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ABSTRACT

Several analytical techniques have shown use for the identification of historical synthetic organic pigments (SOPs) in samples. However, as the techniques differ—for example, in the extent of sample intervention, modes of detection, and limits of detection—so do they differ in results and insights into the colorants and colorant derivatives in a sample. Liquid chromatography (LC) is infrequently applied to the task of SOP identification, despite its ability to differentiate similar molecules, detect at low concentrations, and separate of complex samples and its established usage for organic dyes. This research compared results obtained with micro-Raman spectroscopy and pyrolysis gas chromatography with results from ultra-high performance (UP)LC coupled with photodiode array detection (UPLC-PDA), and high resolution mass spectrometry (UPLC-HRMS) to judge the quantity and quality of SOP information obtained by each technique.

In this study, 67 historical samples were analyzed from historical samples and sample books (1918–1950), consisting of 10 oil paint tubes, 45 oil-bound paint-outs, and 13 gum-bound pigment washes using sample sizes less than a milligram. As few studies have used LC for SOP identification, special attention is also paid to issues around sample preparation and interpretation of results from UPLC-PDA and UPLC-PDA-HRMS results. Finally, archival sources and other contemporary documents are used to contextualize and evaluate the plausibility of the analytical results. The results indicate that specific combinations of analytical techniques are required for confident SOP identifications. While Raman results were accurate and independent of sample solubility, they relied heavily on database completeness and were not sensitive to mixtures or differences in relative amounts of SOPs. UPLC-PDA was an effective complement for these shortcomings, except for a few samples that were insoluble. The use of HRMS was critical for the elucidation of unknown SOPs.

1. Introduction

The use of newly-developed synthetic organic pigments (SOPs) in artists' paint began in the latter half of the nineteenth century [1]. For manufacturers such as Lefranc, Schmincke, Winsor & Newton, Roberson's and (Royal) Talens, SOPs brought attractive new colors to the market at lower prices which required less pigment than traditional inorganic pigments or natural organic lakes [2,3]. In 1931 the paint manufacturer Talens, for example, began the advertisement of

Organische Pigmentverfstoffe in their artists' paints, although glimpses into archival documentation of their paint formulations have revealed that they began experimenting with SOPs in fine artists' paints even earlier [4]. Reports of artists' paints "enhanced" with less lightfast coal-tar colors were common during the period, such that an artists' manual from 1887 listed coal-tar colors as potential adulterants found in yellow ochre paints [3].

Presently, the addition of SOPs to the set of artists' materials and the documentation of their use by artists faces diverse challenges.

Identifying SOPs will not only support art historical research but can also help understand how deterioration affects the current appearance. Since the most standard and traditional analytical methods in conservation science focus on inorganic pigments, identification of the SOPs in art objects occurs less readily. Identification of organic colorants might only occur if organic analyses are pursued for other reasons or if an explanatory inorganic pigment is absent. In many cases, technical studies in the field have been content with labeling a pigment as an organic color without further pursual of the identification. One possible effect of this is that disproportionately few SOPs have been identified in artists' paintings relative to the SOPs documented in archival manufacturer's logs [4]. There are additional explanations for this gap in the technical art history, but it is clear that there is work to be done on the side of the analytical chemist to ensure detection and identification of SOPs when they are present. More discerning approaches in organic analysis must become common in order to understand the spread of SOPs in the art world.

SOP detection and identification is most commonly performed using Raman spectroscopy [5–9], perhaps followed by pyrolysis-gas chromatography-mass spectrometry (Py-GC–MS) [10–12]; these approaches are advantageous for the accessibility of the instrumentation, the minimal sample preparation needed, the time and effort required to undertake an analysis, and the simultaneous detection of other paint components. Raman spectroscopy requires minimal instrument maintenance and can be non-destructive and even portable. Raman also detects scattering of inorganic molecules, including pigments, extenders, and dye substrates. Although the efficacy of spectral matching by Raman is database-dependent, spectra have been amassed for a large number of diverse pigments as flow-charts and in an openly-available database [6,13,14]. Py-GC–MS is the most commonly-used mass spectrometric technique in cultural heritage analysis, as its usage is well-established for binders and varnishes. Several publications have outlined characteristic fragments for particular SOP structural classes [10–12]. Other approaches to SOP detection and identification include laser desorption mass spectrometry [7,15], direct temperature-resolved mass spectrometry [16], and surface-enhanced Raman scattering [14,17,18]. Techniques used to complement and support SOP identifications include Fourier-transform infrared spectroscopy [8,19] thin-layer chromatography [9,20], and energy-dispersive X-ray spectroscopy [9].

The major analytical challenges presented by SOPs are shared across many of the abovementioned techniques. The structural similarity of distinct SOPs is one such obstacle. Small differences in substitutions can be difficult to distinguish by Raman spectroscopy or high-energy mass spectrometric techniques that result in thermal or chemical decomposition, limiting the possibility of a complete identification. Mixtures of SOPs pose additional challenges. SOP particle sizes are so small that, even under high magnification, distinct particles are difficult to resolve. Unique hues may be created by small additions of SOPs due to their high tinting strength—additions of such low concentrations that they may evade detection [20]. Furthermore, the investigation of colorants takes place amongst the backdrop of other paint components, which can obscure the SOPs of interest.

The differentiation of similar molecules, detection at low concentration levels, and separation of complex samples are tasks for which liquid chromatography with on-line detectors, such as photodiode array detection and/or mass spectrometry (LC-PDA-MS), is well-suited. Despite its broad use in academic and industrial analytical research of organic dyes, there have been only a few reports on the use of LC-MS for SOP identification [21–23]. Although LC-MS is well-established in its capacity of unraveling complex microsamples, the instrumentation is advanced and can be time-consuming to develop expertise in and to maintain. The chief limitation of LC is the necessary solubility of the analyte. Synthetic dyes, being more soluble in aqueous solvents than pigments, are a more obvious fit for and have been analyzed effectively using LC analysis [22–27]. Nevertheless, the advantages that LC offers for synthetic dye analysis—specifically, separations of intact molecules

and the ability to couple with powerful detectors—are justification enough to further explore its usefulness with the less-soluble SOP counterparts.

In this work we sought to compare the following analytical techniques used for SOP analysis: micro-Raman spectroscopy, Py-GC–MS, ultra-high pressure LC-PDA (UPLC-PDA), and UPLC-PDA online-coupled to a high resolution MS (UPLC-PDA-HRMS). Of particular interest was the quantity and quality of information gained by the use of separative techniques or, the amount of information lost when no separation was performed. To address these questions, microsamples (<1 mg) were taken from a large, diverse set of historical samples to impose the realistic, complex, sample-limited circumstances that affect sample treatment, interference, noise, sample complexity, and data interpretation which are typical for the analysis of artworks. In total, 67 samples were analyzed, consisting of 10 oil paint tubes, 44 oil-bound paint-outs, and 13 gum-bound pigment washes. The samples were studied in the context of current research on production history of artists' paints and stationary products of (artists') paint manufacturer Royal Talens (Apeldoorn, the Netherlands). The historical samples were partly obtained here, and could be related to the manufacturer's production archive [29].

For each technique, we share key points of consideration before SOP analysis and during interpretation of the obtained data, and we assess its efficacy for accurate SOP identification. As relatively few studies have used LC for SOP identification, special attention is paid to issues around sample preparation and interpretation of results from the technique. The application of multiple techniques to a large set of samples highlights important differences between them, the subtleties of which are explained in detail using individual examples, while the results in their entirety expand the set of known SOPs detected in artists' paints. Lastly, the use of historical evidence to evaluate the plausibility of analytical results is emphasized as an important addition to SOP investigations.

