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Analytical studies on commercial artists' colour charts from *Das Deutsche Farbenbuch* (1925)—identification of synthetic and natural organic colourants by Raman microscopy, surface-enhanced Raman spectroscopy and metal underlayer ATR-FTIR spectroscopy

Clarimma Sessa^{1*}, Christoph Steuer², Diego Quintero Balbas³, Giorgia Sciutto³, Silvia Prati³ and Heike Stege²

Abstract

Historical colour charts provide a rich and often well-dated reference materials source for studying the chemical composition of all kinds of commercial brands of artists' paints. This article presents the results of an extensive analytical study of more than 80 paint hues from 11 colour charts that are included in the German standard book *Das Deutsche Farbenbuch* by H. Trillich (1925, Part II). Our research focused on the identification of synthetic organic pigments, whose quickly increasing significance for artists' paints in the early twentieth century is impossible to evaluate by documentary source research alone. A stepwise procedure combining different non- or minimally invasive vibrational spectroscopy techniques—Normal Raman and Surface-Enhanced Raman spectroscopy as well as Metal Underlayer Attenuated Total Reflection Fourier-transform Infrared Spectroscopy—allowed the identification of 18 different organic colourants in artists' watercolours, tempera and oil colours from six German manufacturers. In addition, micro-X-Ray Fluorescence spectroscopy was applied to determine the elemental pattern of substrates, fillers, and admixed inorganic pigments. In addition to a few traditional natural organic colourants (dark and rose madder lake, cochineal lake), most of the identified compounds comprised synthetic organic pigments or synthetic dyes from various chemical classes (indigo, anthraquinone, monoazo, β -naphthol, xanthene, triarylcarbonium, nitroso, and azine compounds). Some of these have not or only rarely been reported in artists' paints so far. Since the identified organic colourants have mainly poor to fair (only sometimes good) fastness to light according to modern standards and partially also to solvents typically used in conservation treatments, it is evident that works of art from this period should be treated keeping in mind the possible presence of such colourants, when planning both interventive treatments and preventive measures.

Introduction

Historical context

The tremendous modern pigment turn having taken place in commercial paint fabrication of all types within the last decades of the 19th and the first decades of the twentieth centuries is a highly complex and yet not fully explored field of research with major significance for

*Correspondence: Clarimma.sessa@tum.de

¹ Chair of Conservation-Restoration, Art Technology and Conservation Science, Technical University Munich, Munich, Germany
Full list of author information is available at the end of the article

the understanding and preservation of cultural heritage objects [1–7]. Fuelled by the rapid and manifold developments in the coal-tar chemistry—that started after the discovery of mauveine by William Henry Perkin in 1856 [8]—synthetic dyes, lakes and pigments gradually, but inevitably, replaced many of the traditional inorganic pigments in paints of all types of applications. Detailed knowledge of this process is currently of major significance because it targets questions of dating and authentication, and various aspects of active and preventive conservation standards for modern paintings, prints, textiles, etc.; where new, and often insufficiently permanent new colourants, were applied.

Artists' colours were also part of the development; however, in this case and due to their specifically high permanence requirements, not only scientific progress, but also unavailable terminology standards, an increasing complexity of industrial production processes, and a lack of long-term experience with new materials resulted in a complex and confusing situation for paint manufacturers, paint technologists and artists until the 1930s and also lead to early attempts at scientific paint analyses and quality assurance.

Studies on individual artists active in the late nineteenth and early twentieth centuries have demonstrated both the problems associated with fading of early coal-tar derived colourants, such as eosin in Van Gogh's paintings [9], and the acceptance and broad use of the new brilliant colours despite their bad reputation, as shown, for example, for works by the German expressionist Ernst Ludwig Kirchner [10].

A complete and differentiated understanding of when and to what extent a new synthetic organic pigment (SOP) was introduced into artists' paints (and when it possibly disappeared) obviously requires in-depth documentary and archival source research but indispensably also a dense mesh of scientific analyses on well-documented historical production references such as historical paint tubes and colour charts as primary sources. Over the past years, numerous researchers have started to study systematically such references from twentieth-century material collections, artists' estates, or factory archives, many with a focus on SOPs, e.g. [11].

A worthwhile subject of study presented here is *Das Deutsche Farbenbuch* (DFB; English title: The German Book of Colours) by Heinrich Trillich, published in three parts between 1923 and 1926, containing many hand-painted colour charts of different brands of watercolour, tempera, and oil paints produced by various German artists' paint manufacturers [12]. The first part of this paper introduces the *Farbenbuch* and summarises the historical background of its genesis in the context of the activities of the *Deutsche Gesellschaft zur Beförderung*

rationeller Malverfahren (DGzBrM; Engl. Society for the Promotion of Rational Painting Techniques) in Munich and discusses its approach towards coal-tar pigments. The second part is dedicated to the results of vibrational spectroscopy and micro-X-ray fluorescence spectroscopy (μ XRF) carried out either in situ or on micro-samples, evaluation of the performance of the three applied techniques—Normal Raman, Surface-Enhanced Raman Spectroscopy (SERS), and Metal Underlayer Attenuated Total Reflection Fourier-transform Infrared Spectroscopy (MU-ATR)—and the individual discussion of the identified organic colourants.

Das Deutsche Farbenbuch: historical context and approach towards SOP

Das Deutsche Farbenbuch represents an important historical document on the intense preoccupation with commercial paints and their quality around and after 1900 in Germany, specifically in Munich. The book—ambitiously planned to be a comprehensive compilation of materials used for the production of commercial paints of all application types—is a result of the long-term activities of the *Deutsche Gesellschaft zur Beförderung rationeller Malverfahren*, which was founded by Adolf Wilhelm Keim in Munich in 1886 [13]. The DGzBrM was organised in several technical committees and aimed at laying a scientific base on painting techniques; to fight deficiencies in the production, trade, and use of paints; to provide information and to promote exchange of experience between scientists, paint producers, artists and commercial painters. Between 1888 and 1941, the society published the periodical journal *Technische Mitteilungen für die Malerei* (Engl. Technical communications for painting) [14]. Furthermore, Keim led a *Versuchsanstalt für Malerei* (Engl. Testing Institute for Painting), which was taken over in 1903 by the Technische Hochschule München (today: the Technical University of Munich). It was first headed by Gustav Schultz, who was a renowned dyestuff chemist and author of the standard work "*Farbstofftabellen*" [15–21], and was then headed by the paint chemist Alexander Eibner from 1907 [22, 23]. From 1884/85, the DGzBrM already attempted to establish a *Normalfarbenskala*, i.e. a fixed choice of approved pigments for artists' paints that became a quality brand of the society and later on was also included in a revised form in *Das Deutsche Farbenbuch*. Further milestones of the engagement of the DGzBrM were the *1. Kongress für Maltechnik* in Munich in 1893 as well 12 years later a *Kongress zur Bekämpfung der Farben- und Malmaterialienfälschung* in Munich with 250 participants—paint technologists, producers, chemists and painters—who discussed issues of material quality and paint deception [13]. In 1907, a new commission led by the DGzBrM suggested the publication of the

DFB to promote quality assurance and correct denotation standards for commercial paints of all kinds as well as to fight against “*Farbenschwindel*” (paint deception) as a presumption for solid painting techniques and permanence. However, it took almost two decades until the book was eventually published by the chemist, paint producer and voluntary secretary of the DGzBrM Heinrich Trillich between 1920 and 1938. It was published in 3 parts between 1923 and 1926, with the second part from 1925 (Fig. 1) being dedicated to artists’ colourants and binding media [12, 24].

The purpose and the scope of the book were strongly debated over a long period, and the *Normalfarbenskala* was revised several times, e.g. by Eibner in 1915 [25]. Progress was hampered by the highly confrontative positions of the different actors as well as massive criticisms and excessive demands of the DGzBrM on paint producers, such as for the general dispensation of fillers. Moreover, the rapid and dynamic pace of the booming coal-tar chemistry, the expanding level of industrialisation of paint production and the growing market for commercial paints made it impossible for the DGzBrM to catch up appropriately with the latest industrial developments. In 1921/22, Max Doerner, at

the time professor for painting technique at the Munich Academy of Fine Arts, declared the *Normalfarbenskala* as failed [26] and the concept of the DFB—aiming to cover all kinds of commercial paints—as too broad [27]. Eibner shared these criticisms, and, in parallel to Trillich, attempted to establish as an alternative a German *Künstlerfarbengesetz* (Law for Artists’ Paints), which for several reasons was not successfully introduced until the Second World War [27].

