

Article

Is There an International Klein Pink?

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Abstract: Yves Klein (1928–1962) is best known for his intensely blue monochromatic works made with International Klein Blue (IKB), a synthetic ultramarine blue pigment bound in a poly(vinyl acetate) binder. However, he also made monochromes in other colors, including red and pink, the pigments of which have never been elucidated. Analysis of one sculpture, three paintings, and one screenprint by micro-Fourier transform infrared spectroscopy (μ -FTIR), Raman and surface-enhanced Raman (SERS) spectroscopies, portable X-ray fluorescence spectroscopy (p-XRF), and scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectrometry (EDX), revealed that Klein used, knowingly or unknowingly, a variety of pink and red pigments, including Para Red, rhodamine 6G, rhodamine B, eosin Y, and alizarin lakes. The unexpected variety of pigments contrasts with his use of a single blue pigment and suggests he may not have held a singular vision of what constituted an iconic red or pink color.

Keywords: Yves Klein; pigments; μ -FTIR; Raman; SERS; SEM-EDS

1. Introduction

Yves Klein (1928–1962) was an artist who sought to free painting from historic constraints of subject matter, media, and methods of paint application. In the early 1950s, he began experimenting with monochromatic works in green, yellow, blue, pink, red, and orange. These works were first publicly presented in his 1954 books *Yves Peintures* and *Haguenault Peintures* [1,2]. As he continued to create monochromes, Klein became frustrated that the color of pure pigments dulled upon mixing with a binder, saying: “I did not like colors ground with oil. They seemed to be dead. What pleased me above all were pure pigments in powder like the ones I often saw at the wholesale color dealers. They had a burst of natural and extraordinarily autonomous life . . . What upset me was to see this incandescent powder lose all its value and become dulled and lowered in tone once it was mixed with glue or whatever medium was intended to fix it to its support” [3,4].

To overcome this difficulty he collaborated with Édouard Adam, a Parisian color-man, to create a paint using synthetic ultramarine blue ($\text{Na}_{8-10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}$; Pigment Blue 29) bound in poly(vinyl acetate) (Rhodpas M 60 A manufactured by Rhône Poulenc, [PVAc]) dispersed in ethanol and ethyl acetate [5], and in 1960 they submitted the recipe of their new paint, International Klein Blue (IKB) to the French Institute National de la Propriété Industrielle and received a Soleau envelope number 63,471 [6]. Although not an official patent, this attested to the importance of their invention and served as proof of priority for this new paint [6,7]. Subsequent studies of paint samples taken from Klein’s objects painted with IKB, including paintings, sculptures, and paint rollers by researchers at the Centre National de la Recherche Scientifique in Paris, France confirmed the identity of the medium as PVAc and the pigment as ultramarine [6].

While Klein is best known for his IKB paintings and eventually came to also favor a monochromatic trinity created through the use of blue, pink, and gold [4], he never



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abandoned other colors. However, few analyses have been performed on his non-IKB monochromes. In 1993, Sonoda, Rioux, and Duval analyzed *Monochrome orange* (June 1955), *Monochrome jaune* (1957), *Monochrome vert* (1957), and *Monochrome blanc* (1958), in addition to *Monochrome IKB 3* and *Anthropométrie*, all of which contain a PVAc binder [5]. Analysis was carried out on samples by pyrolysis gas chromatography (Py-GC) and Fourier-transform infrared spectroscopy (FTIR). Other than the IKB works, *Monochrome blanc* was the only one of these monochromes to contain a single pigment, lithopone ($\text{BaSO}_4 \cdot \text{ZnS}$; Pigment White 5). The other three works contain more complex mixtures: in *Monochrome orange*, Hansa orange ($\text{C}_{18}\text{H}_{18}\text{N}_4\text{O}_5$; Pigment Orange 1) and calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$); in *Monochrome jaune*, zinc yellow (ZnCrO_4 ; Pigment Yellow 36) and lithopone; and in *Monochrome vert*, Hansa Yellow 10G ($\text{C}_{16}\text{H}_{12}\text{Cl}_2\text{N}_4\text{O}_4$; Pigment Yellow 3), phthalocyanine blue ($\text{C}_{32}\text{H}_{16}\text{CuN}_8$; Pigment Blue 15), and lithopone. It is unclear whether Klein purchased these mixtures ready-made or if he mixed fillers such as calcium sulfate dihydrate and lithopone with pigments to create a specific tonality or to modify the handling properties of the paint. It is also unclear if Klein knew he was choosing to use organic pigments that might prove more prone to light-induced fading than inorganic pigments.

At the time of writing, no published work identifying Klein's red and pink pigments could be found in the literature, and Klein also provided little information about his materials. In his self-published newspaper from 1960, *Dimanche: Le Journal d'un Seul Jour*, he described the use of carmine and madder pinks and indicated that the term "IKP" or "International Klein Pinck" [sic] referred to a pink madder lake (literally "lacque de garance rose") (Figure 1) [8]. However, this has not been confirmed through scientific analysis of artworks. It is also unclear if he used a single pigment across all his pink works, similar to his use of a single blue pigment, and if the colorants in his red and pink works are the same, with tonality differences arising from different pigment to filler ratios.

To address this void, five red and pink works by Klein were analyzed (Table 1, Figure 2): *Untitled Red Monochrome (M 63)* (1959) at the Solomon R. Guggenheim Museum, New York, NY, USA; *Grand Monopink (MP 16)* (1960) at the Louisiana Museum of Modern Art, Humlebaek, Denmark; *Red Rain (Pluie Rouge) (S 37)* (1961) and *Untitled Shroud Anthropometry (ANT SU 4) (Anthropométrie suaire sans titre [ANT SU 4])* (ca. 1960), both at the Menil Collection, Houston, TX, USA; and a pink silkscreen print from 1961 held by The Museum of Modern Art, New York, NY, USA. Klein had already shown monochromatic works in orange, yellow, red, pink, and blue at the Club des Solitaires in Paris in October 1955 and during *Yves: Proposition monochromes* at Gallery Colette Allendy in February 1956 [6,9]. So, while the works studied here are not amongst his earliest monochromes and span a relatively short time frame of three years, they nevertheless present a variety of formats in which Klein used the colors red or pink.

While *Untitled Red Monochrome (M 63)* and *Grand Monopink (MP 16)* are quite different in scale (23.5×33 cm and 199×153 cm, respectively), they represent what is most emblematic about Klein's style: a textured painted surface that appears a single, vibrant color. These two paintings follow Klein's classic approach to the creation of two-dimensional monochromes [6]. Both pictures utilize a stiff board as a support, and in the case of the larger work Klein applied an additional fabric layer to the board; he typically used fine cotton gauze. Klein then applied his paint using a lambskin roller to achieve the richly textured surface he preferred.

