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Portrait of an artist at work: exploring Max Ernst's surrealist techniques

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Abstract
Max Ernst was one of the most influential artists associated with both the Dada and Surrealist movements. However, until now, only few scientific studies have been devoted to his works. This paper presents the results of a multi-analytical investigation on six oil paintings, made between 1927 and 1942, belonging to the Peggy Guggenheim Collection in Venice (Solomon R. Guggenheim Foundation, New York). Through a combined art historical and scientific approach, this study aims at understanding Ernst's painting techniques, including *frottage*, *grattage*, *dripping*, and *decalcomania*, the used materials, and the state of conservation of the artworks. Non-invasive in situ investigations were performed by means of Vis–NIR multi-spectral imaging, X-ray fluorescence, external reflection FTIR and Raman spectroscopy. Imaging analysis revealed important information about Ernst's painting methods while the other techniques provided useful information about the ground layer, the painting materials and the presence of alteration products. Ernst's palette discloses great freedom in his use of materials and evolution during the time. This investigation demonstrates that an integrated, non-invasive, diagnostic approach provides a thorough analysis of materials and execution techniques of Ernst' masterworks allowing an in-depth knowledge of his highly skilled work.

Keywords: Max Ernst, Surrealism, Vis–NIR multi-spectral imaging, XRF, Raman spectroscopy, ER-FTIR

Introduction

Maximilian Maria Ernst (Brühl, 1891–Paris, 1976) is considered one of the most influential German artists of the twentieth century. Early on in his career, he was part of the Rheinische Expressionisten group in Bonn and, after World War I, he produced his first collages and co-founded the short-lived Cologne Dada group. Following his move to Paris, he became a pioneer of the Surrealist movement, creating his own idiosyncratic Surrealist visual idiom. Like many other artists associated with the Surrealism group, Ernst was affected by the horrific war experience, which revealed the moral weakness, social injustice, and political dysfunctionality of the world. Ernst thus rejected a rational vision of life and the prevailing values in society, choosing to pursue alternative avenues: the irrational, dreams, the subconscious, and even magic and alchemy. For him, they were powerful ways to stimulate and free the mind from any imposed limitations.

In the 1920s, when Ernst was fully embracing Surrealism, his experimental approach to art-making resulted in his invention of several techniques.

The diverse, often novel artistic techniques such as *collage*, *frottage*, *grattage*, *dripping*, and *decalcomania*, facilitated, and indeed marked, the evolution of Ernst's unique visual vocabulary. Actually, his oeuvre merged imagination and subconscious with memory and elements of reality in his paintings such as *The Kiss* (1927), *Zoomorphic Couple* (1933), *Garden Airplane Trap* (1935–36), *The Entire City* (1936–37), *Attirement of the Bride* (1940) and *The Antipope* (December 1941 – March

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1942) that are part of the Peggy Guggenheim Collection (PGC) in Venice (Solomon R. Guggenheim Foundation, New York). These paintings have been analyzed in this study as examples of the aforementioned techniques. It should be noted, however, that the present article will not include Ernst's collages, since *collage* is a complex topic in the scholarship of Dada and Surrealism, and Ernst's oeuvre, and a separate article should be dedicated to it.

Thus far, only a few scientific studies on Ernst's paintings can be found in literature [1–5]; therefore, this study sheds light on the amazing pictorial technique of this master painter, by presenting multi-analytical and non-invasive investigation of the above-mentioned six oil paintings completed by Ernst between 1927 and 1942. The in-situ investigation, which involves portable techniques such as Vis–NIR multispectral imaging, External Reflection Fourier Transform Infrared Spectroscopy (ER-FTIR), Raman and X-ray (XRF) spectroscopies is focused on the understanding of his painting materials together with the evolution of his pictorial practice as well as the condition of these works.

Materials and methods

The paintings: art historical context

In *The Kiss* (129 × 161.2 cm, 1927) Ernst celebrates uninhibited sexuality and his relationship and marriage with the young Marie-Berthe Aurenche in 1927. This may have inspired the erotic subject matter of this painting (Fig. 1a). Furthermore, the pyramidal group in the centre and the enveloping gesture of the figure on the top might be compared with Renaissance compositions, in particular with Leonardo da Vinci's painting *Sant'Anna con la Vergine e il Bambino* (1510–13, Louvre Museum, Paris) [6].

In the painting *Zoomorphic Couple* (91.9 × 73.3 cm, 1933), one can distinguish a form akin to that of a bird (the male part) caressed by a humanoid form (the female part) and an octopus that encircles the two figures (Fig. 1b). Yet even if zoomorphic animal features are present, the scene suggests the unity of matter of which they are composed. It evokes a process of evolution and geological formation. It may have alchemical connotations since Ernst was interested in alchemy and the occult. The figures seem to emerge from a *prima materia* substance, appearing as poetic and dreamlike image.

Garden Airplane Trap (54 × 64.7 cm, 1935–36) is one of the fifteen works on this theme in which ribbon-like broken airplanes, flowers, and lush foliage are scattered across a landscape composed of geometric, boxlike structures (Fig. 1c) [7]. The landscape and its elements gain in hostile, menacing features, becoming, in the words of M.E. Warlick, "claustrophobic mazes of entrapment" [8]. Ernst's construction of space here and the landing strips can be compared to the arctic ice landscape, depicting a shipwreck, portrayed by Caspar David Friedrich in the painting The Sea of Ice (1823–24, Hamburger Kunsthalle, Hamburg).

The Entire City (96.5 × 160.4 cm, 1937) is one of thirteen canvases depicting panoramas of cities frequently in decay, where the texture effect is mainly created with the frottage technique (Fig. 1d). Thanks to a trip in South-East Asia in the mid-1920s, Ernst discovered exotic plants and animals as well as extravagant artistic expressions that he then seems to have re-envisioned in his paintings in a personal way. Here, the ruins of pyramidal structures, covered with vegetation, recall archaeological remnants, and become uncompromising symbols of the decaying state of civilization, but also of the cyclical regeneration of life. On the left of the composition, among the leaves, a headless woman's body and a form akin to an iguana can be seen [7].

The painting *Attirement of the Bride* (129.6 × 96.3 cm, 1940) (Fig. 1e), created in 1940, shortly after the start of the Second World War and just before Ernst fled Europe for the U.S., is the epitome of his artistic pursuits and his interest in topics related to the occult. With the execution of the *Attirement of the Bride*, Ernst places himself in the long tradition of artists exploring the ancient ritual of marriage. In the painting a "chemical wedding" between King and Queen is depicted, describing an alchemical archetype beloved by the Surrealists. Here, the bride may represent Ernst's then partner, the British Surrealist artist Leonora Carrington, while the green bird-man on the left may be Ernst himself. The female figures are inspired by Northern Renaissance painting, and the chequered pattern on the floor seems to adhere to the Renaissance notion of perspective, instilling the work with space and depth.