Exploration of the full content of the DFB is left to the interested reader because, for this essay, we restrict ourselves to a discussion of how far synthetic organic colourants found entrance into the second part of the DFB on artists’ materials. From today’s point of view, the DGzBrM retained a strictly conservative and critical attitude towards SOP in general for an exceedingly long period. Thus, Trillich claimed: “*Unfortunately, many of these new colours [coal-tar colours], in spite of the lack of knowledge about their durability, were also used in the first fervour for purposes which they later proved to be unsuitable or overestimated [..]*” [28]. Based on the decisions of the DGzBrM (Hanover 1907), coal-tar colourants were not included (with a single exception) in the DFB and the *Normalfarbenskala* due to the lack of long-term tests to prove their sufficient permanence, especially to light. Moreover, light-ageing tests of Eibner carried out in 1911 had revealed as a general phenomenon that the lightfastness of many coal-tar pigments significantly decreased when used in an admixture with zinc white [24]. The accomplishment of further long-term tests until the publication of the DFB was apparently hampered by the First World War [26]. However, a closer look at the *Normalfarben* included in the DFB in 1925 reveals that “*Alizarinkrapplack*” (lake of alizarin madder) is listed among the suitable materials for water, tempera, oil, and wax-based paints. In brief comments on the *Normalfarben* few other synthetic organic pigments (or rather brands) are mentioned as partly suitable, e.g. Echtlichtgelb and Hansarot for watercolours or indanthrene for tempera, but the passage on oil and oil-resin/wax colours, enamel, and wax painting explicitly warns against the presence of unstable coal-tar colours in many “*geschönte*” (brightened) paints.

From a modern point of view on the pigment turn of the twentieth century and the success story of SOPs also in artists’ paints, the DGzBrM and its book did not manage to catch up appropriately with the actual developments of the pigment industry, especially concerning the introduction of numerous and ever improving coal-tar colourants. Interestingly, Trillich being a paint producer himself, seems to have been aware of this problem and apparently tried to take the latest advancement of coal-tar chemistry into account by adding on his own



Fig. 1 Cover of H. Trillich, *Das Deutsche Farbenbuch*, Part II (1925), Munich

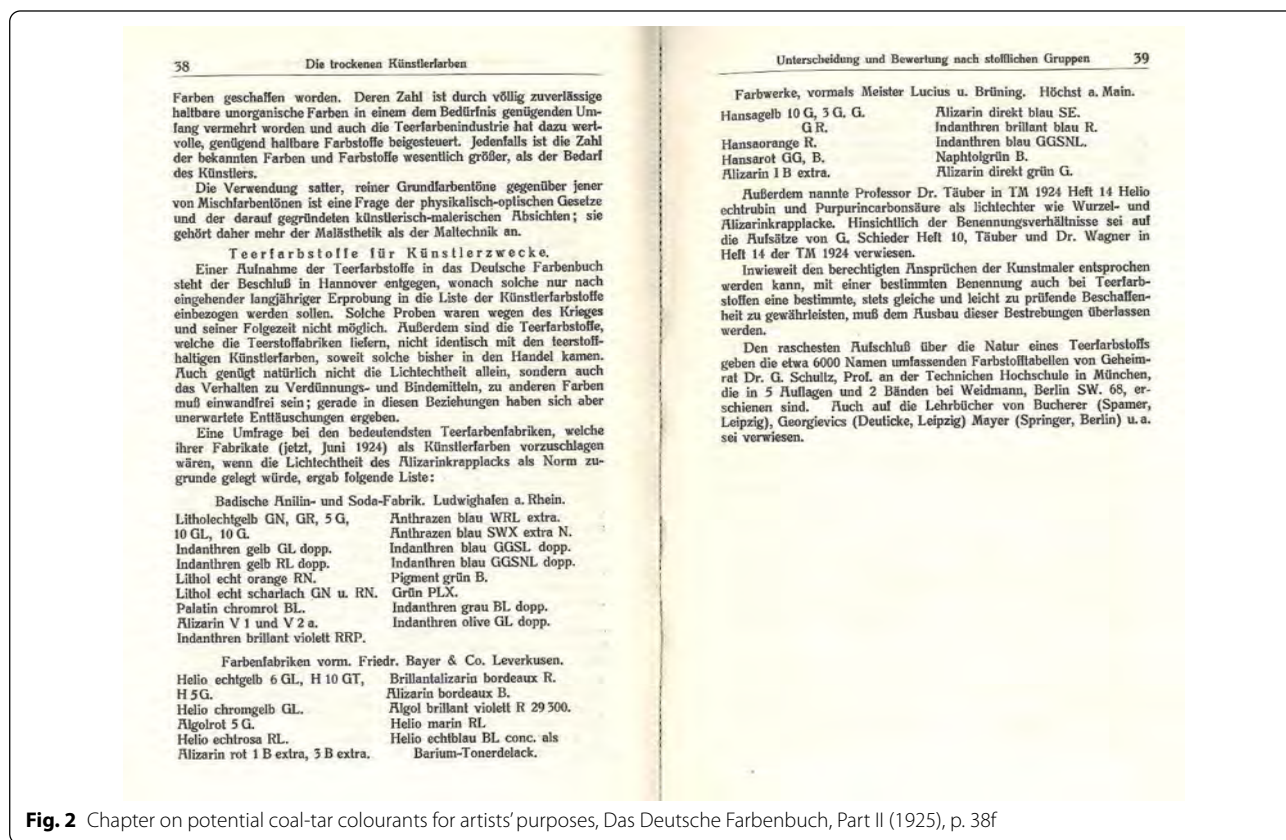


Fig. 2 Chapter on potential coal-tar colourants for artists' purposes, *Das Deutsche Farbenbuch*, Part II (1925), p. 38f

responsibility, a brief chapter on potential SOPs for artists' paints in the DFB (Fig. 2).

Based on an actual questionnaire on the advisement of SOPs of sufficient permanence for potential artists' purposes at three renowned pigment producers, the author published trade names of the following 27 or so coal-tar dyes and pigments (the correspondence to modern Colour Index International pigment/dye names was researched by Schäning, p. 105) [3]:

PY 23, Monoazo-like PY 1, PY 2, PY 3, PY 6, Vat Yellow 1, monopyrazolone, PO 5, PR 3, PR 6, PR 60, alizarin, Vat Red 42, PR 89, Mordant Red 45, Mordant Violet 26, Vat Violet 1, Vat Violet 17, Vat Blue 4, Acid Blue 43, Acid Blue 68, other Acid Blue, Mordant Blue 32, Acid Green 1/PG 12, Vat Green, Acid Green of anthraquinone type, Vat Black 29.

Some of them, such as PY 1 (monoazo yellow), PR 3, and PO 5 (both β -naphthols), are familiar components of modern artists' brands, but many of this list (especially the dyes without a pigment equivalent) are not.

Thus, to what extent did the *Normalfarbenskala* of the DFB as well as the latter last-minute industrial recommendations match the real practice of artists' paint

fabrication in 1925? Here, the 16 historical colour charts being part of the DFB are valuable primary sources that reflect, at least in part, the "true" commercial situation on the paint market around 1925 and thus add to a more realistic view on artists' materials in this significant period of "pigment turn". The colour charts were provided to Trillich by six German paint companies, the majority of them being commercial brands of artists' water, tempera, and oil colours (Redeker & Hennis A.-G. Nürnberg, Dr. Schoenfeld & Co. Düsseldorf, Pelikan Günther Wagner Hannover und Wien, Vereinigte Farben- und Lackfabriken vorm. Finster & Meister München, Herrmann Neisch & Co. Dresden, G. Siegle & Co. Stuttgart, Feuerbach and Besigheim, H. Schmincke & Co. Düsseldorf) (Fig. 3). More than 80 different hues were chosen for analyses based on the denotation of the specific hue (e.g. *Echtröt*, *Indischgelb imit.*) as potentially containing organic colourants as a major constituent. However, one must be aware that this approach is certainly selective and that more synthetic or natural colourants are likely to be present in the charts e.g. in admixtures with inorganic pigments.



Fig. 3 10 (of the 11) colour charts of different German brands of watercolour, tempera, and oil paints being part of *Das Deutsche Farbenbuch*, Part II (1925)

Experimental

Materials and methods

Raman spectroscopy/Surface-Enhanced Raman Spectroscopy (SERS)

The Raman/SERS measurements were performed using a Horiba Scientific Raman Microscope XPLora equipped with three diode lasers (532 nm/25 mW; 638 nm/24 mW; 785/90 mW). Raman spectra were acquired using the 785 nm laser which is best suited for SOPs in general. SERS spectra were recorded with 532 or 638 nm; only the spectrum of the optimum laser line for each colourant is shown. The analysis was carried out with the 100× (Raman) and 50× (SERS) microscope objectives, a holographic grating with 1200 lines/mm, laser power filters between 0.1 and 10% as well as an acquisition time of 10-60 s at 1-5 accumulations. Normal Raman measurements were performed using an external objective adaptor, which permits acquisition of spectra without sampling.

The metal substrate for SERS was prepared according to the Leopold and Lendl method [30] using AgNO₃ (purity N 99%, S8157) and NH₂OH·HCl (379921) purchased from Sigma Aldrich (Germany). The particle size distribution of each silver colloid solution (1:9 dilution with ultrapure water) was tested using a UV/Vis

spectrometer (SPECORD® Plus Analytik Jena) between 300 and 800 nm. More details on the optimisation of the method are published in [31]. Before the SERS analysis, the micro-sample was exposed to hydrofluoric acid (HF) vapour for 5 min in a closed micro-chamber. The pre-treatment procedure had been successfully applied by Pozzi et al. as a non-extractive gas/solid hydrolysis method [32].

