Identification of Pre-1950 Synthetic Organic Pigments in Artists' Paints. A Non-Invasive Approach Using Handheld Raman Spectroscopy

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Abstract: There is little information on the actual use of early synthetic organic pigments (SOPs) in art objects, especially those from before 1950. Their presence can, however, pose a challenge to conservation because their chemical composition, as well as their lightfastness and sensitivity to solvents, are often unknown. Here, a study on the non-invasive identification of SOPs in historic pre-1950 varnished paint-outs from artists' materials manufacturer Royal Talens is presented. The paints were analysed using a handheld Raman device. Spectra were evaluated by recording the spectra of the same samples with a benchtop instrument. This study demonstrated that the identification of SOPs in varnished oil paints with a non-invasive approach is possible and rather straightforward. The handheld Raman device allowed us to identify fourteen SOPs from eight pigment classes. Besides the occurrence of expected and the known SOPs of this time period, there were also some surprising results, like the detection of the triarylcarbonium pigments PG2 and PB8, and the monoazo Mordant Yellow 1.

Keywords: synthetic organic pigments; royal talens; handheld raman spectroscopy; microraman spectroscopy; modern artist oil paint

1. Introduction

After the accidental discovery of mauveine in 1856, a new class of dyestuffs and pigments was developed and introduced to the market. These were formerly defined as coal-tar dyes and are nowadays called synthetic organic pigments (SOPs). SOPs are "manufactured colourants that have a carbocyclic ring skeleton" [1]. In contrast to natural organic pigments, they are synthesized in a laboratory environment and produced on an industrial scale, so that natural organic pigments like indigo and alizarin can be considered as SOPs when they are produced industrially [1].

After their introduction, paint manufacturers started to use SOPs for their tube paints, which led to new shades in artists' colours and to the imitation of traditional pigments [2–4]. As it was initially not mandatory for manufacturers to indicate the use of SOPs in their paint formulations, artists often lacked knowledge of the exact content of their supplies. Considering the minor fastness characteristics of the early SOPs compared to traditional pigments, their use also led to material problems previously unknown to the artists, who tended to take a critical view on these new pigments [2,5]. In contrast to the traditional artists' pigments, the availability of certain SOPs is linked to an exact date of introduction, which can be traced by means of patents. Therefore, the identification of SOPs can not only provide information about the dating of an artwork, but can also expose forgeries [6]. Furthermore, knowledge of the occurrence of certain SOPs can provide useful information for restoration and conservation approaches or art technological studies.

SOPs can be difficult to detect in paint samples, because, due to high tinting strength, relatively small amounts are generally present [7]. Furthermore, these pigments have a very

small particle size and are usually part of a complex system of ingredients in artists' tube paints. Therefore, traditional methods for pigment identification, such as polarised light microscopy, can hardly be used. Identification with Fourier transform infrared (FTIR) spectroscopy may be equally complicated, because the strong and broad peaks of paint binders, inorganic substrates, or extenders can interfere with the SOPs' information [8]. Invasive and destructive methods like pyrolysis gas-chromatography/mass-spectrometry (Py-GC/MS) can sometimes provide useful information on the presence of certain SOPs, such as azo-pigments. Others may not be suitable for this technique due to their thermal and chemical instability [9,10]. High performance liquid chromatography-mass spectrometry (HPLC-MS) can be challenging too, as getting the pigment to dissolve can be difficult and the effects of dissolution on the pigment structure may be problematic for interpretation [11]. MicroRaman spectroscopy (μ-RS) has been demonstrated to be a suitable analytical tool for the identification of SOPs. It is relatively sensitive towards these pigments, requires little sample material, and allows samples to be used for further, complementary analysis [12–14]. Approaches for μ-RS SOPs identification in samples from artworks are under constant development [9,10,15,16]. The main limitation in using μ-RS to identify SOPs in artists' paints, however, is related to the fluorescence associated with organic binders, varnish layers and additives, or sometimes even with the target pigments themselves. In order to obtain an interpretable spectrum, it is important to perform measurements in equilibrium between fluorescence and the intensity of the Raman signal, which makes this approach time-consuming [8,17].

All these analytical techniques, however, require the sampling of small paint fragments, which, besides being destructive, can be challenging, as the probability that the samples are not representative for the materials studied might be quite high [18]. An analytical approach using non-invasive devices that allow for unlimited measurements therefore seems desirable [19]. The use of visible reflectance spectroscopy and visible-excited spectrofluorimetry was successful for the non-invasive identification of contemporary SOPs [20]. Yet, for the non-invasive study of artworks, Longoni et al. [20] recommend the use of further complementary non-invasive analysis. The usage of portable Raman systems seems to be promising [21,22]. A portable device that minimizes fluorescence and can operate at low energy is needed. Damage by strong laser absorption should be avoided to prevent local burns, which may occur especially on opaque or dark materials [8].

Different handheld Raman systems have been reviewed and tested for their application in the field of cultural heritage [19,23–25]. Technological developments have countered the most difficult problems, such as low Raman signal, high fluorescence, and environmental interactions, as well as the positioning and focusing of the laser [26,27]. To date, the Bravo handheld Raman instrument developed by Bruker seems to be the most promising device [19] and its applicability to the study of modern art was evaluated [28]. This device employs a DUO Laser system (785 nm and 853 nm), recording spectra in two separate spectral ranges of 300–2200 and 1200–3200 cm^{-1}, respectively. The patented sequential shifted excitation (SSETM) works by temperature-shifting the lasers over a small wavelength range and recording three spectra per laser, finally merging them into a seventh averaged spectrum. In this way, and through the use of near infrared lasers, the system is able to reduce fluorescence and excite colour with low efficiency, also enabling the measurement of, for example, varnished paint samples [19,23,27]. However, Pozzi et al. [19] observed that if the peaks and curves of the individual spectra differ too much from each other, there is a risk of creating artefacts within the averaged spectrum. Another disadvantage of the device is related to the fact that the only two adjustable settings are exposure time and acquisition number, but not the energy of the laser, which can be a risk for certain art-technological studies [19]. These aspects, regarding the spectral quality and applicability, are discussed within this study.

The aim of this research is to study the potential of a handheld Raman device in identifying SOPs in historical varnished paint-outs (1932–1950) with consideration to future applications in the non-invasive study of early SOP-containing paintings.

Ongoing work on the collection of SOPs Raman reference spectra (https://soprano.kikirpa.be, accessed on 30 June 2021 [14,29]) enables and simplifies pigments' identification. These reference spectra were often obtained by studying modern artists' supplies and can give an idea of the actual SOPs that can be expected.

Before 1950, the following SOP groups were already developed and established: β-Naphthol pigment lakes; BON pigment lakes (pigments produced with 2-hydroxy-3-naphthoic acid as coupling component); β-Naphthol; Pyrazolones; Hansa Yellows; Diarylides; Naphthol AS; Iron complex Pigment Green B; Phthalocyanines; Nickel Azo Yellow [30]. However, as already mentioned, the actual distribution and use of this "new" group of pigments within artists' materials is still unclear today. Attempts to provide an overview of the SOPs that were known before 1950 and of their occurrence in artists' paints demonstrated the need for more research [7,30]. A starting point could be the study of the production archives of artists' material suppliers.

Our research in the archives of Royal Talens and its main pigment suppliers before 1950, BASF and Bayer, shows that there are considerably more SOPs used in artists' paints than hitherto known [4,11,31]. Notably, most of them have not been traced in paintings.