2. Methods

2.1. Reagents

Tetramethyl ammonium hydroxide (TMAH, Sigma-Aldrich) was used as a derivatizing agent for Py-GC–MS. Extractions were performed using dimethyl sulfoxide (DMSO, Fisher Scientific, >99%) or hydrochloric acid (Acros Organics), methanol (LC-MS Chromasolv®-Sigma-Aldrich), and pure water (Millipore Simplicity® UV-purified, 18.2 MΩ-cm). UPLC-PDA mobile phases consisted of methanol ($\geq$ 99.9%, HPLC grade, Sigma-Aldrich), pure water, triethylamine ($\geq$ 99%; Fisher Scientific, UK), formic acid ($\geq$ 96%, Sigma-Aldrich), and 1 M NaOH ($\geq$ 98%, Sigma-Aldrich). Mobile phases for UPLC-PDA-HRMS used acetonitrile (ACN, Honeywell, MS grade, $\geq$ 99.9%), formic acid (Acros Organics, MS grade, 99%), water (H_2O, MS grade, Fisher Chemical), and ammonium formate (Fluka Analytical, >99.0%)).

2.2. Samples

Samples were selected in coordination with a parallel project that surveyed Talens archival production logbooks from 1922 to 1950 [30]. The paints selected for analysis were those suspected to contain SOPs based on the pigments named in the recipes. Samples of the paints of interest were obtained from historical paint swatches created by Talens for marketing purposes (Fig. 1) and paint tubes in the reference collection of the Cultural Heritage Agency of the Netherlands (RCE), acquired from private collections and from the archive of paint manufacturer Royal Talens [29]. Historical pigment samples corresponding to the pigments listed in Talens recipes were also studied for comparison. Historical pigment washes were sampled from copies of Hans Wagner's *Die Körperfarben* (1928 and 1938 editions, and 1960 edition revised by Hans Kittel). The books contain inserts with pigment charts provided by different pigment manufacturers. The charts consist of sample cards with preparations of minimally-bound pigment protected by transparent

Fig. 1. Examples of paint-outs in historic Talens color charts sampled for SOP analysis.

sheets. Samples of inorganic pigments were excluded from the study.

Reference pigments were obtained from the reference collection of the RCE, whose identities were substantiated by UPLC-PDA and HRMS analyses across several references of different origins with the same reported composition. Other pigments absent from the RCE collection were donated by Historische Farbstoffsammlung Dresden (Dresden Historical Dye Collection).

A subset of four paints and respective references representative of common SOP molecular classes, comprising ten samples total, were selected for analysis by Py-GC–MS.

Sampling. Paint-outs were sampled by removing small oil paint chips from the paper substrate with a scalpel (<1 mg), while pigment washes were sampled by scraping from the surface. Loose reference pigments necessitated even less sample due to the absence of binders and other fillers. Sample sizes were restricted to reflect realistic sampling of artworks, subjectively determined by a conservator to minimize damage and by the analyst to produce sufficient instrument signal.

Sample preparation. For Raman analyses of loose pigment, the sample substrate (a glass microscope slide) was covered with aluminum tape (Kelfort) to reduce unwanted scattering due to the probe spot size being larger than sample. Samples analyzed by Py-GC–MS were measured both with and without thermally-assisted hydrolysis and methylation (THM) using 5% TMAH. For UPLC-PDA(-HRMS) analysis, the samples were prepared using one or both of two extraction procedures (see Considerations on sample preparation): (1) dissolved in DMSO and centrifuged, from which the supernatant was collected for analysis; (2) extracted in a 1:1:2 mixture of H_2O:MeOH:HCl at 100 °C for 10 min, evaporated to dryness under a nitrogen stream, resuspended in DMSO, and centrifuged, from which the supernatant was collected for analysis.

2.3. Instruments and protocol

2.3.1. Micro-Raman spectroscopy

Samples were analyzed using a PerkinElmer RamanMicro 300 microscope system using the 50x objective and a RamanStation 400F spectrometer equipped with a 785 nm laser (Waltham, MA). Spectra were recorded between 150 and 2700 cm^{-1} with an approximate resolution of 4 cm^{-1}. Length of exposure, intensity of exposure, and number of spectral accumulations were determined on a case-by-case basis. Laser power on the sample ranged between 1.7 and 21.4 mW. Exposure time was between 6 and 15 s with accumulated measurements between 10 and 30. Results were compared with the Belgium Royal Institute for Cultural Heritage (KIK-IRPA) Modern SOP database (**soprano.kikirpa. be**) [31] and/or an internal reference library for identification.

2.3.2. Py-GC–MS

Samples were pyrolyzed with a Frontier Lab 3030D pyrolizer unit (Koriyama, Japan) at 480°C and separated on a Supelco SLB-5 ms 5% diphenyl column (20 m × 0.18 mm, 18 μm film thickness; Bellefonte, PA) ramped between 35°C and 315°C using a ThermoFisher Focus GC–MS (Waltham, MA). Spectra were interpreted in Xcalibur™ software.

2.3.3. UPLC-PDA and UPLC-PDA-HRMS

Chromatographic separations and PDA detection were performed using a Waters Acquity H-class UPLC-PDA system (Milford, MA) fitted with a 15-cm ZORBAX Eclipse Plus C18 column (Agilent, Santa Clara, CA). The mobile phase system consisted of two solvents, 95:5 and 5:95 buffer:MeOH. The buffer contained 5 mM triethylamine, 1 mM formic acid, and 1 mM NaOH and was adjusted to pH 3 [32]; the gradient used

is presented in the Supplementary Information (SI), Table S1. UPLC-PDA data were interpreted using Waters Empower™ software, and all identifications were made using a spectral library generated from the RCE reference collection. UPLC-PDA-HRMS analyses were performed on the same UPLC system and chromatographic column coupled to a ThermoFisher Orbitrap Q Exactive (Waltham, MA). The potential for damaging effects from triethylamine in the HRMS necessitated a second mobile phase system, which consisted of 94.9:2.5:2.5:0.1/ 5:47.45:47.45:0.1 H_2O:MeOH:ACN:formic acid mixture with 20 mM ammonium formate, the gradient used is presented in the SI (Table S2). UPLC-PDA-HRMS data were interpreted using Chromeleon™ Chromatography Data System and Xcalibur™ software.

2.4. Recipes, patents, contemporary texts, and other historical references

Historical context from archival materials is an important piece to establish relevance and validity of SOP analyses. A collaboration between the RCE and Royal Talens allowed RCE researchers access to archival materials regarding paint formulation dating up to 1975. Further information regarding this research may be found in [30]. Additional access to BASF and Bayer pigment production archives was obtained by R. Pause. Other contemporary technical literature was found in [33–35].

3. Results and discussion

3.1. Considerations on sample preparation

The differing degrees of sample preparation necessary for the analytical techniques studied is significant in its consequences. SOP analysis by micro-Raman spectroscopy is advantageous in that sample preparation does not require chemical modification of the sample, only physical preparation to expose its contents. Leaving the solid structure of the pigment intact, unique and informative sample components may be preserved, including the substrates, salts, or co-precipitants. The rapid development of dye substrate technologies was an important part of the advancement of early SOPs and can be extremely indicative of chronology [28].

By contrast, the sample preparation required for LC is extensive. Studies on the LC of colorants have primarily focused on identifying organic dyes, not pigments. Consequently, extraction procedures of unknown SOP samples have not been fully addressed by current literature. Thus far, the most diverse collection of SOP samples studied using LC is a 2017 article by Degano et. al., in which all powdered pigment or paints were sonicated in DMSO for 5 min at 60°C [21]. A more gentle extraction is ideal to avoid modification of the colorant, which could lead to an incorrect identification or an incorrect assessment of sample degradation.

Despite initial concerns of pigment solubility for UPLC analysis, of the 67 historic samples, only the five phthalocyanine-containing samples were completely insoluble. Nevertheless, some pigment samples were encountered for which extraction solely in DMSO was insufficient. For the barium salts PG12 and PR60, we observed that extraction in DMSO was insufficient to break the organometallic complex, resulting in poor chromatography, and a stronger extraction with diluted HCl was necessary in those instances (Fig. S1). More generally, when analyzing small chips of oil paint, a stronger extraction in HCl (Section 2.3.2, extraction protocol 2) was used before dissolving in DMSO to break down the highly cross-linked oil binder and maximize extraction. However, more reliable results are obtained when the gentlest possible extraction is used.

