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Paul Delvaux: The Study of Nine Paintings by Non-Invasive Methods

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Abstract: Paul Delvaux (1897–1994) was a Belgian Surrealist painter known for his dreamlike and enigmatic compositions. His works often featured nude or semi-nude women and deserted urban landscapes, evoking a sense of mystery and intrigue. Delvaux's meticulous attention to detail and masterful use of light and shadow added depth and realism to his surrealistic style, making him one of the leading figures of the Belgian Surrealist movement. Although writings about Paul Delvaux's work are not lacking, the literature mainly deals with the stylistic and iconographic aspects of his work. Taking an interest in painting materials and the painter's technique allows us to understand his personality and to apprehend his work in a different way. In order to collect such information, the early painted production of Delvaux was studied in situ with imaging methods (high-resolution photography, infrared reflectography and X-ray radiography) and non-invasive analytical techniques (MA-XRF and Raman spectroscopy). The results obtained for nine oil paintings produced from 1928 to 1958 are discussed in terms of the support, the preparatory layer, the preparatory drawing, the changes in composition and reuse of paintings, the pictorial layer and the dripping phenomenon.

Keywords: Paul Delvaux; painting analysis; non-destructive analysis; pigment identification; painting material; pictorial technique

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1. Introduction

Paul Delvaux was a Belgian painter born on 23 September 1897 in Antheit (Belgium) who passed away on 20 July 1994 in Veurne. Known for his surrealistic style, Delvaux was one of the leading figures of the Belgian Surrealist movement.

Born into a bourgeois family with a lawyer father, Delvaux had difficulty convincing his family to let him pursue a career as an artist [1–5]. In October 1919, thanks to the support of painter Franz Courtens (1854–1943) [1–9], Delvaux entered the Royal Academy of Fine Arts in Brussels in the decorative painting class of Belgian symbolist painter Constant Montald (1862–1944) [1–8,10–12]. He also attended the evening drawing classes led by Belgian symbolist painter Jean Delville (1867–1953) [2–5,7,8,12,13]. The latter is well known for the quality of his drawings, as well as for his attraction to large-format paintings.

He drew inspiration from various sources, such as Renaissance masters; classic literature; and the works of his contemporaries, including Giorgio de Chirico and René Magritte.

One of the key elements of Delvaux's style was his portrayal of the female figure. He frequently depicted nude or semi-nude women in his paintings, presenting them as mysterious and ethereal beings. These female figures often appeared as passive objects of desire, evoking a sense of intrigue and vulnerability. Delvaux's portrayal of women sparked discussions and debates around gender dynamics and objectification in art.

Another notable aspect of Delvaux's style was his choice of settings. He often depicted desolate urban landscapes with deserted streets and empty squares. These urban environments, devoid of human presence, added to the eerie and uncanny atmosphere of his

works. The juxtaposition of solitary figures against deserted backdrops created a sense of isolation and heightened the dreamlike quality of his paintings.

Delvaux also drew inspiration from classical art and literature. His works often referenced mythological and historical themes, incorporating elements from ancient Greek and Roman culture.

The use of light and shadow was integral to Delvaux's style, adding a sense of mystery and drama to his compositions. He skillfully employed chiaroscuro, a technique that emphasizes the contrast between light and dark, to enhance the visual impact of his works. The play of light and shadow heightened the depth and three-dimensionality of his figures and contributed to the overall haunting ambiance of his paintings.

Despite facing criticism for his unique style, Delvaux remained true to his artistic vision throughout his career. His works continue to captivate audiences with their enigmatic narratives, skillful execution and thought-provoking themes. Paul Delvaux's artistic style not only exemplified Surrealism but also established him as one of the most renowned painters of the movement, leaving a lasting impact on the art world.

Although important, the academic training of the painter is not sufficient to understand his technique and the material he used. The study of his painted production through complementary imaging methods and non-destructive analysis makes it possible to deliver relevant information on this subject. Focusing on paintings from the first part of his long career allowed us to pinpoint the importance of his training and his own technique. Following the presentation of the studied *corpus* and the analytical protocol carried out systematically on each painting, we present the main results with respect to the support, the preparatory layer, the preparatory drawing, the changes in composition and reuse of paintings, the pictorial layer and the dripping phenomenon.

2. Materials and Methods

In order to study Delvaux's painting materials and pictorial technique, artworks covering the first thirty years of the painter's career, from 1928 to 1958, were analyzed. This paper discusses the results obtained for this first *corpus* belonging to the collection of the Royal Museums of Fine Arts of Belgium in Brussels (RMFAB) (Table 1) : *Couple avec enfant dans la forêt* [Couple whith child in the forest] (Figure 1a), *Le couple* [The couple] (Figure 1b), *Jeune femme rêvant* [Dreaming young woman] (Figure 1c), *Sans titre* [Untitled] (Figure 1d), *L'incendie* [Fire] (Figure 1e), *Pygmalion* (Figure 2a), *Nocturnes* (Figure 2b), *La voix publique* [Public voice] (Figure 2c) and *L'hiver* [Winter] (Figure 2d). The same analytical methodology was applied to the whole *corpus*, thanks to the mobile laboratory available at the Centre Européen d'Archéométrie (CEA) of the University of Liège.

Table 1. *Corpus* of the studied paintings of Paul Delvaux.

Title	Title Translation	Technique	Year	Size	Inv. #
Couple avec enfant dans la forêt	Couple whith child in the forest	Oil on canvas	1928–1929	150 × 178 cm	11,936
Le couple	The couple	Oil on canvas	1929	150 × 135 cm	7004
Jeune femme rêvant	Dreaming young woman	Oil on canvas	1931	110 × 99 cm	7340
Sans titre	Untitled	Oil on canvas	1935	148 × 76 cm	11,541
L'incendie	Fire	Oil on canvas	1935	140 × 86 cm	12,517
Pygmalion	Pygmalion	Oil on trilex	1939	117 × 148 cm	7544
Nocturnes	Nocturnal	Oil on wood	1939	94 × 123 cm	11,947
La voix publique	Public voice	Oil on multiplex	1948	153 × 254 cm	7094
L'hiver	Winter	Oil on multiplex	1958	119 × 153 cm	11,565

Figure 1. Photographs of paintings by Paul Delvaux under study: (**a**) *Couple avec enfant dans la forêt* [Couple whith child in the forest], 1928–1929; (**b**) *Le couple* [The couple], 1929; (**c**) *Jeune femme rêvant* [Dreaming young woman], 1931; (**d**) *Sans titre* [Untitled], 1935; (**e**) *L'incendie* [Fire], 1935.

Technical imaging was performed on the whole set of paintings. First, high-resolution photographs were acquired using a digitization system designed by the CEA [14]. For images in visible light and under ultraviolet light (induced fluorescence), a Nikon® Z7-II camera with a Z-MC 105mm f/2.8 Nikkor® lens was used to capture images, with each close-up recording a small area of the painting (3 × 4 cm). The images were then assembled using PTGui software®. Infrared reflectography (IRR) was performed using an Osiris® camera sensitive in the 0.9–1.7 µm range and halogen lamps. X-ray radiography (XRR) was performed with the use of an Oxford-Instrument® 5000 series X-ray source operating between 40 and 50 kV at 1 mA, with two flat panels from X-Ris® and Balteau NDT®. Figure 3 shows the different imaging methods used for the female figure on the left in *Couple avec enfant dans la forêt*. The surfaces of the paintings were also examined with Dino-Lite® digital microscopes.

Figure 2. Photographs of paintings by Paul Delvaux under study: (**a**) *Pygmalion*, 1939; (**b**) *Nocturnal*, 1939; (**c**) *La voix publique* [Public voice], 1948; (**d**) *L'hiver* [Winter], 1958.

Figure 3. Technical imaging of the left female figure in *Couple avec enfant dans la forêt*: (**a**) photograph; (**b**) photograph with raking light; (**c**) photograph with through light; (**d**) photograph under UV light; (**e**) IRR; (**f**) XRR.

Scanning-mode XRF spectroscopy (MA-XRF) has become an essential tool to visualize the elemental distribution of a surface in recent years [15–18]. The device used is composed of a Moxtek® Magnum X-ray source (with a Ag anode, 40 kV voltage and a current of 120 µA and a Silicon-Drift 123SDD Amptek® X-ray detector. The scanning step was set to 1 mm with a dwell time of 300 ms. The obtained spectra were processed in batch mode using PyMCA [19]. The second technique is Raman spectroscopy (RS), enabling the characterization of the molecular composition of the analyzed material [20,21]. This analysis was performed with an Enwave Optronics® device (I-Dual-G portable Raman analyzer), with a 785 nm laser with power varying between 30 and 300 mW and a spectral resolution of 6 cm^{-1} in the spectral domain of 100–3000 cm^{-1}. For each point of analysis, three acquisitions generally lasting 30 s with a laser power of ≈100 mW and a 500 µm spot size were carried out. The spectra were then processed using GRAMS®.