This study focuses on SOPs in Royal Talens' artists' oil paints from before 1950. Soon after its foundation in 1899, Talens developed into a major international player on the market, already selling more than 1,500,000 oil paint tubes in 1918 [32]. European artists such as van Dongen, Kirchner, Appel, and Munch used Talens' Rembrandt oil paints [33]. In this position, Talens declared the use of SOPs in fine artists' oil paint publicly in the beginning of the 1930s.

Based on pre-1950 oil paint recipes [4,16], a selected set of paint-outs (1932–1950) from the Royal Talens' archive was investigated. For the assessment and evaluation of the handheld Raman spectra, micro samples of the historic Talens paint-outs were also analysed with a benchtop microRaman spectrometer.

Handheld Raman spectra were evaluated, taking into account their major points of criticism, like background fluorescence, the intensity of the Raman signal, spectral resolution, and the risks of laser energy induced damages.

2. Materials and Methods

2.1. Samples

The sample selection consisted of paint-outs from 1932 to 1950. These were included within colour charts specifically dedicated to coal-tar pigments, labelled as unalterable Teerkleurstoffen [coal-tar dyes] (Figure 1), which were published in six editions of the book Kunstschildersmaterialen en Schildertechniek [Painting materials and painting technique] [34–40]. The books deal with Talens' fine Rembrandt artists' oil paints, which were on the market since 1904 [4,33]. In addition, some paint-outs that were listed under inorganic names within the inorganic paint colour charts, but suspected to contain SOPs according to recipe interpretation, were examined as well. To obtain results on a larger data set, it was decided to measure (if available) the same set of 42 potentially SOP-containing paint-outs in each Kerdijk edition, even if, according to the recipes, the same SOPs were to be expected. In total, 193 samples were analysed with handheld Raman spectroscopy and for comparison with benchtop microRaman spectroscopy. Samples were labelled with a "K" (Kerdijk) and the year of publication. All paint-outs were varnished.

2.1.1. Instrumentation

The handheld Raman measurements were conducted with a Bravo Spectrometer (Bruker). The device works with two excitation wavelengths, recording spectra in two separate spectral ranges of 300–2200 and of 1200–3200 cm^{-1} with a DUO Laser system (785 nm and 853 nm). The near infrared lasers (NIR) aid in reducing fluorescence, as the photon does not possess enough energy to induce high molecular fluorescence [22,41]. Furthermore, using two lasers enables researchers to obtain better quality data in the overlap region of 1200–2200 cm^{-1} and lowers fluorescence interference [19]. The energy

reaching the surface during the measurement is officially stated to be less than 100 mW (Table 1). Since the energy cannot be set manually, this indication is too unspecific to be taken as a guide value when analysing delicate cultural heritage objects. In order to estimate the energy that actually reaches the surface of the sample, measurements were carried out with a "Power and Energy Meter" from Thorlabs, using the same settings of the historic Talens paint-outs analyses. The measured energy value was about 45 mW, with measurements conducted at a distance of about half a millimetre, with a spot size of 1 mm. This value also agrees with that determined by Pozzi et al. of about 50 mW [19].
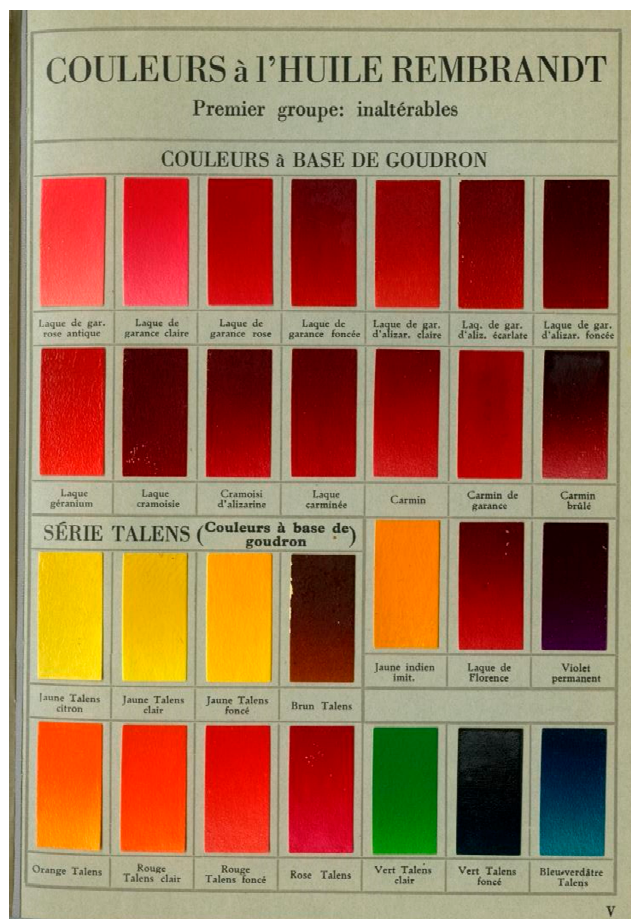

Figure 1. Kerdijk colour chart from 1932, presenting a selection of Talens' Rembrandt artists' oil paints 'à base de goudron' (based on coal tar). Please note that the colours are defined as 'inaltérables' (unalterable).

Table 1. Characteristics of the microRaman and handheld Raman devices.

Name/Producer	MicroRaman [a]	Handheld Raman [b]
Laser system	350 mW near infrared laser (class3B laser device)	Dual laser excitation
Wavelength	785 nm	785 nm and 853 nm
Max. laser power of device	100 mW	<100 mW (both lasers)
Max laser output on sample	21.7 mW (50× magnification)	45 mW (working distance)
Spectral range	95–3500 cm^{-1}	300–3200 cm^{-1}
Spectral resolution	4 cm^{-1}	10–12 cm^{-1}
Spot size	10–20 μm	10–15 μm [c]
Working distance	(depending on magnification)	ca. 0.5 mm

[a] Perkin Elmer, RamanMicro 300, coupled to Raman Station 400F; Available online: https://www.perkinelmer.com/CMSResources/Images/46-74804SPC_RamanStation400RRamanStation400F.pdf (accessed of 14 July 2020). [b] Bravo Bruker [13,23,32]. [c] Due to the lack of a camera and the size of the laser pinhole of 3 mm, it was not possible to precisely focus on this spot size.

To evaluate the handheld device's performance for the identification of SOPs, the colour charts were also analysed with a benchtop microRaman instrument. These reference spectra were recorded with a RamanMicro 300 in combination with a RamanStation 400F (Perkin Elmer, Waltham, MA, USA) and an Olympus BX51M microscope (Table 1). Micro-Raman spectra were acquired from very small samples of the same paint-outs. After the mechanical removal of the varnish from the sampling area, minute paint fragments were taken at the upper right edge where the paint film is thickest. The samples were placed on an aluminium tape, mounted on a glass slide, and positioned as close to perpendicular to the optical axis as possible to reduce fluorescence [42].

Spectra were recorded in the range of 300–2000 cm^{-1}, in order to perform the analysis within the same range as the handheld Raman. The microRaman reference spectra were only baseline corrected when necessary for their readability.