Analyses by Py-GC–MS were done with and without THM. For the pigments selected, THM was observed to preserve pigment structure, likely by improving volatility. Py-GC–MS analyses were most successful with data from both sample preparation approaches, as discussed in the Section 5.3.3.

3.2. Pigment identification

Tables 1-4 contain data subdivided by hue and relate the sample information, sample extraction procedure, analyses performed, compounds identified by each technique, and historical recipes and references that support the identifications (cited in superscript). Sample names refer to the source of the sample using the naming convention described in the SI (Table S3). SOP identifications are reported as the

Table 1
Sample information of red and orange pigments reported by Raman spectroscopy, UPLC-PDA, and UPLC-PDA-HRMS. Samples are divided into subsections by color, each discussed in detail in Section 5.2 "Pigment identification". SOPs detected as the major component of a mixture are formatted in bold. Sources providing historical evidence of use are in superscript. UPLC results in the shaded cells were from extraction with HCl in addition to the default DMSO extraction.

Sample name	Date	Paint/pigment name	Raman	UPLC-PDA/*UPLC-PDA-HRMS*
PT6	1922–1931	*Vermiljoen licht* (Light vermilion)	PR51, unknown components	**PR51**, PR49 components/ ***PR51**, PR49 components*
PT104	after 1930		PO5[33,44]	PO5[33,44]
PT149	after 1930			
PT81	after 1932	*Talensrood* (Talens red)	PR3	**PR3**, trace unknown β-naphthol
PT173	1940–1945			**PR3**, PO5-like/ ***PR3**, trace unknown components*
C1-II-6,1 (148)	1918–1927	*Harrisonrood* (Harrison red)	PR3	PR3
C10-3,10 (41)	~1931	*Scharlakenlak* (Scarlet lake)	PR49:1	**PR49**, PR3
C1-II-1,3 (20)	1918–1927	*Alizarine oranje* (Alizarin orange)	Unknown	**MO1** component/ ***MO1***[33],a*, nitroaniline*
K32-IV-3,1	1932			MO1 components/ ***MO1***[33],a*, nitroaniline*
K37-III-4,1	1937			
K41-III-4,1	1941			
K44-III-4,1	1944			
K50-III-4,1	1950			**MO1 components**, AY1, MR11 (PR83)/***MO1***[33],a*, nitroaniline, AY1*
C1-II-6,2 (98)	1918–1927	*Geraniumlak* (Geranium lake)	PR60:1[35,44]	MR9(PR60)[35,44]
C5-I-3,4	1922–1949	*Talens Rosa* (Talens rose)	PR81[44]	BR1(PR81)[44]
PT160	1930′s		PR57:1	PR57
K50-IV-3,7	1950			**PR57**, trace NB1, trace unknown β-naphthol
Kittel-VI-3,2	1960	*Sieglerosa D443* (Siegle rose D443)	PR81	BR1(PR81)

a pigment recipe.

Table 2

Sample information of yellow pigments reported by Raman spectroscopy, UPLC-PDA, and UPLC-PDA-HRMS. SOPs detected as the major component of a mixture are formatted in bold. Sources providing historical evidence of use are in superscript. UPLC results in the shaded cells were from extraction with HCl in addition to the default DMSO extraction.

Sample name	Date	Paint/pigment name	Raman	UPLC-PDA/*UPLC-PDA-HRMS*
K37-IV-3,1	1937	*Talensgeel citroen* (Talens lemon yellow)	PY3	**PY3**, PY1
K50-IV-3,4	1950			PY3
PT107	before 1949	*Cadmiumgeel oranje imitatie* (Cadmium yellow-orange imitation)	PY4	**PY4**, PO5
PT109	before 1949			
PT32	1920's	*Indischgeel imitatie* (Indian yellow imitation)	MY1	**MY1**, trace unknown yellows
C1-I-6,1 (42)	1918–1927		Unknown	No signal
K32-V-3,5	1932			**Unknown yellow**, PY1/*Unknown yellow (311 m/z), PY1*
C6-I-2,3	1947–1949	*Indischgeel* (Indian yellow)	PY1	**PY1**, trace indigotin, trace PY3
Wagner28-p448-1,3	1928	*Hansagelb G* (Hansa yellow G)	PY1	PY1
Wagner28-p448-1,4	1928	*Hansagelb GR* (Hansa yellow GR)	PY2	PY2
K37-IV-3,4	1937	*Talens geel donker* (Talens dark yellow)	PY2	**PY2**[35], trace unknown β-naphthol[44]
Kittel-I-1,1	1960	*Fanalgelb* (Fanal yellow)	PY18	BY1(PY18)/*BY1 (PY18)*
Wagner28-p272-1,4	1928		BY2	Trace unknown yellow/*BY2 or BY3*

Table 3

Sample information of green pigments reported by Raman spectroscopy, UPLC-PDA, and UPLC-PDA-HRMS. SOPs detected as the major component of a mixture are formatted in bold. Sources providing historical evidence of use are in superscript. UPLC results in the shaded cells were from extraction with HCl in addition to the default DMSO extraction.

Sample name	Date	Paint/pigment name	Raman	UPLC-PDA/*UPLC-PDA-HRMS*
Wagner28-p400-8,4	1928	*Fanalgelbgrun GG* (Fanal yellow-green GG)	PG1, BY2	**Unknown yellow***, BG1 (PG1)/*BG1 (PG1), BY2 or BY3**
Kittel-I-2,4	1960	*Fanalgelbgrün G supra* (Fanal yellow-green G supra)	PG1, PY18	**BG1(PG1)**, BY1 (PY18)
K32-IV-4,5	1932	*Talens groen licht* (Talens light green)	PG9, PY3	PY3
K37-IV-4,4	1937		PY3	
K44-IV-4,2	1944		PG7, PY3	
C9-II-5,4	1936–1937		PG9, PY3	
Wagner28-p448-7,3	1928	*Hansagrün GS + Hansagelb 10 GT* (Hansa green GS + Hansa yellow 10 GT)		
K32-V-4,6	1932			**BG1(PG1)**[44], unknown yellow*/*BG1 (PG1)*[44]*, BB1*[44]*, C.I. 48010**paint recipe,b
C9-II-5,5	1936–1937	*Talens groen donker* (Talens dark green)	PG1[44], unknown yellow	*BG1(PG1)*[44]*, BB1, C.I. 48010*[44],b
K37-IV-4,5	1937			**BG1(PG1)**[44], unknown yellow*/*BG1 (PG1)*[44]*, C.I. 48010**[44],b
K41-IV-4,3	1941			
K42-IV-4,4	1942			*BG1(PG1)*[44]*, BY1 (PY18)*[33],b*, BY21*a*, C.I. 48010*[44],b
K44-IV-4,3	1944			**BG1(PG1)**[44], **unknown yellow***/*BG1 (PG1)*[44]*, BY1 (PY18)*[33],b*, BY21**b
C6-I-1,9	1947–1949			*BG1(PG1)*[44]*, BY21*b
Kittel-I-7,1	1960	*Rembrandtgroen* (Rembrandt green)	PG7	No signal
C1-V-4,4 (285)	1918–1927	*Vert de vessie/ Sapgroen* (Juice green)	PG12	**AG1(PG12), AY1**
K32-III-4,3	1932			
C1-IV-6,4 (279)	1918–1927	*Vert de olive/ Olivegroen* (Olive green)		AG1(PG12), nitroaniline, **MY1**
K32-IV-2,7	1932			
C1-V-5,2 (276)	1918–1927	*Groenlak licht/ Lacque vert clair* (Light green lake)		AG1(PG12), **AY1**
K32-III-4,4	1932			
K50-III-3,5	1950			
C1-V-5,3 (275)	1918–1927	*Groenlak donker/ Lacque vert foncee* (Dark green lake)		**AG1(PG12)**, AY1
K32-III-4,5	1932			
K50-III-3,6	1950			

a pigment recipe.
b pigment archive.

abbreviations[1] of Color Index numbers (e.g. PR60 stands for C. I. Pigment Red 60). Reference PDA spectra and exact masses of all identified SOPs are presented in the SI (Tables S4 and S5 respectively)

For UPLC analyses, a subtle distinction must be noted regarding the reporting of some SOP identifications. SOPs have variable forms, including insoluble organic structures, metallo-organic complexes, as well as water-insoluble salts of dyes, especially as Ba^{2+}, Ca^{2+}, or heteropolyacid salts [1]. If the method of pigment synthesis was to convert a dye to an insoluble salt, when those samples are prepared for UPLC analyses, the pigment is solubilized back into its dye form. To be most accurate, the identifications from solubilized samples are presented as the dye with the pigment(s) it corresponds to. For example, solubilization of PR60 converts it to MR9 and the PDA and/or the MS detects MR9, so the identification would be reported as MR9(PR60). For pigments without a dye equivalent, the pigment is reported without the salt specified, e.g. PR49 instead of PR49:1, and pigments with insoluble organic structures, e.g., PY1, are reported as such.

