Article

Exploring Liu Kang’s Paris Practice (1929–1932): Insight into Painting Materials and Technique

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Abstract: This paper presents the results of an extensive study of 14 paintings by the pioneering Singapore artist Liu Kang (1911–2004). The paintings are from the National Gallery Singapore and Liu family collections. The aim of the study is to elucidate the painting technique and materials from the artist’s early oeuvre, Paris, spanning the period from 1929 to 1932. The artworks were studied with a wide array of non- and micro-invasive analytical techniques, supplemented with the historical information derived from the Liu family archives and contemporary colourmen catalogues. The results showed that the artist was able to create compositions with a limited colour palette and had a preferential use of commercially available ultramarine, viridian, chrome yellow, iron oxides, organic reds, lead white, and bone black bound in oil that was highlighted. This study identified other minor pigments that appeared as hue modifications or were used sporadically, such as cobalt blue, Prussian blue, emerald green, cadmium yellow, cobalt yellow, and zinc white. With regard to the painting technique, the artist explored different styles and demonstrated a continuous development of his brushwork and was undoubtedly influenced by Modernists’ artworks. This comprehensive technical study of Liu Kang’s paintings from the Paris phase may assist art historians and conservators in the evaluation of the artist’s early career and aid conservation diagnostics and treatment of his artworks. Furthermore, the identified painting materials can be compared with those used by other artists active in Paris during the same period.

Keywords: Liu Kang; SEM-EDS; MA-XRF; FTIR; IRFC; X-RAY; RTI; hidden paintings; pigments

1. Introduction

Liu Kang (1911–2004) was one of the most influential figures in the early development of modern art in Singapore. He was born in Yongchun, Fujian province, China. After graduating from Xinhua Arts Academy in Shanghai in 1928, he moved to Paris, where he stayed from February 1929 to April 1932. In the early decades of the 20th century, there was a growing enthusiasm in China towards the study of Western culture. Western art appealed to Chinese educational modernisers because of its realism and supposed association with science and progress [1]. Hence, the Chinese government encouraged graduates as well as established artists to further their art education in France and to promote modernisation ideas in a rapidly transforming China upon their return [2]. Liu Kang’s stay in Paris had a significant influence on his career. He attended the Académie de la Grande Chaumière in Montparnasse and studied Impressionist, Post-Impressionist, and Fauvist styles [3]. In an essay from 1970, Liu Kang made a reference to his Paris phase: “We visited fine art museums and studied the masterpieces of past generations of artists, toured famous art galleries to admire recent works by contemporary artists, and gained much from this initiation” [4].
Although his Paris paintings may seem to show a chaotic mixture of different styles at first glance, a close examination reveals a variety of influences and the search for an individual technique. Liu Kang was attracted to Post-Impressionist and Fauvist styles for their expressive use of colour and form to depict a subjective view of the world [5,6]. It is worth noting that his artistic explorations of the Western painting styles achieved some success—his works were accepted by Salon d’Automne in 1930 and 1931. The variety of styles adopted by the artist in Paris invites the question of whether he actively explored different painting materials. Hence, this study aims to characterise Liu Kang’s painting technique and the pigments he used during the period under review. This study expands the scope of the earlier preliminary investigation of two of Liu Kang’s paintings [7,8] and the overview of his painting supports from Paris phase [9]. The collected data contribute to the knowledge of Liu Kang’s painting materials. It may be useful to art historians exploring Liu Kang’s workmanship and conservators planning conservation treatments of his paintings.

2. Materials and Methods

2.1. Materials

2.1.1. Investigated Paintings

The discussion focuses on seven paintings from the National Gallery Singapore (NGS) and six paintings from the Liu Kang Family Collection (Figures 1 and 2). The inclusion of the paintings from the Liu collection ensured that the overall research base represents a range of the artist’s genres and painting technique during the period from 1929 to 1932. It needs to be noted that the Paris phase also includes artworks he painted during a trip to Saint Gingolph on the French–Swiss border between 8 August and 20 September 1929 [10]. The painting supports of the investigated artworks are not in the scope of this research as a comprehensive study of the supports was carried out earlier [9].

2.1.2. Samples

A total of 59 samples of the paint layer were collected only from the NGS paintings (Figure 1). There was no intention of carrying out any invasive sampling procedures on the paintings from the Liu collection.

2.2. Methods

The range of the applied analytical methods differed between the NGS and Liu collections, mainly due to the Liu family’s wish to conduct only non-invasive in situ examination of their paintings. Thus, only visible light (VIS) photography of the characteristic features of the paint layers was conducted on paintings from the Liu collection to provide further insights into the artist’s painting technique. The NGS paintings were studied first by means of non-invasive imaging techniques, comprising VIS, ultraviolet fluorescence (UVF), reflected ultraviolet (UVR), and near-infrared (NIR) photography. The aim of these non-invasive techniques was to conduct a preliminary characterisation of the pigments by recording their optical features under different wavelengths of the electromagnetic spectrum. An investigation of the paint textures was conducted with reflectance transformation imaging (RTI). To verify the presence of underlying paint layers, NIR and X-ray radiography (XRR) were carried out. The obtained results guided a sampling of the paint layers from the areas with prior loss, for characterising the paint mixtures in detail. Thus, the samples were analysed using optical microscopy (OM), polarised light microscopy (PLM), and field emission scanning electron microscope with energy dispersive spectroscopy (FE-SEM-EDS). A handheld portable X-ray fluorescence (XRF) was used to analyse some areas of the Countryside in France where sampling was not safe. A macro X-ray fluorescence (MA-XRF) scanner was engaged to perform the elemental mapping of Landscape in Switzerland and to support interpretation of data collected from the painting. The initial indication of the organic components of the paint samples was given by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR). The results are summarised in Appendix A, Table A1.
Figure 1. Paintings by Liu Kang from the collection of National Gallery Singapore: (a) Autumn colours, 1930, oil on canvas, 38.3 × 45.3 cm; (b) Countryside in France, 1930, oil on canvas, 46 × 54.7 cm, gift of the artist’s family; (c) Landscape in Switzerland, 1930, oil on canvas, 45.6 × 55.7 cm, gift of C Y Hwang; (d) Village scene, 1931, oil on canvas, 46 × 55 cm, gift of the artist’s family; (e) French lady, 1931, oil on canvas, 60.7 × 45.8 cm; (f) Boat near the cliff, 1931, oil on canvas, 53.7 × 72.4 cm, gift of the artist’s family; and (g) Breakfast, 1932, oil on canvas, 46 × 54 cm. Images courtesy of National Heritage Board. White arrows indicate sampling areas.
Figure 2. Paintings by Liu Kang from the Liu Kang Family Collection: (a) St Gingolph, Lac Leman, Switzerland, 1929, oil on canvas, 45.5 × 37.5 cm; (b) Landscape, 1930, oil on canvas, 46 × 38 cm; (c) Still life with books, Paris, 1931, oil on canvas, 45 × 38 cm; (d) Portrait of a man with his pipe, Paris, 1931, oil on canvas, 45 × 38 cm; (e) Self-portrait, 1931, oil on canvas, 55 × 46 cm; and (f) My landlady, Madame Normand, 1932, oil on canvas, 54 × 45 cm. Images courtesy of Liu family.
2.2.1. Technical Photography

High-resolution technical images were acquired according to the workflow proposed by Cosentino [11–13]. A Nikon D90 DSLR modified camera with a sensitivity of between about 360 and 1100 nm was used. The camera’s white balance preset for VIS photography was created with the X-Rite White Balance Target. The American Institute of Conservation Photo Documentation target was used to additionally finetune the white balance and determine optimum exposure for the VIS imaging. The photographs were shot RAW and further processed by Adobe Photoshop CC according to the standards described by the American Institute of Conservation [14].

VIS and UVF photography at 365 nm were taken with X-Nite CC1 and B + W 415 filters mounted together. NIR photography at 1000 nm, with an additional aim of false-colour infrared imaging (IRFC), was taken with Heliopan RG1000. UVR photography was achieved with Andrea “U” MK II filter.

A pair of 500 W halogen lamps were used for the VIS and NIR illumination system. The light source for UVF and UVR imaging consisted of two lamps equipped with eight 40 W 365 nm UV fluorescence tubes.

2.2.2. RTI

RTI was carried out according to the workflow proposed by the Cultural Heritage Imaging [15]. The images were processed using Adobe Photoshop CC, followed by RTI-Builder and RTIViewer software, as proposed by the Cultural Heritage Imaging [16,17].

2.2.3. XRR

The paintings from the NGS collection were digitally XRR using a Siemens Ysio Max digital XRR system with a detector size of 350 × 430 mm and a resolution of over 7 million pixels. The X-ray tube operated at 40 kV and 0.5–2 mAs. The images were processed with iQ-LITE imaging software and then exported to Adobe Photoshop CC for final alignment and merging.