2.1.2. Acquisition of Spectra

As the Bruker Bravo does not include a camera, the measurement preparation demanded precise positioning. To locate and define the measuring spot on the paint-outs, a Melinex$^{®}$ template in the shape of the optical head was used. Measurements were taken at the closest possible distance without touching the surface, which was approximately half a millimetre. Since this study was undertaken to investigate the possibility of analysing SOPs in real artworks where focusing on well-defined paint spots is mandatory, it was decided not to use the de-focusing tip. Handheld Raman spectra were recorded with initial settings of 100 ms and 20 acquisitions within the spectral range of 300–2000 cm^{-1}. These settings proved to be efficient to verify the Raman signal and fluorescence. Depending on the signal to noise ratio of the spectrum, these settings were tuned to: acquisition times 100–300 ms; 50–200 acquisitions.

A common limitation of portable Raman devices is the reduced possibilities to control the measurement settings [19]. For the Bravo spectrometer, the lack of direct control of the laser energy was considered potentially problematic. As the maximum energy reaching the surface is quite high in comparison to the Perkin Elmer microRaman instrument (Table 1), the measurement spot was checked under the microscope before and after analysis in order to be able to track possible laser induced damage.

Measurements were recorded without removing the varnish layer from the paint-outs at the upper middle edge of the samples, in order to measure a spot with high pigment density.

2.1.3. Interpretation of Raman spectra

Handheld Raman spectra were interpreted using reference spectral databases. Raman reference spectra of SOPs have been published listing the peaks with their relative intensity or in digital databases [10,14,29]. Furthermore, the continuously updated in-house built Raman spectral library was used.

It should, however, be taken into account that reference spectra are mostly acquired on pure materials, like pigment powders. When compared with paint systems, differences in heat dispersion or fluorescence behaviour may lead to slight differences in the spectra [43,44]. The excitation wavelength and power of the laser can influence the reference spectra too. As KIK-IRPA documents the exact measurement settings for each reference spectrum (https://soprano.kikirpa.be, accessed on 21 August 2020), their database was used as the main reference for the interpretation of the spectra, in addition to the in-house database.

In some cases, it was not possible to interpret the Raman spectrum and assign it to a defined pigment. In these specific cases, additional methods, such as ultra-high performance liquid chromatography mass spectrometry (UHPLC-MS), were used to try to identify the unknown samples. These results were verified by analysing corresponding references from the in-house reference collection.

3. Results and Discussion

As a pre-interpretation step of the Raman spectra acquired from the Kerdijk paint-outs, production recipes collected at the Talens' archives were studied and evaluated and a list of expected SOPs was made [4]. Where possible, the commercial names used in the recipes were related to the Colour Index definitions, e.g., the pigment Hansa Geel 10 [Hansa Yellow 10] corresponds to PY3. Then, the acquired Raman spectra were compared with the reference spectra of the expected SOPs.

Table 2 gives a detailed overview of the analysed paint-outs and their interpretation. The expected SOPs according to the recipes are reported. The settings for acquisition refer to the averaged settings yielding the best result. It was found that the handheld Raman produces readable and interpretable spectra with defined peaks at almost constant settings of 150–200 ms exposure time and 100–200 acquisitions.

3.1. Identified SOPs

The Talens Rembrandt oil paints of the Kerdijk colour charts were revealed to contain the SOPs of eight different pigment groups. Furthermore, it was also possible to identify paints that contained a mixture of SOPs (Table 2).

Some of these SOPs belong to groups that are already well known to have been used in fine artists' materials and can be expected in this time period. This concerns SOPs belonging to the BONA, monoazo, and phthalocyanine group as well as the ß-Naphthol pigments PR3 and PO5, which have indeed been found in artworks from before 1950 [30]. In other cases, the Kraplak [madder], Karmijn [carmine], and Alizarine [alizarine] paint-outs provided well defined spectra, but the SOPs have not yet been identified and are labeled as "unknowns".

Among the identified SOPs, there are also some pigments that were not yet known to have been used for the production of fine artists' paints dated before 1950. The occurrence of the mordant dyes and triarylcarbonium pigments are among the most surprising results of this study and emphasizes the importance of searching unexpected possible pigment groups in pre-1950 artists' materials. Three examples are discussed in more detail.

The paint-out Gamboge from 1932 was revealed to contain Mordant Yellow 1. This SOP was discovered by Nietzki in 1887 and is also known as Alizaringelb GG [Alizarine Yellow GG] or Beizengelb TG [Mordant Yellow TG] [45]. Wagner (1928) reports that this pigment was not very popular because of the elaborate preparation needed to obtain a pure product. It is therefore surprising that, according to the recipe records, Talens has used this SOP for fine artists' material production for almost 20 years [34,46]. Figure 2 displays the handheld Raman spectrum of the paint-out Gamboge and the microRaman spectrum of Mordant Yellow 1 from the in-house reference collection. The handheld Raman spectrum displays the peaks that allow an interpretation, but also contains artifacts.

Within the paint-out Talens Groen Licht [Talens Green Light] the pigment PG9, a SOP belonging to the group of Indamine, was detected. This pigment, a barium salt of an iron complex, was discovered in 1909 and labelled as Hansagrün GS [45]. It was recommended by the Colour Index to be used "particularly in mixture with CI PY 1 or 3" [45–47]. Schultz (1931) describes the pigment as a "very lively green when mixed with Hansa Yellow for all purposes (almost as fiery as Schweinfurter Green)" [48]. This suggests its use in artists' colours in mixture with monoazo yellows as a substitute of the toxic inorganic pigment and fits therefore to Talens' application, documented in the recipe of Talens Green Light.

Figure 3 shows the handheld Raman spectrum of the paint-out Talens Green Light and, for comparison, the microRaman spectrum of a Hansagrün GS reference (paint-out from Wagner, 1928). The peaks of the PY3 component in the reference spectrum are very faint, which can be related to different PY3 and PG9 ratios within the samples.

Table 2. Summary of the results obtained with the handheld Raman device on Kerdijk colour charts with Talens' Rembrandt oil paint-outs dated 1932–1950.

Sample Name [English Translation]	Commercial Name of the SOPs from the Recipe [a]	CI	Kerdijkbook	Exposure Time (ms)/Accumulations (No.)	Identification
Kraplak rose antique [madder lake pink antique]	Wurzelkrapplack 30101 Huber	-	K32-K50	200/200	Unknown A
Kraplak licht [madder lake light]	Wurzelkrapplack B6	-	K32-K44	200/200	Unknown A
	Kraplak 31417	-	K50	200/200	PR83 + Unknown A
Kraplak rose [madder lake pink]	Kraplak B6/Kraplak donker 30029 Huber	-	K32-K37	250/100	Unknown A (?)
	Kraplak 30101/Kraplak 30992	-	K41-K50	250/200	Unknown A (?)
Kraplak donker [madder lake dark]	Kraplak donker Huber 30029	-	K32-K44	200/100	Unknown A + Unknown C
	Kraplak 30992	-	K50	200/200	PR83
Alizarine Kraplak Licht [Alizarine madder lake light]	Kraplak IWG	-	K32-K42	200/100	PR83 + Unknown A
	Krapplack 3077	-	K44-K50	150/200	PR83 + Unknown A
Alizarine Kraplak donker [Alizarine madder lake dark]	Alizarine Kraplak 72	-	K32-K37	200/200	PR83 + Unknown A
	Permanentviolet/Karmijnlak/Kraplak	-	K41-K50	200/200	PR83 + Unknown A
Alizarine Crimson [Alizarine crimson]	Kraplak HE	-	K32-K50	150/200	PR83 (+Unknown A?)
Geraniumlak [Geranium lake]	Hansarood B/Kraplak Z	PR3 +?	K32	200/200	PR3 + PO5 [d]
	Isolechtrood B/Kraplak Z	PR3 +?	K37	200/200	PR3 + PO5 [d]
	Karmijnlak fijn/Cadmium red mid	-	K41-K44	200/200	PR3 + PR83
	Talens donker fijn/Karmijnlak fijn	PR3 +?	K50	200/200	PR3 + PR83
Karmijnlak [Carmine lake]	Alizarine madder 34549	-	K32-K50	200/200	PR83 + Unknown A
Crimsonlak [Crimson lake]	Alizarine Kraplak 45	-	K32	200/200	PR83 + Unknown A
Karmijn [Carmine]	-no recipe-	-	K32-K50	200/200	PR83