In a 1957 show, *Pigments purs*, at the Galerie Colette Allendy, Klein exhibited a tray of ultramarine blue pigment on the floor, something he considered to be a painting on the ground, with the pigment fixed in place by gravity [1]. Over this tray, he installed a sculpture, *Blue Rain*. The first version of the sculpture was lost or destroyed, and Klein later created a second version of *Blue Rain* for his 1961 retrospective *Monochrome und Feuer* at Museum Haus Lange, Krefeld (now part of Kunstmuseen Krefeld, together with Haus Esters and Kaiser Wilhelm Museum) where it was accompanied by *Red Rain (S37)* (1961) [9]. These sculptures consist of around a dozen thin, painted wooden dowels approximately two meters long that were meant to be hung from the ceiling using thin filaments with

their bottom edges hovering over a tray of pigments. These works summon pigments from the void and also reflect his contemporaneous interest in dissociating himself from the act of creation. In his 1961 Chelsea Hotel Manifesto, he wrote “I felt the urge to register the signs of atmospheric behavior by recording the instantaneous traces of spring showers on a canvas, of south winds, and of lightning . . . ” [10]; with his sculptural rains, Klein conjures such an atmospheric imprint.



Figure 1. Image from the front page of (a) *Dimanche: Le Journal d'un Seul Jour*, which additionally shows *Le saut dans le vide* (*Leap into the Void*), Fontenay-aux Roses, France, 23 October 1960, and (b) detail image of the section describing “I.K.P” as “International Klein Pinck”[sic] (highlights added by authors). Digital scan courtesy of the Hirsch Library, Museum of Fine Arts, Houston. Credit for *Dimanche: Le Journal d'un Seul Jour*: © Succession Yves Klein c/o Artists Rights Society (ARS), New York/ADAGP, Paris 2023. Credit for *Le saut dans le vide* (*Leap into the Void*): Artistic action by Yves Klein © The Estate of Yves Klein c/o ADAGP, Paris 2023 Collaboration Harry Shunk and János Kender © J. Paul Getty Trust. Getty Research Institute, Los Angeles (2014.R.20). All reproductions of this work are excluded from the CC: BY License.

Table 1. Materials identified in red and pink artworks by Yves Klein.

Title	Institution	Dimensions	Media Description	Binding Media	Pigments and Fillers	Analytical Techniques
<i>Untitled Red Monochrome</i> (M 63) (1959)	Solomon R. Guggenheim Museum	23.5 × 33 cm	Dry pigment in synthetic resin on board	PVAc	Top layer: Eosin-Y lake, aluminum sulfate Bottom layer: Rhodamine B, aluminum sulfate	μ-FTIR, Raman, SERS, SERS, p-XRF

Table 1. Cont.

Title	Institution	Dimensions	Media Description	Binding Media	Pigments and Fillers	Analytical Techniques
<i>Grand Monopink (MP 16) (1960)</i>	Louisiana Museum of Modern Art	199 × 153 cm	Pure pigment and synthetic resin on fine canvas mounted on panel	PVAc	Alizarin lake, calcium sulfate, aluminum sulfate, ultramarine	μ-FTIR, Raman, SERS, SEM-EDX
<i>Red Rain (Pluie Rouge) (S 37) (1961)</i>	The Menil Collection	208.9 × 27.9 × 1.1 cm	Dry pigment in synthetic resin on eleven separate hanging wood dowels	PVAc	<i>Top Layer:</i> Para Red, Synthetic alizarin, aluminum sulfate <i>Bottom Layer:</i> Synthetic alizarin lake, Rhodamine 6G, aluminum sulfate	μ-FTIR, Raman, SERS, SEM-EDX
<i>Untitled Shroud Anthropometry (ANT SU 4) Anthropométrie suaire sans titre [ANT SU 4] (ca. 1960)</i>	The Menil Collection	65.4 × 94 cm	Dry pigment in synthetic resin on fabric	PVAc	Para Red, synthetic alizarin, aluminum sulfate	μ-FTIR, Raman, SERS, p-XRF
<i>Plate from Monochrome und Feuer (1961)</i>	The Museum of Modern Art	31.8 × 23.4 cm	Screenprint	Oil-based printing ink	Rhodamine 6G, calcium carbonate	μ-FTIR, SERS

Dissociation from the act of creation also lies behind Klein's anthropometry series, of which *Untitled Shroud Anthropometry (ANT SU 4)* is a prime example. In these works, Klein created paintings through the use of 'living brushes,' often nude women, who smeared themselves or rolled in paint and then imprinted their figures onto canvas as verbally directly by Klein. Through this non-traditional use of the traditional artist's model, Klein sought to accomplish two objectives. Firstly, to recreate a practice he had learned about during his stay in Japan where artists used their bodies as brushes [10]; and secondly, to use the presence of these women in his studio to prevent himself from "secluding himself in the overly spiritual spheres of creation" and avoid what he termed the "terrifying mirror" created when an artist faces their canvas alone [10].

The final work in this study is a pink monochrome screenprint that was included along with blue and gold leaf monochromes in a 1961 exhibition catalog that accompanied *Monochrome und Feuer* at Museum Haus Lange [9]. Although Klein reportedly created the gold monochrome print himself, they were actually prepared by the museum staff, and it is unclear who printed the pink and blue prints [4]. Incidentally, this was Klein's only museum retrospective during his lifetime, and featured many of the artist's signature works, such as architectural drawings, his *Mur de Feu*, as well as blue, pink, and gold monochromes. Interestingly, two works from that exhibition include "IKP" in their titles as described in the accompanying catalog: a painted sponge sculpture titled *Lecteur I.K.P.* (1960), now held in the collection of the Buffalo AKG Art Museum, and *Grand Monopink (MP 16)*, under study here, which was listed under the title *I.K.P. 1960*.