3. Results

3.1. Support

Following his Academy teachers, Delvaux undeniably favored large formats. In the studied corpus, the smallest painting is *Jeune femme rêvant*, with dimensions of 110 × 99 cm, and the largest is *La voix publique*, with dimensions of 152 × 254 cm.

In consulting catalogs of Delvaux's oil paintings [5–9,22,23], it is remarkable that two-thirds of his oil production is on canvas. The rest comprise paintings on wooden panels, as well as on plywood (triplex, multiplex, unalite, masonite), which was a rather modern support in the 20th century. We observed some careless phenomena on plywood, such as glue drippings on the back of the sheets. On one of the paintings studied in this work (*Nocturnes*) features a handiwork in the lower left corner.

3.2. Ground Layer

Analysis of the ground layer was performed on the edges of the paintings. All the canvases of the studied *corpus* have a white ground layer, as shown in Table 2. The white coloring is due to the presence of two white pigments for the two earliest paintings of the *corpus* (*Couple avec enfant dans la forêt* and *Le couple*), namely lead white ($(PbCO_3)_2 \cdot Pb(OH)_2$) and zinc white (ZnO). The narrow absorption band at 1050 cm^{-1} in the Raman spectrum is characteristic of the presence of lead white [24–26]. Zinc white was identified based on the presence of zinc only. In the case of *Jeune femme rêvant* and the two parts of *L'incendie*, lithopone ($ZnS \cdot BaSO_4$) was identified on the basis of the joint presence of zinc, barium and sulfur. However, we cannot rule out the possibility of a combination of zinc white and barium sulfate. As shown in Table 2, calcium is also present but as a trace element when the ground layer is composed of the supposed lithopone [25].

Table 2. Composition of the ground layer deduced from Raman and XRF analysis. Concerning XRF, K lines were detected for S, Cl, Ca, Co and Zn, with L lines detected for Ba and Pb and M lines for Pb.

Title	Support	Color	Raman Band (cm^{-1})	Detected Elements	Supposed Pigment(s)
Couple avec enf. dans la forêt	canvas	white	1050	Pb(L,M), Zn	Lead white, zinc white
Le couple	Canvas	White	1050	Cl, Pb(L,M), Zn	Lead white, zinc white
Jeune femme rêvant	Canvas	White	no peak	Ba, Ca, S, Zn	Lithopone
L'incendie	Canvas	White	No peak	Ba, Ca, Pb(L,M), S, Zn	Lead white, lithopone
Sans titre	Canvas	White	No peak	Ba, Ca, Pb(L,M), S, Zn	Lead white, lithopone
Nocturnes	Wood	Not present			
Pygmalion	Triplex	Green	980	Ba, Ca, Co, S, Zn	Lithopone, green cobalt pig.
La voix publique	Multiplex	Not available			
L'hiver	Multiplex	Not present			

Unlike canvases, a preparation layer is not necessarily present on plywood, as we observed for *Nocturnes* and *L'hiver*.

Pygmalion is a special case of the *corpus* because the preparation layer that composes it is green. MA-XRF performed on the edge of *Pygmalion* revealed the presence of barium, sulfur, zinc and cobalt. The Raman spectra obtained for the ground layer show a narrow vibrational band at 980 cm^{-1}, which testifies to the presence of barium sulfate [24]. As a reminder, barium sulfate is part of the composition of lithopone. Again, the presence of lithopone or zinc white accompanied by barite can be proposed. In both cases, these pigments give a white color and therefore do not justify the green color. Microscopic enlargements show that a single green pigment is present and not a mixture of blue and yellow pigments. As cobalt and zinc are correlated in the MA-XRF spectra, the use of cobalt green pigment (CoO·ZnO) in this ground layer can be proposed.

With respect to the use of a colored ground layer, we find in the literature the testimony of Danielle Canneel, Delvaux's model from 1966 to 1984 [2], relating that Delvaux had already sketched all the sets and most of the characters in white on a dark canvas [2]. Moreover, in the painting *La pose* (1979) (Figure 4a), several characters are represented in the process of painting a nude model. The preparations of their canvases are dark gray, and they execute their sketches in white (Figure 4b). These pieces of evidence are posterior to the studied paintings, showing the application of a white preparation. The technique of preparing the canvas therefore evolved during his career, but we do not yet know when he began to use a dark preparation layer. As for the green color in particular, the literature does not mention whether canvases other than *Pygmalion* benefited from a similar colored ground layer.

Figure 4. (**a**) Paul Delvaux, *La pose* [The pose], 1979, oil on canvas, 150 × 150 cm, collection of the Foundation Paul Delvaux; (**b**) detail of the lower right corner of *La pose*.

3.3. Preparatory Drawing

Before making this preparatory drawing, Delvaux attached great importance to the study of his subject by making a number of sketches and drawings [2–5,8].

IRR shows the presence of a preparatory drawing made using dry carbon material, such as charcoal or pencil, in three paintings of the studied corpus: *Couple avec enfant dans la forêt*, *Jeune femme rêvant* and *Le couple*. For the first two, a grid drawn in carbon pencil is visible. Therefore, the paintings anterior to *L'incendie*, 1935, have a preparatory drawing executed with dry carbon material. For the rest of the corpus, the preparatory drawing is an oil sketch (Table A1). Figure 5 emphasizes the black line of the nude female figure wearing foliage from *Pygmalion*, overhung with flesh-colored paint, which means that Delvaux painted the guidelines of his composition before applying the pictorial layer. We are tempted to underline a parallel with the studies of the paintings. The literature states that until 1932, Delvaux carried out his studies in carbon pencil or charcoal, and afterwards, he used Indian ink [2,27].

Figure 5. Highlighting the oil sketch in *Pygmalion*.

At the preparatory drawing stage, Delvaux had already made the first corrections, such as adjustment of the position of the main characters or even corrections to their silhouettes. The most reworked preparatory drawing is that of *Couple avec enfant dans la forêt*. As an example, Figure 6 shows a photograph and the IRR of the bust of the main male figure in *Couple avec enfant dans la forêt*; the position of the nipples changed seven times, and that of the navel changed six times, with several thicknesses of the hips and different positions for the arms.

Figure 6. Photograph (**left**), IRR (**center**) and annotated IRR (**right**) of the bust of the main male figure in *Couple avec enfant dans la forêt*. Red arrows and circles show the main changes.

3.4. Changes in Composition and Reuse of Paintings

Writings alluding to the painter's technique report that he frequently changed elements during pictorial execution [2,3]. Indeed, one can observe reliefs on the surface of the paintings that do not coincide with the visible composition. XRR revealed the presence of pentimenti throughout the *corpus* (examples are shown in Figures 3 and 7).

XRR shows some drastic changes in composition, such as the addition or deletion of personages. We often observe a correction at the level of the main figures (Table A1), i.e., changes to features, a modified position of the face, and adjustments to the curves of the body and the position of the arms or legs. Occasionally, some changes are identified in the background elements of the composition, such as buildings or wall ornaments.

In *L'incendie*, after removing a female figure in a dress, as revealed by XRR (as shown in Figure 7), the artist performed a radical transformation. He cut the painting in order to keep the right part with the subject of the fire [23]. This part, which was dated and signed, has been in the possession of the RMFAB since 1994. The second part, which was thought to be lost, was found by Pierre Ghêne and given to the museum in 2014 [6]. The state of this part testifies to its poor conservation conditions. According to Debra's book, when a

painting did not find favor with the artist, he would remove the canvas from its stretcher, roll it up and store it in a loft until it was recycled [1].