Metal Underlayer-ATR Fourier-transform infrared spectroscopy (MU-ATR)

MU-ATR analyses were performed by placing a micro-sample (around 300 µm) over a gold-coated glass slide (76×26 mm; 200 nm Au thickness) purchased from Ssens bv™ and pressing it using a metal roller wheel to obtain a thin layer. More details about the methods are available in [33]. ATR-FTIR analyses were performed using a Ge ATR crystal and a Thermo Scientific Nicolet iN 10MX spectrometer. Spectra were recorded in the range 4000 to 675 cm⁻¹ with an optical aperture of 150×150 µm (analysis area of 37.5×37.5 µm), and a spectral resolution of 4 cm⁻¹ and 64 scans. All data were acquired as replicates according to the sample size. Spectra were processed with Omnic Picta™ and Omic32™ software.

Micro X-Ray Fluorescence (μ XRF)

The XRF measurements were carried out with a M6 Jetstream (Bruker) with Rh tube, 50 kV voltage, 200 μ A current, no filter, in a He atmosphere using single-point mode with 100 μ m spot size, for a total measurement time of 100 s.

Results and discussion

A stepwise procedure for the colourant identification was followed: as a first step, all selected colour washes were systematically analysed in situ by normal Raman accomplished by qualitative XRF for the major inorganic elements (from substrates, fillers or other pigments). If no Raman spectrum was obtained, in a second step SERS was performed on a small sample from the specific colour wash. In case of unsuccessful SERS identification, as a third step, MU-ATR measurements were performed. A summary of the results obtained from the colour charts of artists' watercolours, tempera, and oil colours from six German paint manufacturers is presented in Table 1. The SOP findings are organized by the analytical technique successfully used for identification as main category and within this colour-wise.

The identification of the different colourants by means of Raman/SERS was performed by comparing the recorded spectra with reference spectra of pure dyes, pigments, and lakes, which are included in the Raman/SERS spectral database of the Doerner Institut. This library is the result of systematic studies of historical dyes [34], SOPs, reference colourants and realia. The Raman spectra recorded with the 785 nm laser are also available online through the SOP spectral library create thanks to the SOPrano project [35]. In addition to a few traditional natural organic colourants (dark and rose madder lakes, cochineal lakes), most of the identified compounds comprises SOPs or synthetic dyes from various chemical classes, such as indigoid, anthraquinone, monoazo, β -naphthol, xanthene, triarylcarbonium, nitroso and azine compounds.

Indigoid

Indigo

Indigo (C.I. 73000) is a widely used textile dye and it has a great archaeological and historical importance. In this study, it was found in watercolour alone or mixed. An interesting example is the *Paynes grau* hue from Turm, in which indigo was identified together with Basic Violet 1 (BV1, C.I.42535, Triphenylmethane class, see in section "Triarylcarbonium class" using normal Raman and SERS respectively (Fig. 4). This particular case has demonstrated the complementarity of the two approaches. The

selectivity of the water-based silver substrate may explain the detection of BV1. The SERS spectra of indigo have been published e.g. by Shadi et al. [36]. As the authors discussed, since the indigo is uncharged and relatively insoluble in most solvents, they successfully obtained a SERS spectrum of the molecule only after modifying the colloid substrate by adding methanolic solutions to aqueous silver sols. Since the molecular structure of natural and synthetic indigo is the same, differentiation by means of spectroscopic methods is not possible. The synthetic substitute was discovered in 1878–80 and subsequently patented by different companies [37]. This means that, in our study, the presence of both varieties is plausible.

Anthraquinone class

Madder-/Alizarin-based lakes

A synthetic form of alizarin (PR83, C.I. 58000) was first prepared in 1868 by Carl Graebe and Carl Lieberman. Until then, it was obtained from the root of the madder plant, *Rubia tinctorium* L. Alizarin lake is described in the DFB as sufficiently permanent for *Normalfarben* to be used in water, tempera, oil, and wax-based paints. Indeed, it was identified very frequently alone or in a mixture (with purpurin and/or carminic acid and eosin), on various colour charts.

The DFB here does not explicitly differentiate between dark (alizarin-rich) natural madder lakes and synthetic alizarin lakes, which were both available on the artists' paint market in a large variety in the first decades of the twentieth century. The approved lightfastness of natural madder lakes was sufficient testimony for the early acceptance of its synthetic pendant for the use in artists' paints.

In most of the cases, we obtained a SERS spectrum of pure alizarin, which probably indicates its synthetic nature (Fig. 5a). On the other hand, the SERS spectra obtained for the *Krapplack Alizarin hell nr.4* (watercolour by Schoenfeld—Sorte 1000) and *Krapplack, dunkel 242* (watercolour by Pelikan) (Fig. 5b), which are comparable, show the typical signals of alizarin (duplet at about 1290–1330 cm^{-1} and a strong signal at about 1460 cm^{-1}) as well as broad unassigned bands that indicate a more complex colourant mixture probably hinting toward the lakes' natural origin. Based on XRF almost all alizarin-based colourants are lakes precipitated on aluminium hydroxide (except for *Krapprosa I* of Bössenroth Tempera) and contain some phosphorus from the colourant(s). In addition other inorganic elements were detected that may be attributed to the presence of fillers/white pigments used to modify the colour's intensity/hue (mainly baryte, chalk or gypsum).

Table 1 Summary of SOP findings in the colour charts of the Deutsches Farbenbuch, Part II (1925)

Analytical technique	SOP name	Colour index number	Chemical class	Discovery/first synthesis	Colour charts	Hue/s label	Main elements detected by XRF/ Information on admixture	
Normal Raman spectroscopy	Pigment Red 1	12070	β -Naphthol	1885	Siegle, oil colours	Moderot 3	S, Ba, Sr	
						Moderot 1	S, Ba, Zn	
	Pigment Red 3	12120	β -Naphthol	1904	Neisch Tempera-farben, Sorte 700, tempera colours	Echtrot deckend	Al, Si, Fe, Cd, Se	
						Flamuco, tempera colours	Echtrot	Admixture with cadmium red Al, P, Ca, Ba
							142 Heliorot I	Al, Ca, Cl, Pb, Zn, Hg, S
						Rubensölfarben, oil colours	Echtrot deckend	Al, Si, Fe
	Pigment Red 4	12085	β -Naphthol	1906	Siegle, oil colours	Echthellrot PR	S, Ba, Sr	
	Pigment Red 40	12170	β -Naphthol	1878	Siegle, oil colours	Dunkelbordeaux 30	S, Ba, Sr	
	Pigment Red 49	15630	β -Naphthol	1899	Siegle, oil colours	Corallenrot 5	S, Ba, Zn	
						Corallenrot RCO	Ba, S	
	Pigment Red 54	14830	Monoazo	1910	Siegle I, oil colours	Carmoisinlack BL	Ba, S, Zn, Sr	
	Pigment Red 57 (PR57:1?)	15850	BONS (Ca?)	1903	Turm, watercolours	Karminlack	Al, Si, S, Ba, Fe, P	
	Acid Green 1/Pigment Green 12	10020/10020:1	Nitroso dye	1883	Turm, watercolours	Saftgrün blaulich,	S, Ba, Si, Fe, Pb	
						Saftgrün gelblich	Al, S, Ba (Fe not det.)	
	Indigo	73000	Indigoid	1878/80 (synth.)	Turm, watercolours	Indigo	S, Ca, Si, Al	
Paynes grau						Al, Si, K, Ba, Fe		
Pelikan, watercolours						Indigo	Admixture with Basic Violet 1 (see below) Zn, Si, Cl	
						Paynes grau	Al, Si, P	
Surface enhanced Raman spectroscopy	Carminic acid-based colourants	75470	Anthraquinone	1991 (synth.)	Turm watercolours	Krapplack, dunkel	Al, Si, S, Ba, Fe, P	
					Flamuco, watercolours	Karmin gebrant	P, Al, Ca	
						Pelikan, watercolours	231 Carmin fein	Admixture with alizarine and purpurin Hg, S
					Schoenfeld, watercolours	8 Karmin	Admixture with vermilion Ba	

Table 1 (continued)

Analytical technique	SOP name	Colour index number	Chemical class	Discovery/first synthesis	Colour charts	Hue/s label	Main elements detected by XRF/ Information on admixture
	Alizarin-based colourants		Anthraquinone	1868 (synth.)	Flamuco, watercolours	Krapplack, dunkel Karminlack Violetter lack Karmin gebrant	P, Al, S, Ca, Ba P, Al, Ca Na, Al, Si, S, P, Ca Admixture with ultramarine blue P, Al, Ca Admixture with carminic acid and purpurin
					Bössenroth, tempera colours	125 Krapprosa I 129 Krapplack, dunkel I 138 Krapplack purpur I	Zn, Ba, S, Ca, P Al, Si, P, Ca, Ba, S Al, Si, P, Fe, Ca, Ba, S Admixture with purpurin
					Neisch, tempera colours	Krapplack tief	Al, Si, P, Fe
					Pelikan, watercolours	Krapplack, dunkel (242)	Al, P, K, Ca, Pb
					Schoenfeld, watercolours	Krapplack Alizarin hell (Nr.4)	Al, P, Ba
	Acid Red 87/pigment Red 90	45430	Xanthene	1876	Turm, watercolours	Rosalack	Al, Ba, Pb, Fe, Br
					Flamuco, tempera colours	Krapplack dunkel	Al, P, Ba, S, Ca
		45380	Xanthene	1871			Amixture with Alizarine
	Basic Red 5	50040	Azine	1849	Mussini, oil colours	Wurzel-Krapplack mittel Nr. 5	Fe, Pb, Al, P, S
	Basic Violet 1 (or homologue)	42535	Triarylcarbonium	1861	Turm, watercolours	Payne's grey	Al, Si, K, Ba, Fe in Admixture with Indigo
						Neutraltinte	S, Si
					Siegle, oil colours	Oelviolet 970 Violet 6	Al, Si, Ba, Zn, Pb, Sr Al, Si, Zn
	Basic Violet 2 (or homologue)	42520	Triarylcarbonium	1889	Pelikan, watercolours	Neutraltinte rötlich	Si, P, Ba, S, Fe, Zn
	Basic Violet 10 or Basic Violet 11	45170/45175	Xanthene	BV 10–1905/BV 11–(?)	Flamuco, tempera colours	Krapplack rosa	Al, P
					Flamuco, watercolours	Paynes-grau	Ca, S, P, Al, Si Admixture with ultramarine blue
	Pigment Violet 5	58055	Anthraquinone	(?)	Turm, watercolours	Violett	Al, Si, S, Ba