2.2.4. XRF

XRF measurements were performed using Thermo Scientific™ Niton™ XL3t 970 spectrometer with a GOLDD+ detector and an Ag anode X-ray tube with a 6–50 kV voltage and up to 0.2 mA current. A mining mode with four elemental ranges and a measurement duration of 50 s each (total acquisition time of 200 s) was used to better differentiate the light elements from the heavy ones. The spectra were collected from a 3 mm diameter spot size. The acquired spectra were collected and processed using Thermo Scientific™ Niton Data Transfer (NDT™) 8.4.3 software.

2.2.5. MA-XRF

The elemental mapping of Landscape in Switzerland was conducted with the M6 Jet-stream from Bruker Nano GmbH. The instrument’s measuring head is equipped with a Rh-target microfocus X-ray tube (30 W, maximum voltage of 50 kV, maximum current of 0.6 mA), and a 30 mm² active area XFlash Silicon Drift Detector (energy resolution of <145 eV for Mn-Kα). The measuring head is mounted on an X-Y-Z motorised stage with a maximum travel range of 800 × 600 × 90 mm. The instrument offers an adjustable spot size from 100 µm to approximately 500 µm [18]. The paintings’ elemental distribution maps were acquired with a dwell time of 10 ms/pixel, a pixel size of 300 µm, and an anode current of 599 µA. The data were collected and analysed with the Bruker’s M6 software.

2.2.6. FE-SEM-EDS

The paint samples’ cross-sections were mounted on carbon tapes and examined with a Hitachi SU5000 FE-SEM coupled with Bruker XFlash® 6/60 EDS. The SEM, backscattered electron mode (BSE) was operated with 60 Pa chamber pressure, accelerating voltage of
20 kV, 50–60 intensity spot and a working distance of 10 mm. The acquisition of data and processing were performed using the Bruker ESPIRIT 2.0 software.

2.2.7. ATR-FTIR

ATR-FTIR analyses were performed using a Bruker Hyperion 3000 FTIR microscope equipped with a mid-band MCT detector, coupled to a Vertex 80 FTIR spectrometer. For each sample, 64 scans were recorded in the spectral range of 4000–600 cm$^{-1}$ and resolution of 4 cm$^{-1}$. The spectra were interpreted with Bruker Opus 7.5 software.

2.2.8. OM and PLM

The samples’ structure was studied in reflected VIS and UV light on a Leica DMRX polarised microscope at magnifications of ×50, ×100, ×200, and ×400 coupled with a Leica DFC295 digital camera. PLM was carried out in transmitted VIS light at magnifications of ×100, ×200, and ×400 using the methodology developed by Peter and Ann Mactaggart [19].

2.2.9. Preparation of Samples

The samples selected for the cross-sections were embedded in a fast-curing acrylic resin, ClaroCit from Struers (Cleveland, OH, USA), and fine polished. The PLM pigment dispersions were prepared with a Meltmount nD = 1.662 mounting medium from Cargille (Cedar Grove, NJ, USA).

2.3. Archival Sources

The technical examination of paintings was supplemented with materials from the Liu family archives to elucidate the artist’s painting practice. These materials include Liu Kang’s photographs, watercolours artwork, and a Lefranc artists’ colourmen price list of oil colours from October 1928. The latter may reflect the artist’s interest in Lefranc colours as he had brought the price list home [8]. However, firm conclusions about any links between the Lefranc colours and materials used by Liu Kang should not be made due to weak evidence at the current stage of the research. From observing the advertisement sections of Le Salon’s 1930 and 1932 exhibition catalogues [20,21] and Salon des indépendants 1930 [22], it is deducible that Liu Kang might have had access to a great range of painting materials from other local manufacturers and retailers [9]. He also might have had an opportunity to purchase the overseas brands from retailers, such as Lechertier Barbe LTD, Paris American Art Co., and S. C. & P. Harding (Paris) LTD (Figure 3). The advertisements of these retailers listed a selection of local brands such as Lefranc, Bourgeois Ainé, as well as imported materials from Rowney, Winsor & Newton (W&N), Talens, and Schmincke. While it remains uncertain what brand of colours the artist used, some references are made to the contemporary colourmen catalogues, such as the W&N catalogue from 1928, Lefranc catalogues from 1928 to 1931, and Bourgeois Ainé catalogue from 1929 to provide insights into the availability of certain pigments that are found in the paintings under investigation.
Figure 3. Advertisements by official retailers of local and overseas art materials, available in Paris in 1930 and 1932: (a) Lechertier Barbe LTD; (b) Paris American Art Co.; (c) Talens and Zoon, S.A. advertisement indicating Paris American Art Co. as its Paris representative; and (d) S. C. & P. Harding (Paris) LTD.

3. Results and Discussion
3.1. Pigments
3.1.1. Blue

Blue painted areas of the examined paintings are very often imaged purple in an IRFC, suggesting a use of ultramarine and/or co-containing blue. The analyses confirmed that the different blue hues primarily involve ultramarine (sulphur-containing sodium aluminium silicate), observed with PLM by particles with low refractive index that appear red with Chelsea filter and by SEM-EDS detection of Na, Al, Si, and S. Admixtures of viridian (hydrated chromium oxide) were confirmed by the detection of Cr and coincident PLM observation of large and rough particles with high refractive index. The presence of ultramarine and viridian is compliant with the purple appearance of the paint mixture in IRFC. Admixtures of cobalt blue (cobalt aluminium oxide) were confirmed with SEM-EDS by the concomitant presence of Co and Al as well with PLM (particles with a high refractive index that appear red with Chelsea filter) in Boat near the cliff (sample 26) and French lady (sample 20). Very dark blue in Countryside in France (sample 5) was probably made by mixing ultramarine with carbon black. It is worth noting that no Prussian blue (hydrated iron hexacyanoferrate) was found in the investigated blue mixtures, despite its discovery in the earlier study [7]. Prussian blue is known for its high tinting strength, which may be easy for artists to handle. It also produces dark greenish-blue shades that Liu Kang
probably did not find suitable for painting sky or water. He might also be aware of the Prussian blue’s tendency to fade or change in colour over time [23,24].

In almost all examined blue paint samples, except those from Landscape in Switzerland and Boat near the cliff, a high concentration of Pb seems to point to the consistent use of lead white (lead carbonate) for achieving lighter tints. Meanwhile, the presence of Ba, S, and Zn elements could be related to lithopone (a mixture of barium sulfate and zinc sulfide) and/or zinc white (zinc oxide) and barium white (barium sulfate), a common extender for lead white [25] as well as for viridian [26].

3.1.2. Green

The acquired PLM and SEM-EDS data revealed that viridian was Liu Kang’s consistent choice for green. However, it is very often present in combination with other pigments. For instance, positive identification of emerald green was possible in sample 18 from Autumn colours with SEM-EDS detection of Cu and As elements and with FTIR by absorption bands at 1555, 1451, 816, 762, 690, and 635 cm\(^{-1}\) (Appendix A, Figure A1) [27]. However, based only on the concomitant presence of Cu and As, elements in other green paint mixtures, emerald green (copper acetoarsenite), and/or Scheele’s green (copper arsenite) were considered.

According to Bourgeois Ainé and Lefranc’s catalogues of oil paints, Vert Veronese (emerald green), vert de Scheele (Scheele’s green), and its variant, vert minérale, were available during that time in Paris (Appendix A, Figures A3 and A4). Emerald green was also offered by W&N (Appendix A, Figure A2). Although it is known that some grades of emerald green were commercially adulterated with chromium pigments [28,29], MA-XRF distribution maps of Cr and Cu elements from Landscape in Switzerland showed only a partial co-location of Cu and Cr in the green areas (Figure 4). Hence, it could be said that the Cu–As-based green was not modified by the manufacturer but deliberately mixed with viridian where it suited the artist.

The analyses of the light and warm green hues of the investigated paintings confirmed a consistent use of chrome yellow (lead chromate) as an admixture of viridian. This can be exemplified by sample 3 from Village scene (Figure 5a). In this sample, besides viridian, chrome yellow was detected with PLM by anisotropic, rod-shaped particles with a high refractive index. The SEM-EDS analyses of the green and yellow clusters of not properly mixed paint indicated a varied intensity of Pb-, Ca-, and Cr-peaks contributing to viridian and chrome yellow, probably extended with chalk (calcium carbonate) or calcium chromate [30]. The presence of viridian in the examined paint is in agreement with the purple imaging of the sampling area (Figure 5b,c).