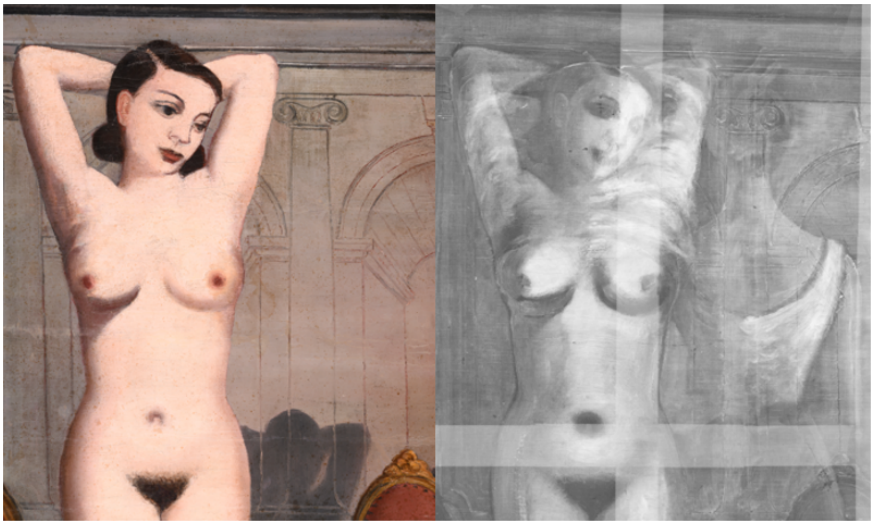

Figure 7. Photograph (left) and XRR (right) of the untitled part of *L'incendie*.

These paintings on canvas are not the only ones to be recycled. XRR of *La voix publique* revealed a double composition, as evidenced by rotating the XRR by 180 degrees, as shown in Figure 8. The red frames highlight the underlying composition. In the upper left corner, a female figure is visible, and the right frame emphasizes the presence of a frame, as well as the bust and head of an imposing reclining nude female figure.

Figure 8. Photograph and XRR of *La voix publique* rotated 180 degrees. The underlying characters are visible in the red rectangles.

Pictorial Layer

The results obtained during the study of the paint layer of the paintings of the *corpus* will be presented below by color.

It is important to mention that Delvaux had a preference for oil-based colors, despite the arrival of acrylic in the middle of the 20th century. According to his nephew, Charles Van Deun, the painter favored Rembrandt oil-based colors by Royal Talens [28].

His classmate, Jules Payro (1899–1971), already an experienced painter, advised Delvaux on how to make his first palette [1,2]. The colors that make it up, in addition to white and black, are as follows: ultramarine blue, English red, yellow ocher and emerald green. He would remain faithful to this palette for a long time before adding cadmium yellow, vermilion and cobalt blue [1].

3.4.1. White

The following white pigments (Table 3) were identified thanks to the performed analyses according to the obtained RS spectra (Figure 9): lead white, zinc white, lithopone, calcium carbonate ($CaCO_3$) and titanium white (TiO_2) in the form of anatase . RS effectively differentiates anatase from rutile. Indeed, rutile has two major narrow absorption bands at 440 cm^{-1} and 610 cm^{-1}, while the most intense and narrow absorption band of anatase is at ≈140 cm^{-1}, with lesser narrow absorption bands at 194, 326, 393, 512, 635 and 794 cm^{-1} [24,29]. Calcium carbonate is identified by the presence of a narrow absorption band located at 1080 cm^{-1} in the Raman spectrum [24].

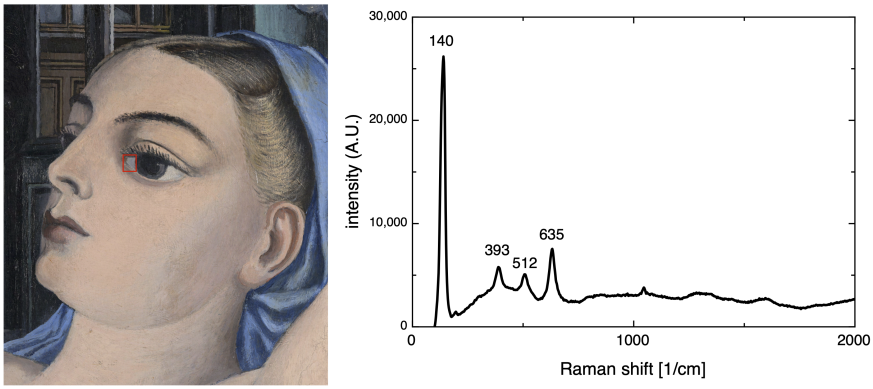

Figure 9. Raman spectrum obtained from the white of the eye of the naked female figure from *La voix publique*, allowing for the identification of the anatase phase of titanium white.

Table 3. White pigments identified in the pictorial layers deduced from the Raman and XRF analysis. Concerning XRF, K lines were detected for S and Zn, L lines were detected for Ba and Pb and M-lines were detected for Pb.

Title	Principal Raman Bands (cm^{-1})	Detected Elements	Main Supposed Pigment(s)
Couple avec enf. dans la forêt	1050	Pb(L,M)	Lead white
Le couple	1050	Pb(L,M)	Lead white
Jeune femme rêvant	1050	Pb(L,M)	Lead white
L'incendie	1050	Ba, Pb(L,M), S, Zn	Lead white, lithopone
Untitled	1050	Ba, Pb(L,M), S, Zn	Lead white, lithopone
Nocturnes	not available	Ba, Zn	Zinc white, barite
Pygmalion	345, 450, 980	Ba, Zn	Zinc white, barite
La voix publique	140, 390, 510, 640, 1050, 1080	Ba, Pb, Ti, Zn	Barite, lead white, titanium white (an.), zinc white, calcium carbonate
L'hiver	98, 430, 1080, 1280	Zn	Zinc white, calcium carbonate

Lead white was used in all the canvases studied herein. We were able to observe the gradual replacement of this pigment in the painter's palette in accordance with the trend of the time. Indeed, for the three earliest paintings in the corpus, dated 1928–1931, it is the only white pigment used in the pictorial layer. For both parts of *L'incendie*, it is

accompanied by lithopone, given the joint presence of barium, sulfur and zinc, although we cannot exclude that these are zinc white and barium sulfate.

The white pigment of the pictorial layer of the two plywood boards dated 1939 is zinc white accompanied by barite. For *L'hiver*, the most recent painting in the corpus, we identified zinc white and calcium carbonate. We can note the absence of lead white in these three paintings.

Three white pigments are part of the composition of the pictorial layer of *La voix publique*: lead white, zinc white and titanium white in the form of anatase. As this is a reused painting, the analyzed pictorial layer is doubled, which explains the number of identified white pigments. In this painting dating from 1948, several observations can be made about the use of titanium white by Delvaux. Historically, in Europe, titanium white was marketed for the first time in fine paint in the form of pure anatase in 1925. Its marketing in the form of pure rutile dates from 1946 [29,30]. Note the late use of titanium white by the artist and the use of anatase, although rutile was already available at this time. Also, contrary to previous literature [1], it was not Delvaux's students who advised him to use titanium white, given that Delvaux's teaching career began in 1950 [1–3,9,10] and that *La voix publique* was produced before this date.

3.4.2. Black

Carbon black was identified in all the studied paintings (Table A1). In RS, two wide absorption bands located at ≈1350 cm^{-1} and ≈1580 cm^{-1} characterize the presence of carbon black [24,31], as shown in Figure 9. Carbon black was identified in many of the Raman spectra obtained in this study. Although MA-XRF cannot identified carbon [18], calcium is the most common secondary element of the various carbon blacks [25,31]. By comparing calcium distributions obtained by MA-XRF with those obtained by IRR, which highlights the carbonaceous matter, the presence of carbon black was effectively identified.

The Raman spectra, the IRR and the calcium distribution obtained by MA-XRF show that in general, carbon black was used for the black elements of the composition, as well as to create shadow effects. The calcium distributions shown in Figure 10 effectively demonstrate the presence of calcium in areas of darker skin tones.

Figure 10. (**a**) Photographs, (**b**) IRR and (**Ca**) calcium distribution of: the female figure on the right of *Nocturnes* (**above**) and the central dressed female figure in *La voix publique* (**below**). The color scale in the elemental distribution is the count number in the XRF spectrum.

3.4.3. Red

The red pigments identified in the pictorial layers of the studied paintings are red iron oxide pigment, cadmium red (Cd(S,Se)) and vermilion (HgS). The first was identified due to the presence of iron in the pictorial layer. The identification of cadmium red is due to the joint presence of cadmium and selenium [25,26,32]. Vermilion was identified thanks to the detection of mercury by MA-XRF and the presence of two narrow absorption bands located at 252 cm^{-1} and 343 cm^{-1} in the Raman spectra [24,25,33]. As shown in Table 4, red iron oxide pigment is the most used, unlike vermilion, which was identified only in *L'hiver*. Despite the fact that cadmium red was an expensive pigment at the time, Delvaux seemed to favor it over vermilion. He sparingly used it for details like the elastic hair of the sculptress in *Pygmalion*, to color the skin of faces or draw contour lines, as shown in the selenium and cadmium distributions of the woman on the left in *Couple avec enfant dans la forêt* (Figure A1).