Finally, *The Antipope* (32.5 × 26.5 cm, 1941–42) (Fig. 1f) encourages a biographical interpretation and may reveal the complex relationship between Ernst, Carrington and Peggy Guggenheim, who was his partner at the time. Knowing of Carrington's fascination with horses, Ernst may have portrayed himself as the blue horse-headed figure, alluding to his love for her. One may speculate that the pink-clad figure leaning toward "Ernst" is Carrington; the face of the green totemic figure recalls her features as well. Guggenheim could be the second, estranged horse-headed figure on the left. Her separation from the artist is graphically represented by a diagonal (a spear) which splits the canvas in two parts [6]. Generally, the overlap between plant, animal, and human life in this work reveals the deceptive construction of reality and the continuity of nature's underlying manifestations. Nature was a source of mystery and wonder for Ernst, and its decay metaphoric of human relationships. Plants or

Fig. 1 A selection of paintings by Max Ernst, the Peggy Guggenheim Collection (PGC), Venice: **a** *The Kiss 76.2553 PG 71* © *Max Ernst, by SIAE 2008* (1927), **b** the *Zoomorphic Couple 76.2553 PG 75 © Max Ernst, by SIAE 2008* (1933), **c** the *Garden Airplane Trap* 76.2553 PG 76 © Max Ernst, by SIAE 2008 (1935–136), **d** the *Entire City 76.2553 PG 77© Max Ernst, by SIAE 2008* (1937), **e** the *Attirement of the Bride* 6.2553 PG 78 © Max Ernst, by SIAE 2008 (1940) and **f** *The Antipope* 6.2553 PG 80 © Max Ernst, by SIAE 2008 (1941–42)

fossils, appear to be decomposing, being a possible metaphor for the deteriorating relationships between Ernst and both women at the time.

Max Ernst's painting techniques

The analysed paintings are representative of a variety of materials and techniques (*frottage, grattage, dripping*, and *decalcomania*) and can demonstrate the evolution of Ernst's works over 15 years.

In 1921, by rubbing on the back of a telegram, he unexpectedly discovered the *frottage* technique (the French term for 'rubbing'). *Frottage* consisted of placing paper on a textured surface of found material, such as a board, wooden floor, or textiles, and rubbing it with graphite or other media. This innovative method perfectly adhered to Breton's definition of Surrealism as "psychic automatism in its pure state, by which one proposes to express… the actual functioning of thought. Dictated by thought, in the absence of any control exercised by reason, exempt from any aesthetic or moral concern" [10]. In line with this Surrealist notion of 'automatism' and embrace of the random, the outcome of rubbing was accidental, with bizarre shapes emerging, as if evoked by the unconscious, and forming fresh pictorial possibilities. When Ernst began working with *frottage*, he described the surprising patterns that emerged in the following way: "my eyes discovered human heads, animals, a battle that ended with a kiss (the bride of the wind), rocks, the sea and the rain, earthquakes, the sphinx in the stable, the little tables around the earth, the palette of Caesar…" [11].

In 1926–27, Ernst extended the method to oil works on canvas: after applying a thick layer of paint on canvas, he scraped it over a rough textured surface or objects, dubbing the process *grattage* (the French term for 'scratching') and revealing the underlying colour laying underneath. Then, he modifies the resulting composition by adding further details or contours with a brush. As Diane Waldman posited, for Ernst "the process of *grattage* uncovered images which provided him with inspiration and helped him to overcome the terror he claims to have felt when confronted with a bare canvas" [12].

Then, the *decalcomania* technique, a transfer technique using paper or glass, invented by the Spanish painter Oscar Domínguez in 1935, was also taken up by Ernst [6, 13, 14]. In *decalcomania* diluted paint is pressed onto a surface with an object (pane of glass, aluminum foil, paper) that distributes it unevenly. As in *frottage* and *grattage*, the resulting irregular paint surface suggests images that might then be developed further by the artist. In the early 1940s, Ernst employed this technique in many paintings. For instance, *Attirement of the Bride* bears one of the most visible uses of the *decalcomania* [7] and an in-depth description of this painting is reported in literature [9].

In 1942, he began working with the technique of *dripping* (or oscillation), in which paint is sprayed on the canvas and left to drip on the surface [12]. *Dripping* (or oscillation) paint is sprayed on the canvas and left to drip on the surface with the canvas in a vertical position. As described by Ernst himself: "It is a children's game. Attach an empty tin can to a thread a metre or two long, punch a small hole in the bottom, fill the can with paint, liquid enough to flow freely. Let the can swing from the end of the thread over a piece of canvas resting on a flat surface, then change the direction of the can by movements of the hands, arms, shoulder, and entire body. Surprising lines thus drip upon the canvas".

Analytical techniques

All the artworks were analysed with portable instruments. Firstly, all works were examined by a careful visual observation, photography and microphotography, followed by Vis–NIR multispectral imaging. Subsequently they were investigated with ER-FTIR, XRF and Raman spectroscopy. To obtain data on the overall palette used by the artist, specific points referred to different colours/tones were selected. For three paintings—*The Kiss*, *Garden Airplane Trap* and *The Entire City*—XRF, Raman and, ER-FTIR analyses were performed on the same colour tone, exactly in the same point (see point details in Additional file 1: Figure S1, S2, S3 in Supplementary materials). While for the other three works—*Zoomorphic Couple*, *Attirement of the Bride* and *The Antipope*—these analyses were carried out on the same tone but not always in the same point due to the operative conditions and to the different moments in which the analyses were carried out (see point details in Additional file 1: Figure S4, S5, S6).

The macro images were acquired with a portable digital microscope manufactured by Skybasic. The Multispectral Imaging system was equipped with a high-resolution Moravian G2-8300 camera (CCD detector KAF-8300, imaging area 18.1×13.7 mm, pixel size 5.4×5.4 μm) with a high dynamic range (16 bits). The sensor is cooled for reducing the electronic noise during the acquisition. The spectral resolution was obtained using interferential filters with ± 25 nm pass-bands around the central wavelengths: 450, 500, 550, 600, 650 nm, in the visible range and 850, 950, 1050 nm in the near infrared.

XRF experiments were carried out using the Elio portable XRF Analyzer (XGLab), equipped with a 10–40 keV/5–200 μA X-ray tube (Rh anode, 1 mm collimated beam on the sample) and a large area Energy Dispersive Si-Drift detector (130 eV FWHM at Mn K).

Raman measurements were carried through a portable instrument i-Raman® Plus (BWTEK, USA) which presents a diode laser source emitting at 785 nm. Spectra were acquired between 60 and 3300 cm^{-1} with a spectral resolution of ~ 3.5 cm^{-1} @ 614 nm, with an exposure time of 10 s per acquisition and a laser power below 2.5 mW.

ER-FTIR was carried out by using the Alpha Bruker portable spectrometer. Spectra were recorded in the reflection mode in the range of 7500–400 cm^{-1} with 160 scans and a resolution of 4 cm^{-1}. The investigated area is about 20 mm^2. Smoothing was carried out by using the OPUS software.

Results and discussion

In the subsequent sections, the results of the study will be reported and discussed as follows. Firstly, the Ernst' painting techniques used in the different paintings will be explained according to the outcomes from the visual observation, thanks also to the use of microphotography. The multispectral imaging, instead, allowed to emphasize hidden details, preparatory drawings and/or overpainting. Later, the findings about the materials (used by the artist or alteration products) obtained by means of spectroscopic investigations (XRF, Raman and ER-FTIR) will be presented. The common features, such as the composition of the substrate, the used binder and the alteration products will be discussed first. Once these aspects have been clarified, the palette of each artwork will be illustrated separately and, finally, its evolution through time will be described.