The co-location of Cr- and Cd-signals recorded with MA-XRF of Landscape in Switzerland (Figure 4) suggested an addition of cadmium yellow (cadmium sulfide) to viridian. This observation was corroborated with red UV fluorescence of the yellow particles [11], SEM-EDS detection of strong Cd- and S-signals, and PLM observation of sample 21 from Landscape in Switzerland (yellow, anisotropic particles with a high refractive index turn green in crossed polarised filters) (Figure 6). However, the presence of S, Ba, and Zn in the investigated mixture may suggest that, instead of pure cadmium yellow with lithopone and/or zinc and barium whites, zinc-modified light cadmium yellow or cadmopone (co-precipitated cadmium sulfide and barium sulfate) was used [31]. A high concentration of Pb in most of the examined light-green samples may suggest concurrent admixtures of chrome yellow and/or lead white to viridian. A combination of viridian and lead white to obtain a light-green tone was detected in Breakfast (sample 4). Meanwhile, strong Zn-signals recorded in the light-green brushstrokes of Landscape in Switzerland (sample 20) and Boat near the cliff (sample 11) suggest an admixture of lithopone and/or barium white and zinc white.
Figure 4. Visible light image and MA-XRF maps of *Landscape in Switzerland*, showing the distribution of the major elements. The greyscale corresponds to the intensity of the signal of each element: white equals high intensity, black means low intensity. The colour maps combine distribution of Cu- and Cr-based pigments and Fe- and Sn-based pigments.
Figure 5. SEM-EDS spectra of: (a) green and yellow areas in sample 3 extracted from Village scene and inset microscopy image of the cross-section with marked areas of analyses; (d) dark-green paint from sample 2 extracted from the same painting and inset microscopy image of the cross-section with the marked area of analysis. The detail of the painting shows the sampling spots (b) and infrared false-colour image of the same areas, revealing the distribution of viridian (purple) and the mixture of Prussian blue with viridian and lead white (tints of violet) (c).
Based on the SEM-EDS and PLM analyses, dark green was very often achieved by mixing viridian with Prussian blue in combination with lead white and/or chrome yellow. This can be exemplified by sample 2 in Village scene (Figure 5d). The SEM-EDS analysis of the dark-green paint revealed that it is rich in lead, chromium, and iron, which can be assigned to lead white, viridian, and Prussian blue. The latter was observed with PLM by dark-blue isotropic particles with a low refractive index that appear dark green with a Chelsea filter. This pigment mixture is consistent with the IRFC imaging, as the dark-violet colour is determined by the purple representation of viridian, combined with a dark-blue representation of Prussian blue (Figure 5b,c). A similar pigment mixture was identified with PLM and SEM-EDS in dark-green paint from Countryside in France (sample 11). However, FTIR did not depict any peaks attributable to viridian due to overlapping bands of other compounds; the most intensive peaks of this pigment fell in the range of 500–400 cm\(^{-1}\), behind the spectral range of the measurement. Although the artist did not employ Prussian blue in the blue painted areas, he preferred it for his hue modification of the green colours. Interestingly, in French lady (sample 15), in addition to Prussian blue, a cobalt blue was added to the green paint to produce the desired hue.

The green colour, obtained by mixing blue and yellow, was found in Landscape in Switzerland (sample 20). The green sampling area appears blue in the IRFC, suggesting the presence of Prussian blue. The SEM-EDS detection of Pb, Cr, and Fe elements, combined with PLM and FTIR analyses, confirmed chrome yellow by absorption peaks at 1061, 967, 826, and 626 cm\(^{-1}\) and Prussian blue by absorption peak at 2086 cm\(^{-1}\). The paint mixture also contains yellow iron oxide observed with PLM (anisotropic yellow particles with a high refractive index). However, its FTIR confirmation was inconclusive due to overlapping bands of chrome yellow. Moreover, there is a possibility that the artist used a commercial chrome green composed of Prussian blue and chrome yellow [26,32]. Such composite paint was available from Bourgeois Ainé in three different hues and from Lefranc in five hues under the name of vert anglais (Appendix A, Figures A3 and A4). It was also listed by
W&N as chrome green, available in three hues, and as cinnabar green, available in five hues (Appendix A, Figure A2).

3.1.3. Yellow

The analyses of the samples of yellow paints revealed the use of four different yellow pigments, but it is evident that chrome yellow was a prevailing pigment. It was identified as a principal component of sample 9 from Countryside in France and sample 8 from Village scene. It appears as an ingredient found together with yellow iron oxide in Autumn colours (sample 3) and Breakfast (sample 3). Nevertheless, it is difficult to ascertain if chrome yellow and iron oxide were deliberately mixed by the artist on the palette or commercially prepared. It is known that the ochres were tinted during the manufacturing process with the addition of chrome yellow [30,33], which also has its own extenders, such as barium white, gypsum, kaolin, and calcium chromate [30].

Analyses of the yellow paint mixture from Landscape in Switzerland (sample 23) allowed features consistent with cadmium yellow or its variants—light cadmium yellow or cadmopone—to be detected. As visualised by the MA-XRF Cd-distribution map, a usage of this pigment for painting yellow areas was very limited; however, it occurs extensively as an admixture in light-green passages (Figure 4).

The SEM-EDS detection of Co and K in the samples of yellow paint from Landscape in Switzerland (samples 23, 36) allowed their attribution to cobalt yellow (potassium cobaltinitrite), later confirmed with PLM by observation of isotropic, yellow, and dendritic particles with a high refractive index (Figure 7). The use of cobalt yellow by Liu Kang seems to be unusual as the pigment is known for its undesirable low hiding power in oil medium. Therefore, its main application was usually a watercolour technique [34,35]. Cobalt yellow was available from Bourgeois Ainé and Lefranc only as a dry pigment and in watercolour and gouache paints. However, it appears in W&N catalogues of oil paints (Appendix A, Figure A2).

![Figure 7. Cobalt yellow particles from sample 23, extracted from Landscape in Switzerland, photographed in plane-polarised light.](image)

3.1.4. Brown

Brown passages were painted using predominantly brown and yellow iron oxides. Lighter tints were produced with a small addition of lead white and/or Cr-containing yellow(s). Darker-brown brushstrokes in Boat near the cliff (sample 14) contain Ca and P elements that can be assigned to bone black admixture, confirmed with PLM (anisotropic...
black and grey particles). In addition, the co-location of Fe and Mn recorded with SEM-EDS suggests the presence of umber. The SEM-EDS and PLM of the dark-brown colour from the armrest of the chair in Breakfast (sample 10) suggested a mixture of red iron oxide with Prussian blue and organic red pigment (unique low refractive index). FTIR completed this outcome by detecting of some absorption bands indicative of organic red at 1656, 1623, 1545, and 1270 cm\(^{-1}\). However, more peaks typical for organic red fall in the range from 1200 to 1000 cm\(^{-1}\) and were interfered by the presence of red iron oxide. In addition, the paint mixture contains a good deal of starch grains with an extinction cross, which were visible in cross-polarised light (Figure 8a–d). However, FTIR measurements detected only one peak at 3270 cm\(^{-1}\) that is related to starch, while further identification was hampered by the intensive peak of red iron oxide at 1005 cm\(^{-1}\) and overlapping characteristic bands of starch at 1014 and 995 cm\(^{-1}\). Starch was frequently added to the organic reds during the manufacturing process to improve its handling properties and to obtain a lighter tint [36,37]. The PLM and FTIR analyses of the paint sample correlate with the occurrence of Sn, detected with SEM-EDS, suggesting the presence of a tin-containing substrate for the organic red, which was usually cochineal lake or brazilwood lake pigment (Figure 8e) [38,39]. A composition containing alizarin crimson and brazilwood on starch and tin substrates was reported in the earlier study of Liu Kang’s painting [8]. Lefranc listed a tin-containing organic red *laque anglaise* composed of *carmin* and *oxyde d’étain* (tin oxide); it was one of the most expensive, priced at 22 francs for a No. 6 tube and 9.50 francs for tube No. 2, whereas blanc d’argent (lead white) was at 3.75 francs for a tube No. 6. (Appendix A, Figure A4). *Laque anglaise* from Bourgeois Aïné had a comparable price (Appendix A, Figure A3).

### 3.1.5. Red

The analytical results showed that Liu Kang employed three types of organic red pigments in most of the examined paintings. They were used as primary reds or in combination with other pigments added to modify hue. An Sn-containing organic red on starch substrate was confirmed with SEM-EDS, PLM, and FTIR in Village scene (sample 9) and Landscape in Switzerland (sample 35, layer 1) and resembled the aforementioned mixture from Breakfast (sample 10).

The FTIR of sample 9 from the Village scene showed low intensity peaks at 1562 and 1545 cm\(^{-1}\), which are indicative of organic red; however, an in-depth molecular characterisation was not possible due to overlapping signals of other compounds present in the investigated sample. A similar issue concerns the identification of starch. Although starch was well observed with PLM, only two FTIR peaks, at 3280 and 1649 cm\(^{-1}\), were considered conclusive. Additionally, detection of Fe and co-location of Pb-, Cr-, and Ca-signals, suggested that an organic red was used in a combination with red iron oxide (absorption peaks at 1026, 1007, 935, 911, 798, 777, and 753 cm\(^{-1}\)), chrome yellow (absorption peaks at 1031, 844, 834, and 624 cm\(^{-1}\)), chalk (absorption peaks at 1410, 870, and 712 cm\(^{-1}\)), and probably lead white (1410 and 677 cm\(^{-1}\)) (Figure 9).