Table 4. List of detected pigments.

Title	Raman Bands [cm^{-1}]	Detected Elements	Main Supposed Pigment(s)
Red			
Couple avec enfant dans la forêt		Cd, Fe, Se	Cadmium red, red iron oxide
Le couple	290, 405, 600	Ba, Cd, Fe, Se	Cadmium red, red iron oxide
Jeune femme rêvant	215, 285, 400, 600	Fe	Red iron oxide
L'incendie		Fe, Si, Sr	Red iron oxide
Sans titre		Fe	Red iron oxide
Nocturnes		Fe	Red iron oxide
Pygmalion		Fe, Cd, Se	Cadmium red, red iron oxide
La voix publique		Fe	Red iron oxide
L'hiver	250, 295, 343, 430, 600	Cd, Hg, S, Se	Cadmium red, vermilion
Blue			
Couple avec enfant dans la forêt		Co	Cobalt blue
Le couple		Co	Cobalt blue
Pygmalion	535		Ultramarine blue
La voix publique	540	S, Si	Ultramarine blue
L'hiver	540	S	Ultramarine blue
Yellow			
Le couple	1170	Fe	Yellow iron oxide
Jeune femme rêvant		Fe	Yellow iron oxide
Green			
Couple avec enfant dans la forêt		Ba, Cr, Mn	Chrome-based green, barite, manganese oxide
Le couple		Ba, Cr	Chrome-based green, barite
Nocturnes		Ba, Cl	
Pygmalion	≈1350, ≈1580	Ca, Cl, Fe, P	Yellow iron oxide pig., carbon black
La voix publique		Cr	Chrome green
L'hiver	≈1350, ≈1580	Ca, Cd, P, S	Cadmium yellow (PY37), carbon black
Purple			
La voix publique		Co	Cobalt violet
L'hiver		Co, Mn, P	Cobalt violet, manganese violet
Brown			
Couple avec enfant dans la forêt		Fe, Si	Brown iron oxide
Le couple		Fe, Si	Brown iron oxide
Jeune femme rêvant		Fe, Sr	Brown iron oxide
L'incendie		Fe, Mn, Si, Sr	brown iron and manganese oxides
Sans titre		Fe, Mn, Si	brown iron and manganese oxides
Nocturnes		Fe, Mn	brown iron and manganese oxides
Pygmalion		Fe, Mn	brown iron and manganese oxides
La voix publique	405, 445, 600	Fe, Mn	brown iron and manganese oxides

In fact, using red to draw contour lines at the level of the flesh of the characters is a common practice in the paintings of Delvaux. We observed this in all the paintings studied with the exception of *L'hiver*. Figure 11 shows such a red line on the face and arm of the female figure in *Untitled*, as well as the iron distribution of an area of the canvas. The red color of these lines associated with iron shows the use of an iron oxide pigment. In the earliest paintings of the *corpus*, the line is easily noticeable and thick. With practice, the painter made it more discreet; in *La voix publique*, it is visible in the ears of female figures and more difficult to see elsewhere.

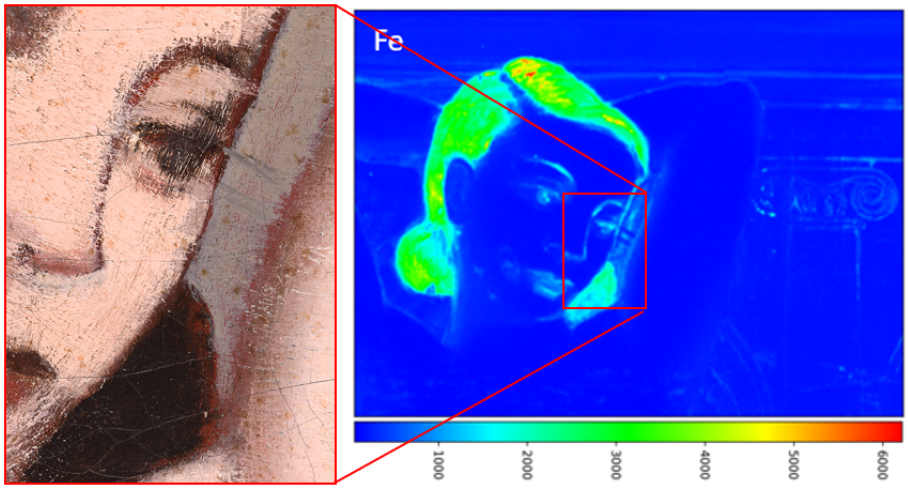

Figure 11. Details of the red contour lines of the female figure in the *Sans titre* painting and the iron distribution of the studied area. The color scale in the elemental distribution is the count number in the XRF spectrum.

White, black and red are used in the flesh tones of the characters in the compositions. The results make it possible to affirm that Delvaux mixed the white and red already present on his palette. In other words, he did not add an extra color to achieve the desired tone. As already stipulated, the addition of black made it possible to induce a light effect by shading of the skin. He used this technique for all the studied painting in the *corpus*, with the exception of *Couple avec enfant dans la forêt*. In order to make the pink tone of the skin, Delvaux added red (Cd and Se distributions in Figure A1), and to lighten it, he added a bit of white.

3.4.4. Blue

The performed analyses revealed the use of two blue pigments by the painter, namely cobalt blue ($CoO{\cdot}Al_2O_3$) and ultramarine blue ($Na_7Al_6Si_6O_{24}S_3$). The first, cobalt blue, was marketed as a substitute for natural ultramarine in the early 19th century. Cobalt blue pigment remains an expensive pigment, even though it is less expensive than genuine ultramarine [31]. The second, artificial ultramarine blue, was industrialized in 1830 and dominated the market until the arrival of phthalocyanine blue ($C_{32}H_{16}CuN_8$) in 1935 [33]. Cobalt blue was identified in the two earliest paintings in the *corpus* (*Couple avec enfant dans la forêt* and *Le couple*). We assumed the use of this pigment because only cobalt was detected in the blue area by MA-XRF [31]. Ultramarine blue was found in *Pygmalion*, *La voix publique* and *L'hiver*, as shown in Table 4. Ultramarine blue was identified by RS, with a narrow absorption band located at 540 cm^{-1}, as shown in Figure 12 for the blue signature of *L'hiver*, indicating the presence of this pigment [24,33,34].

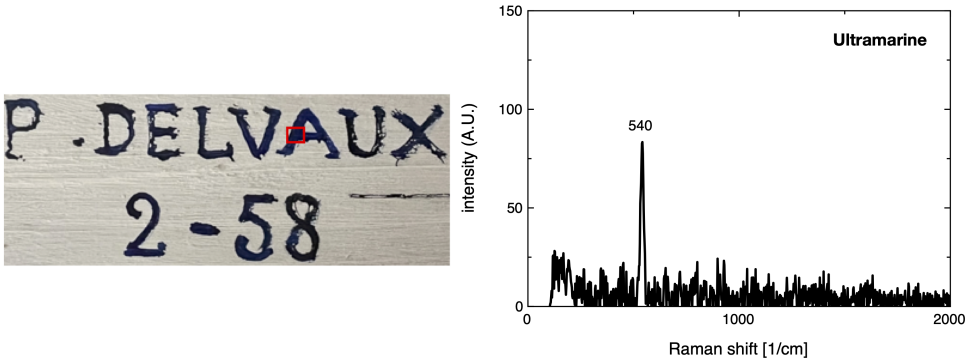

Figure 12. Raman spectrum obtained from the study of the blue signature of *L'hiver*, showing the presence of ultramarine.

For the blue pigments used by Delvaux, note that he used cobalt blue early compared to what is found in the literature. According to Debra's book, Delvaux started using this pigment because it had been recommended by his students at La Cambre school, so after 1950 [1]. Our results show the use of this pigment for *Couple avec enfant dans la forêt*, which is dated to 1928–1929.