3.2.1. Red and orange pigments

Presented in Table 1 are the results from analyses on eighteen red (Vermiljoen licht, Talensrood, Harrisonrood, Scharlakenlak), orange (Alizarine oranje), and pink (Geraniumlak, Talens rosa, Sieglerosa D443) samples, taking the form of oil-bound paint-outs, oil paint tubes,

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1 Abbreviations indicate the colorant type (pigment = P, mordant dye = M, acid dye = A, basic dye = B, or natural dye = N) followed by its color (red = R, orange = O, yellow = Y, green = G, blue = B, violet = V, brown = Br, black = Bk, or white = W) and the unique numerical identifier. Different salts of the same pigment are specified by a colon and an additional number.

Table 4

Sample information of blue and violet pigments reported by Raman spectroscopy, UPLC-PDA, and UPLC-PDA-HRMS. SOPs detected as the major component of a mixture are formatted in bold. UPLC results in the shaded cells were from extraction with HCl in addition to the default DMSO extraction.

Sample name	Date	Paint/pigment name	Raman	UPLC-PDA/*UPLC-PDA-HRMS*
Wagner28-p400-8,2	1928	*Fanalbremerblau (Fanal Bremen blue)*	PG1	**Unknown TAM**/*BG1(PG1)*, BB1 (PB9), trace BB5 (PB3), BB7(PB1)
K32-V-4,7	1932	*Talens groen-blauw (Talens green-blue)*	PB8	**Unknown TAM***, unknown TAMs, trace BB7(PB1), unknown yellow/*BG1(PG1)*, **BB1 (PB9)***, BB5(PB3), BB7(PB1)
C9-II-4,7	1936–1937			*BG1(PG1)*, **BB1 (PB9)**, BB5(PB3), BB7(PB1)
K37-IV-4,6	1937			**Unknown TAM***, unknown TAMs, trace unknown yellow/*BG1(PG1)*, **BB1(PB9)***, BB5 (PB3)*, BB7(PB1)
K41-IV-4,4	1941		PB15,	No signal
C6-II-1,10	1947–1949		PG7	
K50-IV-4,4	1950			
PT129	after 1940	*Rembrandtblau (Rembrandt blue)*	PB15	
Kittel-VI-3,3	1960	*Sieglerotviolett (Siegle red-violet)*	PV2	BV11(PV2)
Wagner28-p272-6,3	1928	*Fanalviolet R neu (Fanal violet R new)*	PV3	BV1(PV3)
Kittel-I-2,1	1960	*Fanalviolet R supra (Fanal violet R supra)*	PV3	**BV1(PV3)**, trace BB7(PB1)

and a pigment wash. Excepting the Alizarin orange paint-outs, the major components identified by both UPLC-PDA and μ-Raman were in agreement. Six of the seven of the red and orange SOPs identified are β-naphthols: PR3, PR49, PR51, PR60, and PO5. PR57 is more specifically classified as a β-naphthoic acid (BONA) pigment, and PR81 belongs to the xanthene class.

Besides detecting the major components, UPLC-PDA revealed the presence of additional trace components that were not detected by Raman, many of which produced PDA spectra similar to those of β-naphthols. The PDA spectra of β-naphthols show qualitative similarities, though further studies would be necessary to determine whether spectral shape is exclusive to the pigment class. Fig. S2 shows the PDA spectra of four β-naphthol pigments identified in red and pink samples for comparison. Fig. 2 shows a typical UPLC-PDA result from a paint tube containing Talens red (Talensrood, PT81). The PDA spectrum at 46.24 min clearly show PR3 as its major component, and the spectrum at 45.16 min shows a minor component that is very similar, likely a degradation product or synthesis byproduct. The minor component at 43.58 min, however, is not similar to PR3, and instead resembles PO5. PR3 is a β-naphthol coupled with *p*-methyl-*m*-nitrophenyl, and PO5 is very similar, having a nitro substitution at the para position instead. Although the presence of the trace PO5-like component was detectable by UPLC-PDA, only an idea of its potential color and chemical class was obtainable from the low signal. HRMS, combined with research into colorants similar to PO5, possible PR3 degradation products, or even PR3 synthesis side-products, would be necessary to identify the molecular formula for the minor components in Talens red.

The use of the same common names for different colorants, and vice versa, has caused confusion almost since their inception [36]. From an analytical standpoint, the names of paints and pigments provided useful suggestions as to possible reference colorants to be obtained to confirm the identity of the unknown. The absence of the correct reference pigment necessitates a more extensive investigation, as was the case for the six Talens' Alizarin orange (Alizarine oranje) paint-outs from 1918 to 1927 through 1950 selected for comparison of their formulations. Identification of the Alizarin orange pigments from Raman spectra was unsuccessful, as there were neither matching spectra in any available databases, nor clear and characteristic bands that would allow for structural elucidation. Analysis by UPLC-PDA isolated two major components in the Talens' samples which did not match the expected reference pigment, the anthraquinone MO14, or any other references already in the PDA spectral library. The alizarin orange formulation from 1950 also contained AY1 and MR11 (or PR83, alizarin crimson). The two unknown components had similar spectra that absorbed
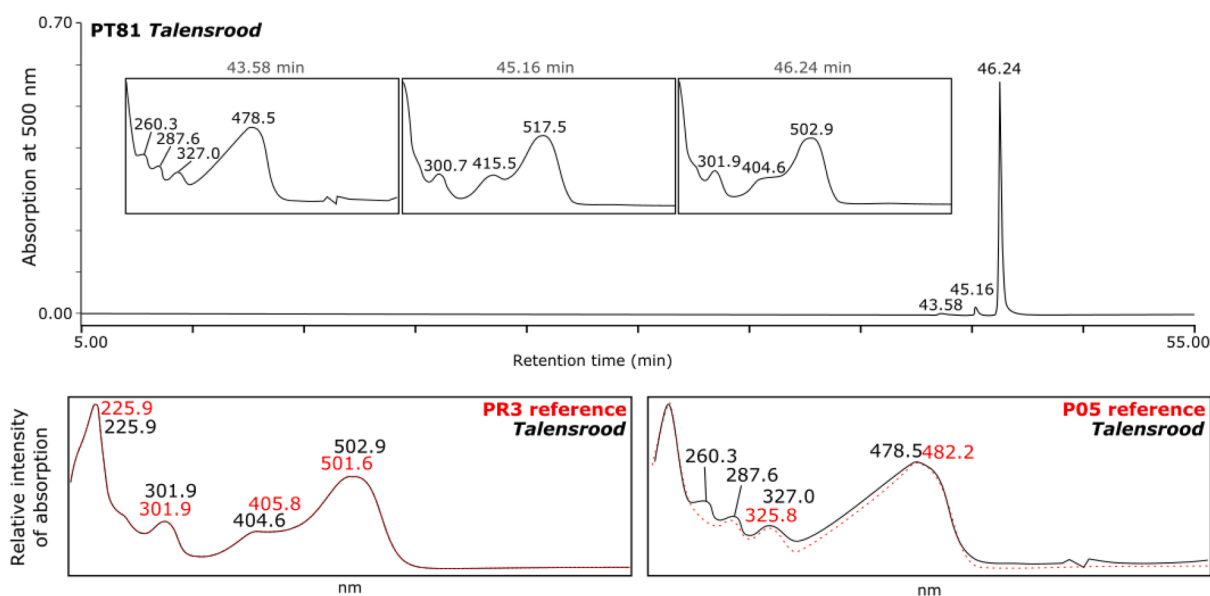
Fig. 2. Above: LC-PDA chromatogram of PT81 (Talensrood) solubilized in DMSO and detected at 500 nm. Above, inset: PDA spectra (200–850 nm) of selected chromatographic peaks. Below, left: overlay of major component spectrum (46.24 min, black trace) with PR3 reference spectrum (red trace). Below, right: overlay of minor component spectrum (43.58 min, black trace) with PO5 reference spectrum (red trace).