Imaging techniques

On *The Kiss* (KI) a *frottage* base was likely applied over the entire surface of the painting. The author used either wood or other heavy material to produce this texture as some parts of the artworks suggest—such as the black shadow to the left of the central figure (see Fig. 2a, b) [7]. The principal lines composing the oeuvres were likely created through the use of a string left falling on the preparatory surface and subsequently partly repainted with brush (see Fig. 2c, e) [15]. The blue tone was applied once the rest of the composition had dried completely (see Figs. 2c, e and 3a–c) [7].

Zoomorphic couple (ZC), on the other hand, was created with a complex technique mostly based on *frottage* and *dripping* [7]. Ernst prepared a base of pastel colours on which several paints were subsequently spattered, blown and dripped (see Fig. 2f, g). In particular, the dark parts were created by placing a paint-laden rope or string over the canvas and spraying over it [6]. Then the cream background was probably applied to define the figures and the outer contours [7] (Fig. 4a).

In *Garden Airplane Trap* (GA), the chroma DI image (1050–650, 650–550, 550–450 nm) [16, 17] can provide information about the technique used by the artist (Fig. 4). In some parts, a pencil preparatory drawing is visible. On the background, created with the parallelepipeds, Ernst overpainted the airplanes and, over them, other elements (flowers, fruit and leaves) are clearly overpainted (see Fig. 4b).

In *The Entire City* (EC), in the upper left of the sky, the false colour image reveals a clearer stain (Additional file 1: Figure S7) that could be related to a moon/sun, which was successively covered during the painting process. In most of the works belonging to this series, a moon/sun is present in the sky, moreover, to achieve a continuous pattern of the city walls, Ernst employed decorated relief blocks (for textile printing). The flattening and the abrasion of the surface of this specific Entire City obliterate both design and texture, making it difficult to observe the rich technical process that is present in other examples (see Fig. 2h, i).

The *Antipope* (AP) was built with a combination of techniques such as *decalcomania*, traditional brushwork, and the printing of leaves into wet paint (Fig. 5). The lower landscape with birds, fossil-like vegetation, moss, shells, frogs, and rocks was created with a decalcomania base on which Ernst then added brushwork (Fig. 4a, b). Other elements such as the red dress, the horse-headed figure with an owl mask on the left, and the skeletal figure in the centre were obtained with similar technical combinations [7]. The complexity of the execution technique is highlighted in photographic details reported in Fig. 2j-m.

Results regarding the *Attirement of the bride* (AB) are thoroughly discussed in a paper dedicated to it: the imaging shows some preparatory drawing, such as prospective construction lines and afterthoughts (*pentimenti*) [9].

Materials characterization

Common features

In general, XRF reveals the presence of Zn, S, Ba, and Pb distributed overall in works studied. This evidence suggests the presence of a ground layer composed by lithopone, $BaSO_4 + ZnS$, and lead white, $2PbCO_3{\cdot}Pb(OH)_2$. Signals due to overtones and combination bands of $SO_4^{=}$ in barite ($2\nu_3$ at ≈2230 cm^{-1}, $\nu_1 + \nu_3$ at ≈2194–2137-2065 cm^{-1} and $2\nu_1$ at ≈1965 cm^{-1} [18]) were detected by ER-FTIR (Fig. 6a, b) in all the canvases, except for KI. In this painting the absence of barite' signals could be ascribed to a thicker pictorial layer than the one present in the other paintings. Another common feature, highlighted by XRF, is the ubiquitous presence of Ca. Ca can be associated with the presence of calcite, as confirmed by Raman ($\nu_1$at 1086 cm^{-1}) and, except for ZC, by ER-FTIR ($\nu_1 + \nu_4$ at ≈1796 cm^{-1}), as illustrated in Fig. 6. In