The sample 35 from Landscape in Switzerland contains two distinguishable layers. Based on the PLM, SEM-EDS, and FTIR, the top red is composed mainly of red iron oxide with an admixture of Sn-containing organic red, detected by absorption peaks at 1620, 1563, 1555, 1529, 1471, 1290, 1265, 1246, and 588 cm\(^{-1}\), and chalk. This top layer was applied over dry paint predominantly consisting of the organic red, detected by peaks at 1621, 1562, 1552, 1531, 1310, 1265, 1247, and 604 cm\(^{-1}\). In addition, a presence of starch was confirmed with PLM observation and FTIR by absorption peaks at 3294, 1639, 1370, 1341, 1247, 1204, 1150, 1077, 1016, 931, 861, 759, and 704 cm\(^{-1}\), while Sn-based substrate was confirmed with the SEM-EDS. Moreover, the analysed paint contains some admixtures of lead white and probably Cr-containing yellow(s) (Figure 10). The MA-XRF map of Sn distribution in Landscape in Switzerland shows that some passages were initially painted with a heavy use of Sn-containing organic red (Figure 4) and finally covered with different colours as visualised on the cross-section of sample 25 (Figure 11).
Figure 8. Microscopy images of the cross-section of sample 10, extracted from Breakfast, photographed in: (a) VIS; (b) UV. Circular, blue-fluorescing particles of the starch substrate are visible in layer 4 and marked with arrows (b). The PLM pigment dispersion from layer 4 is photographed in: (c) plane-polarised light; (d) cross-polarised light. The clumps of starch particles are marked with arrows. The corresponding SEM-EDS spectra of the red paint from layer 4 (e) shows a strong Sn-signal, suggesting the presence of tin substrate.
Another organic red was detected in *Boat near the cliff* (sample 29). PLM allowed the observation of red particles with a low refractive index, which is characteristic of organic reds. An intense orange fluorescence in UV light (Figure 12b) suggests natural madder [38]; however, the SEM-EDS detection of bromine, based on Br Lα and Br Kα signals (Figure 12c), indicates that the red may be a compound related to eosin red—commercially known as geranium lake—which is also characterised by the orange UV fluorescence [40–42]. A comparison of the FTIR spectra of the investigated red with the reference sample of eosin Y revealed some degree of matching. Typical FTIR features consistent with the organic red were identified by absorption bands at 3335, 1561, 1455, 1345, 1221, 1174, 981, 877, 802, 766, 717, 667, and 634 cm$^{-1}$. However, the overlapping bands at 1455, 1174, 981, 802, 717, and 634 are also attributable to lithopone and/or barium white, oil, and acrylic resin, the latter of which is considered to be a varnish and applied during the conservation treatments in 2006 (Figure 13) [43]. Other elements present in the sample, such as Pb, Ba, Al, and S, were difficult to interpret. They can be assigned to lead white admixture and barium white extender. However, it is known that eosin was used to produce lake pigments (such as geranium lake), usually precipitated on an Al- or Pb-containing substrate [32,44–47]. Thus, Ba and S could be assigned to barium white, which is a common extender of lake pigments. Nevertheless, a presence of lithopone is suggested based on the FTIR detection of characteristic peaks at 1174, 1116, 1077, 981, 634, and 607 cm$^{-1}$. 

Figure 9. Microscopy image of the cross-section of sample 9 extracted from *Village scene*, photographed in VIS and UV, followed by SEM-EDS maps showing the distribution of the detected elements. The greyscale corresponds to the intensity of the signal of each element: white equals high intensity, black means low intensity. A high intensity of Sn can be assigned to the tin substrate of organic red while the co-location of Ca-, Cr-, and Pb-signals in the centre of layer 2 suggests the presence of chrome yellow.
Figure 10. Microscopy image of the cross-section of sample 35 extracted from *Landscape in Switzerland*, photographed in VIS and UV, followed by SEM-EDS maps showing the distribution of the detected elements. The greyscale corresponds to the intensity of the signal of each element: white equals high intensity, black means low intensity. The high intensity of Sn in layer 1 can be assigned to the tin substrate of organic red, which is probably mixed with chrome yellow based on the co-location of Cr- and Pb-signals. Layer 2 reveals strong Fe- and weak Sn-signals, suggesting a mixture of iron oxide with organic red with tin substrate.

Figure 11. (a) Detail of *Landscape in Switzerland*, showing the sampling spot; (b) microscopy image of the cross-section of sample 25 with the marked area of SEM-EDS elemental analyses; (c) corresponding SEM-EDS spectra of the analysed area from layer 1, indicating a strong Sn-signal from the tin substrate of organic red.
Figure 12. Microscopy image of the cross-section of sample 29 extracted from Boat near the cliff photographed in: (a) VIS; (b) UV. SEM-EDS spectra of the sample and inset backscattered electron (BSE) image with marked area of analyses (c). The spectra shows Br peaks which could be indicative of geranium lake, as well as Pb, Ba, Al, and S, which can be assigned to lead white and barium white extender and/or Pb- or Al-based substrate.

Lefranc marketed the laque geranium (geranium lake) with information that it is aniline-based pigment (Appendix A, Figure A4), although recent research identified eosin in its sample from 1926 [48]. Bourgeois Ainé listed laque geranium and rouge geranium (geranium red) without a chemical description, while geranium lake from W&N was derived from coal tar, according to their catalogue (Appendix A, Figures A2 and A3). Although the investigated red paint from Boat near the cliff exhibits features intrinsic to geranium lake, more analyses are needed to better elucidate its composition.

The organic red was also observed with PLM in the sample extracted from Countryside in France (sample 7). The sample does not fluoresce in UV, and the SEM-EDS detection of Al might be indicative of Al-containing substrate for the organic red detected with FTIR by peaks at 1617, 1576, 1559, 1499, 1447, 1417, 1397, 1343, 1303, 1276, and 1256 cm\(^{-1}\) [49]. However, the insufficient suit of FTIR peaks or low intensity of peaks did not allow a conclusive attribution.

In Autumn colours (sample 7) and French lady (sample 9), red paints are composed mainly of red iron oxide, modified with minor admixtures.

3.1.6. White

UVR photography is a powerful tool for a preliminary differentiation of lead white painted areas from zinc white and titanium white (titanium dioxide). Thus, lead white was observed in almost all paintings, based on its unique ability to reflect UV (Figure 14a,b). Additional SEM-EDS analyses showed that lead white occurs with a calcium carbonate, which was probably added by the manufacturer as an extender. It is worth noting that the examined white from the Countryside in France (sample 29) is a ground layer intentionally exposed by the artist during the painting process. It is composed predominantly of lead white with admixtures of barium, zinc, and titanium whites [9], suggesting it is of a different grade from the lead white identified in the artist’s white paints [28]. Likewise, the white ground skilfully exposed by the artist in Boat near the cliff for describing foamy water is composed of mixture of lead and zinc whites [9]. White brushstrokes that turn dark grey and black in the UVR of Landscape in Switzerland and Boat near the cliff suggested a
use of UV-absorbent titanium white or zinc white (Figure 14c,d). The latter was confirmed by the yellow-green UV fluorescence and SEM-EDS measurements of the white paint cross-sections from both paintings. Additionally, the MA-XRF of Landscape in Switzerland visualised a strong Zn-signal, which correlates with the white painted areas, while the Pb distribution map suggests chrome yellow and admixtures of lead white (Figure 4). The SEM-EDS detection of Ba and S in the sample 22 of Landscape in Switzerland suggests a common admixture of lithopone and/or barium white [50]. A minor and trace presence of Ti identified only in the colour mixtures may suggest a commercial admixture of titanium white.

![Figure 13. ATR-FTIR spectra of red paint from sample 29, taken from the Boat near the cliff, with labelled marker peaks of organic red and spectra of reference samples, identifying oil, eosin Y, acrylic resin, and lithopone.](image-url)
3.1.7. Black

The IRFC photography determined that the black paints were very often mixtures of black with other pigments. The SEM-EDS and PLM analyses revealed that bone black is prevalent only in black brushstrokes of Autumn colours (sample 9). The intense black found in other paintings resulted entirely from mixing carbon blacks with ultramarine, Prussian blue, cobalt blue, and viridian. In Village scene (sample 13, 14) and Landscape in Switzerland (sample 18), it is evident that the role of the black pigment is taken by ultramarine.

3.2. Binding Media and Other Identified Compounds

The FTIR spectra from all the examined paint samples depicted characteristic bands at around 2925, 2850, 1730, 1460, 1160, and 720 cm\(^{-1}\), confirming a consistent use of drying oil. Furthermore, the presence of zinc soap was confirmed by an absorption peak at 1539 cm\(^{-1}\) in Countryside in France (sample 7) and Landscape in Switzerland (sample 20), while lead soap was found in French lady (sample 16) by an absorption peak at 1514 cm\(^{-1}\). The formation of metal soaps can be explained by the probable reaction of free fatty acids from the oil binder with metals present in the lead- and zinc-containing pigments [51,52]. The detection of the acrylic resin in three of the investigated samples may correspond to the varnish applied during the conservation treatments [43,53,54].