Table 2. *Cont.*

Sample Name [English Translation]	Commercial Name of the SOPs from the Recipe [a]	CI	Kerdijkbook	Exposure Time (ms)/Accumulations (No.)	Identification
Krapkarmijn [Madder Carmine]	-no recipe-	-	K32-K50	150/300	Unknown A
Karmijn donker [Carmine dark]	Kraplak donker Huber 30029/Ultramarijn VU 861E/Alizarine oranje 6231	-	K32	200/200	Unknown B?
Florentijn lake [Florentine lake]	Alizarine lak 45/Ultramarijn VU861E	- + PB29	K32	200/200	PR83 + Unknown A
Talens geel citroen [Talens yellow lemon]	Hansageel 10G	PY3	K32-K44	200/200	PY3
	Fanchon Yellow YH4	PY3	K50	200/200	PY3
Talens geel licht [Talens yellow light]	Hansageel GGR/Hansageel 10G	PY1 + PY3	K32-K37	200/200	PY3 +?
Talens geel middle [Talens yellow middle]	Hansageel GR	PY2	K32-K37	200/200	PY2
Talens geel donker [Talens yellow dark]	Hansageel GR/ Permanentrood 2G extra	PY2 + PO5	K32-K37	200/200	PY2 + PO5
Talens oranje [Talens orange]	Hansageel GR/ Permanenentrood 2G extra	PY2 + PO5	K32-K37	200/200	PY2 + PO5
Talens rood licht [Talens red light]	Permanentrood 2G extra	PO5	K32-K44	200/200	PO5
	Siegle Oranje 3TR	PO5	K50	200/100	PO5
Talens rood donker [Talens red dark]	Hansarood B	PR3	K32-K37	200/200	PR3
	Isolechtrood B	PR3	K41-K50	200/100	PR3
Talens rose [Talens pink]	Permanentrood F6R extra	PR57	K32-K44	200/200	PR57:1
	Rhodamin Toner	PR57	K50	200/200	PR57:1
Talens bruin [Talens brown]	Fanalgelb G	PY18 +?	K32-K37	200/200	?
	Jaune electra 100/Ultramarijn dnk 100/Kraplak dnk. 100	-	K41-K50	150/100	?

Table 2. *Cont.*

Sample Name [English Translation]	Commercial Name of the SOPs from the Recipe [a]	CI	Kerdijkbook	Exposure Time (ms)/Accumulations (No.)	Identification
Talens groen licht *[Talens green light]*	Hansageel 10G/ Permanentgroen	PY3 + PG18	K32-K37	150/200	PY3 + PG9
	Talens geel 100/ Rembrandtgroen 100	PY3 + PG7	K41-K50	200/100	PY3 + PG7
Talens groen donker *[Talens green dark]*	Fanalgelbgruen G supra	PG2	K32-K37	200/200	PB8
	-no recipe-	-	K41-K50	150/100	PG2
Talensgroenblauw *[Talens green blue]*	Fanalbremerblau G neu	-	K32-K37	200/200	PB8
	-no recipe-	-	K41-K50	150/100	PB15 + PG7
Indischgeel imit *[Indian Yellow imitation]*	Indischgeel imit Siegle 41258	-	K32-K44	200/200	PY1
	Transparent yellow 6202/Cadm. Dnk 101/Cadm. Oranje 101	-	K50	200/200	PY1 + PY3
Permanentviolet *[Permanent violet]*	Violet A 2145 Remmert	Natural Red 9	K32-K44	200/100	Unknown B
	Maroon 2142/Monastraalblauw B	Natural Red 9	K50	150/300	Unknown B
Rembrandtblauw *[Rembrandt Blue]*	Monastraalblauw	PB15	K41-K50	100/50	PB15
Rembrandtgroen *[Rembrandt Green]*	Heliogengroen G	PG7	K41-K50	100/50	PG7
Paul Veronesegroen *[Paul Veronese green]*	-no recipe-	PG7	K41-K50	200/100	PG7
Paul Veronesegoen tint *[Paul Veronese green tone]*	-no recipe-	PG7	K41-K50	150/100	PG7
Dekgroen *[Deck green]*	Hansageel 10G/ Monastraalgroen G	PG7 + PY3	K41-K50	200/100	PG7 (+PY3)
Dekgroen tint *[Deck green tone]*	Hansageel 10G/ Monastraalgroen G	PG7 + PY3	K41-K50	200/100	PG7 (+PY3)

Table 2. *Cont.*

Sample Name [English Translation]	Commercial Name of the SOPs from the Recipe [a]	CI	Kerdijkbook	Exposure Time (ms)/Accumulations (No.)	Identification
Gamboge [*Gamboge*]	Indgeel 3030 Huber of Echtgelb S	-	K32	200/200	Mordant Yellow 1 [b]
Alizarine oranje [*Alizarine orange*]	Alizarine oranje 6213	-	K32-K50	200/200	Mordant Orange 1 [c]
Groene lak licht [*Green lake light*]	-no recipe-	-	K32-K50	200/200	PG12
Groene lak donker [*Green lake dark*]	-no recipe-	-	K32-K50	200/100	PG12
Stil de grain geel [*Stil de grain yellow*]	Echtgelb S	-	K32-K44	200/200	Mordant Yellow 1 [b]
	Cone Yellow Lake ER 387		K50	200/200	Mordant Yellow 1 [b]
Vert de olive [*Olive green*]	Groene lak 2365/Alizarine oranje/Echtgelb S	-	K32	100/200	PG12
Vert de vessie [*Sap green*]	Groene lak 2548	-	K32	100/200	PG12

