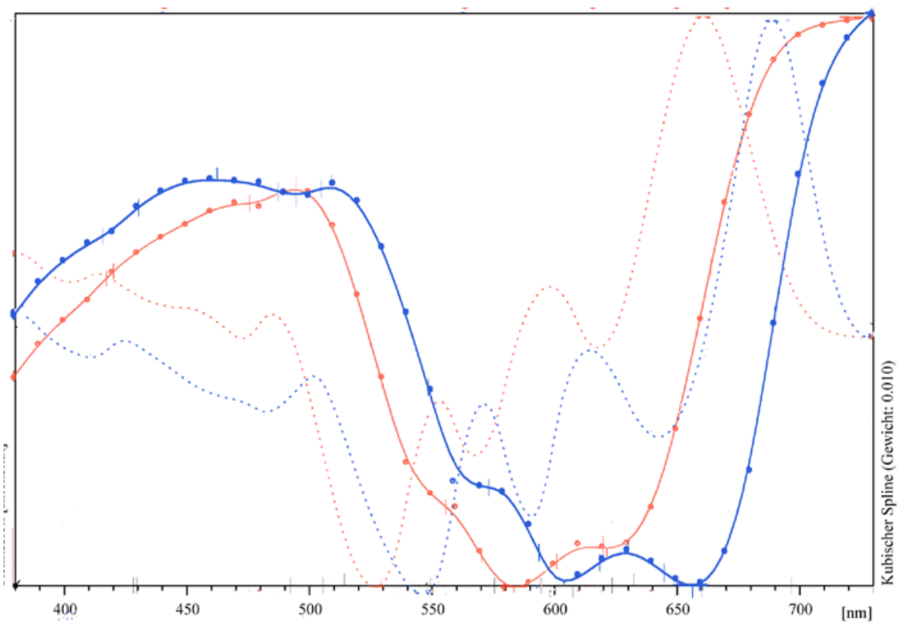


Fig. 2a

Morisot
Child among Hollyhocks
1881, WRM Dep. FC 614

While the spectrum of cerulean blue (blue) resembles that of cobalt blue (red), the minima and maxima of the measured curve (solid line) and the derivative (dashed line) are however characteristically shifted by about 10-20 nm.

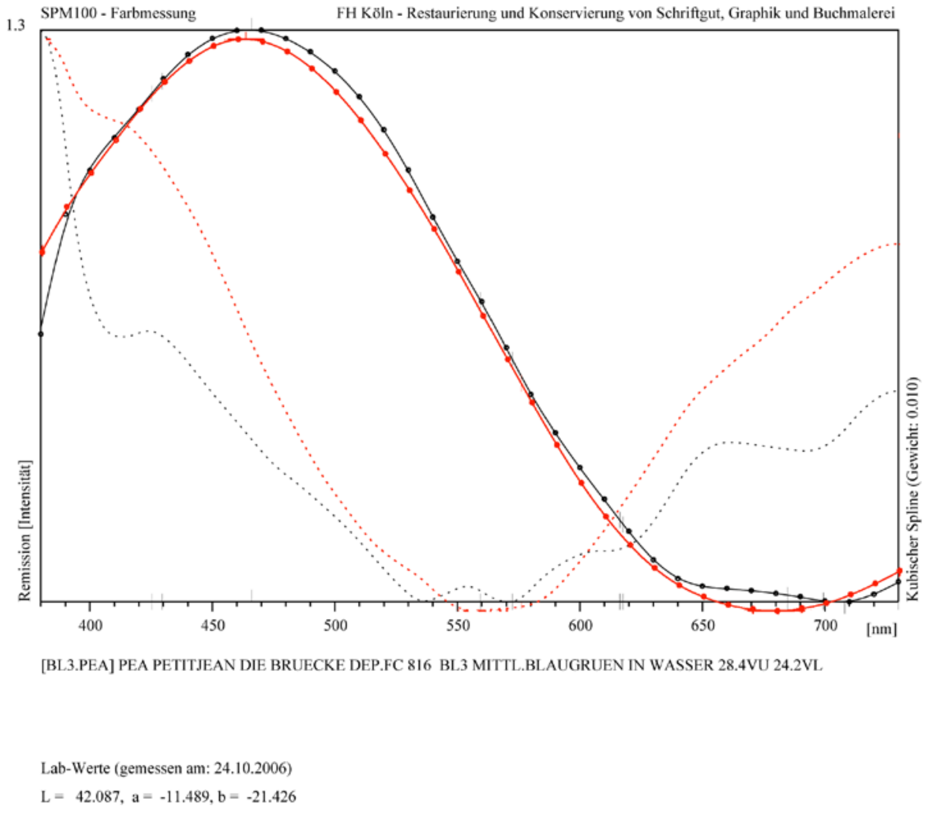
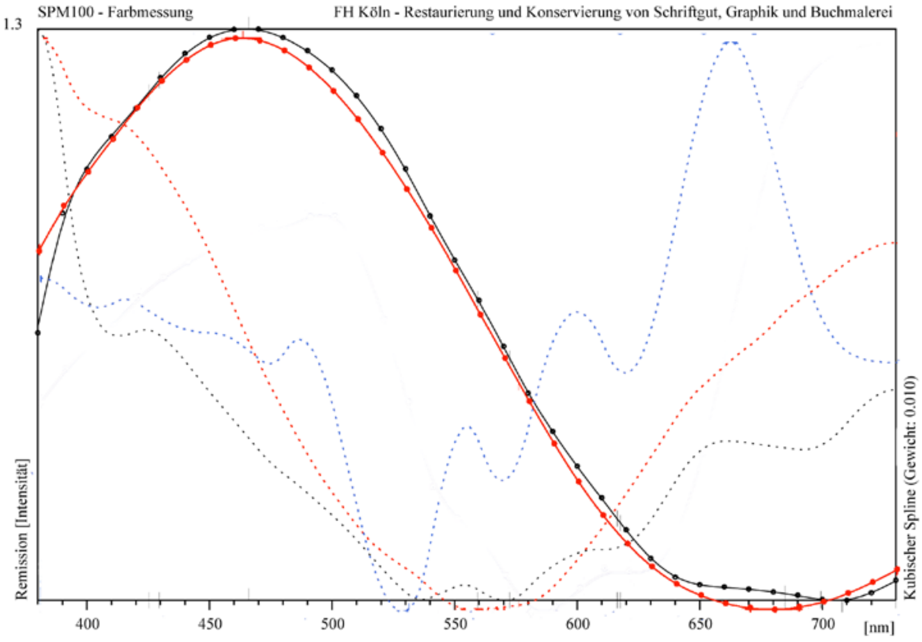