3.3. Painting Process

It is noteworthy that the VIS and NIR photography of the paintings did not detect the presence of the preparatory underdrawings. However, Liu Kang probably studied the subject matter by small-scale sketching prior to painting the composition on the canvas. For instance, a watercolour sketch of Breakfast from the Liu collection reveals an early idea of the composition for the canvas painting Breakfast, which was executed in the same year (Figure 15). Technical evidence from the Countryside in France, Village scene, Breakfast, and Self-portrait indicated that the artist approached the canvas with a clear concept of the general composition, which was established with rough brushstrokes usually of a black paint (Figure 1b,d,g and Figure 2e).
The next step of the painting process involved a gradual colouring in of the outlines of the forms, providing the base for further work, as seen in *Countryside in France* and *Landscape* (Figures 1b and 2b). This method, known as *ébauche* (coloured sketch), was a common practice among Impressionists [55]. Analyses of the brushstrokes revealed that the middle-ground buildings of *Countryside in France* and the foreground house and a tree of *Landscape* were painted first. Then, the artist continued building the colouristic structure around these main subjects. The sky in *Countryside in France* was probably sketched at the end, after the background greenery was completed. Both sketches were conducted in local, vivid colours. A minimal suggestion of light effects observed in the sky of *Countryside in France* was achieved by the increased transparency of the colour, allowing the white ground to show through. The rapid development of the composition during the initial painting phase was facilitated by a few factors observed in *Countryside in France*. The small size of the painting support (number 10) reduced the time required to cover the surface with colours. The use of the absorbent or semi-absorbent ground with the ability to draw the oil from the paint accelerated the drying of the paint layer [9,56]. A thin application of colours mixed with lead white promoted the rapid drying of the paint layer. The presence of the signatures and dates indicates that the artist envisaged the coloured sketches as a completed exercise.

The further painting process can be observed in *My landlady, Madame Normand* (Figure 2f). Here, the artist intensified the colours of the main subject and built-up details with thicker paint. The advanced light effects were achieved by the increased opacity of different tints of white paint. Although the green background is sketchy and transparent, the artist’s signature and date on the painting indicate that he considered the artwork as completed.

Liu Kang’s variety of methods of handling the paint show constant self-development. In *Autumn colours*, his application of the paint using a small brush in short, vigorous, and descriptive paint touches reflects his attention to detail (Figures 1a and 16a). A daring adoption of parallel brushstrokes in *St Gingolph, Lac Leman, Switzerland* is reminiscent of van Gogh’s style (Figures 2a and 16b). The structure of the paint layer with attractive touches is achieved by contrasting juxtaposition of greens with reds and yellows with blues. However, another painting, *Landscape in Switzerland*, shows some modification to this painting method. While the background depicting lake, mountains, and sky was conducted with directional touches, the foreground buildings and fields are depicted by coloured patches (Figures 1c and 16c,d).
The analyses of the paint structure of *Landscape in Switzerland* revealed the hardened brushwork beneath the upper layers, suggesting that the painting, including the signature and date, was executed in a wet-on-dry technique, as illustrated by the microscopic images (Figures 10 and 11b). Hence, two distinct painting sessions can be identified, where the second session, according to the artist’s date and signature, could have been in 1930, at least six months after Liu Kang’s trip to Switzerland. A combination of wet-on-wet and wet-on-dry paint applications was detected in other examined paintings, suggesting that the artist did not attempt to complete the work at one sitting and sometimes worked further on the composition after the initial painting was dry. This tendency could be a result of Liu Kang working on several paintings during one session as documented in the photograph from 1929 taken in Saint-Gingolph, Switzerland. Interestingly, one of the paintings seen in the photograph appears to be unfinished; hence, it can be hypothesised that the artist tended to apply finishing touches later (Figure 17).
A good example of a painting executed rapidly in a single sitting is Village scene. In this artwork, there are significantly few details while the general artistic expression is achieved by directional and highly textured brushwork combined with solid colours (Figures 1d, 5b and 18c,d). Meanwhile, Boat near the cliff is characterised by a synthesis of colours and forms achieved by the broad and flat application of the paint (Figure 1f). Although the painting appears to be spontaneously and rapidly executed, the analyses proved a wet-on-dry execution, suggesting that later modifications were conducted over previous partially hardened touches.

During the painting process, Liu Kang experimented with incorporating the white colour of the ground layer with other paint colours reflecting inspiration from Modernists' techniques [9,57]. A good example is Countryside in France, in which the colour of the exposed ground was utilised for depicting the main building (Figure 14a). In contrast, the ground in Landscape remains exposed between the patches of applied paint, giving the artist a chance to make adjustments of colour and form (Figure 2b). In Boat near the cliff, the ground was used as a highlight and colour in its own right to describe foamy water (Figure 18a). However, Still life with books, Paris, and Village scene exhibit a new experiment with a white ground. Liu Kang enhanced the brilliance of the painted scenes by exposing bright accents of the white ground through the spaces between directional brushstrokes (Figures 5b and 18b,c). This painting method seems to support the notion that the artist sometimes skipped the colour sketching and confidently applied the colours after establishing the general composition with dark outlines. Moreover, to moderate the monotony of a methodical brushwork, the artist creatively produced effects of the broken flow of the paint, by dragging a loaded brush across the textured ground layer (Figures 5b and 18a–c) [9].

An interesting example of the artist's inventive way of utilising the colour and texture of the painting support is Self-portrait (Figure 19). As it was executed on the reverse side of an earlier composition, the brownish canvas made it particularly well suited for providing colouristic unity among the mixed yellows and browns. Moreover, the colour and texture of an un-primed canvas were skilfully exposed to give an impression of the back side of a depicted painting.
Figure 19. Detail of Self-portrait, showing the incorporation of the colour and texture of the painting support in depicting the reverse side of the painting in his artwork. The inset detail shows the structure of the canvas.

Another feature common in the examined paintings is the presence of a strong contour. The lines accompany the painting process from the sketching until the final stage, and they play a crucial role in the aesthetic of the paintings giving greater definition to the forms of the subjects. In Village scene, some of the initial compositional lines describing the highest distant hilltops as well as the shapes of the houses are still visible through the paint layer (Figure 18c,d). In the final stage, the artist usually reinforced the outlines of the subjects with a dark paint composed mainly of bone black with ultramarine and/or Prussian blue, as identified in Village scene (sample 13, 14), Landscape in Switzerland (sample 18), and Breakfast (sample 14).

3.4. Reusing Earlier Paintings

The evidence collected from five examined paintings revealed that Liu Kang had a practice of reusing earlier, unwanted compositions or utilising their reverse sides. For example, a visual inspection of the painted edges of the St Gingolph, Lac Leman, Switzerland revealed the presence of colours to be unrelated to the final image. The raking light and RTI examination of Autumn colours pointed out the surface brushstrokes that skip over the more complex texture of the underlying paint scheme. Subsequent transmitted NIR photography conducted with a camera facing the back of the painting revealed a presence of a still life composition that had been created in the vertical orientation. Further XRR analysis confirmed that the underlying painting depicts plants in flowerpots (Figure 20).

A visual examination of Breakfast provided some indications of another composition underneath. For instance, a different paint scheme was observed in the areas that were not completely covered by the current painting. Moreover, the final paint layer is characterised by several dark paint strokes that do not correspond to the present composition. They are visible on the green table top and red background, probably due to decreasing hiding power of thinly applied upper paint layer (Figure 21) [58]. This feature is similar to the reported case study of Seafood by Liu Kang, in which his hidden self-portrait was discovered beneath [8]. The NIR photography of Breakfast rotated 180° revealed a view that could be interpreted as a riverbank with trees.

Besides the aforementioned examples of paintings over discarded compositions, Liu Kang also utilised the reverse sides of earlier paintings. Self-portrait and Portrait of a man with his pipe, Paris are examples of artworks created directly on un-primed canvases. The
artist’s practice of reusing unsatisfactory compositions or utilising their reverse sides could have been motivated by a temporary shortage of materials or by financial constraints.

Figure 20. Images of *Autumn colours* rotated at 90° anticlockwise and photographed in: (a) VIS; (b) RTI; and (c) transmitted NIR executed with camera facing the back of the painting, then cropped to remove the strainer bars, inverted horizontally, and reproduced with the same relative scale; (d) XRR. The images revealed paint features of hidden still life painting with plants in the flowerpots.

Figure 21. VIS (a) and NIR (b) images of *Breakfast* rotated at 180°. NIR reveals the hidden view of a riverbank with trees.