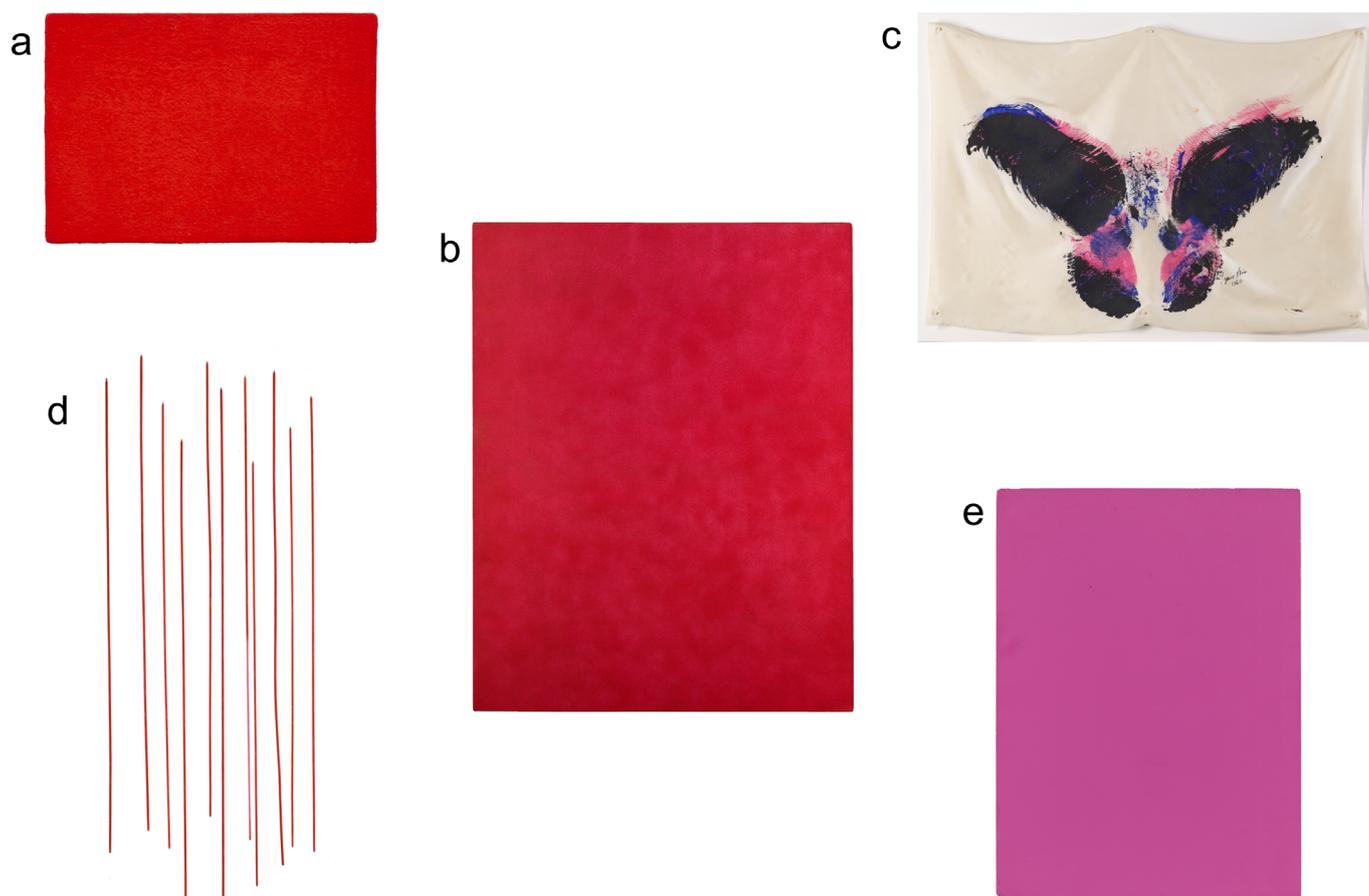


Figure 2. (a) Untitled red monochrome (M 63), 1959. Dry pigment in synthetic resin on board (23.5 × 33 cm). Solomon R. Guggenheim Museum, New York Gift, Andrew Powie Fuller and Geraldine Spreckels Fuller Collection, 1999; (b) Grand Monopink (MP 16), 1960. Pigment on canvas, mounted on board (flock printing) (199 × 153 × 5 cm). Louisiana Museum of Modern Art Long-term loan. Museumsfonden af 7. December 1966; (c) Untitled Shroud Anthropometry (ANT SU 4) (Anthropométrie suaire sans titre [ANT SU 4]), ca. 1960. Dry pigment in synthetic resin on fabric (65.4 × 94 cm). The Menil Collection; (d) Red Rain (Pluie Rouge) (S 37), 1961. Dry pigment in synthetic resin on eleven separate hanging wood dowels (208.9 × 27.9 × 1.1 cm). The Menil Collection; (e) Plate from Monochrome und Feuer, 1960. Screenprint from exhibition catalog with two screenprints and one gold leaf on cardboard, page (each) (31.8 × 23.4 cm). The Museum of Modern Art. © 2023 The Estate of Yves Klein c/o ARS New York/ADAGP Paris/BUS, Stockholm, 2023. All reproductions of this work are excluded from the CC: BY License.

Overall, these five works offer a chance to interrogate Klein's pink and red color choices through a variety of artistic creations and media that encompass much of his oeuvre. Colorants and fillers were identified by Raman and surface-enhanced Raman (SERS) spectroscopy, micro-Fourier transform infrared spectroscopy (μ -FTIR), portable X-ray fluorescence spectroscopy (p-XRF), and scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDX). Binders were also investigated with the use of μ -FTIR. The results presented here show that Klein used a variety of different pigments, and in at least two cases altered the colors in his works from pink to red or made deliberate use of layering to manipulate the visible surface colors.

2. Materials and Methods

2.1. Analysis at the Menil Collection

Cross-section samples were embedded in Epofix epoxy resin (Electron Microscopy Sciences, Hatfield, PA, USA), coarse ground using Micro Mesh MX sheets (120 and 150 grit),

and fine polished using Micro Mesh sheets (1500–12,000 grit) (Scientific Instrument Services, Palmer, MA, USA). Images of the samples under both normal oblique and UV illumination using B-2A or V-2B filter cubes were obtained using a Zeiss AxioCam MRc5 camera controlled by Zeiss Axiovision AC software release 4.5 (White Plains, NY, USA) and mounted onto a Nikon Labophot-Pol optical microscope (Melville, NY, USA) equipped with 10 \times , 20 \times , and 40 \times objectives. Scale bars were created in Adobe Photoshop (Adobe Inc., San Jose, CA, USA) using images of a micrometer scale taken using the same objective.

Dispersive Raman spectra were collected on a Renishaw InVia Raman microscope (West Dundee, IL, USA) running WiRE software version 5.5 using a 785 nm excitation laser operating at powers of 75 to 782 μ W at the sample as measured using a PM100D laser power meter (Thorlabs, Newton, NJ, USA) equipped with an S120C photodiode power sensor. A 50 \times objective was used to focus the excitation beam on the sample supported on a glass microscope slide. The resulting Raman spectra are the average of 1 to 15 scans of 10 s duration. The spectral resolution was 3–5 cm^{-1} across the spectral range analyzed. Sample identification was achieved by comparison of the unknown spectrum to the spectra of reference materials, the KIK/IRPA Raman reference library [11], and those published in the literature.

μ -FTIR spectra were collected in transmission mode using a Bruker Lumos μ -FTIR microscope running Opus software version 8.2 (Billerica, MA, USA). Samples were prepared by flattening them in a diamond compression cell (S.T. Japan, Ft. Myers, FL, USA), removing the top diamond window, and analyzing the thin film in transmission mode on the bottom diamond window. The spectra are the average of 64 or 128 scans at 4 cm^{-1} spectral resolution.