Fig. 3

Petitjean
The Bridge
c. 1890, WRM Dep. 816

Blue in the reflection of the house on the left. The measured curve (black) matches the reference spectrum (red) of Prussian blue very well. The derivative (dashed line) by contrast has considerably more bands. These largely correspond to the characteristic derivative bands of cobalt blue (Fig. 3a, dashed blue line). Some cobalt blue was therefore added to the Prussian blue.



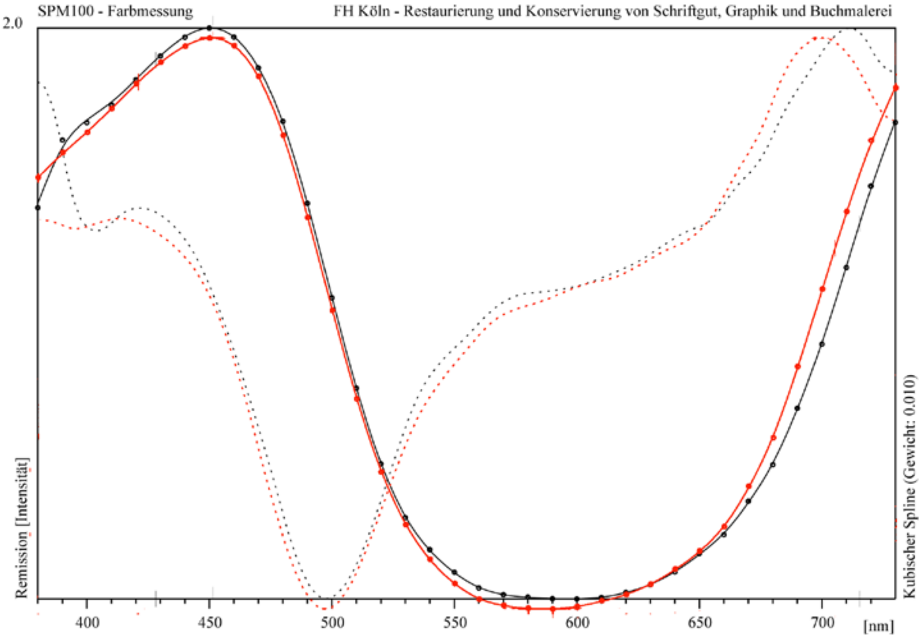
[BL3.PEA] PEA PETITJEAN DIE BRUECKE DEP.FC 816 BL3 MITTL.BLAUGRUEN IN WASSER 28.4VU 24.2VL

Lab-Werte (gemessen am: 24.10.2006)
L = 42.087, a = -11.489, b = -21.426

Fig. 3a

Petitjean
The Bridge
c. 1890, WRM Dep. 816

Blue in the reflection of the house on the left. The measured curve (black) matches the reference spectrum (red) of Prussian blue very well. The derivative (dashed line) by contrast has considerably more bands. These largely correspond to the characteristic derivative bands of cobalt blue (Fig. 3a, dashed blue line). Some cobalt blue was therefore added to the Prussian blue.



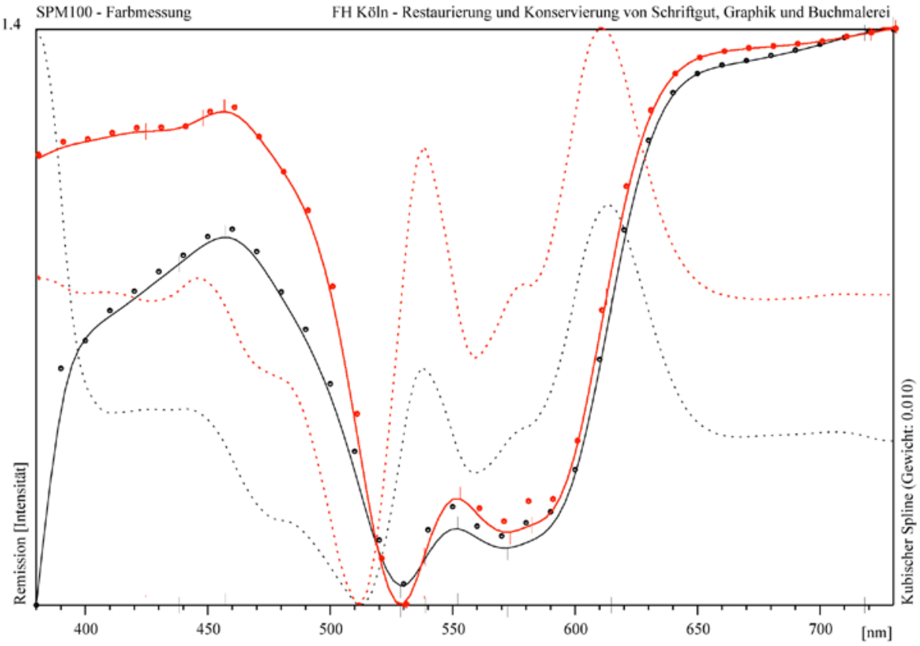
[BL1.LAA] LAA LAUGE PROMENADE DEP FC 757 BL1 DKL BLAU BAUM RECHTS 15.5VU 35.6VL

Lab-Werte (gemessen am: 23.6.2006)
L = 12.768, a = 21.292, b = -37.680

Fig. 4

Laugé
Promenade
1888, WRM Dep. FC 757

Dark blue in the right-hand tree. The measured curve (black) matches the reference spectrum of oil-bound ultramarine (red) very well.