4. Conclusions

The study of Liu Kang’s paintings from the Paris phase provides information about the artist’s choice of pigments and advances our knowledge of his working practice. Selecting artworks from both the NGS and Liu family collections enabled the tracking of the development of the artist’s painting technique during the said period. In addition, the artist’s family archives provided insights into his painting process. The imaging techniques, such as IRFC and UVR, played a crucial role in the tentative identification of pigments and guiding sampling of the material for further detailed analyses. RTI, XRR, and NIR provided valuable information about artist’s painting process by visualising the hidden compositions underlying *Autumn colours* and *Breakfast*. The MA-XRF scanning of *Landscape in Switzerland* highlighted the distribution of elements that are indicative of certain pigments and their role in the evolution of the painting. Additional PLM, SEM-EDS, and FTIR analyses led to the identification of the paint mixtures. The contemporary colourmen catalogues are a precious resource that supplemented the interpretation of certain materials found in the course of paints’ analyses.

The interpretation of the collected data unveiled a restricted palette of colours and the preferential use of ultramarine, viridian, chrome yellow, iron oxides, organic reds,
lead white, and bone black. These major pigments were accompanied with the artist’s admixtures. For instance, cobalt blue was hardly used and was recorded in some blue, green, and black paint mixtures. Prussian blue was used as a tint for green and black colours. Emerald green had a similar role as an admixture of greens. Additions of cadmium yellow and cobalt yellow are interesting as they were found exclusively in Landscape in Switzerland. PLM, SEM-EDS, and FTIR were particularly effective with the detection of three types of organic reds. One could be an organic red on tin and starch substrates. The second is probably a compound related to eosin red on Al- or Pb-containing substrate—known as a geranium lake. The third is probably an organic red on an Al-containing substrate. However, more analyses are needed to better characterise the organic red pigments. Although lead white is a predominant white pigment, its role seems to have been reduced in favour of the lithopone and/or barium white and zinc white in Landscape in Switzerland and Boat near the cliff. Artist also liked to incorporate the white of the ground into the final effect. Carbon black was added to other colours to modify their shade. However, deep blacks usually appear in bold outlines and were achieved by mixing carbon black with ultramarine, Prussian blue, cobalt blue, and viridian.

FTIR analyses additionally confirmed the presence of an oil binder in all investigated paintings from the NGS collection. Moreover, the identification of formation of metal soaps and geranium lake pigment will have some relevance for future conservation diagnostics. This is because metal soaps may contribute to the deterioration process of the paint layers, while geranium lake has a strong fading tendency [59,60].

Studies of the artist’s technique revealed that he adopted coloured sketching; however, he was also able to skip this stage and effectively create compositions with rapid and decisive brushstrokes. It can be speculated that he had conducted small-scale compositional studies in different techniques prior to painting on the canvas. The subsequent progression of painting process can be characterised by constant and generally successful experimentation with brushwork. Ultimately, Liu Kang’s paintings from the Paris phase are defined by continual exploration and learning of different Modernist painting styles. This very mature artistic approach benefitted him upon his return to China, when he felt a strong need to develop his own painting style.

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### Table A1. Overview of the materials identified in the paint samples extracted from the investigated paintings from the NGS collection.

| Title and Inventory Number | Date | Colour | Sample | SEM-EDS * and XRF ** Detected Elements | PLM, SEM-EDS, XRF Assignment | FTIR Identification |
|----------------------------|------|--------|--------|----------------------------------------|------------------------------|---------------------|
| **Autumn colours**, GI-0255 (PC) | 1930 | Blue | 19 | C, O, Pb, Cr, Ca, Si, Al, Na, Ba, S, As, (Sr, Fe, Cu, Zn) | Lead white, lithopone and/or barium white and zinc white, chalk, viridian, ultramarine, emerald green or Sheele's green, Prussian blue | **Emerald green, barium white, lead white, emerald green or Sheele's green, Prussian blue** |
| Green | 5 | Green | 19 | C, O, Pb, Ba, Sr, S, As, Cr, Cu, (Si, Ca, Al, Fe, Na) | Lead white, barium white, chalk, viridian, emerald green or Sheele's green, Prussian blue | **Emerald green, barium white, lead white, possible chrome yellow, oil** |
| Green | 18 | Green | 19 | C, O, As, Cu, Ba, Pb, S, Ca, (Ti, Na, Cr, Cl, Si, Fe, Mn) | Emerald green, barium white, lead white, chalk, viridian, umber, possible Cr-containing yellow(s) and titanium white | **Emerald green, lithopone and/or barium white, lead white, possible chrome yellow, oil** |
| Yellow | 3 | Yellow | 19 | Pb, C, O, Ca, (Cl, Cr, Si, Al, Fe, Ba) | Lead white, chrome yellow, chalk, barium white, yellow iron oxide | **Lead white, chrome yellow, chalk, barium white, yellow iron oxide** |
| Brown | 4 | Brown | 19 | Pb, C, O, Ca, Fe, Al, Si, (Cr, Ba, Sr, Ti, Na) | Lead white, chalk, yellow iron oxide, barium white, possible Cr-containing yellow(s), and titanium white | **Lead white, barium white, yellow iron oxide** |
| Red | 7 | Red | 19 | O, C, Fe, Pb, Ca, Ti, Si, Al, Mg, (P, Na, Sr, Cl, Zn, K, Cr, S) | Red iron oxide, lead white, chalk, titanium white, bone black, possible Cr-containing yellow(s) | **Red iron oxide, lead white, chalk, titanium white** |
| Black | 9 | Black | 19 | C, O, Ca, Pb, P, (Si, Al, Na, Fe, Ba, Mg, Cr, Cl, Zn, As) | Bone black, lead white, lithopone and/or barium white and zinc white | **Bone black, lead white, lithopone and/or barium white and zinc white** |
| White | 2 | White | 19 | Pb, C, O, Ca, (Al, Cl, Si, Zn) | Lead white, chalk, zinc white | **Lead white, zinc white** |
| **Countryside in France, 2003-03365** | 1930 | Blue | 5 | C, O, Sb, As, Pb, Cr, Fe, S, Ca, Si, Al, Ti, (Na, K, Cr, Ti, Sr, Mg) | Lead white, carbon black, ultramarine, lithopone and/or barium white and zinc white, possible titanium white | **Lead white, carbon black, ultramarine, lithopone and/or barium white and zinc white, possible titanium white** |
| Green | 11 | Green | 19 | O, Pb, C, Ba, Cr, Fe, S, Ca, Si, Al, Ti, (Na, K, Zn, Cl) | Lead white, chalk, lithopone and/or barium white and zinc white, viridian, Prussian blue, possible Cr-containing yellow(s), titanium white | **Lead white, chalk, lithopone and/or barium white and zinc white, Prussian blue, possible chrome yellow, oil, acrylic resin assigned to the conservation varnish** |
| Green | 4 | Green | 19 | Pb, C, O, Cr, Ca, Ba, Si, Zn, Al, (S, Fe, Ti, Na) | Lead white, chrome yellow, possible other Cr-containing yellow(s), chalk, viridian, lithopone and/or barium white and zinc white, Prussian blue | **Lead white, chrome yellow, possible other Cr-containing yellow(s), chalk, viridian, lithopone and/or barium white and zinc white, Prussian blue** |
| Title and Inventory Number | Date | Colour | Sample | SEM-EDS * and XRF ** Detected Elements | PLM, SEM-EDS, XRF Assignment | FTIR Identification |
|---------------------------|------|--------|--------|----------------------------------------|-------------------------------|---------------------|
| Yellow                    | 9    | Yellow | Pb, C, O, Cr, (S, Cl, Na, Zn, Al) | Chrome yellow, zinc white     |                                |                     |
| Brown                     | 41   | Brown  | Pb, Fe, K, Si, Ca                | Lead white, iron oxide, chalk  |                                |                     |
| Brown                     | 49   | Brown  | Fe, Ca                          | Iron oxide, chalk              |                                |                     |
| Red                       | 7    | Red    | C, Pb, Ba, O, S, Cr, Al, Si, (Zn, Ni, Sr, Ca, P) | Lead white, chrome yellow, lithopone and/or barium white and zinc white, organic red, bone black | Lead white, chrome yellow, lithopone and/or barium white and zinc white, organic red, oil, zinc soap |
| Black                     | 16   | Black  | O, C, Pb, Si, Al, Na, Ba, S, Zn, Ca, (K, Cr, Ti, Sr) | Lead white, ultramarine, carbon black, lithopone and/or barium white and zinc white |                                |                     |
| White                     | 29   | White  | C, Pb, O, Ba, Ti, Zn, S, Na, (Fe, Si, Al) | Lead white, barium white, zinc white, titanium white | Lead white, barium white, zinc white, oil, proteins |
| **Landscape in Switzerland, P-1229** | 1930 | Blue   | Zn, C, O, Na, Al, Ca, Si, (S, Pb, Sr, Mg) | Zinc white, ultramarine, lead white |                                |                     |
| Green                     | 20   | Green  | Pb, C, O, Zn, Cr, Fe, Na, (Ba, Si, Al, Ca, Cl) | Chrome yellow, yellow iron oxide, Prussian blue, lead white, lithopone and/or barium white and zinc white | Chrome yellow, possible iron oxide, Prussian blue, lead white, lithopone and/or barium white and zinc white, oil, zinc soap, acrylic resin assigned to the conservation varnish |
| Green                     | 21   | Green  | C, O, Cd, Cr, S, Ba, Zn, Cl, (Na, Pb, Al, Si, Sn, Ti, Ca, Sr) | Cadmium yellow, lithopone and/or barium white and zinc white, viridian, chalk, lead white, chrome yellow, possible titanium white |                                |                     |
| Green                     | 24   | Green  | C, O, Pb, Ba, Zn, Cr, Al, Cl, Na, S, Fe, (Cu, Mg, Si, Ti, Ca, As, Sr, P) | Chrome yellow, viridian, Prussian blue, lithopone and/or barium white and zinc white, emerald green or Sheele’s green, possible titanium white |                                |                     |
| Yellow                    | 23   | Yellow | Pb, O, Zn, C, K, Na, Ba, Co, Cd, (Mg, Ca, Fe, Si, S, Al, Cr, Cl) | Chrome yellow, possible other Cr-containing yellow(s), lithopone and/or barium white and zinc white, cobalt yellow, cadmium yellow, yellow iron oxide |                                |                     |
| Yellow                    | 36   | Yellow | Zn, C, O, Pb, Na, Ca, Fe, K, Ba, Co, (Si, As, S, Mg, Al, Cr, Cl) | Lithopone and/or barium white and zinc white, lead white, chrome yellow, possible other Cr-containing yellow(s), yellow iron oxide, cobalt yellow |                                |                     |
| Title and Inventory Number | Date | Colour | Sample | SEM-EDS * and XRF ** Detected Elements | PLM, SEM-EDS, XRF Assignment | FTIR Identification |
|---------------------------|------|--------|--------|----------------------------------------|-------------------------------|---------------------|
| Brown                     | 25, layer 2 | O, Zn, C, Ba, Na, Pb, Fe, Ca, S, Al, Si, K, (Ti, Co, Mg, As, Sr, Cu) | Lithopone and/or barium white and zinc white, lead white, yellow iron oxide, cobalt yellow, possible emerald green or Sheele’s green and titanium white |
| Red                       | 25, layer 1 | C, O, Pb, Ca, Sn, Si, Fe, (Al, Ba, Zn, Na, Cl, Cr, Mg) | Lead white, organic red, red iron oxide, starch |
| Red                       | 35, layer 2 | O, Fe, C, Si, Al, Ca, (K, Sn, Mg, Ti, S, Pb, Zn) | Red iron oxide, organic red, chalk |
| Red                       | 35, layer 1 | C, O, Pb, Sn, (Cr, Fe, Ca, Si, Al, Cl) | Lead white, organic red, iron oxide, possible Cr-containing yellow(s) |
| Black                     | 18 | C, O, Zn, Al, Ca, Ba, S, Na, (Si, Fe, Pb, P, Sr, Mg, Cu, Cl) | Lithopone and/or barium white and zinc white, ultramarine, bone black, Prussian blue |
| White                     | 22 | Zn, C, O, Na, (S, Ba, Mg, Ca, Al) | Lithopone and/or barium white and zinc white, chalk |
| Village scene, 2003-03320 | 1931 | Blue 20 | Pb, C, O, Ca, (Na, Si, Al, Cr, Cl, Mg, Sr, Zn) | Lead white, ultramarine, viridian, chalk, possible zinc white |
| Green                     | 2 | C, Pb, O, Ba, Ca, Cr, S, Fe, (Zn, Al, Na, Si, Ti, Mg) | Lead white, lithopone and/or barium white and zinc white, chalk, viridian, Prussian blue |
| Green                     | 3 | O, Cr, C, Pb, Ca, (Zn, Na, Si, Mg, Al) | Viridian, lead white, chrome yellow, possible other Cr-containing yellow(s), chalk |
| Yellow                    | 8 | Pb, C, O, Cr, (Ca, S, Na, Si, Cl, Al) | Chrome yellow, chalk |
| Brown                     | 5 | Pb, C, O, Ca, Fe, Si, Al, (Zn, Sr, Mg, Cl, Ba, Cr, P) | Lead white, lithopone and/or barium white and zinc white, yellow iron oxide, bone black, possible Cr-containing yellow(s) |
| Brown                     | 10 | O, Fe, C, Ba, S, Ca, Si, (Pb, Al, Ti, Sr, Cl) | Yellow iron oxide, barium white, chalk, lead white |
| Red                       | 9 | C, O, Pb, Sn, Ca, Cr, Si, Fe, (Al, Zn, Ba, P) | Chrome yellow, possible lead white, organic red, starch, chalk, lithopone and/or barium white and zinc white, red iron oxide, bone black |
| Black                     | 13 | O, C, Ca, Si, Pb, Na, Al, S, P, Zn, (Ba, K, Fe, Sr, Cr, Cl) | Ultramarine, lead white, lithopone and/or barium white and zinc white, Prussian blue, bone black |
Table A1. Cont.