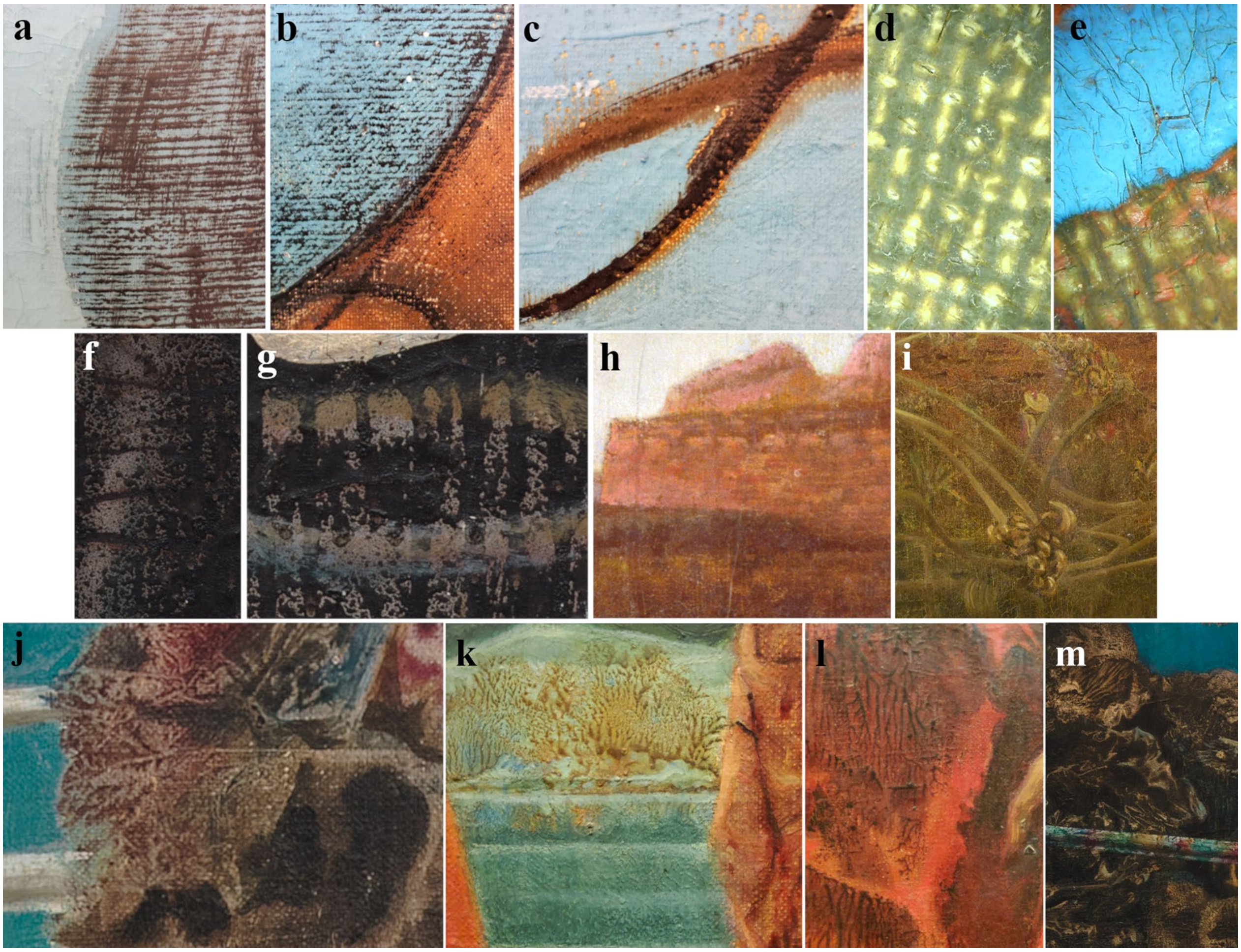

Fig. 2 Details from *The Kiss* (**a**–**e**), *Zoomorphic Couple* (**f**, **g**), *The Entire City* (**h**, **i**) and *The Antipope* (**j**–**m**). The dark texture of wood is visible in (**a**) and (**b**) while in the particulars due to the use of a string are clear in (**c**) and from the digital microscope images (**d**) and (**e**) (100X of magnification). The superimposition of different paint layer, attributable to different painting time, are evident especially in (**a**), (**c**) and (**e**). The *frottage* and *dripping* techniques can be recognized in (**f**) and (**g**). The pattern obtained by using textile blocks is highlighted in (**h**) while the details in (**i**) show the effect of abrasion on design and texture. From (**j**) to (**m**) the patterns obtained by printing of leaf, of the use of a sponge and *decalcomania* are illustrated

all the paintings, the paint binder can be easily identified in ER-FTIR spectra (Fig. 6) by the presence of a well-resolved doublet, at 4320 and 4260 cm^{-1}, attributable to the stretching and bending combination bands ($\nu_{a/s} + \delta_{a/s}$) of the methylene units in drying oils [19]. These signals are combined with the ester asymmetric ν(C=O), at ≈1740 cm^{-1}, which shape suffers the distortions due to the physical features of the pictorial layer (*i.e.,* the execution technique) and to the superimposition with other organic materials (*i.e.,* varnishes from past restoration).

The results above reported underline some common features present in all the paintings. In addition to the use of a drying oil as a binder, the results show that the ground layers, probably commercially applied, are composed of lithopone, and lead white in all instances. Respect to lead white, which was used in Europe from the Roman period onwards as the principal white pigment and employed both as a preparation layer [20] and frequently to give a certain opacity in the flesh tones [21, 22], lithopone was commercialized only since 1874 [20]. In some cases, calcium carbonate was also detected in different areas. However, it might have been present in the paint tube as an extender. The presence of a preparatory layer is confirmed by a previous micro-sampling from AB, which showed the presence of a white ground layer [9]. μ-Raman performed on these micro-samples revealed the presence of lithopone and lead white in one case and lithopone and calcium carbonate in a second case. The use of a commercially applied ground layer is confirmed by an

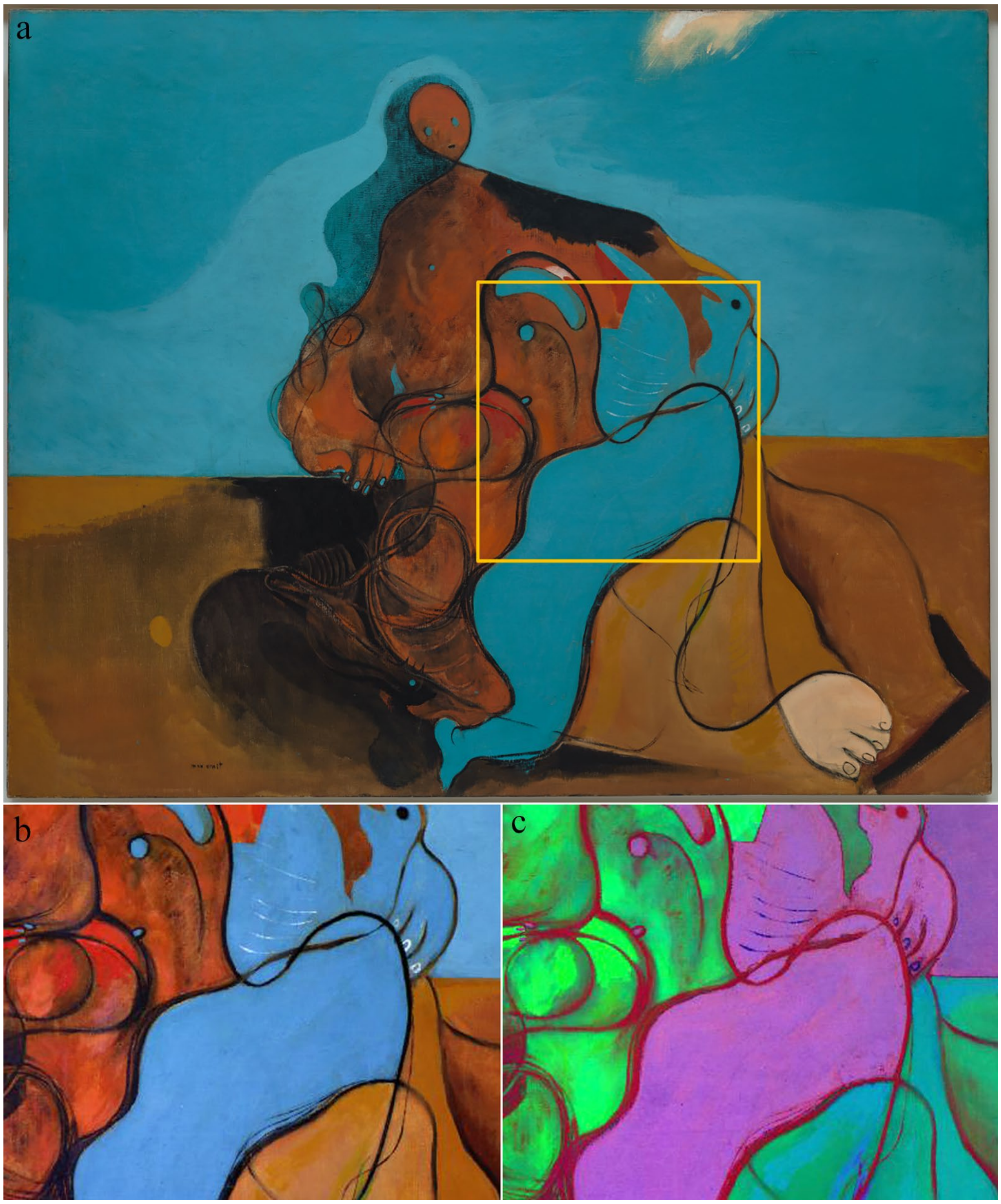

Fig. 3 The *Kiss* (**a**), detail: comparison between RGB (**b**) and Chroma DI images (**c**). The analysis suggests that, probably, the blue tone was applied once the rest of the composition had dried completely. The different shades indicate, in fact, differences in the density, and thus in the quantity, of pigments used

old conservation report [23], indicating the use of a commercial primed canvas, and supported by literature data [5].