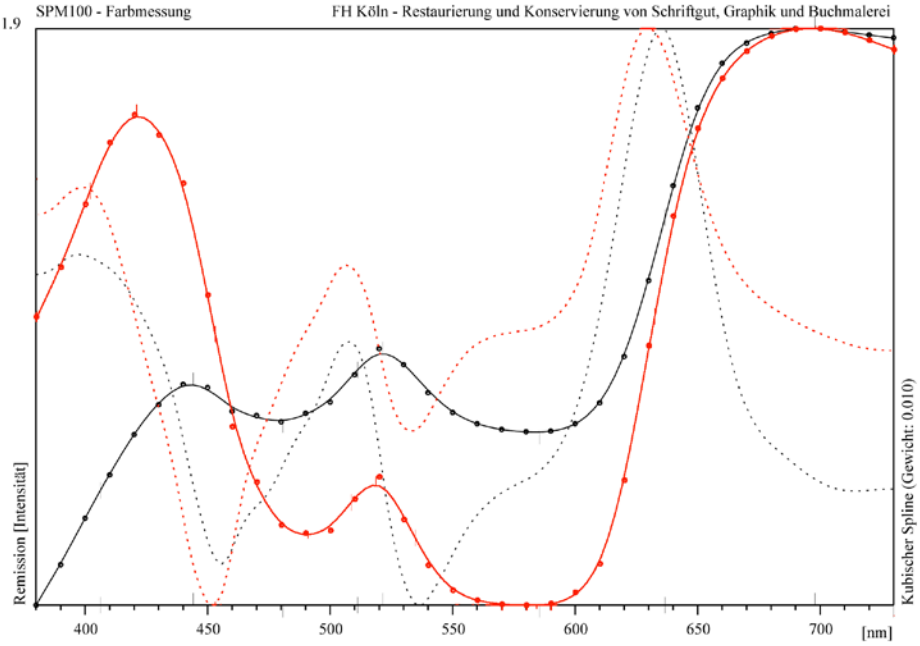
[VI1.MEA] MEA METZINGER RUND.BAUM FC VI1 VIOLETT IM WEG 3.6VU 6.8VL

Lab-Werte (gemessen am: 12.10.2006)
L = 32.335, a = 26.475, b = -17.497

Fig. 5

Metzinger
Landscape with Round Tree
c. 1906 WRM Dep. 847

Violet in the road. The measured curve (black) and the derivative (dashed black) match the reference spectrum of cobalt violet (cobalt arsenate) from the patterns in Wagner 1928, plate following p. 128, almost exactly (red). The steeper gradient of the curve relative to the reference could be caused by the addition of zinc white.



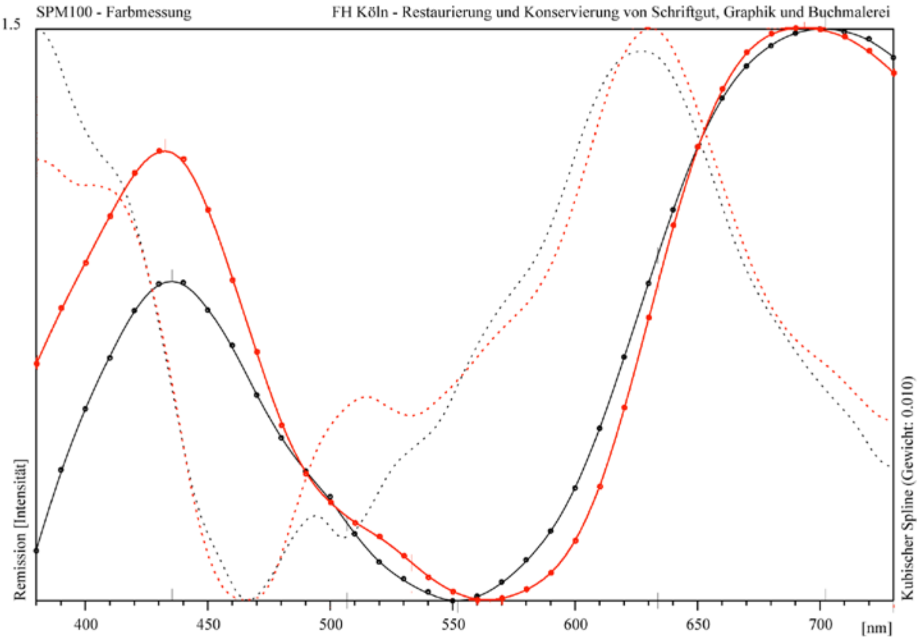
[VI1.MOG] MORISOT ENFANT AU JARDIN DEP. FC 614 VI1 VS DKL VIOLETT VORNE MUG 5.5VU 23.5VL

Lab-Werte (gemessen am: 17.7.2006)
L = 20.872, a = 5.220, b = 1.801

Fig. 6

Morisot
Child among Hollyhocks
1881, WRM Dep. FC 614

Violet in the foreground. The measured curve (black) largely matches the reference spectrum of a cobalt violet produced by Schallfarben (red). Presumably it is a cobalt phosphate, but the reference has not yet been subject to precise chemical identification.



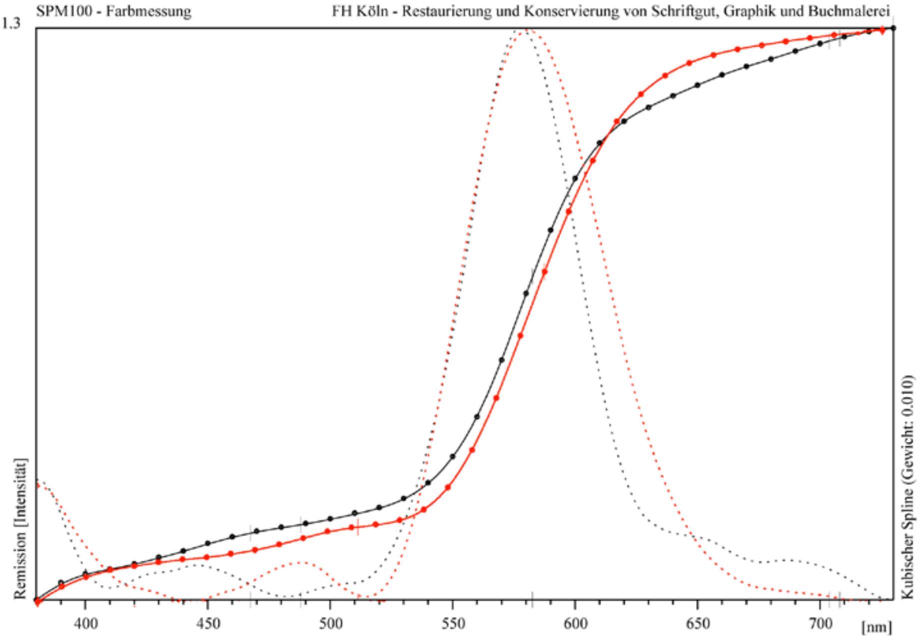
[VI1.LUA] LUCE ST TROPEZ DEP. FC 733 VI1 VIOLETT HORIZONT 13.0VU 24.6VL