Table 1 (continued)

Analytical technique	SOP name	Colour index number	Chemical class	Discovery/first synthesis	Colour charts	Hue/s label	Main elements detected by XRF/ Information on admixture
Metal underlayer attenuated total reflection FTIR spectroscopy	Pigment Yellow 1	11680	Monoazo	1909	Börsenroth, tempera colours	3 Echtgelb II 31 Indischgelb imit. II	Zn, Ba, S, Sr Cr, Sr, Fe, Ca, Cd Admixture with cadmium yellow and strontium chromate

The findings are organized by the analytical technique successfully used for the identification of the colourant as main category and within this colour-wise. The confirmed presence of further pigments/dyes in admixture with the main colorant has been specified

Cochineal/Carminic acid-based lakes

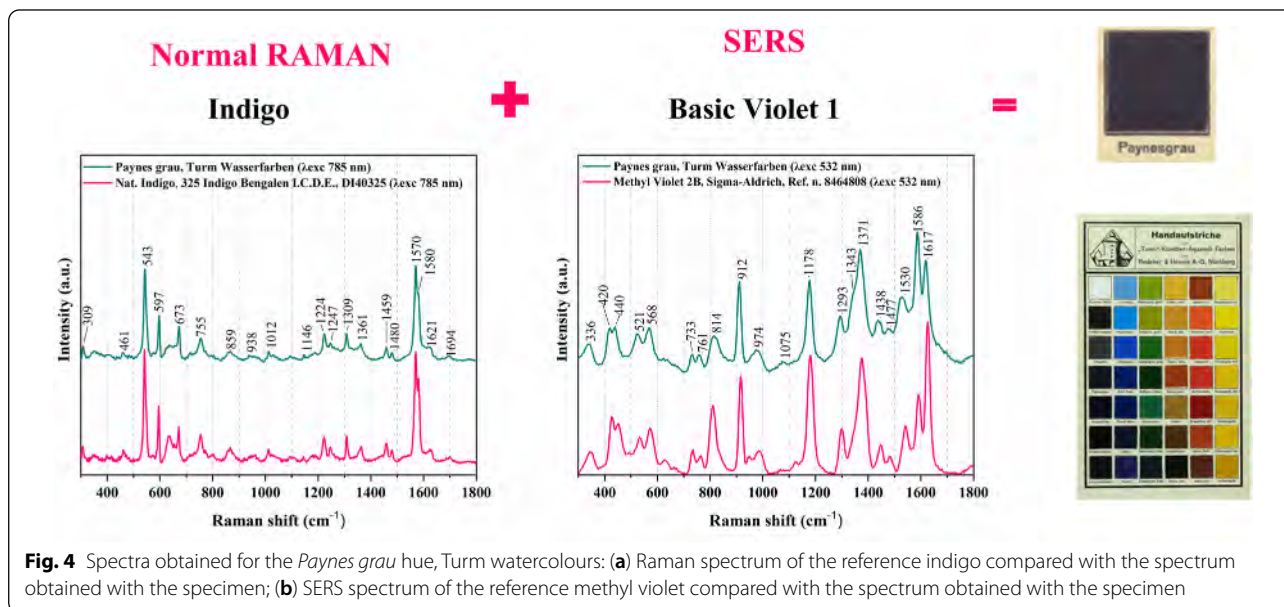
Cochineal/Carminic acid-based colourants have been identified in four watercolour washes of four different brands. It is difficult to establish exactly which preparation procedure/recipe has been followed to prepare the different hues. However, they can be differentiated one from another based on the XRF results and/or SERS spectrum. The XRF results indicate different substrates and thus different lake preparation/precipitation procedures and, in one case, a mixture with a red inorganic pigment. As Kirby et al. discussed, since its exportation from the Americas to the European continent there were many attempts to optimise the precipitation of carminic acid-based lake [38]. Winsor and Newton, for example, devoted great attention to the production of carmines, with many trials [39, 40]. Carminic acid is the major colouring matter of cochineal lakes. In particular, several recipes, which first appear in the late eighteenth century, suggest the use of a little alkali with the alum to precipitate the carmine [39]. This is the case for a colour wash labelled *Krapplack dunkel* by Turm (XRF: Al, Si, P, S, Ba). The recorded SERS spectrum shows a very good match with the spectrum of carminic acid pure dye (Fig. 5c). It is interesting to stress that the label *Krapplack*, which normally indicates a madder/alizarine-based colour, is misleading since no evidence of the presence of such compound has been observed.

The Al-based substrate has also been identified in the *Karmin gebrannt* hue by Flamuco (XRF: P, Al, Ca). In this case, a complex but well-resolved SERS spectrum suggests the presence of a mixture of carminic acid, alizarine and purpurin (Fig. 5d). The capability of SERS to differentiate between closely related red dyes in a mixture has been already demonstrated by Pozzi et al. [41].

Similar SERS spectra have been obtained for the washes labelled *N.8 Karmin* by Schoenfeld (XRF: Ba

and *231 Carmin Fein* by Pelikan (Fig. 5e). Comparable spectra have been published by Pozzi et al. [6] for cochineal-based colourants in Winsor and Newton's nineteenth- and twentieth-century catalogues. The presence of carminic acid in admixture with a more complex mixture could only be detected by chromatographic techniques (results not shown). The presence of vermilion has been confirmed by XRF (Hg, S) in the hue *Carmin fein* by Pelikan. The use of vermilion to adjust the hue of cochineal-based lakes has been already described in the literature of the nineteenth century [42].

The cochineal-based red colourants have also been extensively used during the nineteenth/early twentieth century, and its instability to light is a source of concern for the conservation of many important works of art, e.g. [43, 44]. The fading phenomenon in watercolours has been studied by Berrie et al. [44]. Based on the second Colour Index edition (1956), the lakes are produced with starch, alumina, kaolin or blanc fix. Although they have poor fastness to light, they are transparent and are used as watercolours, for colouring confectionery and cosmetics, and occasionally in printing inks [37]. Moreover, its poor fastness to light and weather was already known in 1890 and was addressed by A.H. Church in his essay "*The chemistry of paints and paintings*" in which he wrote: [...] *Beautiful and rich as are the colours prepared from cochineal, not one of them should ever find a place upon the palette of the artist. They all become brownish and ultimately almost disappear after a short exposure to sunlight or the more prolonged attack of strong diffused daylight* [45]. Natural cochineal carmine is still produced today but owing to its fugitive nature it is used mostly for cosmetics. Synthetic carminic acid is much too difficult to prepare to be of commercial interest [46].



Pigment violet 5

We identified Pigment Violet 5 by SERS in the *Violett* hue of Turm watercolours (Fig 5f) as Al-salt (PV5:1, C.I. 58055, XRF: Al, Si, S, Ba). Based on the second C.I. edition it was used for lacquers, paints, alkyd resin enamels, printing inks and wallpapers. Furthermore, it was occasionally used in emulsion paints, rubber, vinyl products, plastics, and textile printing. PV 5 exhibits very good lightfastness [37]. Even though it was already on the market before 1924 as Siegle blauviolett [2], to the best of our knowledge, it has been identified in art only in a work by Lucio Fontana dated 1963 [47].