Backscatter electron images of the uncoated cross-section samples were taken with a JEOL JSM-IT100 SEM (Peabody, MA, USA) with 20 kV voltage, running under low vacuum mode with a pressure of 50–55 Pa and a probe current of 40–50 (unitless). EDX analysis using the integrated detector was performed under the same voltage and pressure conditions, but with higher probe currents (65–75) to increase the counts.

p-XRF spectra were collected using a Bruker Tracer III-SD handheld energy-dispersive X-ray spectrometer (Madison, WI, USA) equipped with a Peltier-cooled XFlash silicon drift detector (SDD) with a resolution of 145 eV and a 5 mm diameter approximate spot size. The excitation source was a Rh target X-ray tube, operated at 40 kV and 10 μ A current, and spectra were collected over 180 s (live time). Spectra were obtained with Bruker S1pXRF software version 3.8.30 and spectral interpretation was performed using Bruker Artax Spectra 7.4.0.0 software.

2.2. Analysis at the Museum of Modern Art

Optical Microscopy was conducted using a Leica DM IRM microscope using a 10 \times objective. Cross-sections were embedded in BioPlastic[®] (Aldon Corp., Avon, NY, USA), a blend of polyester and methacrylate monomers in a styrene solvent, trimmed with a jeweler's saw, and dry polished with Micro-Mesh[®] (Micro-surface Finishing Products, Wilton, IA, USA) silicon carbide or aluminum oxide abrasives.

μ -FTIR spectra were collected in transmission mode using a Nicolet iS50 μ -FTIR coupled with a Thermo Nicolet Continuum infrared microscope equipped with an MCT detector (Waltham, MA USA). Spectra were collected in the 4000–600 cm^{-1} range with a 4 cm^{-1} resolution and 128 scans using the Thermo Scientific OMNIC 9.0 software package. Spectra were examined using the Spectral Search and Multicomponent Search tools available in Thermo Scientific OMNIC Spectra 2.0 software.

Silver nanoparticles (AgNPs) for surface-enhanced Raman spectroscopy (SERS) were prepared according to a method developed by Lux et al. [12]. A solution of 12.5 mL of 0.5 mM silver sulfate (Ag_2SO_4) ($\geq 99.99\%$; MilliporeSigma, Burlington, MA, USA), 0.5 mL of 1% sodium citrate dihydrate ($\text{C}_6\text{H}_9\text{Na}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$) ($\geq 99\%$; Thermo Fisher Scientific Inc., Waltham, MA, USA), and 1 mL of 1% D-glucose ($\geq 99.5\%$; MilliporeSigma, Burlington, MA, USA) were mixed in a Hydrothermal Synthesis Autoclave Reactor PTFE Tank (Baoshishan, Zhengzhou,

China) previously cleaned with 30% *v/v* nitric acid in distilled water. The starting solutions were all made with 18 M Ω deionized water. Once closed, the vessel was positioned in the center of a Panasonic model NN-SD372S inverter microwave and heated at 810 W for 2 min. Then 1.5 mL aliquots of this stock solution of citrate-capped AgNPs were centrifuged at 12,000 rpm for 15 min. The supernatant containing the citrate solution in excess was removed and replaced by 18 M Ω deionized water to avoid sodium citrate interference in the SERS spectra.

Dispersive Raman spectra were collected on a Renishaw InVia Raman system (West Dundee, IL, USA) equipped with a 785 nm diode laser operated between 0.3 to 3 mW, a 1200 lines/mm grating, and a Leica confocal microscope with a 50 \times LWD or 100 \times objective. Final spectra represent an average of five acquisitions of 10 s. Spectra were examined using the Spectral Search and Multicomponent Search tools available in Thermo Scientific OMNIC Spectra 2.0 software. SERS was carried out using the same Renishaw InVia Raman system, employing here a 532 nm diode laser operating at 0.25 mW with an 1800 lines/mm grating. Spectra were evaluated using the Spectral Search and Multicomponent Search tools available in Thermo Scientific OMNIC Spectra 2.0 software. Sample identification was achieved by comparison of the unknown spectrum to spectra of reference materials, the KIK/IRPA Raman reference library [11], and those published in the literature.

p-XRF spectra of *Untitled Red Monochrome (M 63)* were collected using a Bruker Tracer 5g handheld energy-dispersive X-ray spectrometer (Madison, WI, USA) equipped with a 20 mm² graphene window (SDD), detector area with a resolution of 145 eV and an 8 mm diameter approximate spot size. The excitation source was a Rh target X-ray tube, operated at 40 kV and 4 μ A current, and spectra were collected over 120 s (live time). Spectra were obtained and evaluated with Bruker Artax Spectra 8.0.0.476 software.

3. Results and Discussion

3.1. Red and Pinks Revealed

The results obtained from this multi-analytical campaign show that Klein used a variety of pink and red pigments to achieve his monochromatic surfaces. μ -FTIR analysis (Figure 3) revealed that all four paintings and sculptures contain PVAc as the binder, while the screenprint was made with an oil-based ink (Table 1 lists the materials identified, and Table 2 provides the characteristic FTIR and Raman peaks for these materials, the Raman spectra are shown in Figure 4). μ -FTIR spectra of samples taken from the paintings and sculpture also showed peaks indicative of a hydrated sulfate-based filler or lake-base (Figure 3), with peaks at 3407 and 1642 cm⁻¹ likely corresponding to the stretching and bending vibrations of water, and that at 1120 cm⁻¹ deriving from S–O stretching in the sulfate ion [13,14]. p-XRF and SEM-EDX analysis of the Menil Collection and Louisiana Museum works, in addition to p-XRF of the Guggenheim work, indicated aluminum was the counterion, likely present as hydrated aluminum sulfate (Al₂(SO₄)₃). Calcium carbonate (CaCO₃) was identified as a filler in a pink sample taken from the screenprint associated with *Monochrome und Feuer*. Both calcite and aragonite, two crystal forms of CaCO₃, were observed in the μ -FTIR spectrum, where the latter was identified by the sharp ν_2 (CO₃²⁻) peak at 855 cm⁻¹.

A cross-section sample taken from the earliest of these works, *Untitled Red Monochrome (M 63)*, displays two distinct layers (Figure 5a,b). The first, more orange-hued red layer contains the lake pigment eosin Y (C₂₀H₆Br₄Na₂O₅; Pigment Red 90:1) (Figure 5), which was identified by both Raman and μ -FTIR spectroscopies. The presence of this pigment was further confirmed by the large amount of bromine (Br) detected with p-XRF. Raman analysis of the second, surface layer produced overwhelming fluorescence that necessitated the use of SERS, through which rhodamine B (C₂₈H₃₁ClN₂O₃; Pigment Red 173) was identified. Both of these pigments fluoresce orange under ultraviolet illumination [15], which explains the lack of distinction between the two layers in the cross-section when examined with microscopy.