Lab-Werte (gemessen am: 18.7.2006)
L = 23.598, a = 14.071, b = -9.648

Fig. 7

Luce
Saint-Tropez
1892, WRM Dep. FC 733

The measured curve (black) matches a reference spectrum of cobalt violet (red), which was measured in a 19th-century paint-box, almost completely. It is presumably a cobalt phosphate, but the reference has not yet been subject to precise chemical identification. Trivial deviations from the reference, above all the derivative bands between 480 and 510 nm, are caused by cobalt blue measured at the same time.



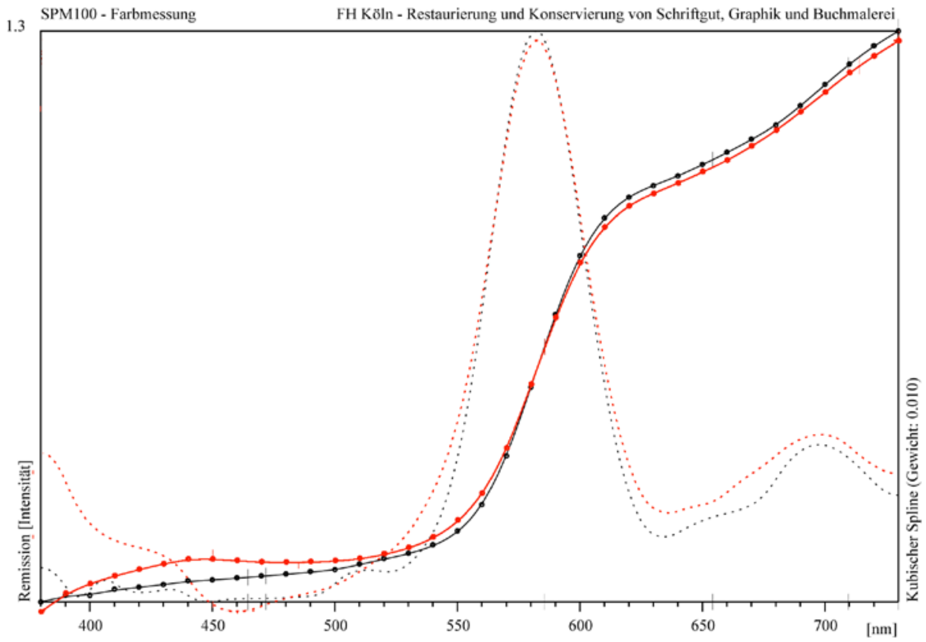
[RO2.RED] RENOIR JEAN COUSANT DEP. FC 680 RO2 HELLROT FALTENWURF AERMEL 18.8VU 8.8VL

Lab-Werte (gemessen am: 10.7.2006)
L = 43.248, a = 30.679, b = 24.781

Fig. 8

Renoir
Jean Renoir sewing
1900, WRM Dep. FC 680

Red fold in the sleeve. The measured curve (black) matches that of chrome red (red) pretty exactly. The shape of the curve of this pigment resembles that of red lead (fig. 10) and vermilion (fig. 11), but the inflections of the three pigments (dashed line) is in a different place in each case. The inflection of chrome red corresponds to that of iron-oxide red (fig. 9), but is usually broader.



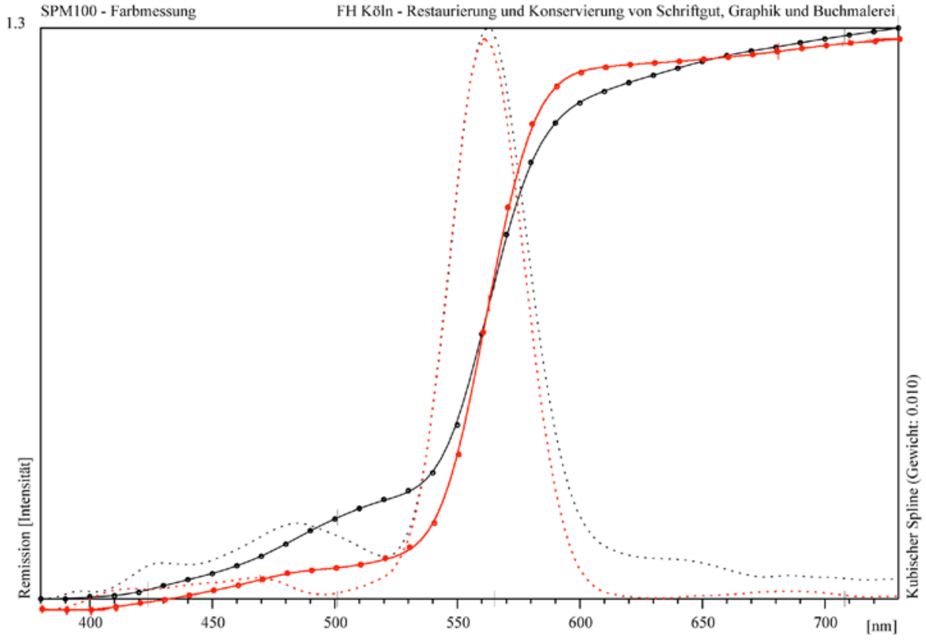
[RO1.GAE] GAE GAUSSON LA RUE DES ETUVES... DEP FC 745 RO1 ROTBRAUN ESSE HAUS RECHTS 12.2VL 11.6VU

Lab-Werte (gemessen am: 4.4.2007)
L = 33.266, a = 17.663, b = 11.730

Fig. 9

Gausson
Rue des Étuves
at Lagny-Sur-Marne
c. 1885, WRM Dep. FC 745

Chimney of the first house on the left, red. The spectrum (black) matches that of reddish-brown iron-oxides (red) exactly.