[a] Information based on archival research [3,4]. Further information will be available in R. Pause, PhD thesis, University of Amsterdam, due in 2022. [b] Identified by A.N, Proaño Gaibor, UHPLC-MS analysis.
[c] Identified by B. Sundberg, UHPLC-MS analysis (Sundberg et al., 2020). [d] Additional peaks at 1343 cm^{-1} and 1368 cm^{-1}, which are not attributable to PR3 or PO5, are not yet interpreted.
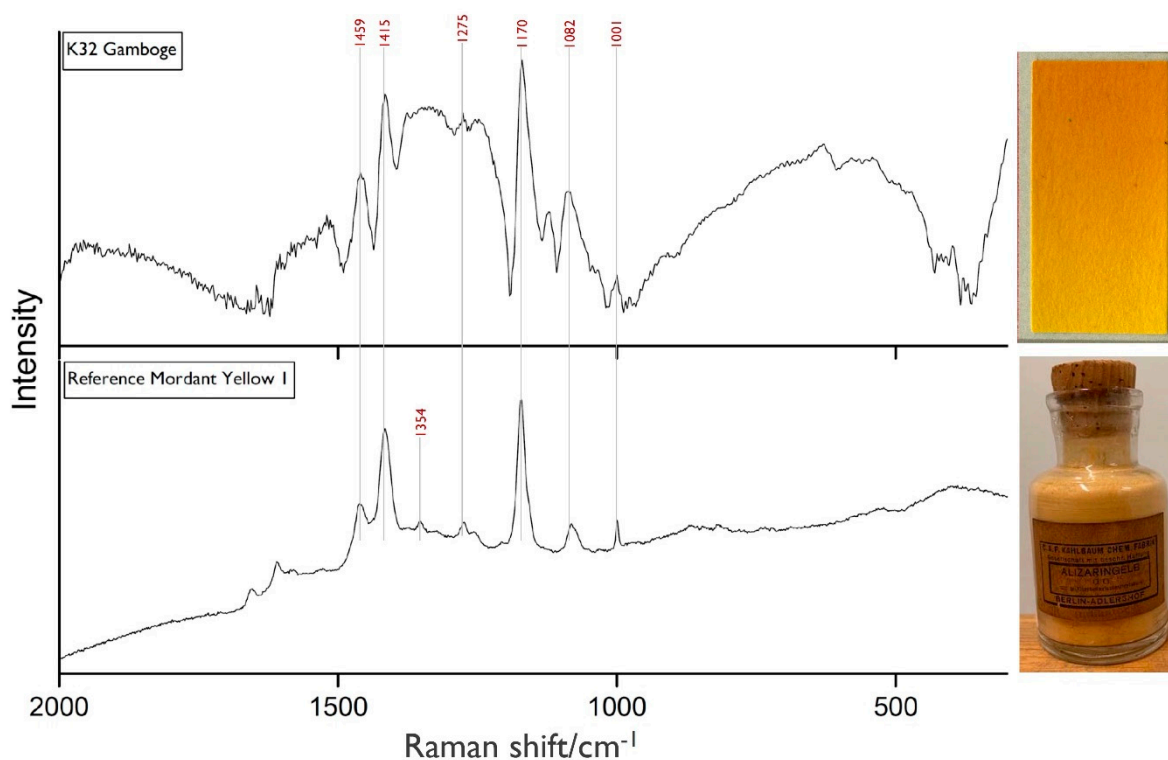
Figure 2. Handheld Raman spectrum of the paint-out Gamboge (K32) and the microRaman spectrum of Mordant Yellow 1, labelled as Alizarine Yellow GG (reference collection of the Cultural Heritage Agency of the Netherlands, Amsterdam, The Netherlands).
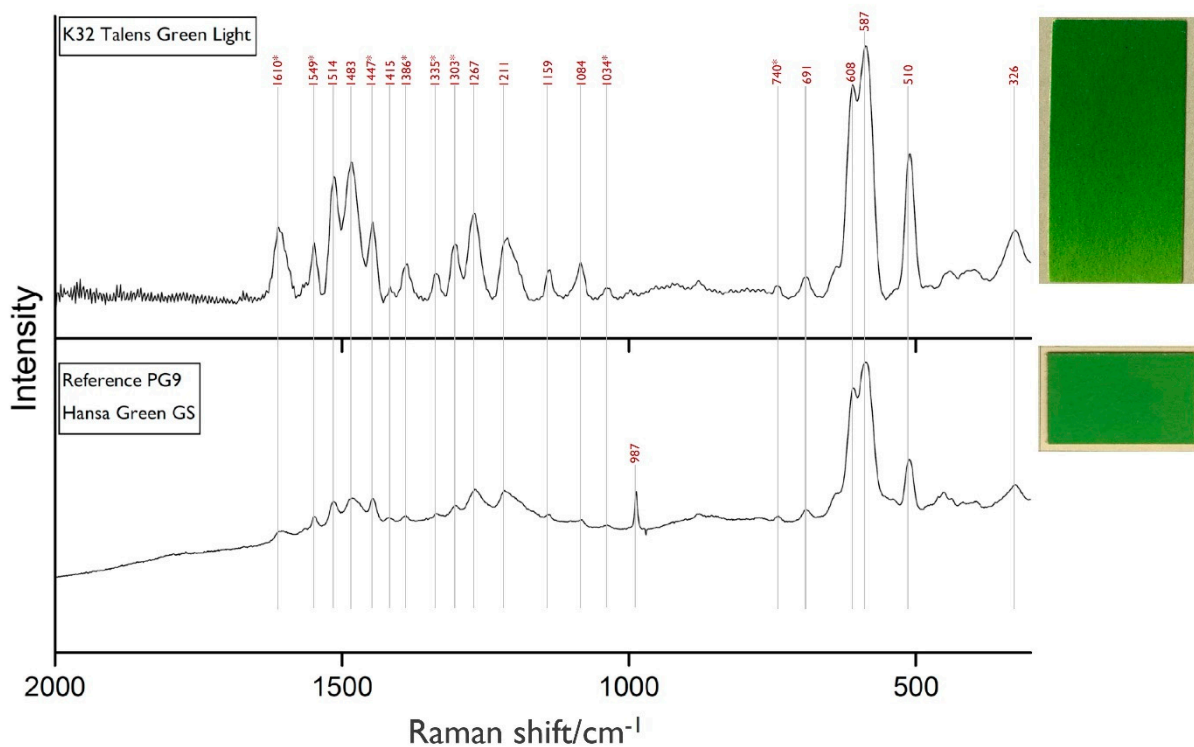

Figure 3. Handheld Raman spectrum of paint-out Talens Green Light (K32) and the microRaman spectrum of reference Hansagreen GS (Wagner, 1927), mixed with barium sulphate (987 cm^{-1}), both showing the characteristic peaks of PG9 in mixture with PY3. The peaks that clearly correspond to the KIK-IRPA reference for PY3 are highlighted with a star.

Two paints of the Talens in-house brand, labelled as "Talens paints", showed triaryl-carbonium pigments. In the paint-out Talens Groen Donker [Talens Green Dark] of the 1941–1950 editions, the green pigment PG2 was identified. PG2, brought to the market under the product name Fanalgelbgrün [Fanal Yellow Green], is defined as either a mixture of Basic Green 1 and Basic Yellow 1, precipitated with phosphotungstomolybdic acid (PTMA), or Basic Green 1 with Auramin O, precipitated with PTMA [31,45,48].