State of conservation

Another interesting aspect, unearthed by ER-FTIR, concerns the presence of alteration products. As matter of fact, except for the GA and the EC, all paintings show evidence to metal soaps and oxalate. In KI, both zinc oxalate ($ZnC_2O_4{\cdot}2H_2O$) and zinc metal soaps are revealed in different tones (Additional file 1: Figure S12). Similar evidence were identified in AB and AP (Additional file 1: Figure S6). In these paintings, both metal soaps and oxalate are uniformly distributed over the surface and the signals due to zinc oxalate are in general more intense in comparison with the stearate ones. ZC presents a different condition: the signals due to $ZnC_2O_4{\cdot}2H_2O$ seem to be more intense in the light tones while the Zn soaps

Fig. 4 **a** Chroma DI (1050–650, 650–550, 550–450 nm) imaging of *Zoomorphic Couple*: in the upper part is clearly visible (in light green) a stain in the sky, due to a discoloration, whereas the different shades suggest an inhomogeneity of the background; **b** Chroma DI (1050–650, 650–550, 550–450 nm) detail of *the Garden Airplane Trap*. The floral detail was clearly done after painting the underside, as seen by the visible striped outlines. Some construction lines are also detectable, as highlighted by the different shades in the chroma DI details

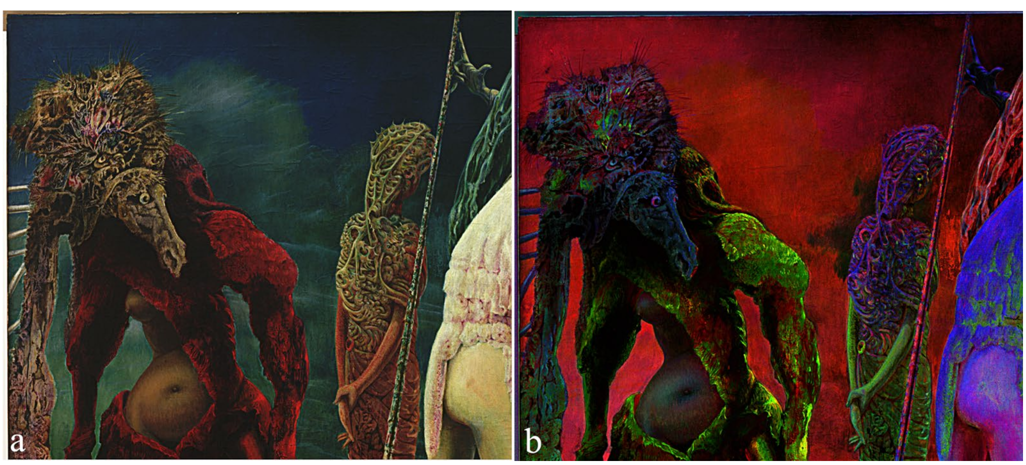

Fig. 5 *The Antipope*, detail: comparison between **a** RGB (450, 550, 650 nm) and **b** chroma DI (1050–650, 650–550, 550–450 nm). Ernst created the horse-headed figure with an owl mask on the left, and the skeletal figure in the centre with a decalcomania base on which then added brushwork

ones are more evident on the dark hues. All the spectra collected in the light tones show the insurgence of a new absorption, centered at ≈1700 cm^{-1}, that can be attributed to the $\nu_a(CO)$ in zinc oxalate. Usually, this signal appears as a derivative band [24], but, probably as consequence of the *frottage*, the rough surface enhances the volume reflection modifying the shape of the absorption.

It should be observed that zinc white was detected only on KI. In all the other artworks the presence of Zn could be related to the use of ZnO as drier [25] or with the presence of zinc stearate as fast wetting and dispersant for pigments [26, 27] in the paint tube formulations. Considering this hypothesis, zinc soaps can be present in the original paint formulation, as observed by Izzo et al. [26] or can be originated from the reaction between ZnO and the free fatty acids generated through ester hydrolysis of triglycerides as proposed by Hermans and co-workers [25]. The formation of zinc stearate can be promoted also by the presence of aluminum stearate, a very common rheology modifier as suggested by Osmond and co-workers [28]. On the contrary, metal oxalates are definitely alteration products: for instance, zinc oxalate was also detected in Pollock's *Alchemy* in the holdings of the Peggy Guggenheim Collection in Venice [29].

Max Ernst's palette

The evolution of the palette, with an overview of the pigments used, is hereafter reported, highlighting the distinctive results. Table 1 reports a synoptic overview of the pigments.

The Kiss (1927) The blue-azure background and part of the vest are realized with Prussian blue; in fact, Raman spectra (Additional file 1: Figure S8a) show the stretching vibration of the lattice Fe–C at 532 cm^{-1} [30] and the stretching vibration of C≡N group at 2093 and 2154 cm^{-1} [31]. The ER-FTIR spectra in the blue-azure areas (Additional file 1: Figure S8b), confirm the presence of Prussian blue; moreover, they are characterized by a strong absorption at ≈512 cm^{-1} (Additional file 1: Figure S2b), tentatively attributed to ν(ZnO) [32]. This hypothesis is supported by XRF data that show an intense peak due to Zn in correspondence to the blue tones. On the brown-yellow paints, ER-FTIR analysis reveals the presence of silicates, probably kaolin, with the characteristic inverted ν(SiO) at 1030 cm^{-1} and the ν(OH) at 3695 cm^{-1} [18] (Additional file 1: Figure S9). This evidence, together with the intense peak of Fe, detected by XRF, supports the use of ochre [33]. In the same tones, XRF also indicates the presence of Cd and S, suggesting the use of cadmium yellow, CdS, to impart the yellow shades. On the contrary, in the brown-orange areas, Raman spectrum (Additional file 1: Figure S10) shows the chromate symmetric stretching (ν_1) at 340, 822 and 845 cm^{-1} that, corresponding to Cr and Pb detected by XRF, are ascribable to the use of a chrome yellow orange ($PbCrO_4 \cdot PbO$) [34–36]. Finally, the black lines correspond to carbon black with typical Raman absorption bands at 1336 and 1590 cm^{-1}, D and G bands respectively; the first one is often called the 'disorder' band, attributed to a mode with A_{1g} symmetry while the second one is assigned to the in-plane stretching vibration mode (E_{2g}) [37, 38].