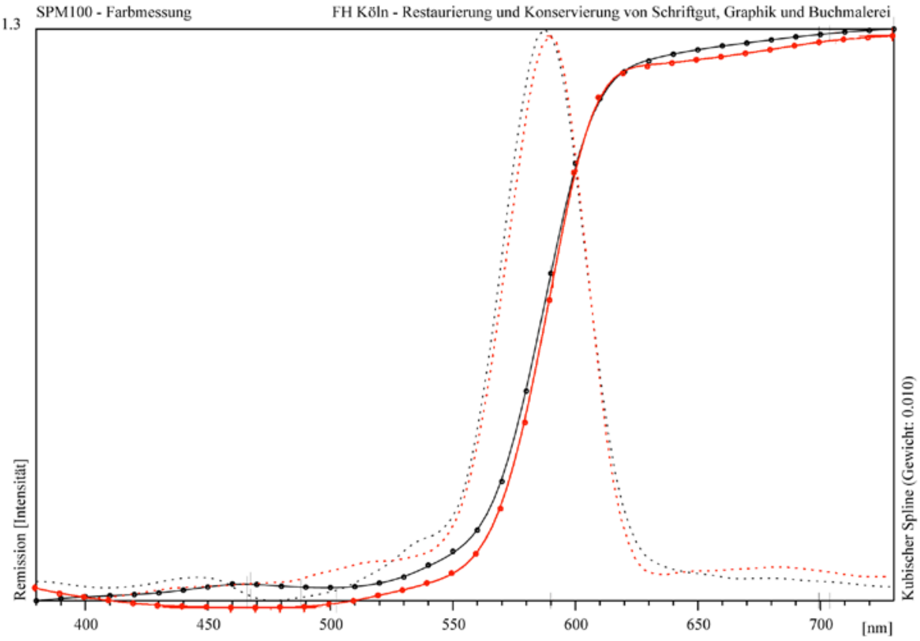
[OR1.GAE] GAE GAUSSON LA RUE DES ETUVES... DEP FC 745 OR1 GEBAEUDE VORNE RE 17.3VL 3.6VU

Lab-Werte (gemessen am: 4.4.2007)
L = 48.865, a = 32.431, b = 37.092

Fig. 10

Gausson
Rue des Étuves
at Lagny-Sur-Marne
c. 1885, WRM Dep. FC 745

Bright orange in the corner of the building in the right foreground. The measured curve (black) matches the spectrum of red lead (red) almost exactly. The gradient of the curve deviates from the reference between 460 and 500 nm, a circumstance which can be explained by yellow components measured at the same time.



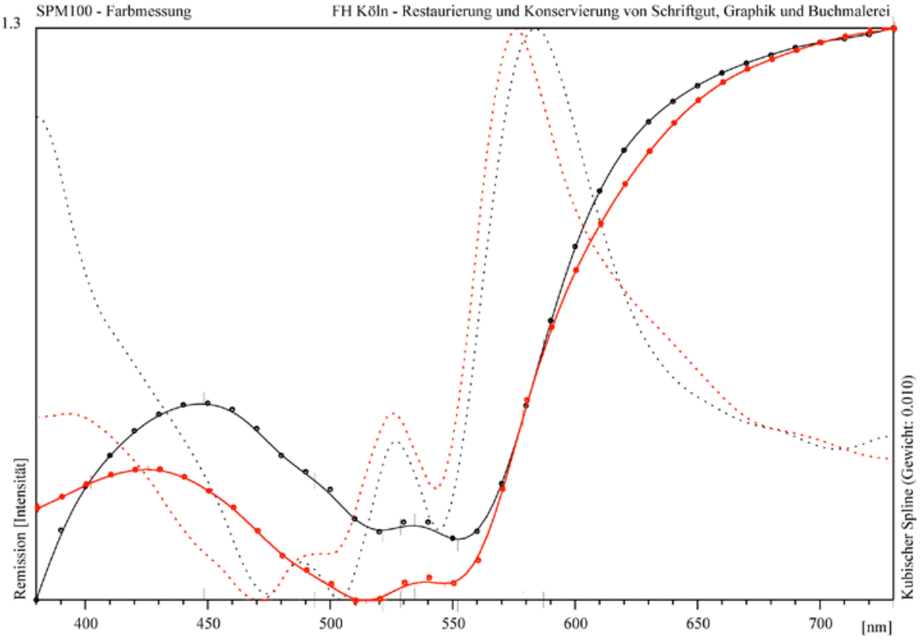
[RO1.CRA] CRA CROSS COUCHER DEP.FC 708 RO1 ROT IN WOLKE 15.2VL 37.9VU

Lab-Werte (gemessen am: 9.1.2007)
L = 43.121, a = 43.810, b = 27.086

Fig. 11

Cross
Sunset over the Sea
1896, WRM Dep. FC 708

Red in the purple band of cloud. The measured curve (black) is identical with the reference spectrum of vermilion (red).