strongly in the yellow range (between 350 and 450 nm) in the mobile phase solution. The absorption data directed inquiries towards other yellow-orange reference pigments. In particular, the single azo dye alizarin yellow R (MO1, 5-(4-nitrophenylazo)salicylic acid) is rusty-orange as a pigment and dark yellow in solution. UPLC-PDA of several MO1 references confirmed that the Alizarin orange samples contained MO1, not MO14. Furthermore, an important industry text from 1931, Schultz's *Farbstofftabellen*, includes alizarin orange as an alternative name for alizarin yellow R [33].

To identify the SOP of the alizarin orange paint-outs, the absence of the correct SOP from any databases was addressed using color clues from sample absorbance spectra, analysis of multiple reference pigments, and support from historical literature. While UPLC-PDA results were able to match Alizarin orange samples and alizarin yellow R reference pigments, the molecular identities of the two main MO1 components were not obtainable by their PDA spectra. It could be reasonably supposed from chromatographic retention data that the more highly-retained component is the full MO1 molecule, but it could not be proven by UPLC-PDA alone.

Py-GC–MS was evaluated for its ability to provide structural information about the MO1 components in the reference and the alizarin orange paint samples. Analysis of the MO1 reference by Py-GC–MS (without derivatization) identified a MO1 azo coupling molecule, *p*-nitroaniline, and decarboxylated MO1. Decarboxylation is a common result of pyrolysis without protective modifications through derivatization. However, the complete, decarboxylated MO1 molecule was undetected in the Talens' paint-outs. Pigment concentration is considerably lower in paint samples than in loose pigment references due to dilution by the binder, which is the most probable explanation for why MO1 was only detected in the references [10].

Analysis by THM-Py-GC–MS identified not MO1 but MY12 in the paint samples and the reference pigment—MY12 is identical to MO1 but with an amine instead of a nitro group. THM is thought to help preserve molecular integrity by lowering the boiling point, which would explain why the MO1-like molecule was detected in the Alizarin orange samples with THM but was not visible without THM. However, the discrepancy in functional groups is also likely the result of derivatization. Both pyrolysis and derivatization procedures introduced elements of

uncertainty into the analytical results, which reduced confidence in the identifications of the components in the Talens' paint-outs.

Experiments by UPLC-PDA-HRMS including MS/MS confirmed the two major components in the alizarin yellow R reference and the Talens' samples are MO1 (Fig. 3) and *p*-nitroaniline and also assigned the molecules to their respective PDA spectra and retention times. *P*-nitroaniline was subsequently identified in an Olive green sample, C1-IV-6,4 (279).

3.2.2. Yellow pigments

The results from the thirteen yellow samples studied are shown in Table 2, which consisted of three oil paint tubes, six oil-bound paint-outs, and four pigment washes. Yellow pigments of a diversity of structures were identified in the samples: PY1 through PY4, all formed through the coupling of a diazotized nitrobenzenamine compound with a 3-oxo-N-phenylbutamide derivative [1], MY1, a precipitant of a single azo dye, and PY18, the phosphotungstomolybdic acid (PTMA) salt of the thiazole BY1. Among these, both PY4 and PY18 are no longer commercially available. Analyses by Raman and UPLC-PDA agreed upon the major sample components; however, wherein Raman always identified single components, separation by UPLC-PDA sometimes revealed the presence of mixtures. For example, UPLC-PDA results indicated a mixture of PY1 and PY3 in Talens lemon yellow (K37-IV-3,1) and the addition of PO5 to PY4 in Cadmium yellow-orange samples (PT107, PT109), while Raman showed only the presence of PY3 and PY4, respectively. Yellow SOPs were also detected as secondary coloring components, especially in green paints.

Several yellow SOPs were detected by UPLC-PDA that were missed by Raman and were absent from the reference library, such that UPLC-PDA-HRMS was necessary to identify them. It has been observed for unknown synthetic dyes that to obtain an identification from HRMS results alone is not straightforward [23]. The addition of PDA data provides an advantage for avoiding pitfalls that might lead to an incorrect identification. For example, three different yellow components were found across seven samples of the paint Talens dark green (Talens groen donker) spanning between 1932 and 1947–1949. The chromatogram in Fig. 4 shows a peak at 27.9 min with *m/z* 331.2175, which appears in the earliest five samples (between 1932 and 1942, K32-V-4,6,
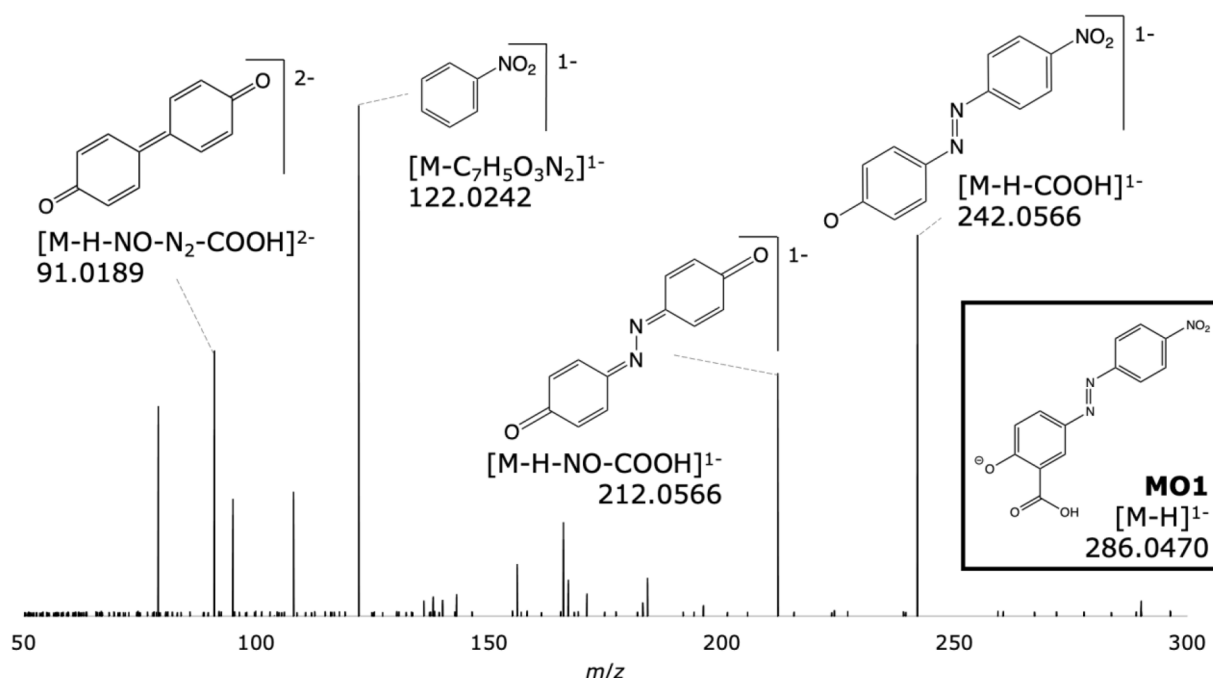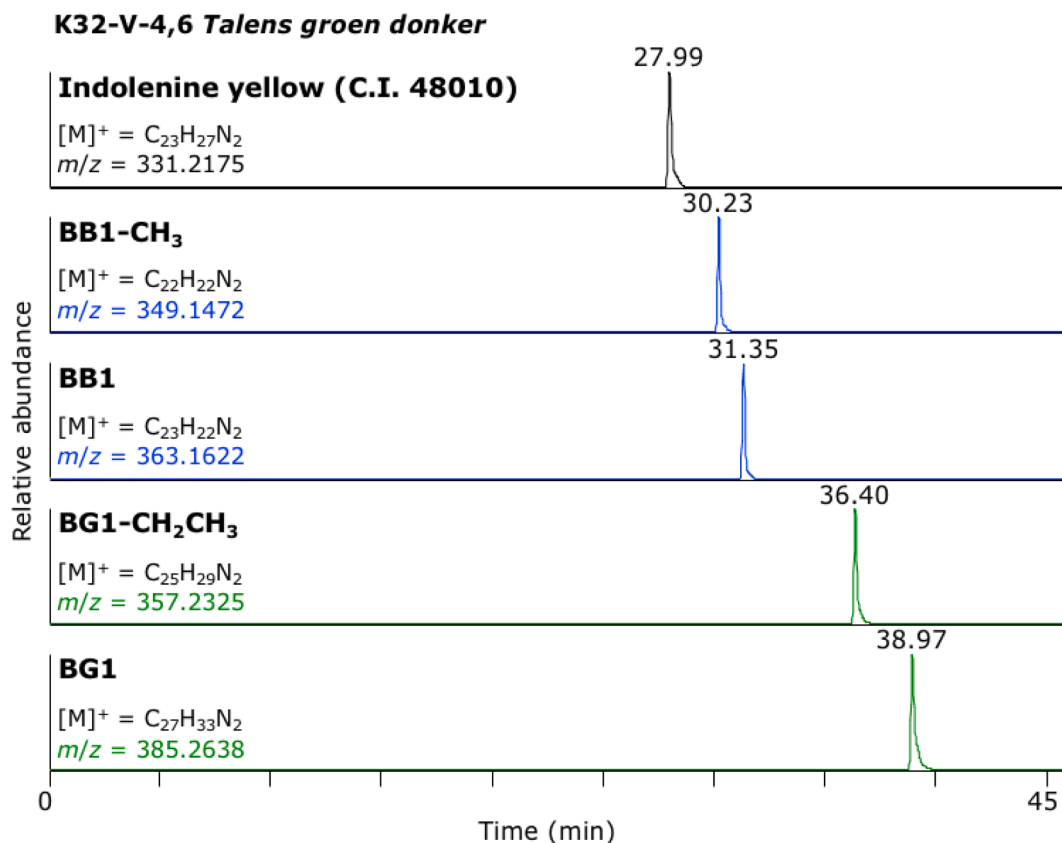