Zoomorphic Couple (1933) Raman and XRF analyses on the white-yellow background show the presence of lithopone. S, Zn and Ba were detected, together with the Raman symmetric stretching of sulphate group (988 cm^{-1}), also in the yellowish shades of the tentacles in the central part

Table 1 Overview of all the pigments identified in the different paintings. Lithopone and lead white are reported when they are used in the pictorial layer, not only in the ground

	The Kiss	Zoomorphic Couple	Garden Airplane Trap	The Entire City	Attirement of the Bride	The Antipope
Execution year	**1927**	**1933**	**1935–36**	**1936–37**	**1940**	**1941–42**
Prussian blue	✓	✓	✓	✓	✓	
Phthalocyanine blue					✓	✓
Cerulean blue						✓
Cobalt-based pigment			✓		✓	
Chrome yellow orange	✓					
Strontium yellow		✓	✓	✓		✓
Barium chromate					✓	
Cadmium yellow	✓		✓	✓		
Ochre	✓				✓	
Raw umber			✓	✓	✓	✓
Chrome-based green				✓		✓
Vermillion		✓				
Iron oxide		✓			✓	✓
Cadmium red			✓	✓		✓
Cobalt arsenate						✓
β-naphthol					✓	
Titanium dioxide					✓	✓
Calcium carbonate			✓	✓	✓	
Barium sulphate				✓		
Lithopone		✓			✓	
Lead white		✓			✓	
Carbon black	✓	✓			✓	

of the canvas. In the same areas, XRF reveals the presence of Sr and Cr, indicative of the use of strontium yellow, $SrCrO_4$ (Fig. 7a). The blue shade of the tentacle is due to Prussian blue, confirmed by both Raman and ER-FTIR techniques, whereas the black tone corresponds to carbon black, identified by Raman as well. Finally, in the red shade on the tentacle, vermilion (HgS) is identified by Raman (Fig. 7b) [39, 40] and confirmed by the presence of Hg peak in the XRF spectrum. ZC presents an evident pinkish stain in the upper left probably due to discoloured reintegration [7]. The chroma DI image (1050–650, 650–550, 550–450) highlights the reintegration (Fig. 3a) together with an evident inhomogeneity in the background, probably due to the use of different shades of pigment. Raman measurements on the stain identify lead white, by the symmetric stretching $CO_3^{=}$ group at 1050 cm^{-1} [39], and hematite, Fe_2O_3, by the Fe–O symmetric bending at 225 and 291 cm^{-1} (figure S11) [41]. At first glance, ZC may appear painted with a limited palette based on light/dark contrast; however, the analyses confirm the use of different pigments to render yellow, blue, and red shades on the dark tentacles of the figures.

Garden Airplane Trap (1935–1936) The paint is dominated by light brownish-yellow tones, whose elemental composition reveals the ubiquitous presence of Sr and Cr and, in some points, of Cd and S. These elements suggest the use of strontium and cadmium yellow, respectively. The palette of the bluish areas is more complex: in the blue areas ER-FTIR and Raman clearly highlight the use of Prussian blue probably together with cobalt blue, as suggested by the Co signal in the XRF spectra and according to the literature [1]. Greenish areas show the use of Prussian blue mixed with strontium yellow and/or cadmium yellow, as suggested by the presence of Sr, Cr, Cd and S in the XRF spectra. The presence of Mn, together with silicates, detected in the ER-FTIR spectra, suggest the use of raw umber in some brownish-green shades. The red shade of the flowers is due to cadmium red, $CdS_{1-x}Se_x$, as suggested by the signals of Cd, S and Se in the XRF spectra (Fig. 7c).

The Entire City (1937) The painting presents an upper part (the sky), characterized by a shade from a lighter green to a white/yellowish tone and a lower part, where the tangle vegetation invades the step/pyramidal ruins, mostly composed by red, brown, and dark green tones. In the upper part, XRF evidences the presence of Cr and Sr; therefore, we can suppose the use of strontium yellow. However, since this part is mostly green and no blue pigment is evidenced, also the use of a chrome-based green (Cr_2O_3 or $Cr_2O_3{\cdot}2H_2O$) cannot be excluded. In the white-yellowish hues, XRF identifies the presence of Cd and S along with Cr and Sr; therefore, the use of both strontium and cadmium yellow can be assumed. Added to these pigments, the Raman technique identifies calcium carbonate and barium sulphate probably to give a lighter shade. The darker green tones in the lower part of the painting are associated with Prussian blue, showed by ER-FTIR analysis, added to strontium yellow and cadmium yellow recognized by XRF. Moreover, the presence of the signals of Fe and Mn in XRF spectrum and silicates peaks in ER-FTIR could be attributed to the presence of a raw umber, also identified by XRF in some red paints. In other red paints, instead, XRF technique reveals both Cd and Se associated with the use of cadmium red.

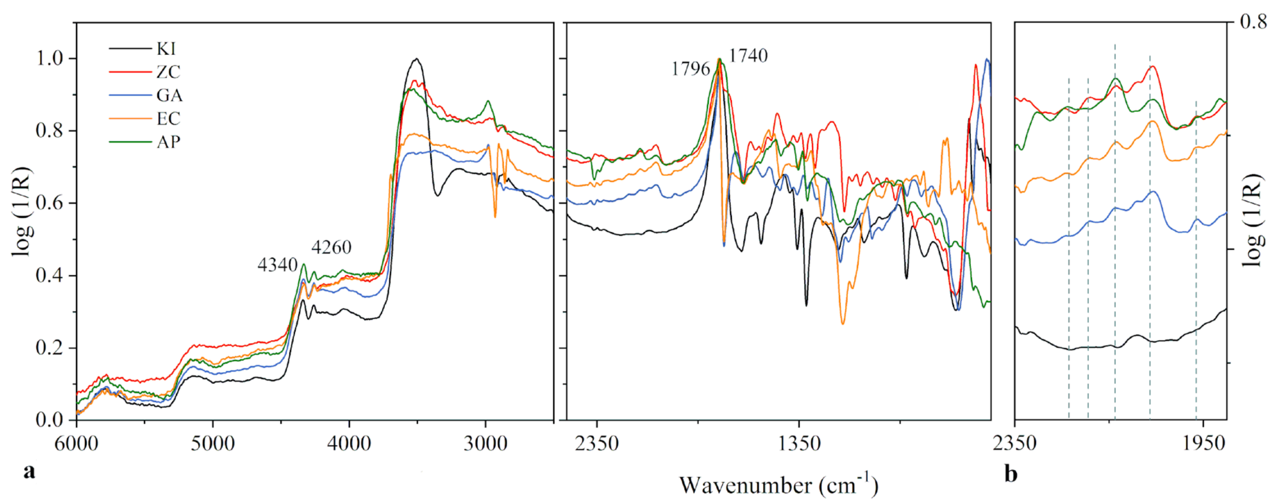

Fig. 6 Representative ER-FTIR spectra collected on KI, ZC, GA, EC and AP. The entire spectra are illustrated in **a**, while **b** is a highlight of the 2350–1900 cm-1 region in which the overtones of SO4 = are reported (green dotted line)

Attirement of the Bride (1940) A detailed characterization of the AB is reported in literature [9]. In this painting, two different blue pigments are used: copper phthalocyanine is identified in the main blue tones, while Prussian blue is mixed with other pigments to obtain several shades (green, violet, flesh and yellow). Two different red tones are recognized: an orange-red one with iron oxide and a more intense tone with an azo β-naphthol pigment. In both cases, also lead white and lithopone are identified. The lead white present in red tone could have been used as a pigment or it could be referred to the white ground layer (see above). The violet tones are a mixture of Prussian blue and iron oxide, while lithopone and calcium carbonate are probably added to give a lighter shade. Furthermore, XRF reveals the presence of cobalt. The yellow tones are obtained with barium chromate and in some points also ochre is recognised. The green paint is probably due to a mixture of Prussian blue and a yellow pigment, likely barium chromate, with the addition of a cobalt-based pigment. The white paints are a mixture of anatase (TiO_2), lithopone, and calcium carbonate. In the flesh tones several pigments are identified: lithopone and/or calcium carbonate, silicates, iron oxide and a raw umber are mixed for the base colour, while several shades are obtained by adding Prussian blue and a cobalt-based pigment. Lastly, the black paints are obtained with carbon black, while the brown paints are a mixture of iron oxide and a raw umber, identified for the presence of Mn.