| Title and Inventory Number | Date    | Colour | Sample | SEM-EDS * and XRF ** Detected Elements | PLM, SEM-EDS, XRF Assignment | FTIR Identification |
|----------------------------|---------|--------|--------|----------------------------------------|-----------------------------|---------------------|
| Black                      | 14      |        |        | O, Pb, C, Si, Al, Na, S, Ca, (K, As, Zn, Ba, Fe, Sr, Cl) | Lead white, ultramarine, lithopone and/or barium white and zinc white, red iron oxide, carbon black |                     |
| White                      | 17      | Pb, C, O, Ca, (Cl, Al, Mg) |        | Lead white, chalk                       |                             |                     |
| *French lady, 1993-00996*  | 1931    | Blue   | 20     | C, O, Pb, Al, Ca, Ba, Si, Co, Na, (S, Cr, Mg, Ti, Sr, K, P, Fe, Zn, Cl) | Lead white, chalk, lithopone and/or barium white and zinc white, cobalt blue, viridian, ultramarine, bone black |                     |
| Green                      | 15      |        |        | C, O, Pb, Cr, Ba, Ca, (As, Si, Al, Na, Cu, Ti, Fe, Co, Cl, S) | Lead white, viridian, chalk, barium white, cobalt blue, Prussian blue, possible emerald green or Sheele's green and titanium white |                     |
| Green                      | 16      | Pb, C, O, Ba, Ca, As, Cr, S, Cu, (Fe, Ti, Na, Al, Si, Cl) |        | Lead white, barium white, chalk, emerald green, Prussian blue, possible Cr-containing yellow(s) and titanium white |                     |                     |
| Brown                      | 17      | Pb, O, C, Ca, Si, Fe, Al, (Zn, Ba, Cr, Cl, Mg, K, Na, Ti) |        | Lead white, yellow iron oxide, Cr-containing yellow(s), lithopone and/or barium white and zinc white |                     |                     |
| Red                        | 9       | Pb, C, O, Ca, Ba, Fe, Si, (Al, Cl, Cr, Ti, Mg) |        | Lead white, chalk, Cr-containing yellow(s), barium white, iron oxide |                     |                     |
| Black                      | 19      | O, C, Pb, Ba, Pb, Al, S, Co, Na, K, Si, As, (Ca, P, Ti, Zn, Mg, Cr, Sr, Cl) |        | Prussian blue, lithopone and/or barium white and zinc white, lead white, cobalt blue, bone black, viridian, possible titanium white |                     |                     |
| Black                      | 6       | O, C, Pb, Si, Al, S, Na, Ca, As, K, Fe, (Sr, Ba, Cl, Mg, Ti, Cr) |        | Lead white, ultramarine, carbon black, Prussian blue, barium white, viridian, possible titanium white |                     |                     |
| *Boat near the cliff, 2003-03249* | 1931    | Blue   | 3      | C, Zn, O, Ba, Na, S, Cr, (Al, Si, Sr) | Lithopone and/or barium white and zinc white ultramarine, viridian |                     |
| Blue                       | 21      | C, O, Na, Zn, Al, Si, S, Ba, (K, Sr, Cr, Ca, Cl) |        | Ultramarine, viridian, lithopone and/or barium white and zinc white |                     |                     |
| Blue                       | 26      | C, O, Ba, Zn, S, Cr, Na, Pb, (Ti, Ca, Al, Si, Co, Mg) |        | Lithopone and/or barium white and zinc white, lead white, viridian, ultramarine, cobalt blue |                     |                     |
### Table A1. Cont.