Fig. 3. Product ion spectrum and proposed structures from the molecular ion, alizarin yellow R (MO1, inset).

Fig. 4. Extracted ion chromatograms of a mixture of colorants and their byproducts identified in a Talens groen donker paint sample by UPLC-HRMS. Indolenine yellow and BG1 may have been sold as the pigment blend PG2.

C9-II-5,5, K37-IV-4,5, K41-IV-4,3, and K42-IV-4,4). The mass and retention time did not correspond to any previously-known colorant. First, PDA data showed that the component has color, and is therefore more likely to be a colorant of interest instead of a different paint ingredient or a contaminant. That the unknown component at 27.9 min showed a PDA spectrum with strong absorbance in the visible range indicated that the component is likely an SOP and should be investigated. Second, PDA data indicates the color of the unknown component, which can assist in the elimination of candidate molecular formulae obtained from its exact mass and isotopic pattern. PDA data narrowed the possible component identities from green, blue, or yellow to only yellow colorants. Lastly, PDA data often indicates chemical class, as in the β-naphthols in the Talens red sample (Section 5.2.1). The spectrum of the unknown yellow component was not of a recognizable chemical class.

The unknown yellow component at 27.9 min in in the Talens dark green samples corresponded with the formula $C_{23}H_{27}N_2Cl$ (331.2169 m/z, <5 ppm mass accuracy), which agrees with an unusual basic dye referred to as Indolenine yellow (C.I. 48010). HRMS/MS fragmentation showed loss of methyl groups and ring expansions characteristic of indoles [37,38]. In addition, Indolenine yellow is described in a 1934 technical manual from I. G. Farbenindustrie as yellow specific to their line of Fanal colors; its application in paints has not been reported elsewhere. While there seems to be a good match between the MS data and the Indolenine yellow structure, its identity as the yellow component in Talens dark green would be made more certain once a reference sample can be obtained and matched.

Results from one particular sample (K42-IV-4,4) indicated a green paint was created using three different yellow SOPs and seemed unlikely at first, but consultation with historical materials rendered the results plausible. The available recipes for Talens dark green from 1932 and 1935 do not list a yellow pigment at all; it is likely that the green

pigment used by Talens was a blended pigment, possibly PG2 (Fig. 4). PG2 is a product derived from BG1 and any basic yellow pigment [1]. The basic yellow pigments in PG2 may have been used interchangeably or in combination. If multiple batches of PG2 were available in the Talens factory, it is quite possible that three different basic yellows were combined.

UPLC-PDA-HRMS did not result in successful identifications in all cases. A yellow component mixed with PY1 in an Indian yellow imitation paint-out (K32-V-3,5) with $[M + H]^+ = 311.0709$ m/z could not be assigned to particular molecular formula that matched with any known yellow colorants. Raman bands could not be matched with any known SOPs.

3.2.3. Green pigments

Twenty-four green samples were analyzed, the results of which are shown in Table 3. Three of these were pigment washes from Wagner and Kittel texts, and the rest came from oil-bound paint-outs of the same six paints spanning decades of production.

Detecting major components in some green samples necessitated a technique that does not require solubilization. In two instances (Talens light green and Hansa green), only the yellow pigments were detectable by UPLC-PDA due to insolubility of the green component. Raman matched sample spectra with references for the insoluble green pigments: the chlorinated copper phthalocyanine PG7 and PG9. The use of PG9 in paints is reported by Wagner and Kittel [34,39], Venkataraman names it as a sulfonated diaminonaphthalene derivative [40], the Color Index categorizes it as an "barium lake of acid dye containing iron" [35], and more current literature describes the pigment as an azo metal complex [6]. Its exact structure has not been published, and this is the first report of its detection in paint samples. Attempts to confirm the structure of PG9 by (THM-)Py-GC–MS were unsuccessful, possibly due to insufficient volatility caused by sulfonation.

While Raman always detected a green pigment component, it did not always detect the additional yellow pigment. Particularly, data from UPLC-PDA showed that AY1 or MY1 were added to PG12 in different ratios to achieve different green hues, which did not appear in the Raman spectra (Light green lake, Dark green lake, Juice green, Olive green, Talens dark green, Fanal yellow-green).

3.2.4. Blue and violet pigments

Results from blue and violet samples are shown in Table 4. The nine blue and violet samples consisted of four oil-bound paint-outs and one oil paint tube from Talens and four pigment washes from historical Wagner and Kittel texts. Raman detected the triarylmethane (TAM)

pigments PV3 and PB8 (a mixture of PB3 and PG1), the xanthene PV2, and the phthalocyanine PB15. UPLC-PDA-HRMS results identified these aforementioned pigments, and in addition, the TAMs BB1(PB9) and BB7 (PB1), which were detected in the Talens green-blue paint-outs (Table 4).