Note that other research has been carried out on *Les nœuds roses* (oil on canvas, 122 × 160 cm,1937) [35], *Faubourg* (oil on panel, 130 × 130 cm, 1956) [21] and *La Genèse* (oil on wall, 661 × 1196 cm, 1960) [36]. The blue pigments used for the first canvas are Prussian blue ($Fe_4[Fe(CN)_6]_3 \cdot xH_2O$) mixed with ultramarine blue [35]. For *Faubourg*, it is a mixture of ultramarine blue, titanium white and phthalocyanine blue [21] while for *La Genèse*, the mixture is composed of ultramarine blue, titanium white and phthalocyanine green [36]. This information is important and makes it possible to construct an initial timeline of the use of blue pigments in the painter's palette: a systematic use of ultramarine blue in paintings can be dated to after 1937.

3.4.5. Yellow

In this section on yellow pigment, we recount Delvaux's words about the yellow in van Gogh's painting *Les Tournesols* : "The yellows that van Gogh sought so long have turned brown there because this one was not rich and could not use good colors. He used chrome. And the chrome yellows don't last. " [7,37,38]. Delvaux therefore seems to have had some knowledge of the quality of pigments. Unlike van Gogh, he had the chance to live from his art. And before that, his parents, as well as his first wife, supported him financially [1]. This allowed him to choose quality materials, in particular quality pigments such as cobalt blue and cadmium red, which are relatively expensive [26,31].

Yellow pigments that were identified in the *corpus* are yellow iron oxide pigment and cadmium yellow (CdS), as shown in Table 4. The yellow pigment based on iron oxide was identified by MA-XRF thanks to the detection of iron [31] in the yellow areas of *Le couple* and *Jeune femme rêvant*. In *L'hiver* and *Pygmalion*, the green color of the vegetation was achieved by means of a mixture of black and yellow pigments. Figure 13 shows the presence of yellow and black grains in the green of the vegetation in the painting. Black is made of carbon black, given the results of RS (broad bands at ≈1350 and ≈1580 cm^{-1}) and MA-XRF. The yellow pigment in *Pygmalion* was identified as yellow iron oxide through the detection of iron by MA-XRF in this green area. The yellow pigment in *L'hiver* is cadmium yellow, given the presence of cadmium in this area [26] and, more precisely cadmium yellow PY37, as MA-XRF does not show the presence of zinc, which, accompanied by cadmium, would have indicated cadmium yellow PY35 [25,39,40].

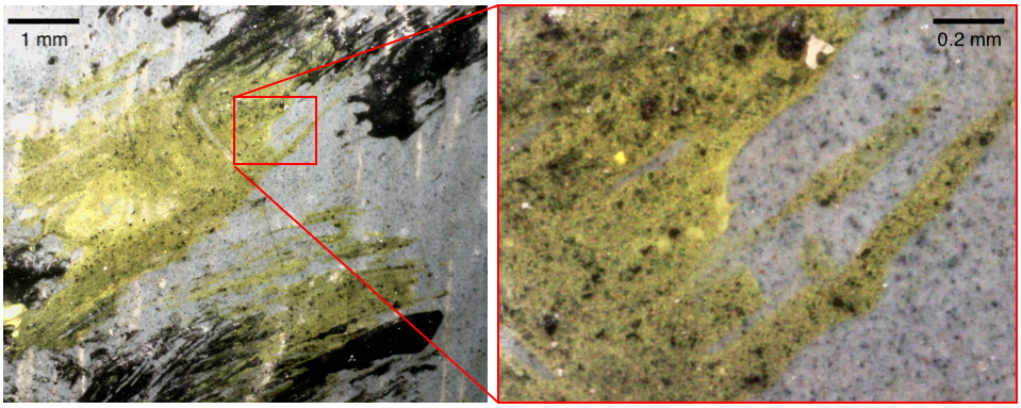

Figure 13. 50× (**left**) and 240× (**right**) enlargements of a vegetation zone of *L'hiver*.

3.4.6. Green

Unlike *Nocturnes* and *L'hiver*, the green color of the other paintings in the *corpus* comes from a single green pigment and not from a mixture of pigments. The presence of a green based on chromium oxide was identified in *Couple avec enfant dans la forêt* (see chrome distribution in Figure A1), *Le couple* and *La voix publique*. This identification was carried out through the detection of chromium by MA-XRF [25,29]. The analyses, unfortunately, do not allow us to advance whether it is a chromium oxide or a hydrated chromium oxide. Table 4 indicates the presence of chlorine in the green of the pictorial layers of *Pygmalion* and *Nocturnes*. Figure 14 illustrates this chlorine distribution for the female figure on the left in *Nocturnes*. We noticed that it is also present in the skin tones and does not seem to be at the origin of the green color of this painting. For the moment, no hypothesis can be proposed on its origin.

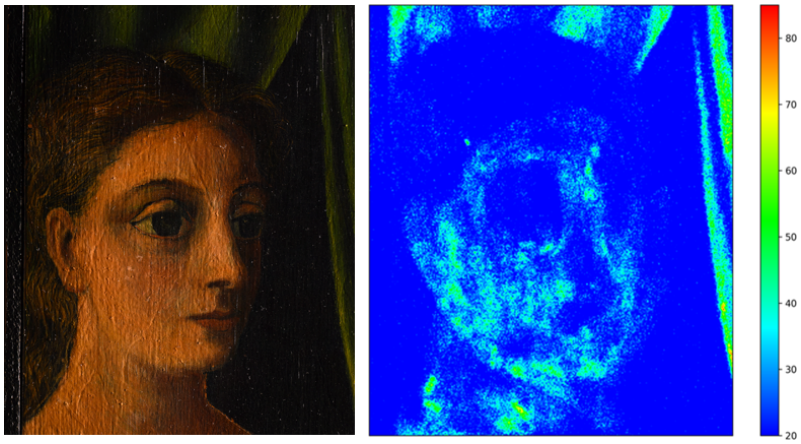

Figure 14. Photograph and chlorine distribution of the left female figure in *Nocturnes*. The color scale in the elemental distribution is the count number in the XRF spectrum.

3.4.7. Purple

The violet color is part of the pictorial layer of two paintings of the studied corpus. In *La voix publique*, it is used to color large purple nodes. Unlike in *L'hiver*, where its presence is more subtle and barely noticeable, it colors a veil of a character in the background. In both cases, digital microscopy showed that the purple comes from a pure pigment and not from a mixture of blue and red pigments. The purple color of both paintings is composed of cobalt and phosphorus according to MA-XRF. Figure 15 clearly shows that the cobalt present in the violet areas is associated with phosphorus and not with arsenic. In view of our results, we can suggest that it is a cobalt violet ($Co_3(PO_4)_2$) [25,41]. In the violet area of *L'hiver*, manganese was detected, in addition to cobalt and phosphorus. For this painting,

a mixture of purple pigments may have been used: cobalt violet and manganese violet ($MnNH_4P_2O_7$).

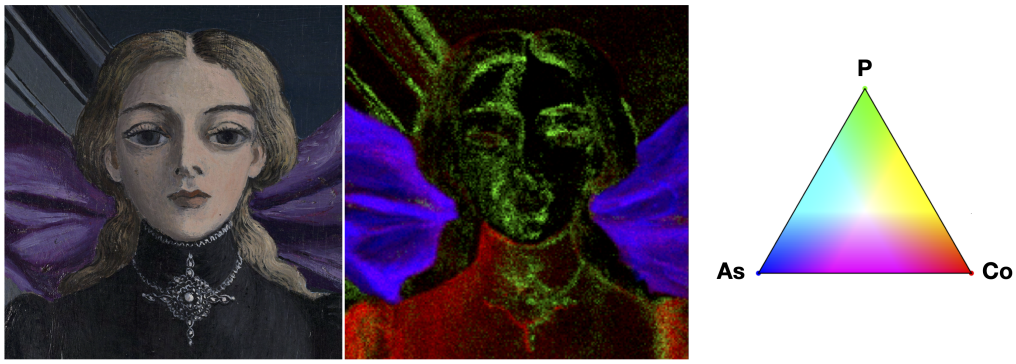

Figure 15. Woman dressed in the center of *La voix publique*: As-P-Co distribution. Superposition of the distributions of arsenic (green color: G = 100 if the As signal is maximum and G = 0 if As is minimum), phosphorus (red color: R = 100 if P the signal is maximum and R = 0 if P is minimum) and cobalt (blue color: B = 100 if the Co signal is maximum and B = 0 if Co is minimum).