| Title and Inventory Number | Date | Colour | Sample | SEM-EDS * and XRF ** Detected Elements | PLM, SEM-EDS, XRF Assignment | FTIR Identification |
|----------------------------|------|--------|--------|----------------------------------------|--------------------------------|---------------------|
| Green                      | 11   | O, C, Ba, Zn, Pb, S, Fe, Cr, Ca, Na, Si, (Al, Ti, Mg, P, Cl, K) | Lithopone and/or barium white and zinc white, chalk, chrome yellow, yellow iron oxide, Prussian blue, viridian, bone black, possible titanium white |
| Green                      | 12   | O, C, Ba, Ca, Pb, S, Cr, Fe, (Ti, Sr, Si, Al, Na, Zn) | Lithopone and/or barium white and zinc white, viridian, Prussian blue, chrome yellow |
| Yellow                     | 25   | O, C, Ba, Ca, Pb, S, Zn, Cr, (Sr, Na, Ti, Mg, Si, Al, Cd, Fe) | Lithopone and/or barium white and zinc white, chrome yellow, cadmium yellow, iron oxide, possible titanium white |
| Brown                      | 14   | C, O, Zn, Fe, Na, Al, Ba, (Ca, P, Si, Mn, Mg, Cr, Pb, Sr) | Lithopone and/or barium white and zinc white, umber, bone black, chrome yellow, possible other Cr-containing yellow(s) |
| Red                        | 29   | C, O, Pb, Ba, Br, Al, S, (Si, Ti, Cl, Ca) | Br-containing organic red on Pb- or Al-based substrate, barium white, possible titanium white | Lithopone and/or barium white, organic red, oil, acrylic resin assigned to the conservation varnish |
| Black                      | 17   | C, O, Zn, Pb, Na, Mg, (Si, Al, Fe, S, Ba, Ca, K) | Lithopone and/or barium white and zinc white, lead white, carbon black, Prussian blue |
| White                      | 22   | Zn, C, O, Na, (Si, Mg, Pb, Al) | Zinc white, lead white |
| Breakfast, GI-0257 (PC) 1932 | 4    | O, Cr, C, Pb, Ba, S, Ca, (Na, Al, Si, Mg, Ti, Sr) | Viridian, lead white, barium white, chalk, possible titanium white |
| Yellow                     | 3    | O, C, Fe, Si, Pb, Al, Ca, (K, As, Cr, Sr, P, Ba, Cl, Ti, Zn) | Yellow iron oxide, chrome yellow, lead white, lithopone and/or barium white and zinc white, bone black, possible titanium white |
| Brown                      | 10   | O, C, Fe, Si, Pb, Al, Sn, Ca, Sr, Ba, K, (Ti, Cr, Mg, Cl, Zn, P) | Red iron oxide, organic red, lead white, chalk, Prussian blue, starch, Cr-containing yellow(s), lithopone and/or barium white and zinc white, bone black, possible titanium white |
| Black                      | 14   | O, Ca, Pb, C, Cr, P, Ba, Si, (Fe, Al, Na, Ti, Mg, K, Cl, Sr) | Lead white, bone black, viridian, barium white, Prussian blue, possible titanium white |
| White                      | 7    | Pb, C, O, Ca, (Cl, Si, Na, Al, Mg) | Lead white, chalk |

* Major elements are given in bold, minor elements in plain type and trace elements in brackets. ** Elements detected with XRF are given in italics.
Figure A1. ATR-FTIR spectra of green paint from sample 18, taken from Autumn colours, with labelled marker peaks of emerald green and spectra of a reference sample of emerald green.
Figure A2. Compositions of pigments, listed in the catalogue of W&N from 1928, used for the manufacturing of oil and watercolours. The highlighted details show carmines, varieties of chrome greens, cinnabar green, cobalt yellow, emerald green, and geranium lake.
Figure A3. Oil colours, listed in the catalogue of Bourgeois Aîné from 1929. The highlighted details show carmines, a range of madder lakes, geranium lake, geranium red, varieties of chrome greens, emerald green, Scheele’s green, and its variant mineral green.
Figure A4. Oil colours listed in the catalogue of Lefranc from 1931. The highlighted details show carmines, geranium lake, a range of madder lakes, varieties of chrome greens, emerald green, Scheele's green, and its variant mineral green.
35. Kirby, J., van Bommel, M., Verhecken, A., Spring, M., Vanden Berghe, I., Stege, H., Richter, M. Natural Colorants for Dyeing and Lake Pigments: Practical Recipes and Their Historical Sources; Archetype Publications: London, UK, 2014; pp. 78, 101.

36. Schweppe, H.; Roosen-Runge, H. Carmine–Cochineal Carmine and Kerme Carmine. In Artists’ Pigments: A Handbook of Their History and Characteristics; Feller, R.L., Ed.; National Gallery of Art: Washington, DC, USA, 1986; Volume 1, p. 37.

37. Callen, A. Techniques of the Impressionists; Orbis: London, UK, 1982; pp. 155, 178.

38. Brill, T.B. Light: Its Interaction with Art and Antiquities; Plenum Press: New York, NY, USA, 1980; p. 89.

39. Kühn, H. Zinc white. In Artists’ Pigments: A Handbook of Their History and Characteristics; Feller, R.L., Ed.; Archetype Publications, ICN Amsterdam: London, UK, 2005; p. 75.

40. Duffy, M.; Martins, A.; Boon, J.J. Metal Soaps and Visual Changes in a Painting by René Magritte—The Menaced Assassin, 1927. In Issues in Contemporary Oil Paint; van den Berg, K.J., Burnstock, A., de Keijzer, M., Krueger, J., Learner, T., Tyle, A., Heydenreich, G., Eds.; Springer International Publishing: Cham, Switzerland, 2014; pp. 197–203.

41. Hermans, J.J.; Keune, K.; Van Loon, A.; Iedema, P.D. Toward a Complete Molecular Model for the Formation of Metal Soaps in Oil Paints. In Metal Soaps in Art: Conservation and Research; Casadio, F., Keune, K., Noble, P., Van Loon, A., Hendriks, E., Centeno, S.A., Osmond, G., Eds.; Springer International Publishing: Cham, Switzerland, 2019; pp. 47–67.

42. Fieberg, J.E.; Knutås, P.; Hostettler, K.; Smith, G.D. “Paintings fade like flowers”: Pigment analysis and digital reconstruction of a faded pink lake pigment in Vincent van Gogh’s Undergrowth with two figures. Appl. Spectrosc. 2017, 71, 794–808. [CrossRef] [PubMed]

43. Van Bommel, M.; Geldof, M.; Hendriks, E. An Investigation of Organic Red Pigments Used in Paintings by Vincent Van Gogh (November 1885 to February 1888). In ArtMatters-Netherlands Technical Studies in art; Hermens, E., Ed.; Waanders Publishers: Zwolle, The Netherlands, 2005; Volume 3, pp. 128, 129.

44. Centeno, S.A.; Hale, C.; Caro, F.; Cesariotto, A.; Shibayama, N.; Delaney, J.; Dooley, K.; van der Snickt, G.; Janssens, K.; Stein, S.A. Van Gogh’s Irises and roses: The contribution of chemical analyses and imaging to the assessment of color changes in the red lake pigments. Herit. Sci. 2017, 5, 18. [CrossRef] [PubMed]

45. Kirby, J. The Reconstruction of Late 19th-Century French Red Lake Pigments. In The Art of the Past: Sources and Reconstruction: Proceedings of the First Symposium of the Art Technological Source Research Study Group; Clarke, M., Townsend, J., Stijnman, A., Eds.; Archetype Publications, ICN Amsterdam: London, UK, 2005; p. 75.

46. Kirby, J.; van Bommel, M. Bright New Colours: The History and Analysis of Fluorescein, Eosin, Erythrosine, Rhodamine and Some of Their Derivatives. In The Diversity of Dyes in History and Archaeology; Kirby, J., Ed.; Archetype Publications: London, UK, 2017; pp. 326–338.

47. Kirby, J.; van Bommel, M. Bright New Colours: The History and Analysis of Fluorescein, Eosin, Erythrosine, Rhodamine and Some of Their Derivatives. In The Diversity of Dyes in History and Archaeology; Kirby, J., Ed.; Archetype Publications: London, UK, 2017; pp. 326–338.

48. Kirby, J.; van Bommel, M. Bright New Colours: The History and Analysis of Fluorescein, Eosin, Erythrosine, Rhodamine and Some of Their Derivatives. In The Diversity of Dyes in History and Archaeology; Kirby, J., Ed.; Archetype Publications: London, UK, 2017; pp. 326–338.

49. Kirby, J. The Reconstruction of Late 19th-Century French Red Lake Pigments. In The Art of the Past: Sources and Reconstruction: Proceedings of the First Symposium of the Art Technological Source Research Study Group; Clarke, M., Townsend, J., Stijnman, A., Eds.; Archetype Publications, ICN Amsterdam: London, UK, 2005; p. 75.

50. Kirby, J.; van Bommel, M. Bright New Colours: The History and Analysis of Fluorescein, Eosin, Erythrosine, Rhodamine and Some of Their Derivatives. In The Diversity of Dyes in History and Archaeology; Kirby, J., Ed.; Archetype Publications: London, UK, 2017; pp. 326–338.