Archival logbooks for Talens green-blue paints between 1930 and 1932 indicated the use of the pigment Fanalbremerblau G neu (Fanal Bremen blue G new), an offering from I. G. Farben's Fanal range of pigments. While Bremen blue is most commonly associated with synthetic azurite [41], recipes/patents indicate that the Fanal Bremen blue pigments contain PB8, a PTMA salt of BG1 and BB5. As a co-precipitation of structurally-similar TAM molecules, PB8 presents a
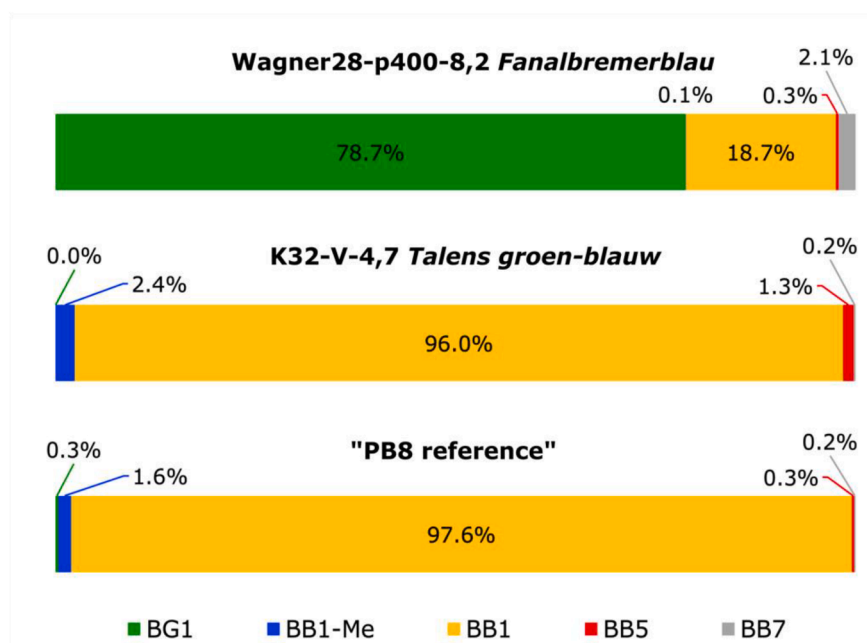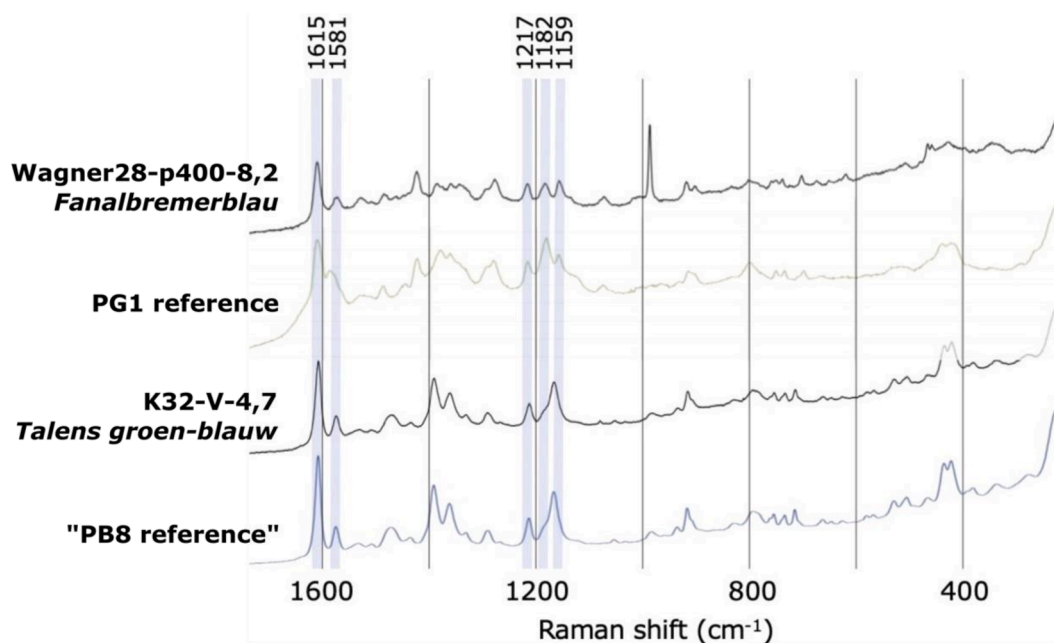

Fig. 5. Comparison of Raman and UPLC-HRMS results for two green-blue samples and corresponding pigment references. Raman spectra of the Wagner28-p400-8,2 sample shows some agreement with the PG1 reference, especially the characteristic triplet highlighted at 1217, 1182, and 1159 cm^{-1}, while no other colorants are evident. HRMS results for the sample indicate that BB1(PG9) and BB7(PB1) are present in significant quantity. The K32-V-4,7 sample shows very good agreement with the PB8 reference, although HRMS results indicate both samples are composed primarily of BB1(PG9). Percentages shown are the ratios of an individual peak area over the total colorant peak area.

considerable analytical challenge, especially once formulated into a paint with other pigments.

(THM)-Py-GC–MS analyses could not distinguish a number of pigments present from the pyrolytic fragments, because of their structural similarity. A similar difficulty is presented by interpretation of TAM pigments by Raman [20]. Raman spectra from the Talens green-blue paint-outs from 1932 through 1937 matched very closely with a PB8 reference loaned from the Historical Dye Collection in Dresden (Fig. 5), while those produced after 1941 contained mixtures of PB15 and PG7. However, analysis of the early Talens green-blue samples (1932–1937) and the PB8 reference by UPLC-PDA-HRMS instead showed BB1(PB9) to be the major component of both, comprising approximately 96–98% of the samples. The next largest component (1–2%) derives from BB1 following the loss of a methyl group. PB9 is absent from the SOPRANO spectral database and current literature, and reliance on the labels of historical references could lead to misinterpretation. The Raman spectra accurately reflected the similarity between the Talens green–blue sample and the PB8 reference; however, accurate identification depended on verification by another technique. The trace components measured by HRMS are BG1(PG1), BB5(PB3), and BB7(PB1). The significance of the trace quantities of pigment are uncertain, as the perceptibility of such small additions of SOPs have not been studied.

The early Talens green–blue paints were compared with another Fanal product, a pigment wash labeled Fanalbremerblau from the 1928 edition of the Wagner text (Wagner28-p400-8,2) (Fig. 5). The Wagner sample's Raman spectrum does not bear close resemblance with the Fanal Bremen blue G new samples, excepting two shared bands at 1615 cm^{-1} and 1581 cm^{-1}, but the triplet in the range of 1225–1150 cm^{-1} corresponds to PG1. UPLC-PDA-HRMS results from the Wagner sample indicate it is comprised of 78.7% BG1(PG1), 18.7% BB1(PB9), 0.3% BB5 (PB3), and 2.1% BB7(PB1). PB9, PB3, and PB1 were not determinable from the Raman spectrum.

3.3. Possibilities and limitations of analytical approaches

3.3.1. Raman analysis

The results shown demonstrated that analysis by Raman spectroscopy, together with access to an extensive database and a large library of references, was successful in identifying most of the major components in an unknown microsample. The importance of the widest-possible database must be underscored—particularly amongst early SOPs, for which the number and variety of possible colorants is extensive. The comprehensive database of Raman spectra reduced the number of unidentifiable colorants to relatively few. Verified reference Raman spectra were absent for MO1, BY21, C.I. 48010, PB8, and PB9, resulting in missing, incorrect, or questionable identifications of SOPs if determined by Raman alone. The absence of definitive structural data from Raman spectra provides little indication to assist in identifying unknown SOPs.

As with all spectral-matching techniques, the accuracy of the identifications depends on the thoroughness of the library, spectral resolution, instrumental settings and the skepticism of the analyst. The magnification and settings selected delivered the best S/N ratio and did not show thermal effects on the analyzed samples. Although a larger magnification (up to 100x) was feasible, we noticed that the energy of the laser beam became too intense. Besides, since the samples were relatively homogenous, a larger magnification did not improved the identification although it must be noted that on paint samples from historical object this magnification might be adapted. One major shortcoming of Raman related to identifications of minor components in mixtures of SOPs. For example, in this study, minimal spectral variation was observed between samples shown by HRMS to contain different proportions of the TAM pigments in the Talens green-blue samples and different basic yellow colorants in the Talens dark green samples. Analysis at multiple wavelengths may improve the potential for Raman identification in these and other cases [4], especially in the case of

pigments that do not respond to the 785 nm laser used. Sampling at multiple locations so as to interrogate more of the pigment particles may also improve the number of minor components detected. All of these approaches require the analyst to suspect that there are other SOPs that have not yet been detected. For cases such as these, UPLC was a very effective complementary technique to supplement Raman.