3.4.8. Brown

As we can see in Table 4, MA-XRF systematically detected iron in the brown of the studied paint layers. This result is not surprising, since many brown pigments are based on iron oxide. For the three oldest paintings in the corpus, the brown pigment is composed of iron oxide only, as we can see, for example, in Figure A1. Therefore, it is composed of a mixture of iron oxide and manganese oxide. In Figure 16, the iron and manganese distributions of part of *L'incendie* illustrate the joint presence of these two elements in the brown hair of the female figure. The detection of manganese by MA-XRF can be interpreted as the use of an umber brown pigment [25,42].

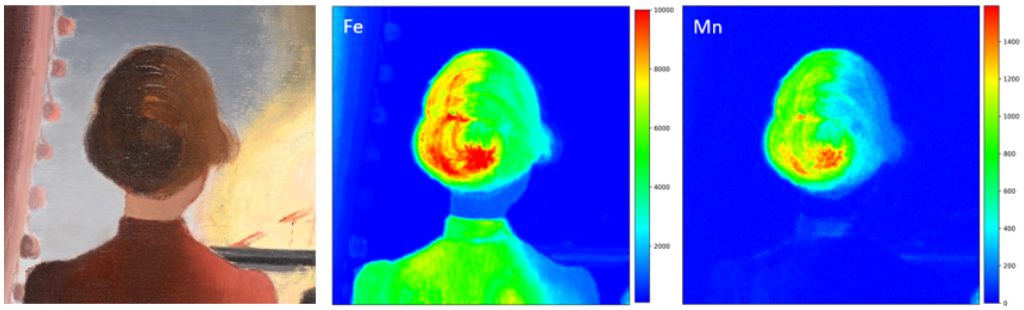

Figure 16. Female figure in *L'incendie*: photograph (**left**), iron distribution (**center**) and manganese distribution (**right**). The color scale in the elemental distribution is the count number in the XRF spectrum.

3.5. Dripping Phenomenon

For the whole *corpus*, with the exception of *Jeune femme rêvant* and the two parts of *L'incendie*, the photographs under ultraviolet light reveal a recurring phenomenon (Table A1). As shown in Figure 17, these are non-pigmented and translucent drips that appear while the pictorial layer is drying. These drips are sometimes even visible to the naked eye, as in *L'hiver*, where they stand out as yellowish on the white tiles.

For the moment, their exact nature remains uncertain. Additional analyses involving mass spectrometry would provide more information about them. We can assume that they come from the addition of a yet undefined component to the oil paint. Indeed, in images from Delvaux's studio, there are bottles of pure linseed oil but also turpentine, charcoal fixative and retouching varnish (shown in Figure 18) [28]. In addition, In Debra's book, Delvaux testified to having only ever used pure linseed oil [1]. This statement by the artist

may mean that he chose tubes of oil paint based on pure linseed oil, which could mean that he was reworking the thickness or the gloss of the oil paint with pure linseed oil.

Figure 17. Visible photograph and photograph under UV light of a part of *Le couple*.

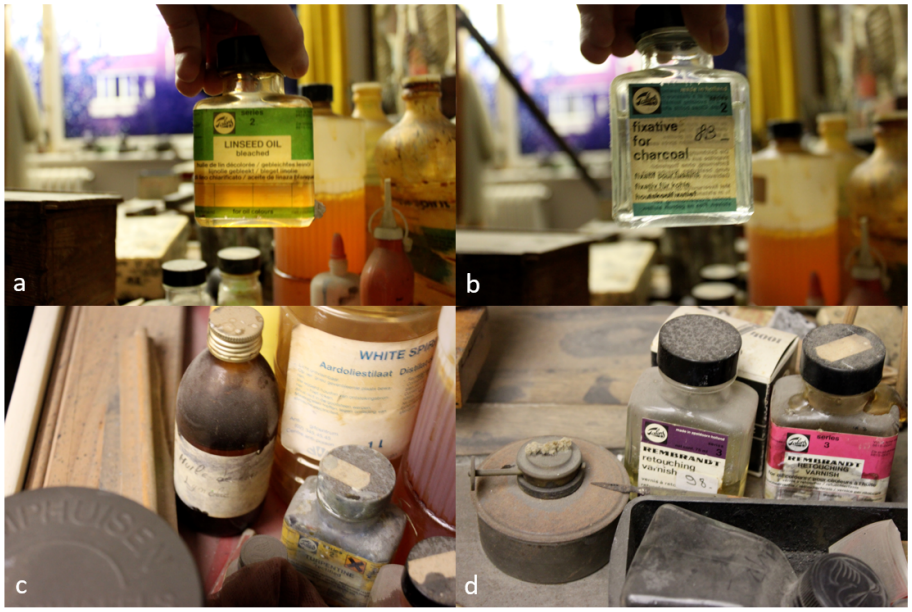

Figure 18. Images of the Delvaux studio: (**a**) linseed oil bleached series 2 by Talens; (**b**) fixative for charcoal series 2 by Talens; (**c**) white spirit, linseed oil and turpentine rectified series 2 by Talens; (**d**) retouching varnish Rembrandt series 3 and retouching varnish for oil colours Rembrandt series 3.

These same drips were observed in the study of *Les nœuds roses* but were not been identified for sure [35]. It is therefore a recurring phenomenon in the oil paintings of Delvaux that deserves to be further explored.

4. Discussion and Conclusions

The study of these nine works provides novel knowledge on the process of elaboration and on the constituent materials of the early works of Paul Delvaux. A summary of the identified pigments is presented in Table 4. A more complete presentation of the overall results is presented in Table A1.

For the elaboration process, the application of a preparation layer is dependent on the type of support. Indeed, all canvases of the studied *corpus* have a white ground layer, unlike plywood, which does not necessarily have one. Moreover, the ground layer can sometimes be colored, as in *Pygmalion*.

For the preparatory drawing, the second stage of the development process, a grid was used in two paintings: *Couple avec enfant dans la forêt* and *Jeune femme rêvant*. The preparatory drawing of the paintings anterior to *L'incendie*, 1935, was done using dry carbonaceous material such as charcoal or pencil. After that, the preparatory drawing was made based on an oil sketch. From then on, a parallel was made with the studies of the works which were carried out in pencil or charcoal until 1932, when the artist began to use Indian ink. It would be interesting to analyze works dated from 1930 to 1934 in order to effectively date this change.

Then, in accordance with what is found in the literature, various changes and corrections were observed in the compositions. Changes were also made during pictorial execution, as evidenced by the many observed pentimenti . They can be discreet, such as are correction of the position of the main characters or even the removal of the elements that make up the ground of the composition. But they can also be more drastic, like the removal or addition of a character. Once the painting is finished, the changes in composition do not end there, as shown in *L'incendie* and in *La voix publique*.

For the pigments that make up the pictorial layer, the palette is relatively poor and composed of inorganic pigments (Table A1). Some technical characteristics of the painter were observed, such as the use of carbon black to create luminosity and shadow in the flesh of the figures or the use of red paint in the lines of the flesh.

The results of the study of these nine paintings allowed a first approach regarding the evolution of the different pigments in the painter's palette. It is particularly noticeable with the blues and the whites.

The last result is the presence of non-pigmented translucent drippings that are visible under ultraviolet light. These drips are recurrent in Delvaux's paintings and appear when the paint layer dries. This phenomenon deserves special attention, requiring other methods of analysis.

To conclude, it is important to remember that the studied *corpus* only covers thirty years of the painter's career, from 1928 to 1958, which is a small part of Delvaux's work, since he began his painted production just after his training at the Academy in 1920 and he stopped painting only shortly before his death in 1994. Although the results revealed in this article already give us a lot of information on the process of creation and on the material used to make them, they are not representative of the painter's career. They bring up a lot of questions. Are there other paintings with a green ground layer? Is it possible to find an explanation for the absence of a ground layer on certain plywood? When did the painter switch to oil sketching? What is the timeline of the evolution of the different pigments in the painter's palette? What is the exact origin of these drippings? We hope that by increasing the number of studied artworks, we can answer these questions with more precision and, perhaps, discover other technical particularities of Paul Delvaux.