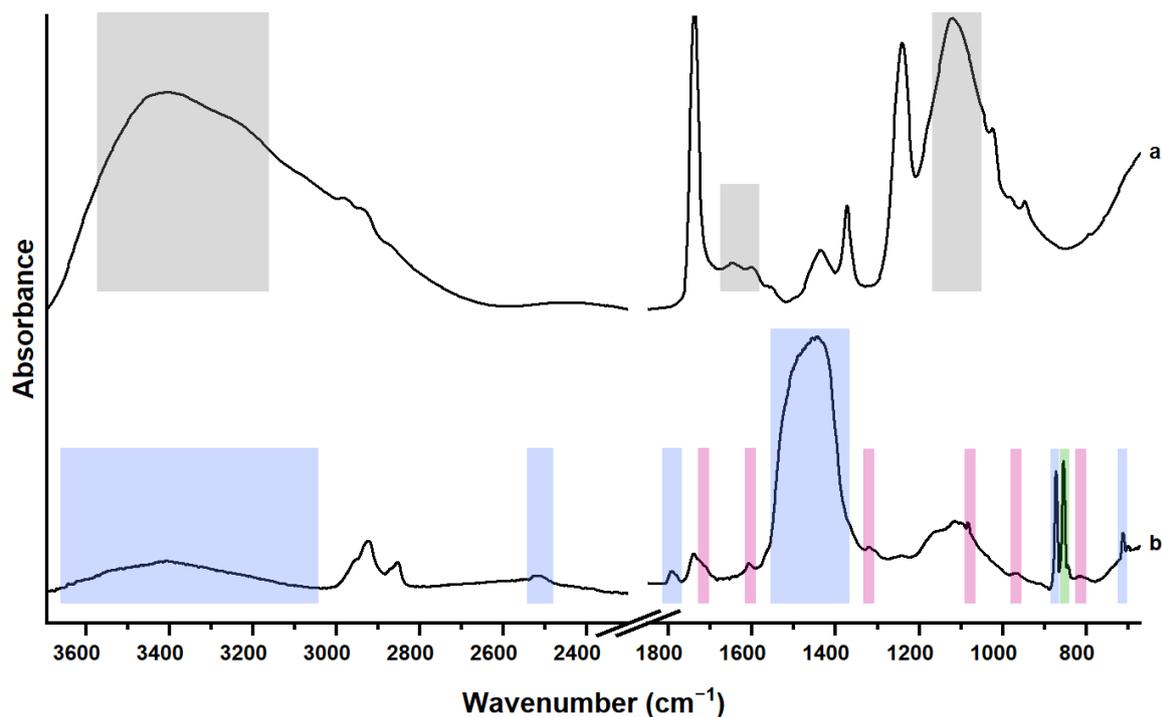


Figure 3. μ -FTIR spectra showing the presence of (a) PVAc in a sample from Grand Monopink (MP 16) and (b) oil-based printing ink in a sample from the screen print associated with Monochrome und Feuer. The peaks highlighted with gray in (a) correspond to hydrated aluminum sulfate, and in (b), the peaks highlighted in blue correspond to CaCO_3 in calcite form, green to a CaCO_3 in aragonite form, and in pink to rhodamine 6G.

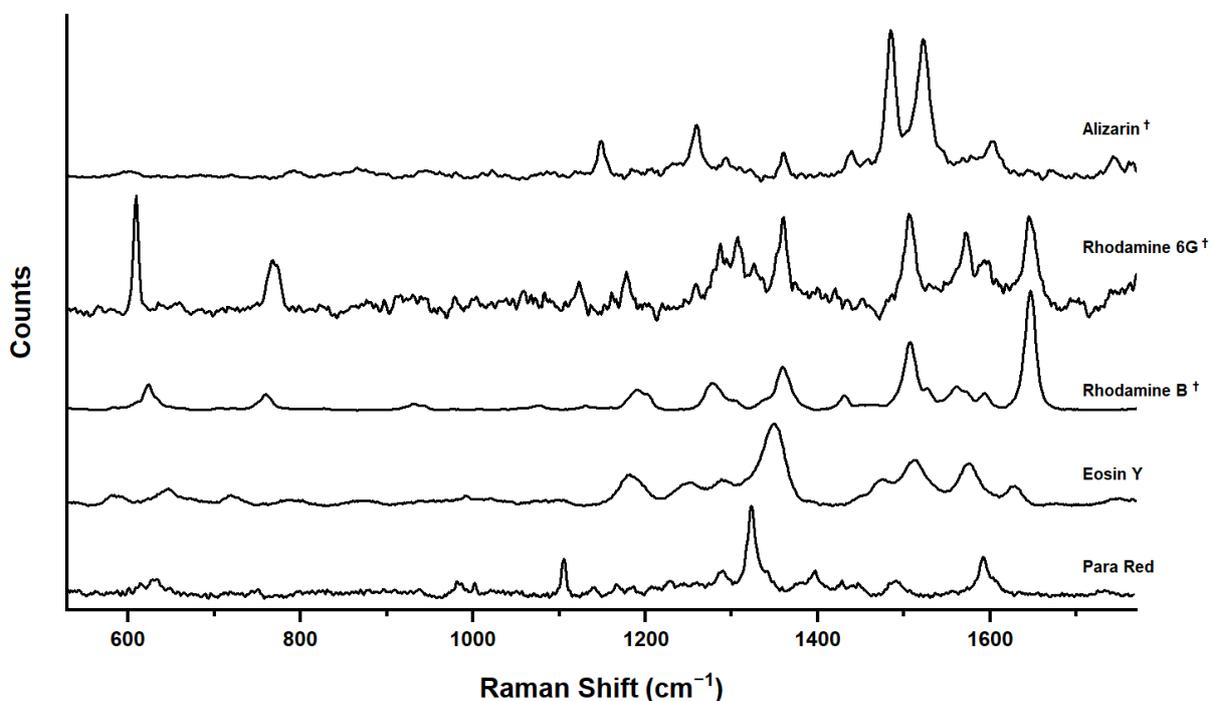


Figure 4. Raman and SERS spectra showing the variety of red and pink pigments used by Yves Klein. Spectra marked with (+) were obtained with SERS.