The other triarylcarbonium pigment that was identified is PB8. It was detected in the paint-out Talens Green Dark (1932), contradicting the recipe (Table 2), and in the Talens Groen Blauw [Talens Green Blue] in the editions from 1932 and 1937. PB8, labelled in the Talens recipes as Fanalbremerblau G neu [Fanal Bremer Blue G new], is a mixture of Basic Blue 5 and Basic Green 1, precipitated with PTMA [17]. Figure 4 displays the handheld Raman spectrum of Talens Green Blue and the reference microRaman spectrum of a reference sample, labelled as a mixture of Basic Blue 5 and Basic Green 1 precipitated with PTMA, provided from the Historic dye collection of the technical university in Dresden.
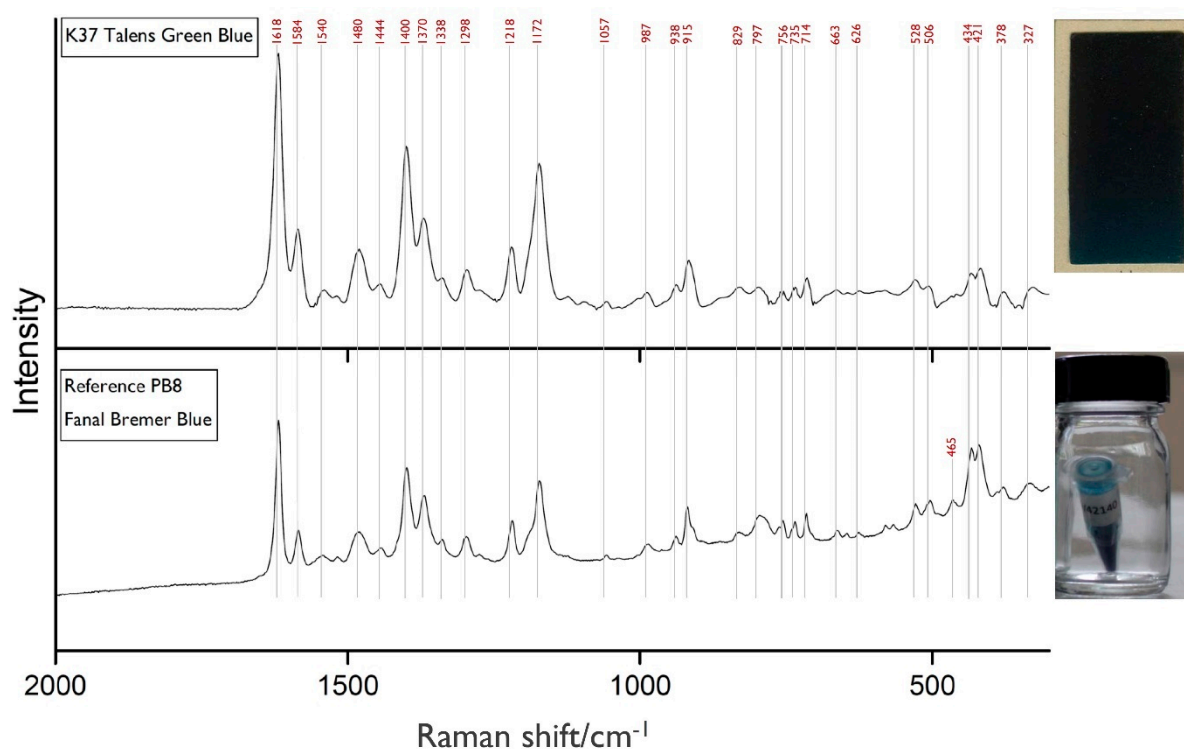

Figure 4. Handheld Raman Spectrum of paint-out Talens Green Blue (K32) and the microRaman spectrum of a reference sample containing Basic Blue 5 and Basic Green 1, precipitated with PTMA (Historic Dye Collection, Dresden, Germany).

Both PB8 and PG2 belong to the Fanal brand, which was introduced by I.G. Farben in 1924 [31]. Lomax et al. [1] point out that "the major use of these pigments [triarylcarbonium] is in the printing ink industry" and it seems surprising that Talens chose these SOPs for their fine artists' oil paint brand. However, Steger et al. detected two pigments (PV2 and PG1), belonging to this group, in a reverse glass painting from 1945 [49].

3.2. Evaluation of the Handheld Raman's Applicability

Raman spectra were not only interpreted for pigments' identification, but also evaluated for readability and quality. When dealing with the handheld Raman spectra that were acquired from our samples, we came across some of the issues that generally arise in the discussions about the applicability of handheld Raman spectroscopy [19].

A common problem which can lead to uninterpretable spectra is the occurrence of strong fluorescence that obscures the Raman scattering signal and affects the accuracy

and sensitivity of the measurements [50]. As mentioned, the Bravo-Raman device uses sequentially shifted excitation, a patented fluorescence minimization method [19].

As an example, a paint-out containing a Hansa Yellow pigment was selected to demonstrate the result of the automatic fluorescence reduction. This important class of SOPs, which is commonly found in modern artworks [30], often exhibits strong fluorescence in Raman spectroscopy. Figure 5 shows the handheld Raman spectrum of the paint-out Talens geel citroen [Talens yellow lemon], where Hansa Yellow (PY3) was identified. The spectrum recorded with the microRaman was not further processed after acquisition and shows a distinct fluorescence, whereas the spectrum recorded with the handheld Raman appears to be corrected in this respect, thanks to the SSE approach and the two lasers. The spectrum presents intense peaks, although the spectral resolution is not very high, as demonstrated by the lack of a peak at ~1593 cm^{-1}, which was present in the microRaman spectrum.
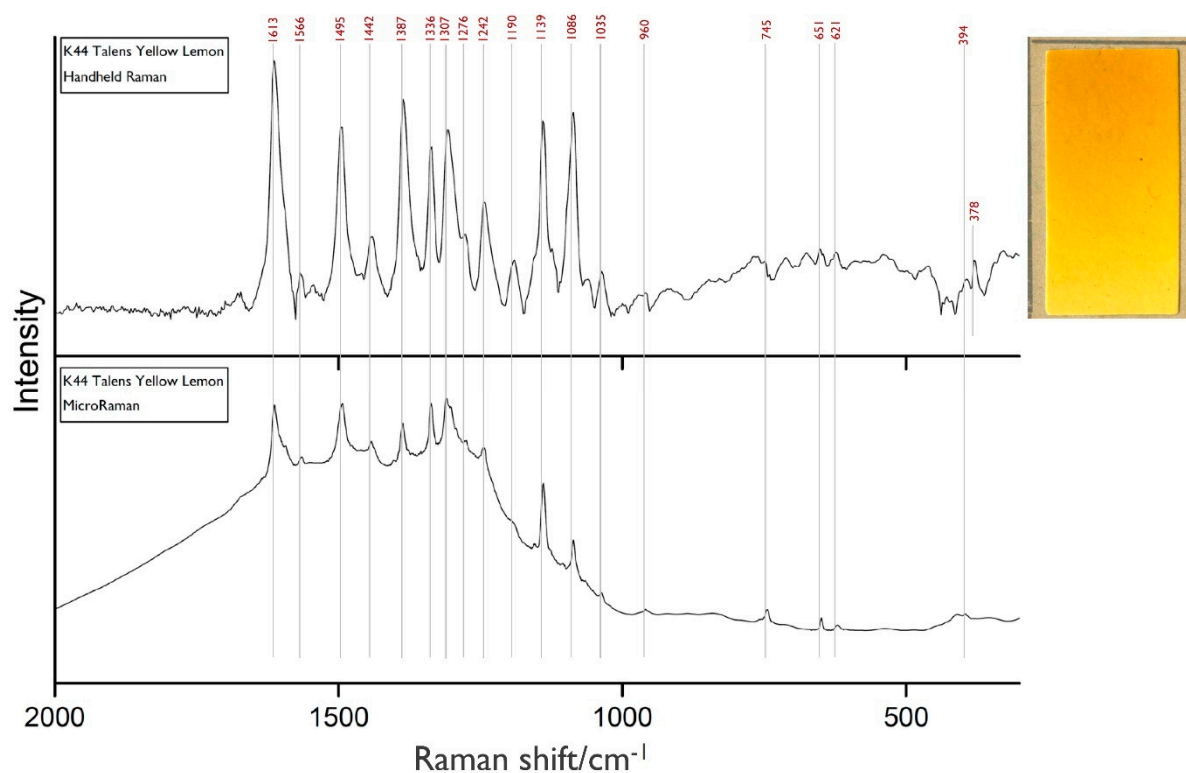

Figure 5. Handheld and microRaman spectra of paint-out K44 Talens Yellow Lemon.