Author Contributions: C.D., D.S., A.D., S.-J.K. and E.D. realized the in situ measurements. E.D., C.D., D.S. and F.V. have interpreted the results of the analysis. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

RMFAB	Royal Museums of Fine Arts of Belgium
CEA	Centre Européen d'Archéométrie (European Center for Archaeometry)
IRR	Infrared reflectography
XRR	X-ray radiography
MA-XRF	Macro X-ray fluorescence
RS	Raman spectroscopy

Appendix A

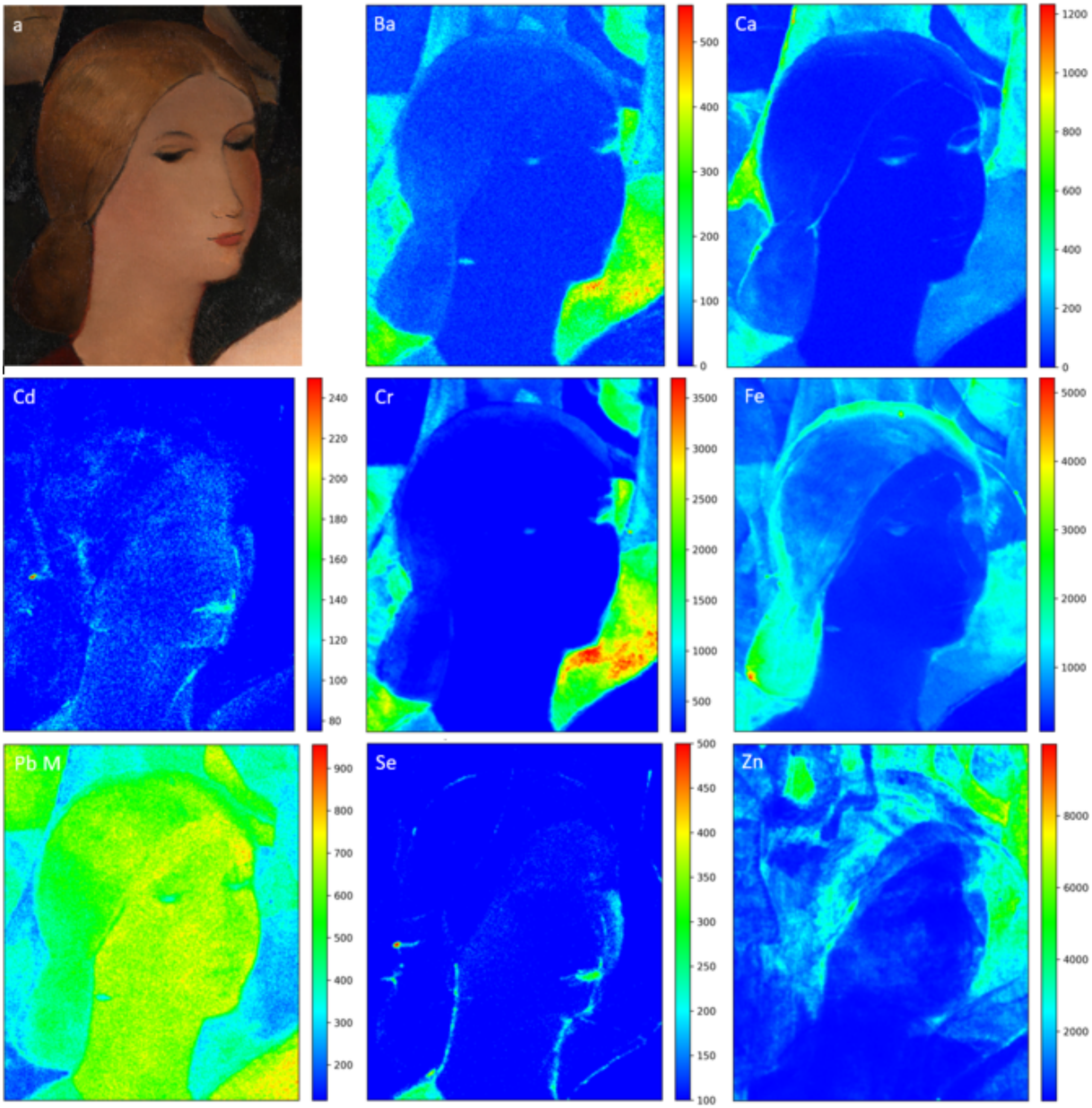

Figure A1. MA-XRF imaging of the left female figure in *Couple avec enfant dans la forêt*: (**a**) photograph and the different elementary distributions. The color scale in the elemental distribution is the count number in the XRF spectrum.

Appendix B

Table A1. Summary of all results for each painting: the type of support, the pigments that make up the ground layer, the characteristics of the preparatory drawing, the type of pentimenti, the pigments that make up the pictorial layer and the type of dripping.

Title	*Couple avec Enfant dans la Forêt* (1928–29)	*Le Couple* (1929)	*Jeune Femme Rêvant* (1931)	*L'incendie* and *Sans Titre* (1935)	*Pygmalion* (1939)	*Nocturnes* (1939)	*La voix Publique* (1948)	*L'hiver* (1958)
Support	canvas	canvas	canvas	canvases	triplex	wood	multiplex	multiplex
Ground layer	lead white, zinc white	lead white, zinc white	lithopone	lead white, lithopone	not present	lithopone, green cobalt pig.	not available	not present
Preparatory drawing	carbon dry matter and grid	carbon dry matter	carbon dry matter and grid	oil sketch	oil sketch	oil sketch	oil sketch	oil sketch
Pentimenti	corrections in the main figures and deletion of secondary figures	corrections in the main figures	indefinite background changes	deletion of a figure (for the untitled part) and change of wall ornaments design	corrections in the main figure	corrections in the main figures	corrections in the main figures	corrections in the main figures
Pictorial layer	lead white, carbon black, cobalt blue, red iron oxide pig., cadmium red, chrome-based green pig., brown iron oxide pig.	lead white, carbon black, cobalt blue, red iron oxide pig., cadmium red, chrome-based green pig., yellow iron oxide pig., brown iron oxide pig.	lead white, carbon black, red iron oxide pig., yellow iron oxide pig., brown iron oxide pig.	lead white, lithopone, carbon black, red iron oxide pig., brown iron oxide and manganese oxide pig.	zinc white, barite, carbon black, red iron oxide pig., cadmium red, ultramarine blue, yellow iron oxide pig., brown iron oxide and manganese oxide pig.	zinc white, barite, carbon black, red iron oxide pig., brown iron oxide and manganese oxide pig	lead white, zinc white, titanium white (anatase), barite, caclium carbonate, carbon black, red iron oxide pig., ultramarine blue, chrome-based green pig., cobalt violet, brown iron oxide and manganese oxide pig.	zinc white, caclium carbonate, carbon black, cadmium red, vermilion, ultramarine blue, cadmium yellow(PY37), cobalt violet, manganese violet, brown iron oxide and manganese oxide pig.
Dripping phenomenon	non-pigmented translucent dripping visible under UV	non-pigmented translucent dripping visible under UV			non-pigmented translucent dripping visible under UV	non-pigmented translucent dripping visible under UV	non-pigmented translucent dripping visible under UV	non-pigmented translucent dripping visible under UV