Azo class

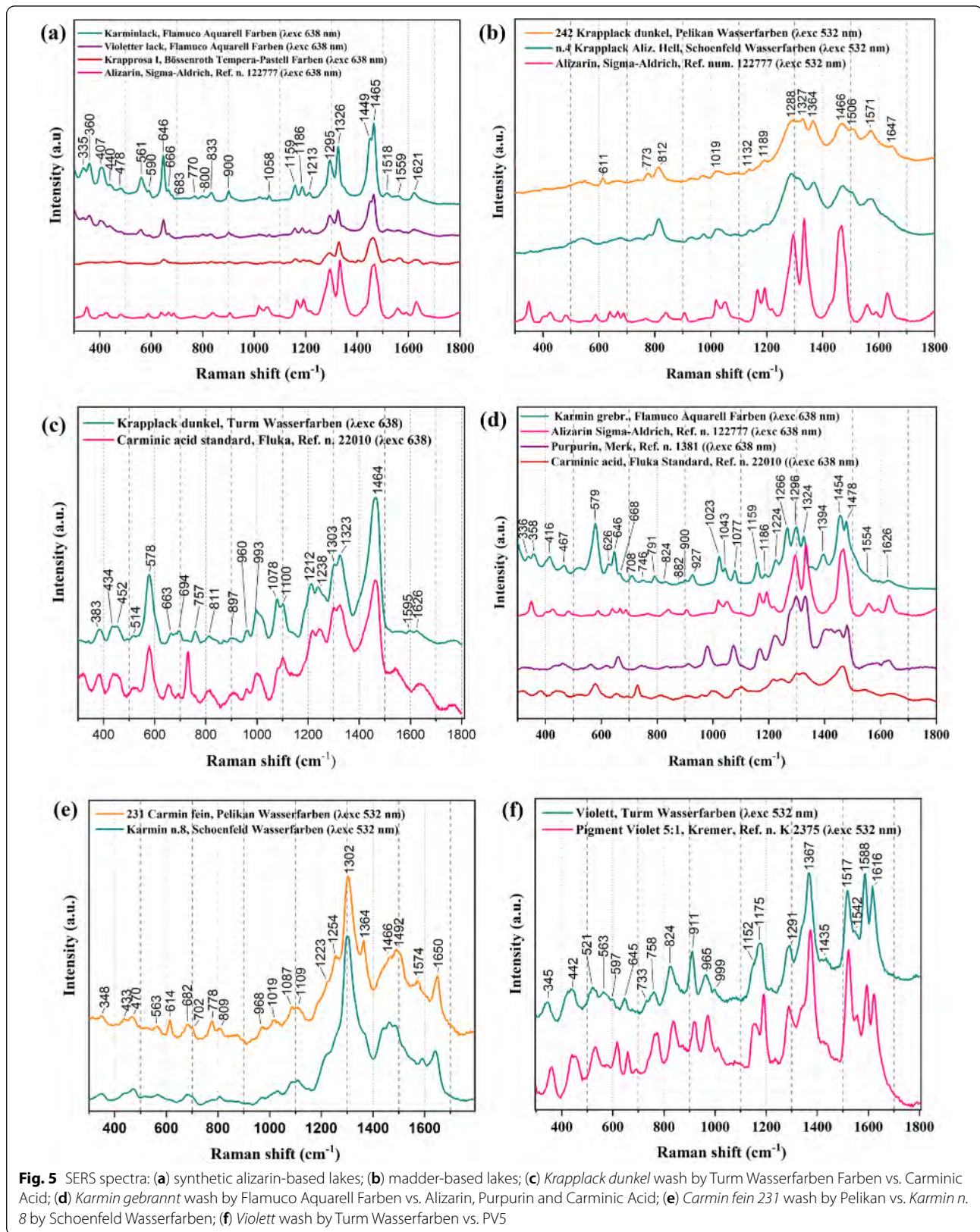
β -Naphthols

In this study, we successfully identified Pigment Red 1 (PR1, C.I. 12070), Pigment Red 3 (PR 3, C.I.12120), Pigment Red 4 (PR4, C.I.12085), Pigment Red 40 (PR 40, C.I.12170), and the Ba salt of Pigment Red 49 (PR 49:1, C.I.15630) in tempera and oil colours by normal Raman (Fig. 6a–e). Especially PR3 and PR4 are frequently found in works of art created in the first half of the twentieth century. The matches are close, often the main signal of the filler baryte (as confirmed by XRF) appears at 980 cm^{-1} .

Among the diversity of SOP of the twentieth century, the β -naphthol representatives constitute one of the most significant and also earliest chemical classes for paint production [48]. Neugebauer et al. and Sessa et al. recently published a very extensive study about the chemical composition of these compounds and their

historical preparation processes, also compiling an actual overview of findings in works of art [49, 50]. The specific features of the Raman and SERS spectra of 18 different β -naphthol colourants from historical material collections were discussed to evaluate the discrimination capability of the analytical methods. As a general observation, it was possible to assess an initial differentiation among pigments/lakes of this class based on the presence or absence of the nitro group substituents and their corresponding Raman signals. The lightfastness of most pure β -naphthol pigments is very good or good—but not excellent—as pure pigments, only the unsubstituted PR40 exhibits poor fastness to light [51]. As discussed above, Trillich published suggestions of three pigment manufacturers, which includes in their lists different trade products of PR3, e.g. Litholechtscharlach RN by Badische Anilin- und Soda-Fabrik, Ludwigshafen am Rhein and Hansarot B by Meister Lucius u. Brüning, Höchst am Main [29].

Other chemists of the time, E. Täuber and P. Kraus, tested the lightfastness of some β -naphthol pigments and described PR3 as sufficiently lightfast for use in artists' paints, whereas PR1 and PR4 were not stable enough, especially admixed with white pigments [52–55]. A. Eibner positively evaluated PR1, PR3, PR4, PR40, PR49. However, he reported that they significantly reduce their lightfastness when mixed with zinc white [23]. Max Doerner described PR49 (Lithol Red) as being 'sufficiently lightproof for artist's colours' [26]. However, since PR49 has been identified as the source of decay of Mark Rothko's Harvard Murals, its fastness to light has been extensively investigated.



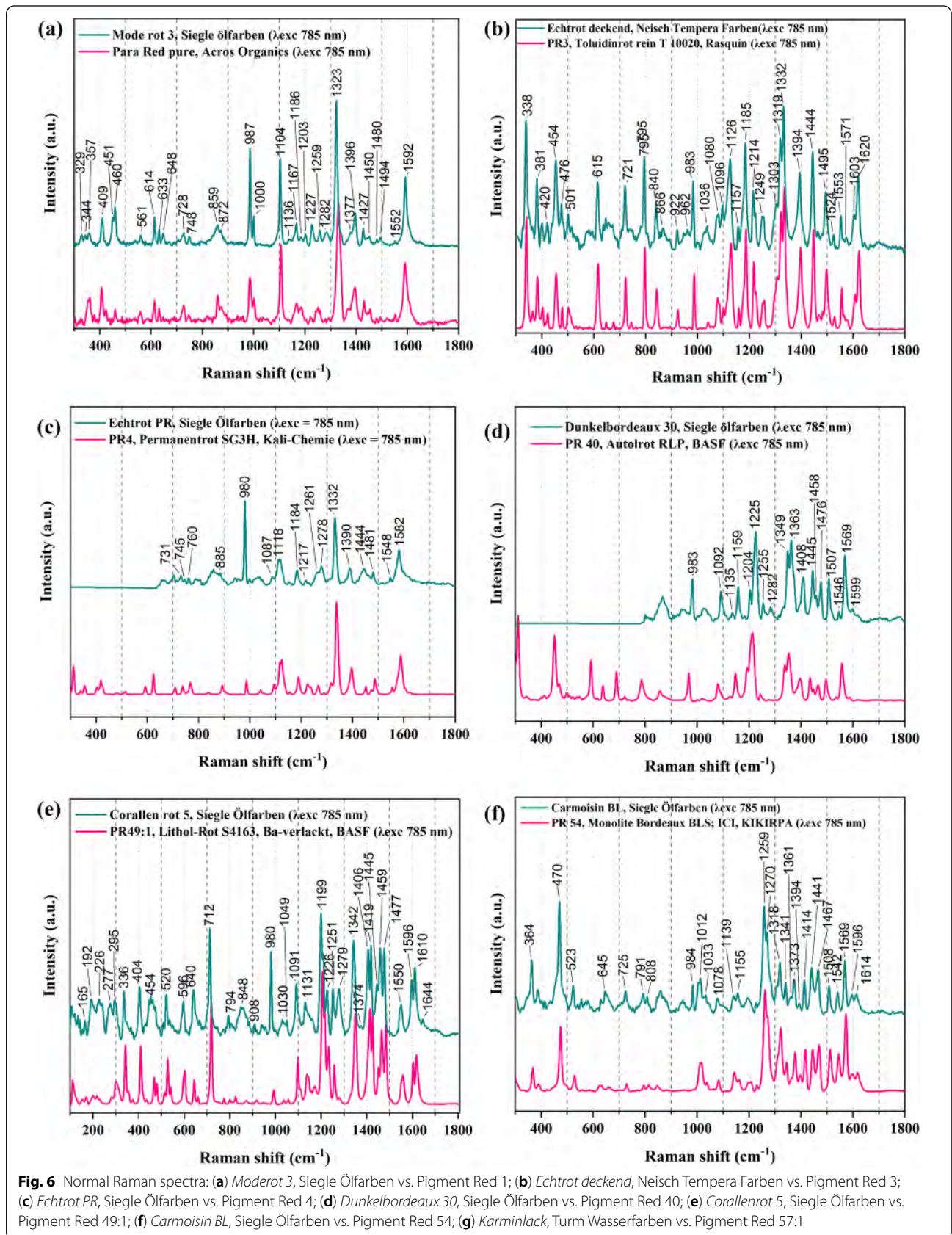


Fig. 6 Normal Raman spectra: (a) *Moderot 3*, Siegle Ölfarben vs. Pigment Red 1; (b) *Echttrot deckend*, Neisch Tempera Farben vs. Pigment Red 3; (c) *Echttrot PR*, Siegle Ölfarben vs. Pigment Red 4; (d) *Dunkelbordeaux 30*, Siegle Ölfarben vs. Pigment Red 40; (e) *Corallenrot 5*, Siegle Ölfarben vs. Pigment Red 49:1; (f) *Carmoisin BL*, Siegle Ölfarben vs. Pigment Red 54; (g) *Karminlack*, Turm Wasserfarben vs. Pigment Red 57:1