Another issue we considered was the merging or shifting of peaks as a consequence of over excitation, when measuring with a high, non-adjustable energy. This was observed in the Handheld Raman analysis of the paint-out Talens Rood Donker (Talens Red Dark), containing PR3 (Figure 6). Peaks that are close to each other and similar in intensity seem to be smoothed. This could be due to the high laser power, which might be responsible for a shift in peaks to lower wavenumbers, peak broadening, or twin peaks merging (for example at 1621 cm^{-1} and 1605 cm^{-1}).

Another example of possible overexcitation is reported in Figure 7. Here the handheld Raman spectrum of paint-out K41 Rembrandtgroen [Rembrandtgreen] is shown where the green copper phthalocyanine pigment PG7 was identified. Analysing phthalocyanine pigments with Raman spectroscopy can lead to overexcitation and peak shifts [29,51]. Fremout et al. (2012) made this observation while analysing the related PB15 pigment and state that the exact reason for this phenomenon is unclear and that a reversible, heat induced deformation of the crystal structure is possible [29]. The handheld Raman and microRaman spectra seem indeed to be shifted when compared to the KIK-IRPA reference spectrum

(https://soprano.kikirpa.be, accessed on 30 June 2021 [30]) (Figure 7). However, the PG7 spectrum published by Schulte et al. fits our Raman spectrum [10]. These discrepancies might be explained by the spectral differences observed for dry pigment powder and paint systems. Defeyt et al. noticed peak shifts when comparing the Raman spectra of blue copper phthalocyanine PB15 as a dry pigment powder and mixed with a binder [43].
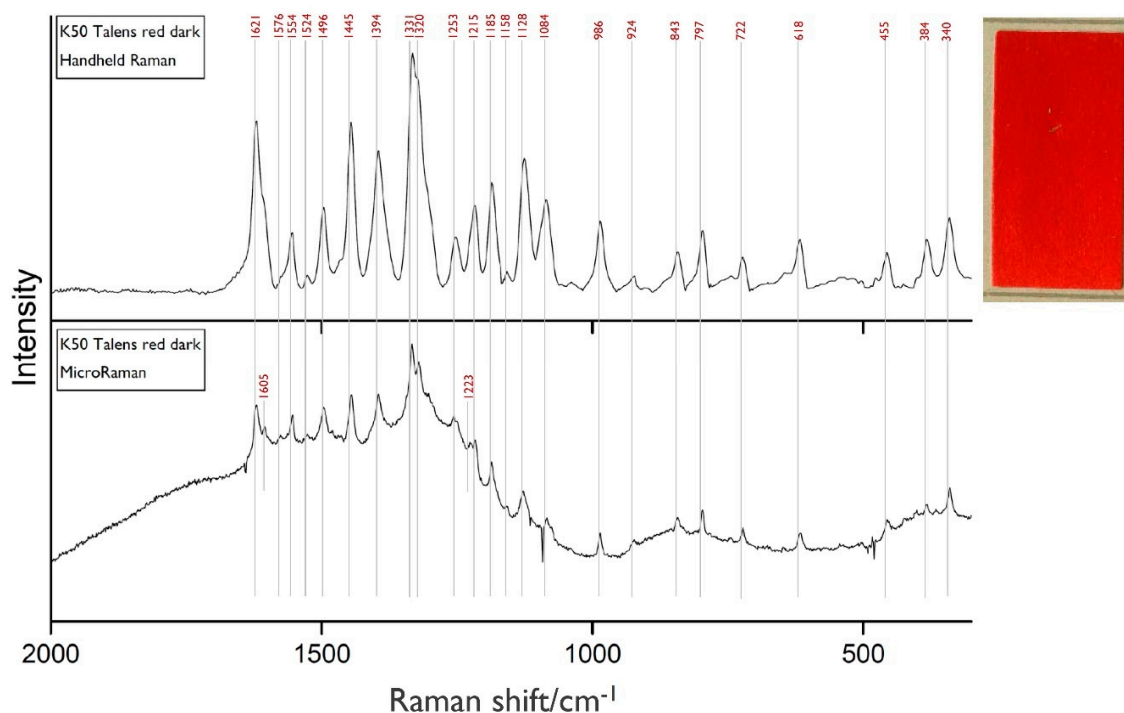

Figure 6. Handheld and microRaman spectra of paint-out K50 Talens red dark, mixed with barium sulphate (986 cm^{-1}).
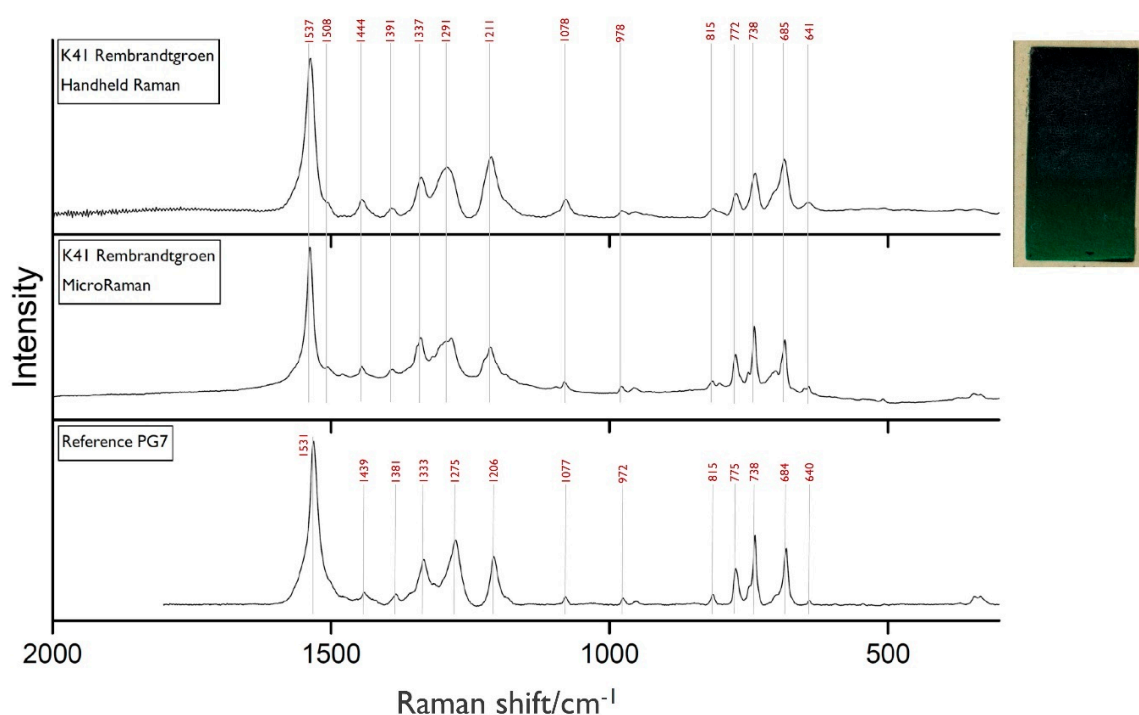

Figure 7. Handheld and microRaman spectra of paint-out K41 Rembrandtgroen and the KIK-IRPA reference spectrum for PG7.