The Antipope (1941–1942) In the flesh tones titanium dioxide, detected by Raman in its anatase form [35] is used along with cadmium red, identified by the presence of Cd and Se in the XRF spectra of the abdomen of the figure on the right, or with iron oxide, revealed by Raman (Fig. 8a). In the legs of the figure on the right, XRF also shows Sr and Cr; therefore, strontium yellow could have been added to give a particular shade. Cadmium red is probably present also in some red paints such as the dress of the figure on the left since XRF identifies Se and Cd. In addition to cadmium red, iron oxide and titanium dioxide [35, 42] were identified by Raman, as reported in Fig. 8a. It is worth noting that the peaks at 1228, 1393 and 1609 cm^{-1} are due to luminescence of coprecipitated titanium white pigment [43] and this is a direct implication for dating the oeuvre, being not present in pigments produced by later preparations.

In two pink tones XRF analysis shows the presence of As and Co; this finding suggests the presence of $Co_3(AsO_4)_2$ (cobalt violet) [44]. In the orange tone of the central figure, XRF shows the presence of Fe and Mn, so the presence of a raw umber can be assumed. Unlike

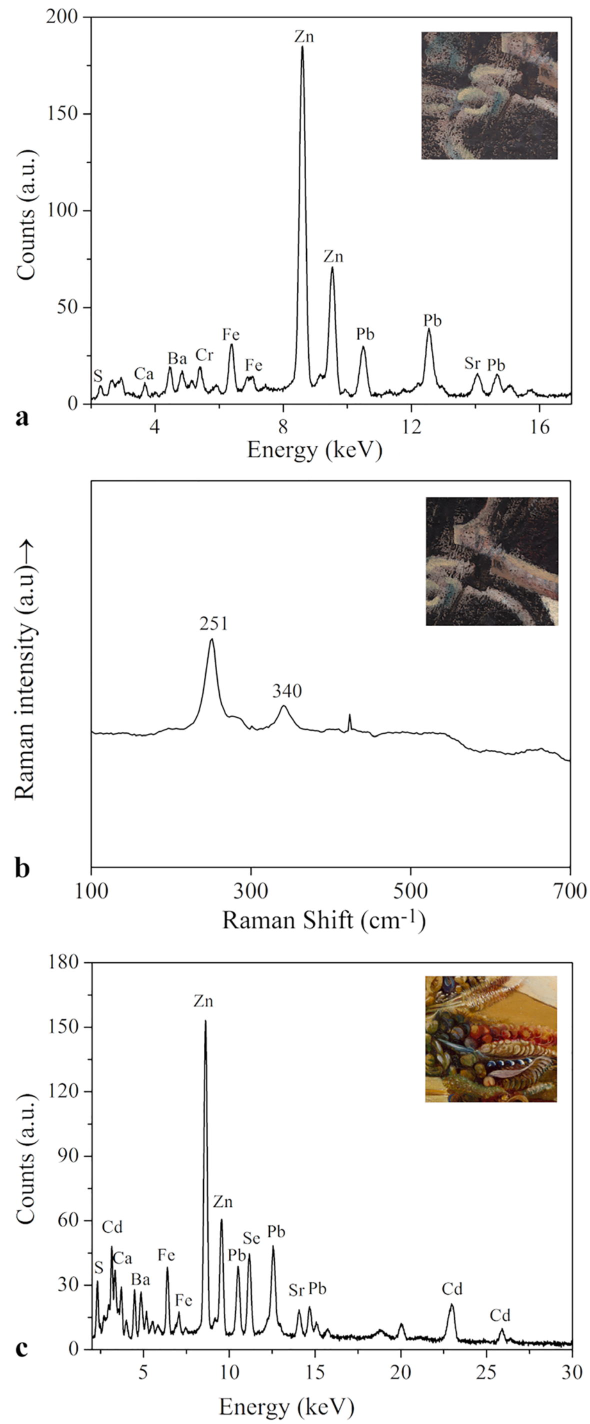

Fig. 7 Spectral features of the ZC and in GA: **a** XRF identifying strontium chromate in a yellow shade of ZC and **b** in-situ Raman spectrum identifying vermillion in a red shade of ZC with the typical bands located at 251 cm^{-1}, attributed to δ(S-Hg-S), and 340 cm^{-1}, ascribed to *ν*(HgS). **c** XRF spectrum of a red paint in GA identifying cadmium red

the previously works, Prussian blue is not present and other blue pigments are revealed. In the blue/green background in the upper part of the painting, XRF identifies Sn, Co and Cr; therefore, a cerulean blue ($CoSnO_3$) and a chrome-based green pigment can be supposed. The use of cerulean blue is also evidenced by XRF results also in some parts of the blue figure on the right. Instead, in the lower part of the background characterized by a different blue/green shade, in the blue figure on the right and at the base of the spear, Raman analysis identifies a copper phthalocyanine. As illustrated in Fig. 8b, the main intense Raman absorption peak at 1526 cm^{-1} corresponds to the main macrocycle stretching vibration [45], while the signals at 680 and 747 cm^{-1} are due to the breathing and deformation vibration of the macrocycle [46] while the band at 1340 cm^{-1} is due to the C–C stretching [46, 47].

In some areas, titanium white was detected, probably used to mitigate the intense colour of copper phthalocyanine. Moreover, Raman analysis identifies the copper phthalocyanine also in some green paints.

The analyses also highlighted an elegant use of both traditional and synthetic pigments to obtain hues, shades, and vibrant colours. As a matter of fact, the Ernst' palette evolves over the years (see Table 1), according to the availability of new pigments, but at the same time, the artist continues to use the traditional ones. For instance, in KI, Ernst uses both traditional pigments, *e.g.,* carbon black and ochre, and synthetic ones such as Prussian blue, firstly synthetized in the eighteenth century [20, p. 315] and cadmium yellow, developed during the nineteenth century [48, p. 65] or chrome yellow orange, first used in the nineteenth century [35]. In ZC, Ernst uses vermillion, carbon black, iron oxide and lead white, with lithopone, strontium yellow and, again, Prussian blue. In GA vermillion is substituted by the cadmium red, introduced in the market at the beginning of the twentieth century [20, p. 76] and the blue tones are still obtained by Prussian blue together with a Co-based pigment, used to obtain particular shade. Corresponding to the palette used in the previous works, strontium and cadmium yellow [5] are still present for the yellow paints, even if a traditional raw umber is also used. This palette is close to the one used in EC, which is dated once year later. The latter one is enhanced by the use of a chrome-based pigment mixed with strontium chromate the green paints [5], and barium sulphate for the white paints. In AB the extensive use of Prussian blue is almost completely substituted by the recently commercialized phthalocyanine blue, synthetized in 1907 [49] but commercialized as monastral fast blue only in the 1930s [50]. AB palette is composed also by titanium white, introduced in Europe in the 1920s [51], azo pigments, developed from the second half of nineteenth century [52], and barium chromate, commercially diffused at the end of the nineteenth century [20, p. 42]. In AP, Ernst introduces the use of cerulean blue and cobalt arsenate, both introduced in the nineteenth century [20, p. 96], [53], to obtain some light blue and light violet tones, respectively. It is worthy to observe, studying the corpus of masterworks conserved at the PGC, the evolution in using Prussian blue: if in the earlier paintings Prussian blue was used to create blue tones, or mixed with yellow to obtain green hues, after the 1941 it was only used in shades, as in AB, or completely eliminated, as in AP. Similarly, Ernst seems to prefer, in both AB and AP, the use of the "new" titanium white in place of the consolidated white pigments. On the contrary, all