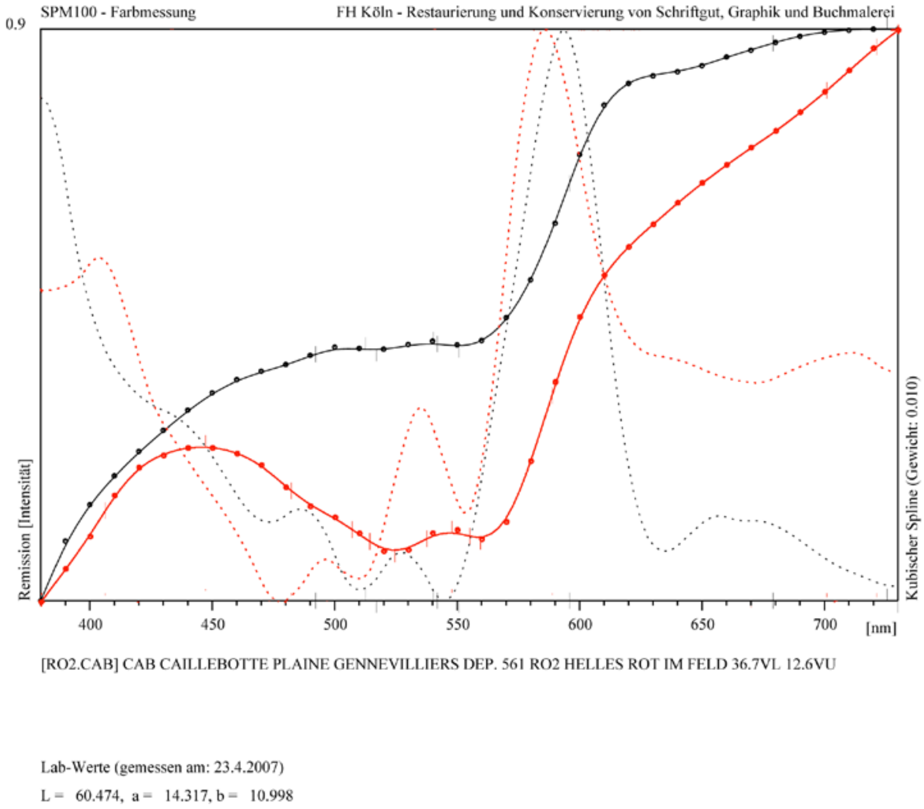
[RO2.CRB] CROSS PAYSAGE DEP.FC 659 RO2 ROTER FARBLACK IN WIESE 39.7VL 2.9VU

Lab-Werte (gemessen am: 16.1.2007)
L = 44.533, a = 40.969, b = 5.965

Fig. 12:

Cross
Landscape in Provence
1898, WRM Dep. FC 659

Red lake in the meadow at the bottom edge of the picture. The measured spectrum (black) largely matches that of rose madder (red). The broad hump at 450 nm may be caused by the particular method of producing the lake. Whether it is a synthetic alizarin lake or a madder obtained from the plant cannot be determined using VIS spectroscopy.



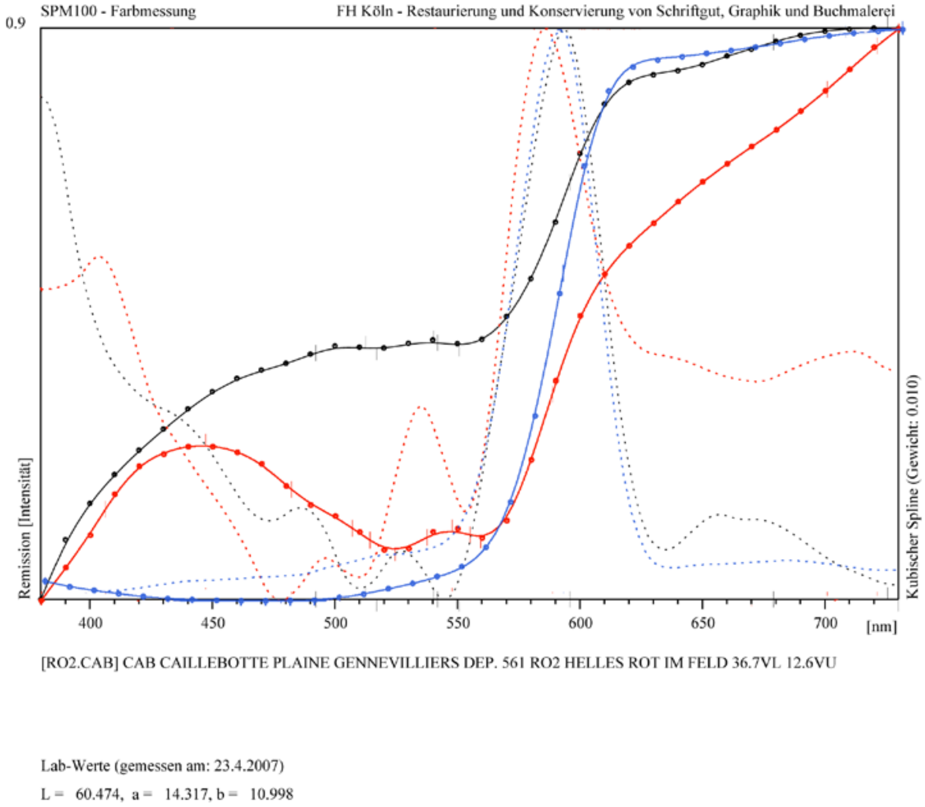
[RO2.CAB] CAB CAILLEBOTTE PLAINE GENNEVILLIERS DEP. 561 RO2 HELLES ROT IM FELD 36.7VL 12.6VU

Lab-Werte (gemessen am: 23.4.2007)
L = 60.474, a = 14.317, b = 10.998

Fig. 13

Caillebotte
The Plain of Gennevilliers
1884, WRM Dep. FC 561

Red in the field of flowers. Above all the derivative (dashed line) shows the close agreement of the measured curve (black) with the reference spectrum of cochineal (red). The deviations, the markedly flatter gradient of the curve from 600 nm and the somewhat shifted inflection point, are caused by the admixture of vermilion (fig. 13a: blue curve).