Figure 8 reports the spectrum of Talens rose [Talens pink] in comparison with the reference spectra of the BON pigment lake Lithol Rubine, precipitated on two different substrates. This example was chosen to illustrate the possible effects of the minor spectral resolution of the handheld Raman device when examining closely related pigments. The KIK-IRPA references of Lithol Rubine PR57:1 (calcium carbonate salt) and PR57:2 (barium salt) show slight spectral differences, allowing a differentiation, given that the recorded spectrum is well defined. The spectral resolution of the Bravo device is 10–12 cm^{-1}, which turns out to be almost three times lower than that of our microRaman device (Table 1). Pozzi et al. also noted that "the inferior spectral resolution compared with benchtop spectrometers may cause difficulties in differentiating among closely related molecules with similar Raman fingerprints, especially if the analyses have poor Raman cross section or their spectra are characterized by low signal-to-noise ratio" [19]. It was, however, shown that the handheld Raman spectrum of Talens rose [Talens pink] contains the small spectral features that allow the assignment to PR57:1. In this case, the minor spectral resolution of the handheld Raman proved to be sufficient to allow a clear identification.
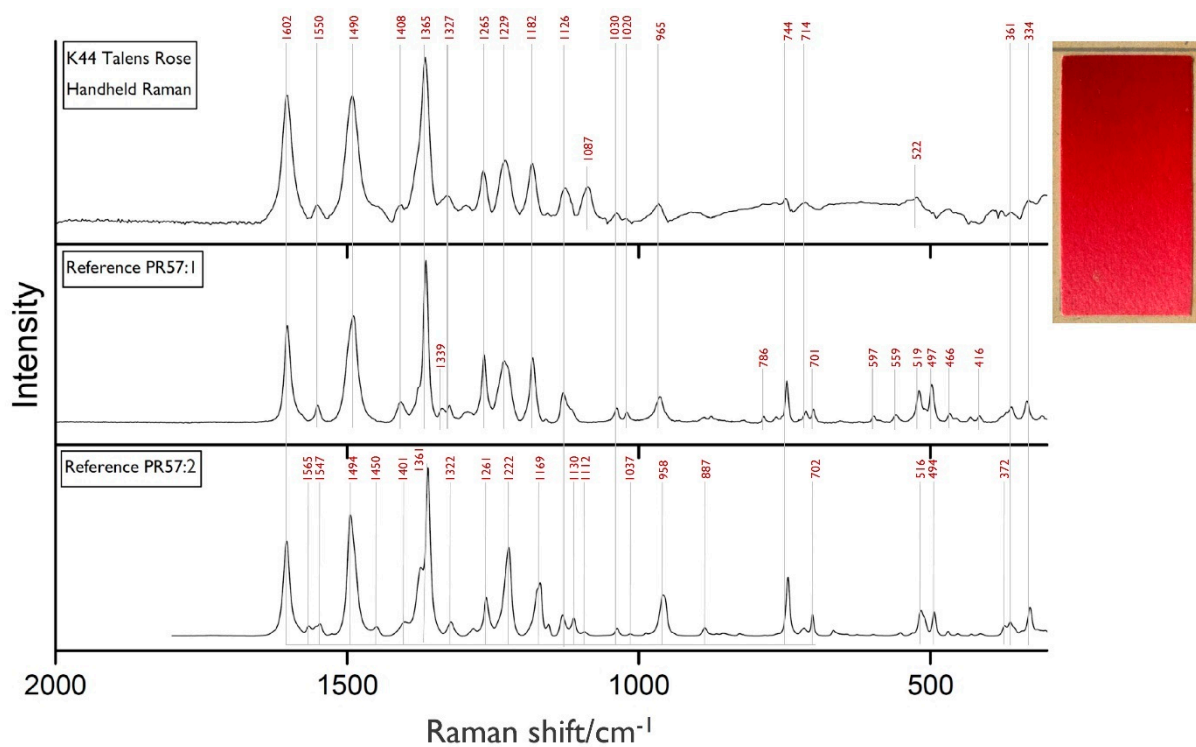

Figure 8. Handheld Raman spectrum of paint-out Talens rose and Raman spectra of the KIK-IRPA PR57:1 and PR57:2 references.

Two paint-outs (K37 Paul Veronesegroen [Paul Veronese Green] and K37 Dekgroen [Dekgreen]) were revealed to be rather sensitive to the handheld Raman lasers. The after-measurement check of the surfaces showed local burns, resulting in a small (~0.5 mm) black discoloration. According to Talens' recipes, these samples should contain a green SOP, but the X-ray fluorescence (XRF) measurements identified a copper arsenic pigment, which is rather sensitive to Raman laser irradiation. The analysis of these paint-outs highlights a strong disadvantage of the handheld Bravo, namely the non-adjustable laser energy, which is about 50 mW, more than two times higher compared to the microRaman instrument we used. The laser power can, however, be reduced by increasing the working distance to 1–2 mm. In this way, potential changes or thermal damage can be minimized or even prevented. Pozzi et al. [19] address this problem by proposing preventive measurement settings for sensitive samples. Other recommended options to avoid damage are the placement of a neutral density filter in front of the laser spot or the use of a defocusing tip.

It is worth mentioning that no SOP-containing paint-out showed any comparable damage. Since the sensitivity of emerald green is known, preliminary elemental analysis with XRF spectroscopy would have raised attention to this risk and demanded preventive action by adjusting the measurements settings.

4. Conclusions

This study demonstrated that identification of SOPs with a non-invasive approach in modern oil paint systems, also in the presence of a varnish layer, is possible. The handheld Raman was able to identify a large variety of SOPs—belonging to eight different pigment groups—within the historic varnished paint-outs of a leading artists' paint manufacturer and provided in the meantime a very useful insight into the use of early SOPs in modern artists' oil paints dated 1932–1950.

This research intends to provide a basis for future research into the non-invasive identification of SOPs in pre-1950 works of art. Detailed knowledge about the type and the characteristics of modern SOPs contributes to a better understanding of artists' materials from this period and helps to assess the restoration and conservation needs. Setting these pigments into their art technological context will contribute to studying the history of certain works of art and add to the knowledge available to detect forgeries.

Some of the SOPs identified within this study have not yet been analytically detected within works of art from before 1950. This outcome emphasizes the importance of further and intensive study of the use of SOPs in modern art. On the one hand, the knowledge of how to analyse SOPs without taking samples in a scan-like examination setup opens up new possibilities for their further investigation. On the other hand, this non-invasive approach can be used to clearly determine adequate spots for sampling, when necessary.

The advantages and drawbacks of the use of handheld Raman spectroscopy in the investigation of SOPs in artists' materials were considered. Thanks to the efficient suppression of fluorescence, varnished paint systems could be analysed and it was even possible to identify the mixtures of SOPs. The rather low resolution was a limiting factor, but turned out to be not too problematic for this set of samples. In some cases subtle spectral differences could still be detected, enabling a distinction between pigment substrates. The issue of non-adjustable energy was revealed to only be risky for one inorganic pigment, but this can be addressed with other non-invasive complementary techniques, such as handheld X-ray fluorescence spectroscopy. Another challenge is the lack of a camera for exact positioning. In this study a Melinex®template was successfully used for the analysis of the paint-outs, but the examination of specific and/or detailed paint areas in artworks could be hindered or difficult, depending on the surface and type of object.

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