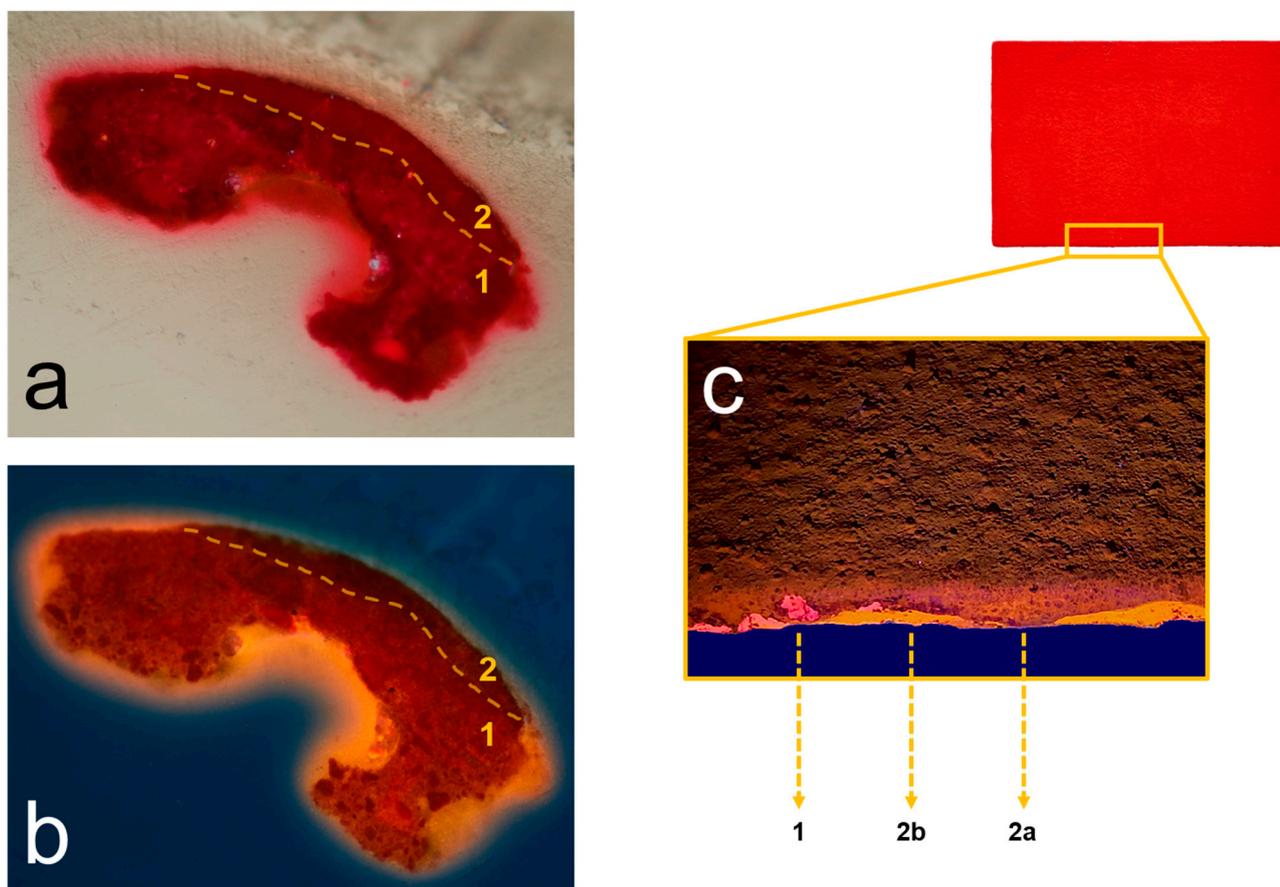


Figure 5. Cross-section of a sample taken from *Untitled Red Monochrome (M 63)* with (a) visible light and (b) UVF showing two layers of paint. Visual examination of the edge under ultraviolet illumination reveals the presence of three layers, where 1 is painted with rhodamine B and 2a and 2b with eosin Y. Panel (c) shows the layering visible at the edge of *Untitled Red Monochrome (M 63)* under UV illumination.

However, closer inspection of the edge of *Untitled Red Monochrome (M 63)* under UV illumination (Figure 5c) reveals more information about the layering of these paints and suggests that there may be three layers in total. Over the bright pink rhodamine B layer, which is revealed through spalling of the surface layers, and which appears to be the lowest paint layer applied, are two additional visibly distinct layers: a middle layer that fluoresces bright orange and the surface layer that fluoresces a muted deep red. Raman analysis of scrapings taken from the middle and surface layers detected only eosin Y. Thus, Klein appears to have applied the final color in two coats, and the surface coat now appears darker under UV possibly due to aging, dirt, or photodegradation in the presence of fillers or white pigments [16].

Analysis of a sample from *Grand Monopink (MP 16)* indicated the presence of an alizarin lake ($C_{14}H_8O_4$; Pigment Red 83). The absence of any definitive signatures for purpurin or pseudopurpurin likely excludes the use of a natural alizarin lake pigment [17], as multiple anthraquinones are usually present in pigments extracted from the madder root [18]. Early in the 20th century, synthetic lakes were beginning to replace natural ones largely due to their superior lightfastness [19–21], so it is likely that Klein would have had easier access to synthetic lakes. His writings do not indicate whether he preferred natural or synthetic pigments. Although Klein used synthetic ultramarine, and synthetic pigments were found in his green and orange monochromes [5], he may simply have chosen what was offered by suppliers at the time.

It is worth noting that the SERS spectra obtained for alizarin in this study suggest a particular bonding mechanism that explains the Raman shifts reported here. Cañamares et al. determined that the pKs of alizarin are 5.25 and 11.5, which give rise to the monoanionic and dianionic species, respectively [22]. Considering that SERS analysis was done under acidic pH with the introduction of HNO₃ for hydrolysis, the resulting SERS spectrum indicates the bonding of negatively charged, monoanionic anthraquinone to the positively charged silver nanoparticle clusters (Ag₃)⁺ [22,23]. This species was observed for all the SERS spectra obtained with alizarin in this study.

Visible inspection of samples taken from Grand Monopink (MP 16) suggested the presence of two layers, a deeper pink top layer and a lighter pink bottom layer (Figure 6). However, visible light microscopy and SEM-EDX analysis of an embedded sample failed to identify the presence of multiple layers (Figure 6), as did SEM-EDX analysis of unembedded flakes. While both pink and red areas contain calcium, identified as calcium sulfate (CaSO₄) by Raman, SEM-EDX shows the amounts to be consistent across the samples indicating that the color difference does not arise from different amounts of calcium-based filler. Klein is known to have applied multiple layers of paint to his IKB monochromes and subtle differences in formulation sometimes result in perceptible color differences in his IKB monochromes [7]. If multiple layers are present in Grand Monopink (MP 16), they are similar enough to be indistinguishable by the analytical techniques used in this study. Visible light microscopy and SEM-EDX analysis of the samples also showed the presence of small, dispersed particles of ultramarine. The apparent heterogeneity in their distribution suggests that the pigment is present as a contaminant, perhaps from powdered pigments in Klein studio, and was not deliberately added to the pink paint.