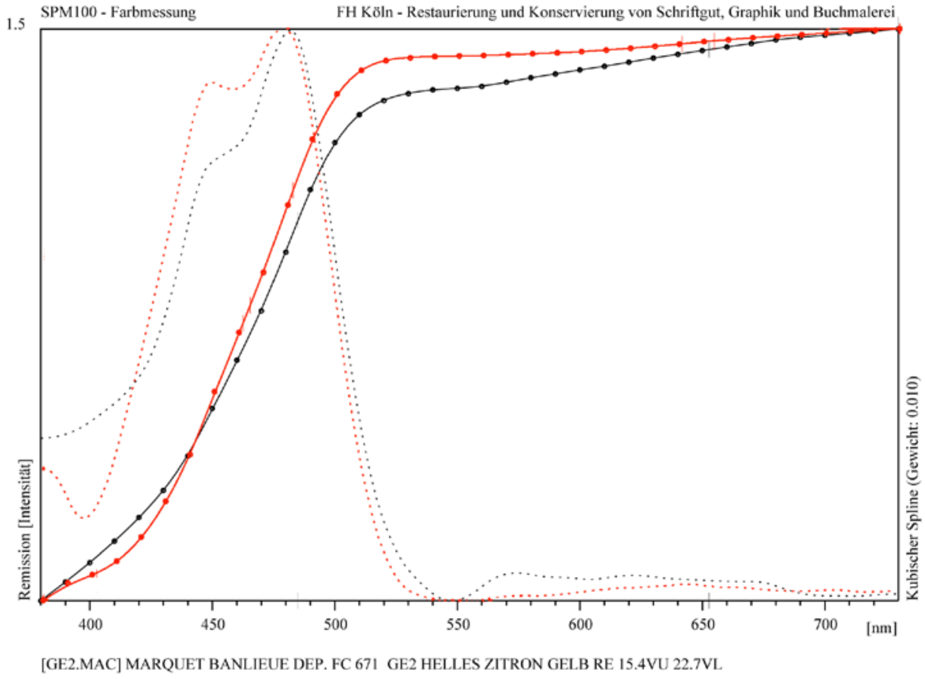
[RO2.CAB] CAB CAILLEBOTTE PLAINE GENNEVILLIERS DEP. 561 RO2 HELLES ROT IM FELD 36.7VL 12.6VU

Lab-Werte (gemessen am: 23.4.2007)
L = 60.474, a = 14.317, b = 10.998

Fig. 13a

Caillebotte
The Plain of Gennevilliers
1884, WRM Dep. FC 561

Red in the field of flowers. Above all the derivative (dashed line) shows the close agreement of the measured curve (black) with the reference spectrum of cochineal (red). The deviations, the markedly flatter gradient of the curve from 600 nm and the somewhat shifted inflection point, are caused by the admixture of vermilion (blue curve).

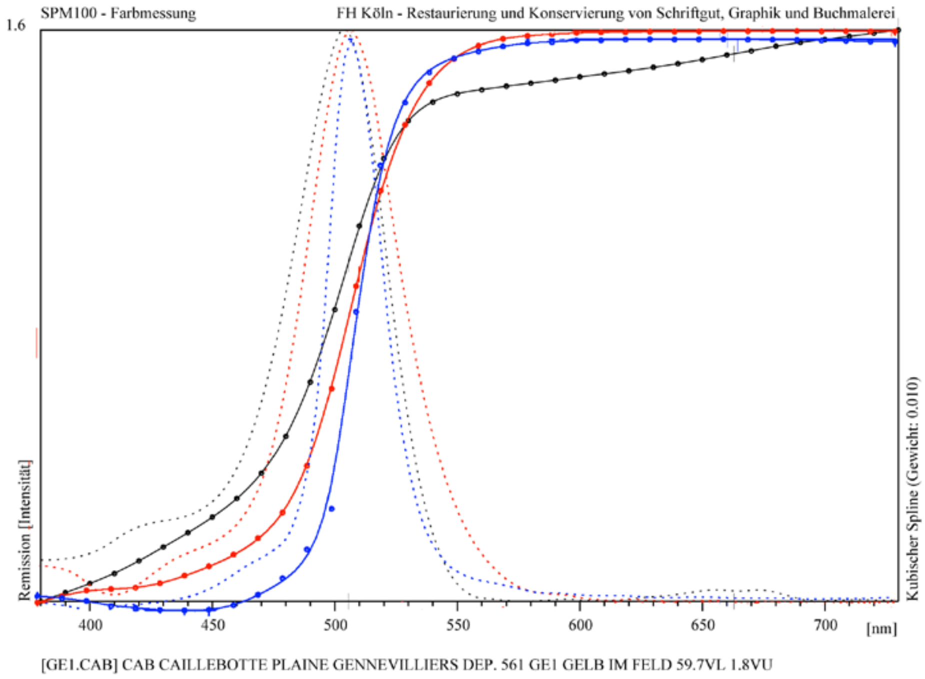


Lab-Werte (gemessen am: 18.6.2006)
L = 72.618, a = -7.535, b = 53.330

Fig. 14

Marquet
Outskirts of Paris
1899, WRM Dep. FC 671

Lemon yellow in the middle. The spectrum (black) is almost identical to that of barium chromate (red).

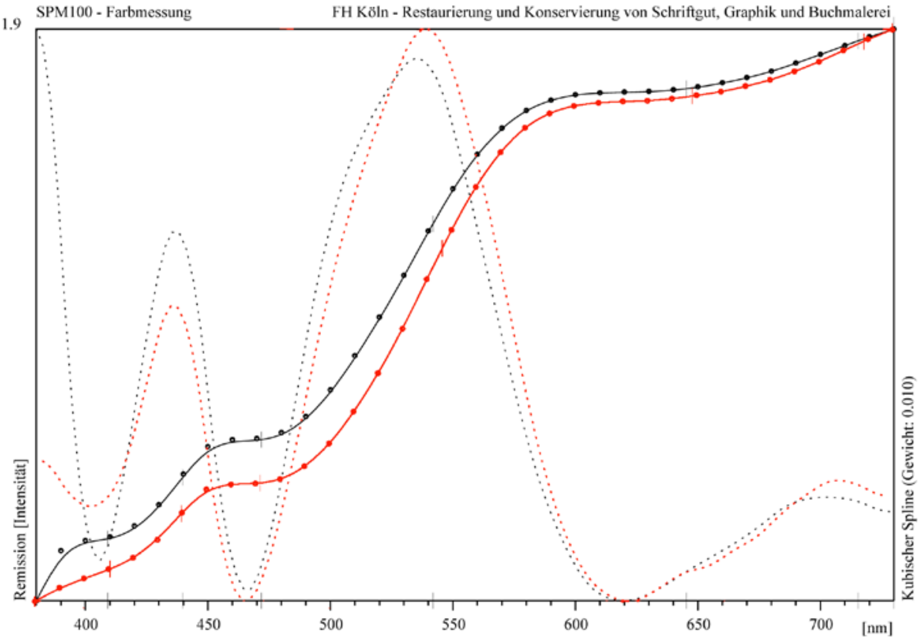


Lab-Werte (gemessen am: 23.4.2007)
L = 67.412, a = -0.557, b = 68.423

Fig. 15

Caillebotte
The Plain of Gennevilliers
1884, WRM Dep. FC 561

Bright yellow at the bottom edge of the picture. The measured curve (black) shows an inflection point at 505 nm, recognizable only in the derivative (dashed line). These characteristics are also found in the spectra of intense yellow types of chrome yellow (red) and cadmium yellow (blue).