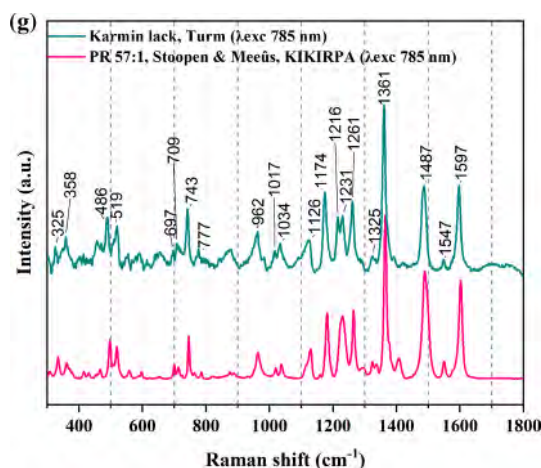


Fig. 6 continued

Recent light-aging experiments showed that the neat powder is very lightfast but that the pigment has poor light stability within paint systems, mainly due to the interaction with the binding media [56, 57].

In oil and watercolours, we furthermore identified Pigment Red 54 (PR 54, C.I.14830) and Pigment Red 57 (PR 57, C.I.15850), respectively, using normal Raman. Both pigments have good lightfastness and very good fastness to oil [37]. PR54 (naphthalene sulfonic acid (Ca salt) was identified in the hue of *Carmoisin lack* in oil paint by Siegle (Fig. 6f). It was synthesised in 1910 and it has been used for paints, printing inks, alkyd resin enamels and lacquer. In the second edition of the C. I. it is indicated as suitable for artists' material but only for students' grade. The Raman spectrum at 785 nm is available online in the SOPrano spectral library [35]. To the best of our knowledge, no information about the use of this pigment in a work of art has been published.

PR57 (BONS) has been identified in the hue labelled *Karminlack* by Turm. The XRF results do not permit clear discrimination between a Ca or Ba form of the pigment. The obtained spectrum (785 nm) shows a good match with the reference spectra of the Ca lake (PR57:1) (Fig. 6g). A comparison with the reference spectrum of PR57:2 (Ba salt) of the KIKIRPA database shows a very different relative intensity of the signals at 1180 and 1260 cm⁻¹. The literature, e.g. Herbst and Hunger (1987) [58] and Fux [2] mention only PR57:1 as a compound used in artists' paint, which makes the Ca form very likely.

This pigment was synthesised for the first time in 1903, and in 1924 it was listed in the C.I. as Lithol Rubin B. Based on the second edition of the Colour Index, it has been used for artists' colours; however, it has been rarely identified, e.g. in the atelier estate of

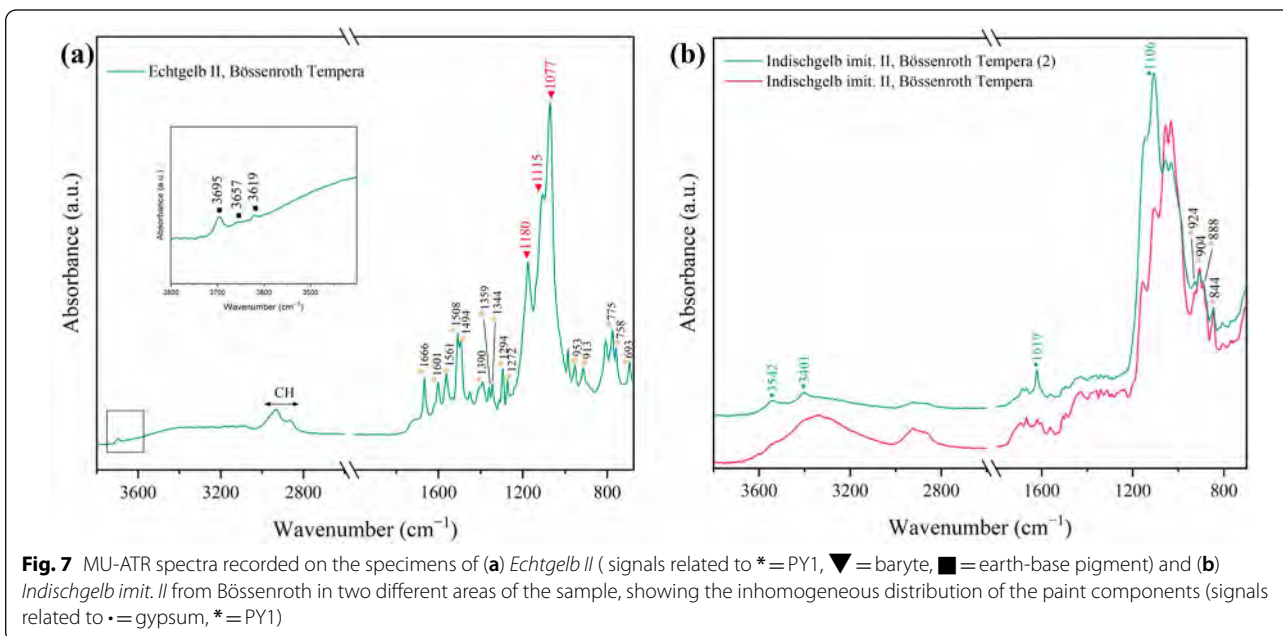
Fritz Winter (1905–1976) [59]. Abraham et al. tested the effect of laser light (Nd:YAG at 1064 and 532 nm) on several SOP classes as dry pigment and in paint medium. They observed that PR57:1 tends to shift to a darker and duller shade after the exposure [60].

Monoazo yellows (arylide yellows)

Pigment Yellow 1 (PY1, C.I. 11680) has been identified by MU-ATR in *Echtgelb II* and *Indischgelb imit. II* by from Bössenroth (Fig. 7). The spectra have been evaluated using the IRUG spectral library [61] Already sold in 1909, it started to be used in artists' paints around 1912 [2, 48]. Neither normal Raman nor SERS were able to obtain a well-resolved spectrum from those specimens. PY1 presents good lightfastness; it is sensitive to most common organic solvents and has poor heat stability [62]. After laser exposure it showed no shift of the L a*b* coordinate [60].

In particular, in a sample of *Echtgelb II* from Bössenroth (Fig. 7a), in addition to PY, we identified baryte as a filler due to the bands at 1180 cm⁻¹, 1115 cm⁻¹, 1077 cm⁻¹, and 982 cm⁻¹, as well as an earth-base pigment rich in aluminosilicates, which was indicated by peaks at 3695 cm⁻¹, 3657 cm⁻¹, and 3619 cm⁻¹ (Fig. 7a).

Indischgelb imit. II from Bössenroth (Fig. 7b) probably contains PY1 mixed with another inorganic pigment. The bands at 924 cm⁻¹, 904 cm⁻¹, 888 cm⁻¹, and 844 cm⁻¹, assigned to asymmetric stretching of CrO₄²⁻ in the MU-ATR spectra, suggest that strontium chromate is also present [63]. The presence of Sr and Cr was confirmed by XRF analyses. In addition, the manufacturer added gypsum as a filler, as indicated by the bands at 3542 cm⁻¹, 3401 cm⁻¹, 1619 cm⁻¹, from OH stretching and bending respectively, and 1106 cm⁻¹ from S=O stretching.



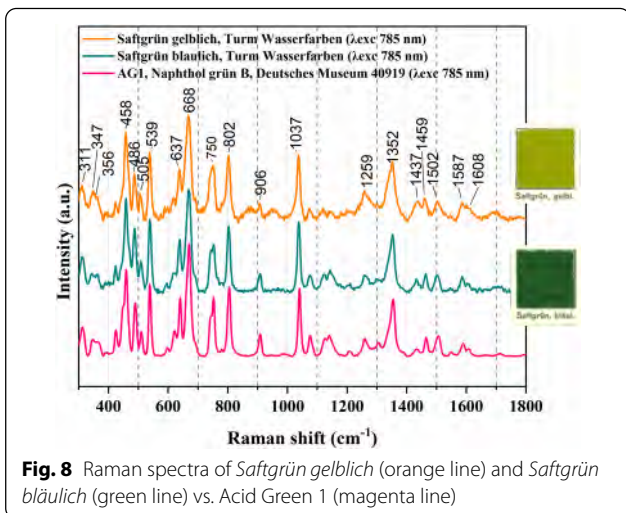
Nitroso class

The synthetic nitroso dyestuff Acid Green 1 (AG1, C.I. 10020) and/or its lake Pigment Green 12 (PG12), was identified by normal Raman in two washes of the Turm watercolours, namely *Saftgrün bläulich* and *gelblich* (engl. Sap green bluish and yellowish; Fig. 8). The label Sap green would generally indicate the presence of a natural dyestuff, which is obtained from different kinds of *Rhamnaceae* [64]. This example is indicative of how the labelling and terminology used for modern artists' colours may be misleading.

