CHAPTER 27

The Elusive and Transitory Materials in Contemporary Drawings

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27.1 INTRODUCTION

Contemporary art, the eclectic descendant of the avant-garde from the early twentieth century, has renewed and surpassed the use of traditional tools and techniques since the 1950s, encompassing endless possibilities and pushing traditional aesthetics to extreme limits with regards to the employment of the most diverse materials, techniques and supports. Contemporary drawings are no exception, finding great use during the twentieth century as an independent and free art form.

The use of paper began to change around the middle of the last century, expanding out of its traditional field as a simple support for studies or sketches. Instead it became the basis of autonomous opera, which were presented at times torn, burned, folded, perforated and wrinkled...yet which maintained, however, an unaltered expressive power of uniquely strong intimate and reflexive aspects. Within such expressive values are housed the styles of three contemporary

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artists-Stefano Arienti, Sandra Vásquez de la Horra and Beatriz Milhazes—all of whom have expressed their artistic drawings as a means of personal expression. This selection of artists is characterized by the complete individuality and significance of their works, yet whose sensitivity and whose modus operandi, although completely unique, have proved representative of several typical problems that may be faced by scientists and conservationists alike when considering contemporary drawings. These artists are united in the originality of their respective techniques and in the implementation of unconventional materials, which at times are difficult to characterize on first glance. This is the case of works by Stefano Arienti, in his opera dedicated to Picasso, in which uncommon techniques appear, such as peculiar burning, stitching, pinholes and wrinkling together with the use of a variety of ochre-brown inks, which can all be investigated and elaborated thanks to modern scientific analyses. Emblematic of works on paper by Sandra Vásquez de la Horra is the distinction of impregnation with beeswax covering and modifying the thickness, appearance, and physico-chemical characteristics of the paper support. The characterizing feature of Beatriz Milhazes with her *Manjary* collage is that it is made up of different types of colored papers, plastic sheets with holographic prints, packaging papers and aluminium, all contemporary materials whose primordial use is uniquely diverted from the norm. In this context, it is crucial to distinguish the execution techniques of such contemporary drawings even when there are no pigments, dyes or materials that are directly correlated to the "fine arts". Nowadays, the vast fields of science and conservation collectively strive towards investigation by analytical methods that are valid for the complete characterization, individualization and comparison of execution techniques and constituent materials.

The distinction of techniques, support media, and materials of contemporary drawings signifies individualizing the universe of the artist with his/her creative approach, style and thought as well as simultaneously creating the ideal housing and storage conditions thanks to an understanding of the properties of employed materials, to their classification and to the rigor when necessary, in arranging the opera's housing, safeguard and diffusion.

This contribution permits, through combined analytical investigations and historical-artistic connections, the examination of the constituent materials and techniques employed by the chosen artists in representative artworks in order to understand their evolution. This work also serves to incite scientific research towards the field of contemporary drawing given that analytical analyses are increasingly practical and ideally suited to capture even the most elusive materials and transient information.

27.2 SCIENTIFIC ANALYSES AND MEASUREMENTS

27.2.1 Stefano Arienti and the Opera Dedicated to Picasso

Stefano Arienti graduated in agriculture and entered the world of art without any formal artistic training. Since the beginning of his artistic career, he focused on the manipulation of images and everyday objects, through drawing them and giving them a new identity and life, transforming both their formal aspect and communicative power. The chosen work for scientific investigation is *Picasso*, a collection of 100 drawings on paper realized in 1989 on photocopies of the graphic work of Pablo Picasso that Arienti individually elaborated with burns, scorches, sewing, pinholes and other techniques such as the use of "magic inks" whose identification has prompted a series of investigations that will be discussed in this chapter. Six drawings from the collection have been analysed, identified respectively as A1, A2, A53, A57, A60 and A91.

27.2.1.1 Characterization of Executive Technique. Selected drawings by Arienti for Picasso were analyzed by non-invasive spectroscopic techniques namely, X-ray fluorescence[†] and infrared spectroscopy,[‡] which permitted multiple representative investigations to be effectuated and ultimately minimized the need for micro-sampling. Among the aforementioned drawings, the study of A57 (Figure 27.1) was revealed to be of particular interest as this piece is characterized by areas of color ranging from yellow to brown for which analyses have failed to detect the presence of common pigments used in the design and painting. This evidence therefore suggested the probable use of an unconventional technique. In all the infrared spectra acquired at various points of the drawing, see Figure 27.1(a), characteristic signals of both cellulose

[†]The portable XRF instrument consists of an X-ray tube (EIS P/N 9910), equipped with a tungsten filament and a Peltier-cooled silicon drift detector having a resolution of 150 eV FWHM at 5.9 keV. It works in non-contact mode at a distance of about 2 cm from the surface and with a spot diameter of 4 mm. This instrumental setup allows the detection of elements with atomic number higher than silicon (Z>14). The excitation parameters usually used during the investigations are: voltage of 38 kV and current of 0.05 mA, while the acquisition time is 120 s. The spectra, corrected for the efficiency of the detector, are expressed as counts per second (cps).

^tThe portable infrared spectrophotometer is an ALPHA (mod.A241/D, Bruker Optics, Germany/ USA-MA) equipped with a SiC Globar source, a rock solid design interferometer (gold mirrors) and a DTGS detector. The mid-FTIR spectral data are acquired in reflection mode and the background correction is performed employing a spectrum recorded from a gold reference sample. This instrumentation is also equipped with an attenuated total reflection diamond crystal accessory (ATR), which allows us to obtain spectra in absorbance mode.