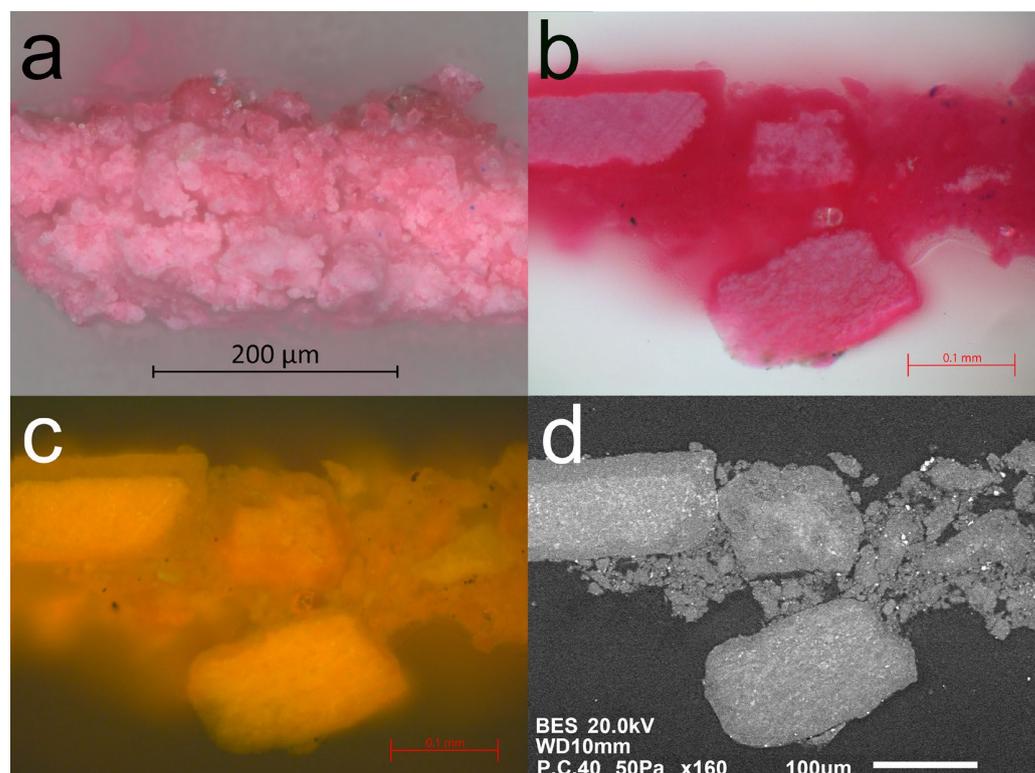


Figure 6. Image of (a) an unembedded sample taken from *Grand Monopink* (MP16). Cross-section of a second sample imaged under (b) visible light; imaged with (c) ultraviolet-induced visible fluorescence using a B-2A filter cube; and (d) SEM electron backscatter. The cross-section sample shows no evidence of the presence of multiple layers.

Spalling of the red surface paint of *Red Rain* (S37) (1961) revealed a pink underlayer suggesting that multiple paint layers were also present in this work. Cross-section analy-

sis using visible and ultraviolet illumination and SEM-EDX confirmed this stratigraphy (Figure 7) and revealed a thick lower layer containing large particles rich in aluminum and sulfur, likely the hydrated $\text{Al}_2(\text{SO}_4)_3$ seen by μ -FTIR. The thin surface layer also contains $\text{Al}_2(\text{SO}_4)_3$, but SEM-EDX showed that small amounts of silicates and barium are also present, the latter likely present as barium sulfate; these are the small, bright white particles visible in the backscattered electron image (Figure 7c). As in Grand Monopink (MP 16), scattered ultramarine particles were observed in both paint layers and on the surface below the over-paint present in other samples analyzed.

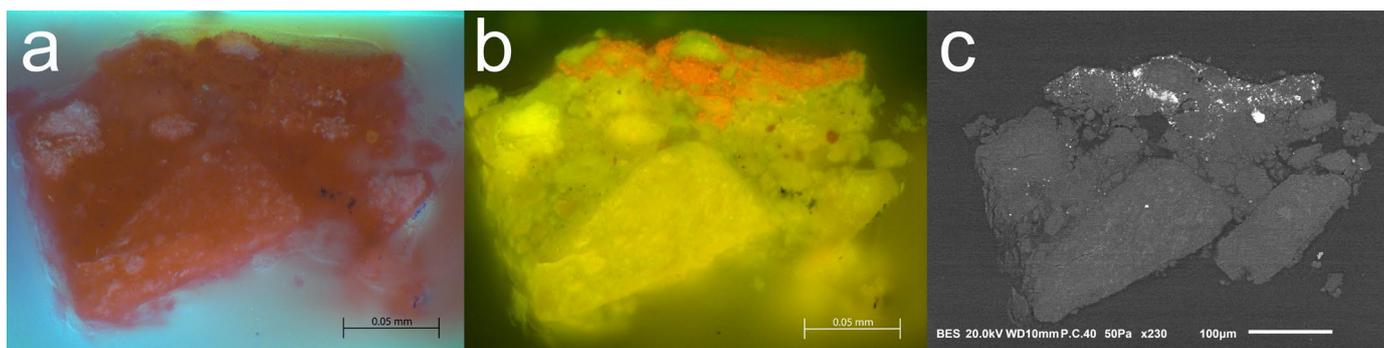


Figure 7. Cross section of a sample taken from *Red Rain* (S37); (a) visible light; (b) ultraviolet-induced visible fluorescence using a B-2A filter cube, the Para Red-containing upper layer exhibits a more orange fluorescence); (c) SEM electron backscatter image, the small bright white particles in the upper layer are barium sulfate.

Analysis of the lower pink layer with SERS (Figure 4) revealed the presence of two lake pigments, rhodamine 6G ($\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3\text{Cl}$; Pigment Red 81) and a synthetic alizarin [23]. The reason for the addition of rhodamine 6G to synthetic alizarin is unknown, although lake pigments were often adulterated with additional synthetic pigments [24]. The large particle sizes revealed by SEM, relatively low amounts of binder, and the hygroscopic nature of aluminum sulfate may account for the observed paint spalling.

The thinner, surface layer of red paint in *Red Rain* (S37) contained a different red pigment, Para Red ($\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}_3$; Pigment Red 1), which was identified by both Raman and μ -FTIR spectroscopies. A peak at 1290 cm^{-1} suggests the presence of synthetic alizarin in the layer as well. There is no evidence to suggest that the thin surface layer is not artist-applied.

The pink paint on *Untitled Shroud Anthropometry* (ANT SU 4) (1961) also contains Para Red and synthetic alizarin on an aluminum sulfate base, although the binder-to-pigment ratio appears to be higher than on *Red Rain* as the pigments were only detected by Raman spectroscopy; Para Red was below the detection limit of μ -FTIR.

The latest of these works, the pink screenprint in the collection at MoMA, was created in 1961. Although Klein's involvement in the choice of printing ink for this work is unknown, the analysis offers an opportunity to compare colorants that Klein personally selected for his artworks with one that may have been chosen or recommended by the printer. Rhodamine 6G was again detected by SERS (Figure 4) and perhaps suggests an evolution towards consistency in the choice of pigment for an artist largely preoccupied with color. This pigment was also detected by μ -FTIR (Figure 3).