3.3.2. UPLC-PDA and UPLC(-PDA)-HRMS results

Results of a typical UPLC-PDA analysis are shown in Fig. 2. Emblematic is one or two major component peaks that have a very clear PDA spectrum and several trace components. The ability to separate sample components through chromatography provided more nuanced insights into the components of an unknown, including degradation products and trace coloring components. Yet, detection of the minor components in a sample did not guarantee identification, due to limitations of the sensitivity and selectivity of the PDA detector and the even larger set of reference spectra entailed by the additional trace components.

The main challenges posed by PDA detection are due to relatively high limits of detection. This is more prominent when dealing with data with low signal-to-noise (S/N), as in the minor component in Fig. 2. Noise in the UV range will distract basic library-matching software that relies solely on the overall numerical similarity of a spectrum from recognizing patterns at longer wavelengths, and it is partially for this reason that many analysts rely on their experience with PDA detection in recognizing spectral patterns that indicate a particular dye class. In spectra with low S/N, the minute spectral traits in the visible range that are responsible for differentiating species in a class of compounds are not reliable. In these cases, the heights of spectral peaks are distorted, making relative height difficult to distinguish. Again, as another spectral-matching technique, the accuracy of the identifications by PDA depended upon a comprehensive spectral library and a skeptical approach.

However, the combination of the retention time and the spectra of the components of interest is a very strong identification tool. Although retention time alone is insufficient to establish an identification, it can provide confidence in ambiguous cases, provided that the component is present in the reference library and has been or can be analyzed using the identical chromatographic system as the unknown.

SOP identifications made by HRMS are facilitated by the high instrumental mass accuracy and the structural data garnered from fragmentation studies. Especially the combination of UPLC and HRMS allows identification based on references materials as well as unknowns when prior knowledge is available obtained via other techniques. However, this does not guarantee that measurement of an unknown colorant would always result in an SOP identification. A major factor limiting the efficiency, ease, and utility of identifying SOPs by UPLC-HRMS is the absence of a searchable database of known (and unidentified) SOPs with molecular formulae. To generate potential structures to be compared with potential molecular formulae, the HRMS results presented relied on Raman results, molecular class and color from PDA data, archival information regarding paint formulation or pigment production, and the colorant structures presented in industrial texts such as the Color Index and Schultz's *Farbstofftabellen*. As previously mentioned, expecting the broadest range of possible materials is key to avoiding misidentification [42]. The process of refuting or confirming results relied upon redundancy, and when possible, MS/MS fragmentation. The addition of on-line PDA and MS/MS fragmentation data greatly improved the possibilities for identification, as with MO1 in the Alizarin orange samples (Section 5.2.1) and C.I. 48010 in the Talens dark green samples (Section 5.2.2).

3.3.3. Py-GC–MS spectra

(THM-)Py-GC–MS was applied to ten samples, including four paints and the related pigments. For the exclusive purpose of SOP identification, (THM-)Py-GC–MS was better suited for providing supporting

evidence. The uncertainty in structure introduced by pyrolysis and/or derivatization seemed surmountable only for identification of pigments with unique, characteristic fragments, such as phthalocyanine pigments. Confident discrimination of the exact TAM or azo pigments from (THM-) Py-GC–MS alone was not possible, although the classes of pigments were determinable. Sample quantity, age, or complexity may be partly responsible for the shortcomings, although such encumbrances are typical of art materials. The main advantage of Py-GC–MS would have been the concomitance of data on binder and varnish, had they been of interest.

THM has been used extensively in the analysis of organic binders, and some implications for identification and interpretation [43] seemed to extend to the SOPs studied here. In particular, methylation seemed to preserve more specific, characteristic pyrolytic fragments and reduce nonspecific fragmentation. One such example was described in Section 3.2.1, in which the complete azo molecule was preserved with THM, while only half the molecule was detected without. However, one of substituents of the complete molecule was modified by the THM, resulting in an incorrect identification nevertheless.

3.3.4. Historical contextualization

Analysis of historical materials dictates that results make sense in a historical context [42]. Thus, validation of results was only possible with access to archives at Royal Talens, BASF, and Bayer and through art technological source research in patents, recipes, and other contemporary literature. For example, surprising results from seven Talens dark green paint samples showed that five different pigment mixtures were used across a seventeen-year period. While all the paints contained BG1 as the major component, three different basic yellow pigments were present in various combinations, and BB1 was also present in two of the samples. However, the formulation workbooks in the Talens' archive showed that the regular re-working of paint ingredients and their quantities was typical. The hundreds of kilograms of prepared pigments that were shipped to Talens' each year were part of a shifting collection of what was available, affordable, and convenient for the larger colorant industry [44]. The hues of the Talens' product line were created using what was available, which changed over time.

4. Conclusions

Using the techniques studied here, the most confident identifications were those that were supported by a spectral technique, a structural technique, and evidence of its usage at the time. The most effective of the workflows explored began with Raman, as it is potentially non-destructive and does not require solubilization and was followed by UPLC-PDA-HRMS. The shortcomings of one technique are compensated for by the other: Raman analyzes the original solid state of the sample and can provide information on precipitant, information that is lost in solubilization for LC. Furthermore, gentler sample extraction for LC analysis can be warranted by the likely detection of insoluble components in the Raman spectrum. LC separates out minor components and mixtures, and unknown components can be interrogated by HRMS data. Together, the colorants are interrogated by multiple chemical properties: Raman scattering, molecular interaction with a stationary phase, UV-Vis absorbance, and *m/z*.

The comparison of techniques used here showed through several examples four general types of data that are gained with the use of LC techniques. First, of the 67 samples analyzed, UPLC-PDA detected 42 of them as composed of mixtures of colorants, while Raman detected 16. The mixtures detected by the two techniques were not the same, as UPLC techniques could not detect the phthalocyanine-containing mixtures. From these numbers, it is likely that mixtures are common to paints made with SOPs, and to detect all of the coloring components, an analytical technique must be able to detect mixtures. Second, and in a similar vein, degradation products were detected by UPLC-PDA and identified by UPLC-HRMS, but not detected by Raman. Furthermore,

UPLC-PDA and HRMS provided semi-quantitative data on the multiple colorant components, which could be useful for comparing paints that differ only in amounts or monitoring degradation phenomena. Lastly, UPLC-PDA-HRMS was used to establish the identities of unknown colorants or degradation products. The usefulness of data on mixtures, degradation products, relative amounts, or structures of unknowns depends on the questions posed to the samples under analysis.

Also emphasized by these experiments is the importance of reporting analytical limitations when reporting results. As multi-analytical approaches and more sophisticated techniques in cultural heritage analyses become more common, the open-ended nature of sample contents has become evident. For example, the Raman spectrum of a major sample component could be obscuring minor and/or less Raman-active components, only discoverable through extensive searching. HRMS can detect miniscule amounts of SOPs and related compounds, the significance of which are yet undetermined. Thus, there are unexpressed levels of confidence for identifications that contingent on the analytical and art technological approaches used. Researchers in such interdisciplinary fields as cultural heritage science are faced with the particular challenge not to bolster misconceptions about the infallibility of scientific data, given the interest of parties from a broad range of scientific training.

Finally, collaborative efforts were key to the successful implementation of analytical techniques and validation of results. Open-access data libraries, such as the Modern KIK-IRPA database (**soprano.kikirpa.be**) [31], and the open sharing of small samples of reference pigments from Dresden Historical Dye Collection easily improved the number and quality of identifications possible. An equivalent SOP data library for PDA and HRMS spectra are much-needed additions to the analysts' toolkit. Currently absent from any such data libraries is the ability to share unknown or unidentified spectra, to pool the efforts of analysts worldwide. The development of effective identification tools, together with progress in minimally-destructive organic analyses, will result in large steps forward for SOP identifications in artworks.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2021.106708.

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