AG1/PG12 was recently identified by Raman on other historical colour charts and in various artists' paints from

the material collection of the Doerner Institut, Munich. However, to the best of our knowledge, no example of the presence of AG1 lakes in specific work of art has been published. Therefore, we dedicated a combined study of historical source research and systematic analytical examinations on surviving realia with the aim of creating a detailed picture of its application in artists' paints [65].

AG1 was first synthesised in 1883 by Otto Hoffmann and then patented in 1884 in Germany as *Naphtholgrün* by Anilinfabrik Gans & Co. for dyeing wool and silk [66]. Historical sources report that the fastness of AG1 lakes to light was fairly good or moderate, even though they were never classified into the group of the most permanent SOPs [67]. Interestingly, its use is nevertheless suggested in the DFB by Meister Lucius u. Brüning, Höchst am Main (Trillich 1925, p. 38, 39).



Triarylcarbonium class

SERS spectra of methyl violet colourants (Basic Violet 1 or homologues) were obtained in different colour hues of both water and oil colours. The photodegradation of this class of colourants has been extensively studied and fading phenomena have already been observed in several works of art, mostly on paper [68, 69].

Based on the second edition of the C.I., the dye Basic Violet 1 (BV1, C.I. 42535) has very poor lightfastness (grade 1 of the Blue Wool scale). The fastness to light was significantly improved around 1925 for the corresponding phosphotungstomolybdic acid (PTMA) lake [70], then denoted as Pigment Violet 3 (PV3, C.I. 42535:2)

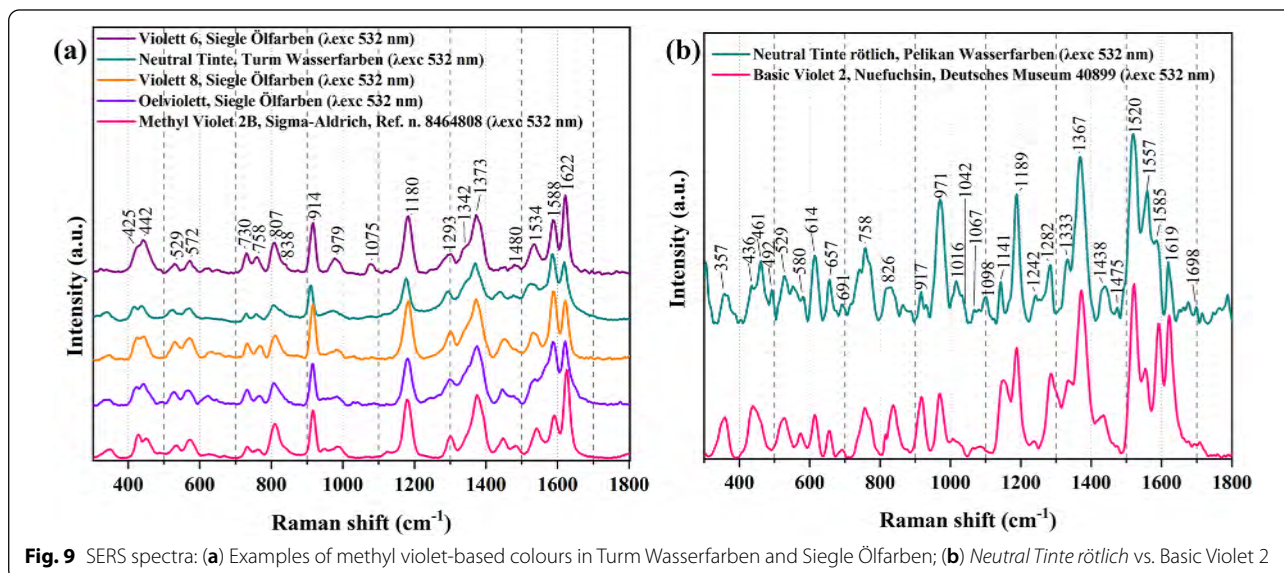


Fig. 9 SERS spectra: (a) Examples of methyl violet-based colours in Turm Wasserfarben and Siegle Ölfarben; (b) *Neutral Tinte rötlich* vs. Basic Violet 2

[37]. However, XRF did not detect P, Mo or W, so BV1 here is probably still present, mainly as Al-based lakes.

It is interesting to observe how the signal of some SERS spectra acquired on the washes present a different relative ratio of the peaks at 1589 cm^{-1} and 1622 cm^{-1} . Such a spectral feature is reported to be due to the material's photo-induced fading and/or to the HF pre-treatment of the sample, which we applied (Fig. 9a) [68].

Basic Violet 2 (BV2, C.I. 42520) has most likely been used for a reddish tone of a grey-blue hue, labelled *Neutraltinte rötlich* (Neutral ink, reddish) in Pelikan watercolours (Fig 9b). Comparison of the SERS spectra of pure BV2 dye as reference and the sample shows spectra with a similar number and position of peaks, however their relative intensities show differences. First synthesised in 1889 by Homolka. (C.I. 1924). The dye was formerly used in watercolour paints, but has since been replaced by colours with better lightfastness properties [71]. It has been identified in two woodblock Japanese prints from the late nineteenth century by Cesaratto et al. [68] and recently by Stege et al. in a painting by Emil Nolde dated 1932 [72].

Xanthene class

Xanthene colourants were identified in rose/purple and grey hues, both in water- and tempera colours. The SERS spectrum recorded on the *Rosalack* wash by Turm (XRF: Al, Ba, Pb, Fe, Br) is comparable to the reference spectrum of Acid Red 87 (AR 87, Eosin Y, C.I. 45380 corresponding to Pigment Red 90, C.I. 45380:1) and also Acid Red 51 (AR51, Erythrosine, C.I.45430 corresponding to Pigment Red 172, C.I. 45430:1). The discrimination of

the two compounds by means of spectroscopic methods is not straightforward (Fig. 10a). The SERS characteristic bands present only small differences in shifts, e.g. Br (Eosin) or I (Erythrosine) substitution of the aromatic ring can be observed between $663\text{--}708\text{ cm}^{-1}$ and $675\text{--}709\text{ cm}^{-1}$, respectively [73]. The XRF analysis help the discrimination based on the detection of one of the two metal. In this case due to the detection of Br, the presence of AR87 can be assumed. There are two possible forms of the two lakes, namely the Pb and the Al lake. Also, in this case, due to the detection by XRF of strong signals of both Al and Pb, no specific form can be discerned.

AR87/PR90 (or similar) has also been identified in the DFB colour charts by SERS in admixture with alizarin in *Krapplack dunkel* wash by Flamuco Tempera (Fig. 10b). The presence of Alizarin (PR83, C.I. 58000) was confirmed by MU-ATR (Fig. 10c). In the SERS spectrum, bands at about $1200\text{--}1250\text{ cm}^{-1}$ can be attributed to phenyl mode OH def. vibration and C-O stretching combinations. Thus, the presence of a third, unidentified colourant may be suggested.

AR87/PR 90, also named Geranium lake, has attracted the attention of the scientific community owing to its presence in famous Impressionist and Post-impressionist paintings, e.g. Van Gogh *Iris* [9]. Those paintings showed evident discolouration phenomena. The role of light exposure, oxidation and the presence of binders on the photochemistry of eosin-based organic pigments have been recently studied by Chieli et al. [69] and Sabatini et al. [74]. The poor lightfastness has been confirmed and a fading mechanism has been proposed. The tests also show that the white pigments have no obvious effect on the stability of the colouring matter [69].