3.2. Technique

Two of the works studied here, *Red Rain* (S37) and *Untitled Red Monochrome* (M 63), have lower layers of pink paint and surface coats of red paint. In a 1956 article by Bernadette Allain about Klein's Galerie Colette Allendy show, she describes a 20×30 cm painting where through the purple-violet surface one can "feel the powerful life of red" (literally "sen la vie puissante du rouge") suggesting that Klein may have deliberately layered colors in this painting [25].

However, in addition to deliberate layering, artists, including Klein, rework their paintings. Stitch notes instances of Klein repainting a pink work to make it yellow, a red painting from 1956 that he covered in blue, and a 1957 painting where he covered blue with bronze [4]. She also describes a red monochrome from 1957 that has an underlayer of pink; this subtle color change makes it difficult to decide if this is a case of deliberate revision or of Klein deliberately layering his colors. The works described by Allendy and Stitch were made from 1955–57, earlier than the works studied here, and if the layering of pink and red in *Untitled Red Monochrome (M 63)* and *Red Rain (S37)* is not an alteration but a deliberate choice, it suggests that Klein continued to explore the possibilities of optical translucency. Stitch also notes that in the case of the red monochrome, the fading of the red surface paint allows the pink underlayer too much prominence and says the monochromatic effect is lost [4]. If such a change happened in Klein's lifetime, the wide variety of pigments found in this study could document his search for more stable colorants.

3.3. Implications for Conservation

Klein's works have always presented problems for conservators because of their unique surfaces and intense monochromatic color [7,26,27]. The presence of organic pigments in these objects adds additional complexity due to potential issues surrounding lightfastness and solubility. The lightfastness of pigments is impacted by many factors including the strength of the tint, the thickness of the paint film, particle size, the identity of the binding medium, and the presence of other pigments [28–30]. However, the identification of a variety of pigments indicates that these pink and monochromes can be expected to be light sensitive in a way that IKB monochromes are not.

Rhodamine B and eosin Y pigments are considered fugitive, equivalent to Blue Wool Scale (BWS) 2–3, meaning that they may show visible fading after 4–10 years of exposure to light that contains an ultraviolet component (unfiltered daylight) and 7–20 years if the UV component is filtered out, as is in museum environments [31,32]. Rhodamine 6G and Para Red are somewhat more lightfast, with BWS ratings of 4–6, and can be expected to exhibit noticeable color change after 23–30 years on display if ultraviolet light is not filtered out, and 67–670 years if it is [30–32]. Synthetic alizarin is more stable than that extracted from plants but is still considered to have only fair lightfastness [33]. Therefore, these works are considerably more fugitive in their colorfastness than IKB works and care should be taken when designing their display and storage conditions.

In addition to issues with lightfastness, organic pigments may also be solvent sensitive and show solubility, limiting potential treatments. For instance, rhodamine 6G and synthetic alizarin are sensitive to polar solvents including ketones and esters, and Para Red is sensitive to water, which may impact treatment choices [30].

4. Conclusions

Analysis of five pink and red works by Yves Klein paints a more complex picture of his working practice with color. His 1960 statement in *Le Dimanche* indicated that madder lake was 'IKP'. However, in the works studied here, alizarin, likely synthetic, was found in only three objects, *Grand Monopink (MP16)*, *Red Rain (S37)*, and *Untitled Shroud Anthropometry (ANT SU 4)*, and is the primary colorant only in the first of these. The other artworks contained different organic colorants, including rhodamine 6G, rhodamine B, and eosin Y, suggesting that he had not yet settled on a singular "IKP" pigment. Perhaps had Klein lived longer, this exploration of the color pink could have led to the same standardized practice he arrived at with IKB, or maybe for reds and pinks he had no defined vision of what the ideal color was, unlike his strong vision of a single, perfect blue.

Table 2. μ -FTIR, Raman, or SERS peaks for pigments and binding media identified in the selection of works by Yves Klein studied here.

Material	Characteristic Peaks
Pigments	
Para Red (Pigment Red 1)	Raman: 185, 358, 410, 462, 615, 631, 647, 750, 981, 1002, 1105, 1141, 1165, 1186, 1207, 1229, 1260, 1289, 1323, 1383, 1396, 1427, 1447, 1489, 1558, 1592 cm^{-1} [34] μ-FTIR: 1624, 1602, 1593, 1449, 1343, 1330, 1203, 1104, 984, 860, 839, 795, 749, 670 (?) cm^{-1} [34]
Eosin Y (Pigment Red 90)	Raman: 216, 383, 449, 482, 582, 636, 719, 992, 1182, 1248, 1289, 1349, 1472, 1512, 1575, 1628, 1752 cm^{-1} [35] μ-FTIR: 1619, 1562, 1501, 1441, 1352, 1111, 1078, 982, 762, 722 cm^{-1} [36]
Rhodamine 6G (Pigment Red 81)	SERS: 403,611, 636, 758, 772, 928, 1084, 1127, 1206, 1223, 1275, 1310, 1362, 1387, 1419, 1431, 1448, 1508, 1572, 1596, 1649 cm^{-1} [35] μ-FTIR: 1716, 1607, 1320, 1244, 968, 815 cm^{-1} [36]
Rhodamine B (Pigment 173)	SERS: 611, 620, 736, 772, 934, 1075, 1133, 1120, 1280, 1359, 1432, 1507, 1529, 1569, 1599, 1647 cm^{-1} [35]
Alizarin (Pigment Red 83)	SERS: 574, 658, 813, 943, 1029, 1056, 1092, 1241, 1289, 1327, 1411, 1479, 1554, 1598 cm^{-1} [23]
Ultramarine (Pigment Blue 29)	Raman: 375, 555, 591 cm^{-1} [37]
Fillers	
Aluminum sulfate	μ-FTIR: 3407, 1641, 1120 cm^{-1} [14]
Calcium sulfate	Raman: 422, 498, 990, 1016, 1142 cm^{-1} [37]
Calcium carbonate	μ-FTIR: 3407, 2518, 1793, 1446, 873, 855, 712, 699, cm^{-1} [36]
Binding Media	
Polyvinyl Acetate	μ-FTIR: 2972, 2923, 1738, 1436, 1373, 1241, 1085, 1024, 947, 795, 634, 608 cm^{-1} [36]
Oil-based printing ink	μ-FTIR: 2960, 2924, 2852, 1740, 1244, and 1162 cm^{-1} [36]

Author Contributions: A.H. carried out microscopy, Raman, SERS, and μ -FTIR at The Museum of Modern Art and p-XRF at Solomon R. Guggenheim Museum. C.E.R. carried out microscopy, Raman, μ -FTIR, p-XRF, and SEM-EDX. Both authors created figures and contributed to the conceptualization, writing, and editing of this manuscript. All authors have read and agreed to the published version of the manuscript.

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