References

1. Debra, M. *Promenades et Entretiens avec Delvaux*; Duculot: Paris, France, 1991.
2. Ghêne, P.; Anrieu, P. *Paul Delvaux Raconte. . . ;* Editions Havaux: Nivelles, Belgium, 2004.
3. Ghêne, P. *Paul Delvaux, Les Jardins Secrets*; Editions Pandora: Anvers, Belgium, 2000.
4. Basch, S.; Clair, C.; Draguet, M.; Farnoux, A.; Jockey, P.; Koutsomallis, K.; Theodoropoulos, T. *Delvaux et le Monde Antique*; BAI: Antwerpen, Belgium, 2009.
5. Engen, L.; VanDeun, C.; Closset, E.; Laroche, P.; Ratz, S.; Warzée, G.; Werpin, F. *Le pays Mosan de Paul Delvaux*; Snoeck-Ducaju & zoon: Gent, Belgium, 1997.
6. Ghêne, P.; Laoureux, D.; Leblanc, C.; Neve, L. *Paul Delvaux, Maître du rêve*; Somogy Editions d'art: Paris, France, 2017.
7. Pire, M. *Paul Delvaux, Inconnu et Mystérieux*; Village Publishing: Bruxelles, Belgium, 1997.
8. Rémon, R.; Canonne, X.; Chariot, C.; Denhaene, E.; DeRycke, J.P.; Hupkens, J.P.; Robert-Jones, P.; VanDeune, C.; Warzée, G. *Paul Delvaux, Peintre des Gares*; Editions Luc Pire: Bruxelles, Belgium, 2009.
9. MRBAB. *Paul Delvaux, 1897–1994*; Blondé s.a.: Wemmeigen, Belgium, 1997.
10. VanDeun, C.; Carels, C. *Paul Delvaux, sa vie*; BAI: Antwerpen, Belgium, 1985.
11. Brasseur, C. Montald. In *Nouvelle Biographie Nationale 13*; Lewin, R.A., Ed.; Académie Royale des Sciences, des Lettres et des Beaux-Arts de Belgique: Bruxelles, Belgium, 2016; pp. 249–251.
12. Brasseur, C. *Paul Delvaux, The Man Who Loved Trains*; Snoeck: Gent, Belgium, 2020.
13. Guégen, D. *Jean Delville, La Contre-Histoire*; Lienart: Paris, France, 2016.
14. Strivay, D.; Clar, M.; Rakkaa, S.; Hocquet, F.P.; Defeyt, C. Development of a translation stage for in situ noninvasives analysis and high-resolution imaging. *Appl. Phys. A Mater. Sci. Process.* **2016**, *122*, 950. [CrossRef]
15. Hocquet, F.P.; Garnir, H.P.; Marchal, A.; Clar, M.; Oger, C.; Strivay, D. A remote controlled XRF system for field analysis of cultural heritage objects. *X-ray Spectrom.* **2008**, *37*, 304–308. [CrossRef]
16. Hocquet, F.P.; Calvo del Castillo, H.; Cervera Xicotencatl, A.; Bourgeois, C.; Oger, C.; Marchal, A.; Clar, M.; Rakkaa, S.; Micha, E.; Strivay, D. Elemental 2D imaging of paintings with a mobile EDXRF system. *Anal. Bioanal. Chem.* **2011**, *399*, 3109–3116. [CrossRef] [PubMed]
17. Alfeld, M.; Janssens, K.; Dik, J.; de Nolf, W.; van der Snickt, G. Optimization of mobile scanning macro-XRF systems for the in situ investigation of historical paintings. *J. Anal. At. Spectrom.* **2011**, *26*, 899–909. [CrossRef]
18. Donais, M.K.; George, D.B. *X-ray Fluorescence Spectrometry and Its Applications to Archeology, An Illustrated Guide*; Momentum Press: New York, NY, USA, 2018.
19. Solé, V.; Papillon, E.; Cotte, M.; Walter, P.; Susini, J. A multiplatform code for the analysis of energy-dispersive X-ray Fluorescence spectra. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2007**, *62*, 63–68. [CrossRef]
20. Lauwers, D.; Hutado, A.G.; Tanevska, V.; Moens, L.; Bersani, D.; Vandenabeele, P. Characterisation of a portable Raman spectrometer for in situ analysis of art objects. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2014**, *118*, 294–301. [CrossRef] [PubMed]
21. Vandenabeele, P.; Hardy, A.; Howel, G.M.E.; Moens, L. Evaluation of a principal components-based searching algorithm for Raman spectroscopic identification of organic pigments in 20th century artwork. *Appl. Spectrosc.* **2000**, *55*, 525–533. [CrossRef]
22. DeBock, P.A. *Paul Delvaux, L'homme, Le Peintre, Psychologie d'un Art*; Jean-Jacques Pauvert: Bruxelles, Belgium, 1967.
23. Gillemon, D.; Draguet, M.; Sojcher, J. *Paul Delvaux Dévoilé*; Snoeck: Gent, Belgium, 1994.
24. Caggiani, M.C.; Cosentino, A.; Mangone, A. Pigments Checker version 3.0 a handy set for conservation scientists: A free online Raman spectra database. *Microchem. J.* **2016**, *129*, 123–132. [CrossRef]
25. Larsen, R.; Coluzzi, N.; Cosentino, A. Free XRF spectroscopy database of pigments checker. *Int. J. Conserv. Sci.* **2016**, *7*, 659–668.
26. Feller, R.L. (Ed.) *Artists' Pigments, Volume 1, A Handbook of Their History and Characteristics*; Cambridge University Press: Cambridge, UK, 1987.
27. Houbart-Wilkin, S. Le dessin de Paul Delvaux, A propos de six dessins offerts aux Musées Rouyaux par Claude Spaak (in French, The drawing of Paul Delvaux, About six drawings donated to the Rouyaux Museums by Claude Spaak). In *Bulletin*, 3rd ed.; Musees Royaux des Beaux-Arts de Belgique: Bruxelles, Belgium, 1966; pp. 189–206.
28. Pesesse, S. La Genèse. Master's Thesis, ESA St-Luc Liège, Liège, Belgium, 2012.
29. Fitzhugh, E.W. (Ed.) *Artists' Pigments, Volume 3, A Handbook of Their History and Characteristics*; Archetype Publications Ltd.: London, UK, 1997.
30. Coupry, C.; Le Marec, J.; Corset, J.; Papillon, M.C.; Lefèvre, R.; Duval, A.; Lahanier, C.; Rioux, J. Analyse de pigments blancs appliquées à l'étude chronologique des peintures de chevalet- blanc de titane (in French, Analysis of white pigments applied to the chronological study of easel paints - titanium white). *Investig. Sci. Des Oeuvres D'art* **1987**, *1*, 25–32.
31. Berrie, B.H. (Ed.) *Artists' Pigments, Volume 4, A Handbook of Their History and Characteristics*; Archetype Publications Ltd.: London, UK, 2007.
32. Buxbaum, G.; Pfaff, G. (Eds.) *Industrial Inorganic Pigments, Third Completely Revised Ed.*; Wiley-VCH Verlag GmbH and Co KGaA: Weinheim, Germany, 2005.
33. Ashok, R. (Ed.) *Artists' Pigments, Volume 2, A Handbook of Their History and Characteristics*; Cambridge University Press: Cambridge, UK, 1993.

34. Osticioli, I.; Mendes, N.F.C.; Francisco, P.S.C.G.; Becucci, M.; Castellucci, E. Analysis of natural and artificial ultramarine blue pigments using laser induced breakdown and pulsed Raman spectroscopy, statisticial analysis and light microscopy. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2008**, *73*, 525–531. [CrossRef] [PubMed]
35. Vandeputte, E. A Multi-Technical Study on the Materials of the Pink Bows (1937), a Flemish Masterpiece by Paul Delvaux in the Collection of the KMSKA. Ph.D. Thesis, University of Antwerp, Antwerpen, Belgium, 2022.
36. Defeyt, C. Copper-Phtalocyanine Blue Pigments in Conservation. Ph.D. Thesis, University of Liège, Liege, Belgium, 2013.
37. Monico, L.; Miliani, C.; Janssens, K.; Brunetti, G.B.; Vagnini, M.; Vanmeert, F.; Falkenberg, G.; Abakumov, A.; Lu, Y.; Tian, H.; et al. Degradation process of lead chromate in paintings by Vincent van Gogh studied by means of spectromicroscopic methods. 3. Synthesis, characterization, and detection of different crystal forms of the chrome yellow pigment. *Anal. Chem.* **2012**, *85*, 851–859. [CrossRef] [PubMed]
38. Monico, L.; Miliani, C.; Janssens, K.; Vanmeert, F.; Brunetti, G.B.; Cotte, M.; Hendricks, E.; Geldof, M. The degradation process of lead chromate in paintings by Vincent van Gogh. *Microsc. Microanal.* **2013**, *19*, 1424–1425. [CrossRef]
39. Monico1, L.; Cartechini, L.; Rosi, F.; Chieli, A.; Grazia, C.; De Meyer, S.; Nuyts, G.; Vanmeert, F.; Janssens, K.; Cotte, M.; et al. Probing the chemistry of CdS paints in *The Scream* by in Situ Noninvasive Spectroscopies Synchrotron radiation X-ray techniques. *Sci. Adv.* **2020**, *6*, eaay3514. [CrossRef] [PubMed]
40. Rosi, F.; Grazia, C.; Gabrieli, F.; Romani, A.; Paolantoni, M.; Vivani, R.; Brunetti, G.B.; Colomban, P.; Miliani, C. UV-Vis-NIR and micro Raman Spectroscopies for the non destructive identification of $Cd_{1-x}Zn_xS$ solid solution in cadmium yellow pigments. *Microchem. J.* **2016**, *124*, 856–857. [CrossRef]
41. Corbeil, M.C.; Charland, J.P.; Moffatt, E.A. The characterization of cobalt violet pigments. *Stud. Conserv.* **2002**, *47*, 237–249.
42. Eastaugh, N.; et Walsh, V.; Chaplin, T.; Siddall, R. *Pigment Compedium, a Dictionary and Optical Microscopy of Historical Pigments*; Elsevier: Oxford, UK, 2008.