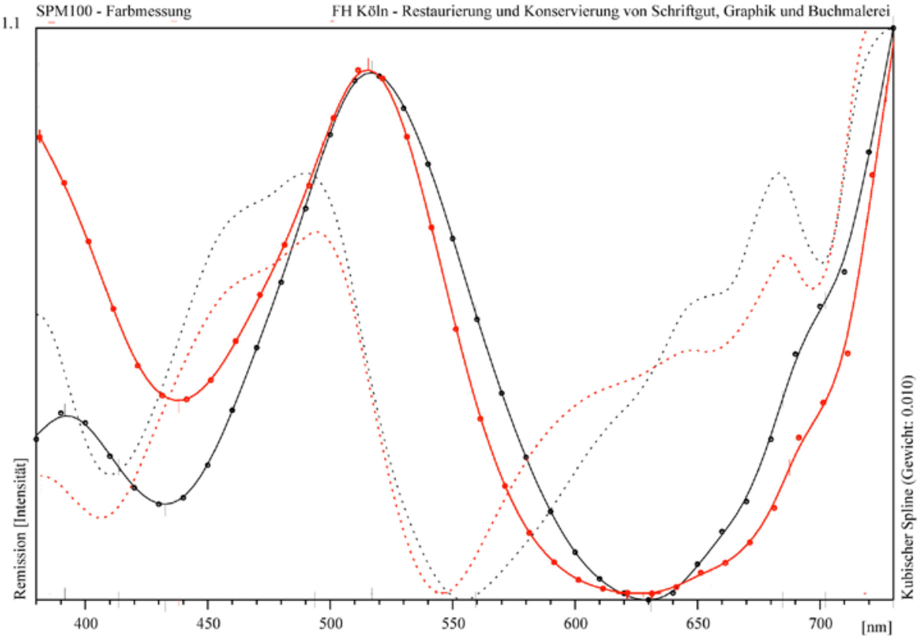
[GE1.CAF] CAILLEBOTTE BORDS DE SEINE DEP. FC 706 GE1 GELB AM UNTEREN UFER 6.2VU 39.0VL

Lab-Werte (gemessen am: 10.7.2006)
L = 45.120, a = 15.326, b = 43.044

Fig. 16

Caillebotte
Banks of the Seine
1891, WRM Dep. FC 706

Warm yellow on the foreground bank. The spectrum (black) exactly matches that of yellow iron oxides (red).



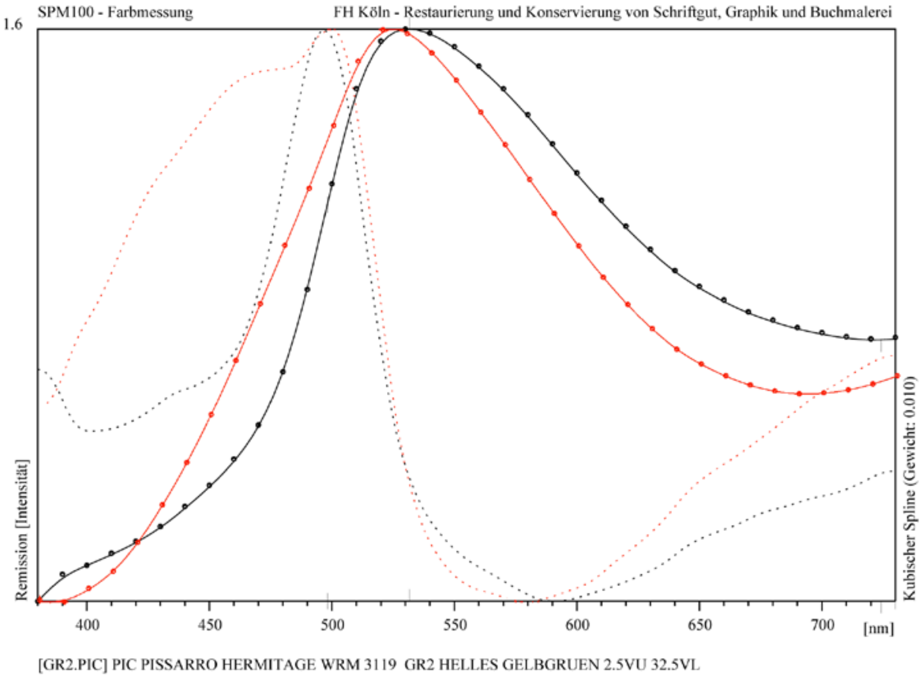
[GR1.BAA] BAZILLE JEUNE FEMME DEP. FC 811 GR1 DKLGRUEN AUSMISCHG REBEN 11.0VU 12.4VL

Lab-Werte (gemessen am: 10.7.2006)
L = 45.240, a = -25.234, b = 6.815

Fig. 17

Bazille
Young Woman
among Grapevines
1869, WRM Dep. FC 811

Green in the grapes. The measured curve (black) almost exactly matches the reference spectrum of viridian (red). Small differences can be explained by cobalt blue measured at the same time.



Lab-Werte (gemessen am: 15.6.2006)
L = 36.345, a = -17.176, b = 23.606

Fig. 18

Pissarro
L'Hermitage at Pontoise
1867, WRM 3119

Yellowish-green in the foreground. The measured spectrum (black) strongly resembles a reference spectrum of chrome green (red). The derivative (dashed line) shows the inflection point of chrome yellow as a maximum.