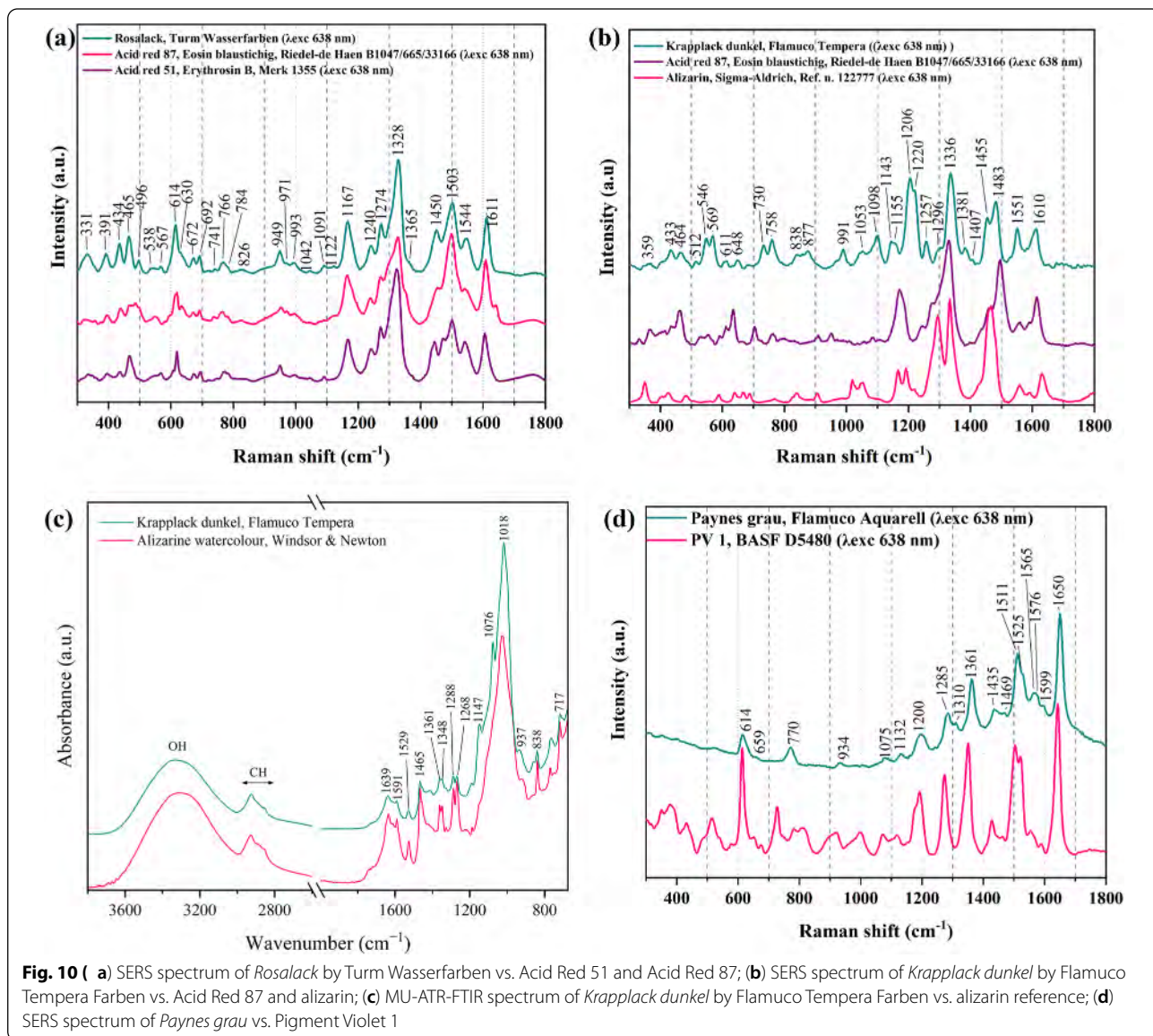


Fig. 10 (a) SERS spectrum of *Rosalack* by Turm Wasserfarben vs. Acid Red 51 and Acid Red 87; (b) SERS spectrum of *Krapplack dunkel* by Flamuco Tempera Farben vs. Acid Red 87 and alizarin; (c) MU-ATR-FTIR spectrum of *Krapplack dunkel* by Flamuco Tempera Farben vs. alizarin reference; (d) SERS spectrum of *Paynes grau* vs. Pigment Violet 1

The aluminium and lead lakes of AR51 are bright red pigments used in cosmetics and occasionally in printing inks. They have poor fastness to light [37]. This colourant has not been identified in specific works of art.

Basic Violet 10 (BV 10, Rhodamine B, C.I.45170) or Basic Violet 11 (BV 11, C.I. 45175) has been identified in the watercolour hue *Krapprosa* (XRF: Al, P) by Flamuco and in the grey-blue hue labelled *Paynes grau* (XRF: Ca, S, P, Al, Si) of the same brand. The SERS spectra of BV 10 and BV 11 are very similar and cannot be distinguished (Fig. 10d). The additional presence of ultramarine blue in the last wash has been confirmed by means of MU-ATR. As discussed for BV1, both dyes (BV10 and BV11) were produced as more stable lakes of

phosphotungstomolybdic acid (PTMA) since about 1925 and then denoted as Pigment Violet 1 and Pigment Violet 2, respectively [70]. However, for the two DFB colour charts, XRF did not detect P, Mo or W, so BV10 or BV11 here is probably still present mainly as Al-based lake.

Azine class

Basic Red 5 (BR5, C.I. 50040) was unexpectedly identified in a hue of Mussini Harzölfarben labelled *Wurzelkrapp mittel n.5*, a designation that normally refers to a natural madder lake (Fig. 11). BR5 was already synthesised in 1879, and to the best of our knowledge, no example of the presence of BR5 lakes in a specific work of art has been published.

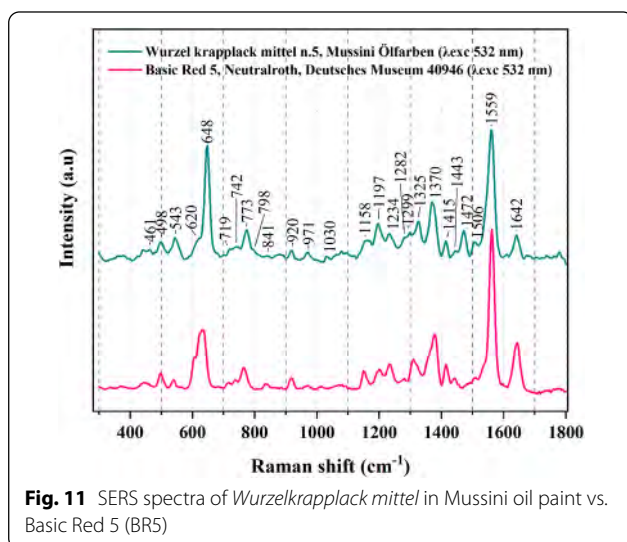


Fig. 11 SERS spectra of *Wurzelkrapplack mittel* in Mussini oil paint vs. Basic Red 5 (BRS)

Conclusions

A stepwise combination of complementary vibrational spectroscopy techniques (i.e. normal Raman, SERS, and MU-ATR), both non-invasive and micro-invasive, allowed us to identify 18 different organic colourants in artists' watercolours, tempera and oil colours from six German paint manufacturers dated 1925. Even though, we are aware that our approach was selective and the true palette of SOPs at the time was probably significantly broader. Minor SOP additions in admixtures are likely to be underestimated by vibrational spectroscopy alone and require further studies with chromatographic techniques.

In addition to a few traditional natural organic colourants (e.g. dark and rose madder lake, cochineal lake), most compounds comprised SOPs or synthetic dyes from various chemical classes (indigo, anthraquinone, mono-azo, β -naphthol, xanthene, triarylcarbonium, nitroso and azine compounds). Most organic dyes/SOPs are present as aluminium lakes. Phosphotungstomolybdic acid (PTMA) lakes, which were introduced around 1925, could not yet be identified in the charts of the *Deutsches Farbenbuch*.

The study also demonstrated the complementarity of both normal Raman and SERS approaches for the comprehensive characterisation of complex SOP mixtures, but also the need for building more comprehensive SERS databases. In fact, in some cases, the interpretation of very good but complex SERS spectra was not possible. The use of MU-ATR in this study was limited to cases in which no results were obtained by Raman/SERS. It was useful for the identification of specific yellow colourants (PY1). Moreover, it was key for identifying further inorganic components, which are not always successfully detected by normal Raman.

The denotations of the commercial colours usually did not give reliable clues regarding the pigment composition. Hitherto, some of the identified dyes and SOPs have not or only rarely been reported in artists' paints, which indicates the need for undertaking further, similar analytical studies. Since the identified organic colourants have mainly poor to fair (only sometimes good) fastness to light and partially also to solvents typically used in conservation treatments according to modern standards [75], it is evident that works of art from this period should be treated keeping in mind the possible presence of such colourant, when planning both inter-ventive treatments and preventive measures.

Abbreviations

C. I.: Colour Index published by the Society of Dyers and Colourists (SDC) and American Association of Textile Chemists and Colourists (AATCC); DFB: Das Deutsche Farbenbuch; DGzBrM: Deutsche Gesellschaft zur Beförderung rationeller Malverfahren (engl. Society for the Promotion of Rational Painting Techniques); SOP: Synthetic organic pigment; SERS: Surface-enhanced Raman spectroscopy/scattering; XRF: X-Ray fluorescence; MU-0ATR: Metal-underlayer attenuated total reflection Fourier-transform infrared spectroscopy.

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Author contributions

CS performed the SERS measurements, was involved in data analysis and interpretation. She wrote and edited the manuscript in collaboration with all the co-authors. HS conceived and led the project, was involved in data analysis and interpretation and wrote part of the article; CS performed the Raman and XRF measurements and was involved in data analysis and interpretation; DQB and GS performed the MU-ATR measurements and were involved in data analysis and interpretation. SP was involved in analysis and interpretation of the MU-ATR measurements and revised the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

The data will be available upon request. The Raman spectra recorded with the 785 nm laser are also available online in a SOP spectral library created thanks to the Belgian Royal Institute for Cultural Heritage (KIK-IRPA) Brussels and the SOPrno Project [35].

Declarations

Competing interests

The authors declare that they have no competing interests.

Author details

¹Chair of Conservation-Restoration, Art Technology and Conservation Science, Technical University Munich, Munich, Germany. ²Doerner Institut, Bavarian

State Painting Collections, Munich, Germany. ³Microchemistry and Microscopy Art Diagnostic Laboratory (M2ADL), Department of Chemistry “G. Ciamician”, University of Bologna—Ravenna Campus, Ravenna, Italy.

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