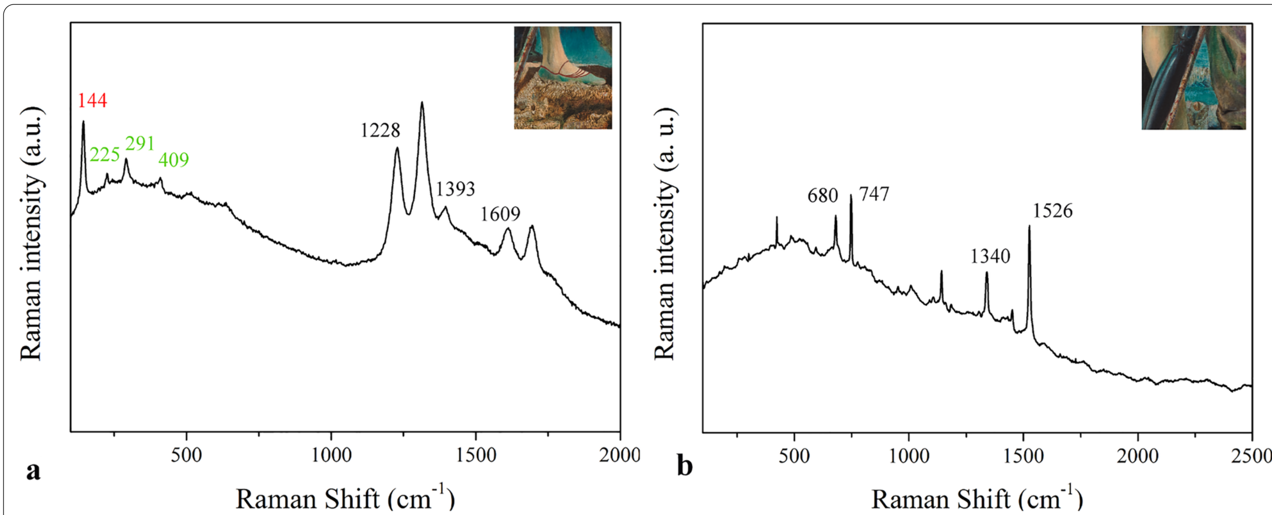

Fig. 8 In-situ Raman spectra of *The Antipope*: **a** flesh paint with iron oxide (green peaks) titanium dioxide (red peak) and **b** blue paint with phthalocyanine blue,

the black areas were painted with the traditional carbon black, underlining the high Ernst's mastery in the experimentation with traditional and new materials.

Conclusion

The present study sheds light on the evolution of the Ernst' painting technique, over a period of fifteen years, by considering six oil-on-canvas paintings, conserved at the PGC in Venice. In particular, the results of the multi-analytical in situ approach allowed to understand the evolution of his palette. The analyses highlighted that Ernst had a great awareness of the creative possibilities offered by both new and traditional pigments, and the results also showed how his palette evolves over time. In fact, in older paintings, some traditional pigments are present, such as vermillion and carbon black; while, in more recent works, Ernst preferred to use new industrial pigments, revealing that he had a good knowledge of the latest developments in the production of the new artistic materials. Alongside his innovative use of various artistic techniques (*frottage, grattage, dripping, decalcomania*), Ernst seems to have searched for the most suitable painting material to express his imagination and feelings, planning his works carefully from the start. He employed both techniques and materials in a conscious way, a "methodological madness" as Spies defined it [13], revealing the remarkable mastery of Ernst at work. In fact, even if apparently different in their approaches, all techniques that Ernst employed are part of the artist's unified vision.

Abbreviations

Vis–NIR: Visible-near infrared; ER-FTIR: External reflection Fourier Transform Infrared Spectroscopy; XRF: X-ray Spectroscopy; PGC: Peggy Guggenheim collection; S: Supplementary materials.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40494-022-00777-4.

Additional file 1: Figure S1. Points analysed on the *Kiss* by the different techniques. **Figure S2.** Points analysed on the *Garden airplane trap* by the different techniques. **Figure S3.** Points analysed on the *Entire city* by the different techniques. **Figure S4.** Points analysed on the *Zoomorphic couple* by the different techniques. **Figure S5.** Points analysed on the *Attirement of the bride* by the different techniques. **Figure S6.** Points analysed on the *Antipope* by the different techniques. **Figure S7.**Chroma DI (1050-650, 650-550, 550-450 nm) of *the Entire city*: the red arrow points at the moon circle, not visible in the RGB image (yellow square). **Figure S8.** Spectral features of Prussian blue recognized in *The Kiss:* (a) in-situ Raman spectrum and (b) ER-FTIR spectrum, the absorption at 512 cm^{-1} is to refer to ν(ZnO). **Figure S9.** ER-FTIR spectra of three yellow tones in *The Kiss* which show the presence of silicates. **Figure S10.** In-situ Raman analysis of *the Kiss* identifying chrome yellow orange. **Figure S11.** In-situ Raman analysis of the *Zoomorphic couple* identifying iron oxide (green peaks) and lead white (blue peak). **Figure S12.** ER-FTIR reflection spectra showing the presence of alteration products in AP (green lines), KI (black line) ZC (red for the spectrum collected in dark tones, cyan for the one collected on light tones), VS (magenta line), GA (blue line) and EC (orange line). Zinc oxalate (magenta dashed line) was identified by the typical inverted doublet at ≈1364 and ≈1320 cm^{-1}, attributable to the νs(CO) and by the derivative ν(OH) at ≈3400 cm^{-1} [1]. Instead, Zn metal soaps, probably zinc stearate (dark cyan dashed line), were rec-ognized by the sharp inverted bands at ≈1540 and ≈1395 cm^{-1} which can be reasonably attributed to the asymmetric and symmetric stretching of the carboxylate group in zinc stearate [2, 3, 4, 5].

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Author contributions

The research was designed by MZ, PT, LN, SL, LPB. Analyses were performed by MZ, PT, LN, SL, GL, BC, VP. Data were processed and interpreted by MZ, PT, LN, SL, and VP. The original manuscript was drafted by MZ, SL, LN, GS and LPB with contributions and subsequent revisions from PT and LS. PT supervised and provided financial support to the project. All authors read and approved the final manuscript.

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Availability of data and materials

All data generated or analysed during this study are included in this published article [and its supplementary information files].

Declarations

Ethics approval and consent to participate

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Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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