Figure 27.1 Drawing A57 by Stefano Arienti for the art work *Picasso*; (a) reflection infrared spectra of the paper, scorched paper and of the residue with signals of kaolin (K) and paper (P) indicated; (b) transmission infrared spectra of the residue, heated lemon juice and citric acid (standard).

and kaolin were identified, the latter used as a fiber filler. In the region between 3575 and 3125 cm⁻¹, it is possible observe the bands attributed to the stretching of the hydroxyl groups of cellulose $O-H^1$ whilst the signal at around 2909 cm⁻¹ and between 1400 and 1300 cm⁻¹ can be correlated to the C-H stretching and bending of the CH₂ and CH₃ groups, respectively. Numerous bands, moreover, are identified between 1300 and 1000 cm⁻¹, which may be related to the stretching of the C-O or C-O-C or the bending of the O-H groups of cellulose. Regarding the assignment of the band at 1645 cm⁻¹, some suggestions indicate a C=O stretching and/or absorbed water.² The presence of kaolin, however, has emerged from the identification of the characteristic signals of hydroxyl stretching (O-H) at 3697 and 3621 cm⁻¹ and by the combination modes at 4528 cm⁻¹.

In the infrared spectra acquired in the vicinity of the yellow and brown areas, see Figure 27.1(a), the appearance of a signal around 1719 cm^{-1} is attributable to the carbonyl C=O. This band, however, was also identified in the vicinity of the burns characterizing the drawings A2 and A91 as a direct result of the combustion process of the paper. The appearance of such a signal may be attributed to

aldehyde and ketone products that are generated following oxidative processes during the combustion process. Indeed, in conditions of high temperature or strong alkalinity, the oxygen in air can react directly with the cellulose leading to a rapid degradation of the amorphous cellulose constituent.^{4–6}

Returning to the nature of the substance used "for coloring", infrared analysis acquired on the dense accummulations present in the upper portion of the drawing has proved fundamental for its identification. In spectra acquired in reflection mode (see Figure 27.1(a)), the band of the carbonyl falls at a higher frequency (1734 cm⁻¹), characterized by an increased intensity and can be, therefore, related to the coloring substance. This signal, therefore, has allowed the sensitivity of the instrumentation used to be defined, given that it was possible to detect the presence of the colored substance only in the vicinity of dense accummulations and not in the lighter yellow or brown areas in where it appears more diluted.

Subsequently, based on this evidence, it was decided to perform micro-sampling from one such residue which was analysed with the bench instrumentation³ by dispersion in potassium bromide (KBr). In transmission mode, see Figure 27.1(b), the signals of kaolin are not observed, but the bands at 1645 and 1075 cm⁻¹ ascribable to the paper are present. Moreover, in the spectrum, some signals pertaining to the unknown compound can be identified. In order to distinguish this material, the search shifted to the analysis of unusual materials such as the so-called "magic inks", namely those substances that once applied to paper become visible upon heating. Among such inks, a good correspondence with lemon juice[§] was noted, whose infrared spectrum, see Figure 27.1(b), corresponds to that of citric acid. In this spectrum, the intense signal at 1734 cm⁻¹ can be attributed to the stretching of C=O of the carboxyl group.⁷

27.2.1.2 Fillers: from Kaolin to Calcium Carbonate. Analyses for the identification of heated lemon juice required the preparation of a series of mock samples to ascertain this particular artistic technique. The samples were made up essentially of white paper from various eras from the 80s to today. The results gave evidence of the presence of kaolin on the paper before the 90s and calcium carbonate on later dated paper. This shift from kaolin to calcium carbonate has inspired us to seek the reason for this change.

[§]Stefano Arienti has confirmed the use of heated lemon juice for the realization of the work dedicated to Picasso and pointed out that the variations of yellow-ochre-brown is due to successive applications of lemon juice followed by various steps of heating, in this case using a gas stove.

Kaolin has always been widely used, and still is, although to a lesser extent, as a loading substance or filler in the manufacture of paper. Yet towards the end of the 80s, calcium carbonate[¶] became systematically used according to the norms in the production of paper,[∥] which favors the manufacture of paper in an alkaline environment. Calcium carbonate improves the optical properties (brightness,** opacity, whiteness), printability (ink receptivity), and mechanical strength of the paper.

In the application of this filler, the mineral is added to the cellulose pulp before it is transformed into a sheet. The load of calcium carbonate is distributed throughout the mass of the sheet increasing its thickness and improving the dimensional stability.^{††} If paper thickness is more important, the amount of cellulose pulp is lower, allowing the manufacturer to economise the quantity of cellulose pulp whose cost^{‡‡} is higher than that of the mineral filler. All such reasons have led the European paper industry to use calcium carbonate thus reducing the use of kaolin.^{§§}

The identification of kaolin on the support of the artwork, in a certain sense, historically places the paper support to an earlier period than the early 90s, but not likely later.

27.2.1.3 Black Ink. In the drawings A53 and A91, the ink of the photocopies in the background of each drawing was analyzed by infrared spectroscopy. In the spectra obtained with the portable instrumentation, signals pertaining to C–H stretching at 2925 and 2854 cm⁻¹ and that of the carbonyl C=O at 1735 cm⁻¹ were identified suggesting the presence of an organic binder. From A53 (Figure 27.2), a small fragment was sampled and analyzed by attenuated

[®]The term calcium carbonate defines the precipitated calcium carbonate (PCC) and ground calcium carbonate (GPP).

Defined in the Norm ANSI Z39.48 1992, later adopted by ISO 9706 in 1994.

^{**}There seems to be a considerable difference between the brightness level obtained with kaolin (about 80 to 90 on the scale of ISO brightness, ISO standard 2470) and that obtained from calcium carbonates (GCC above 90 and CCP between 90 and 95). Only papers that have a brightness exceeding 90 are commercialized.

^{††}EU report: Case No COMP/M.3796 -OMYA/HUBER- PCC REGULATION (EC) No 139/2004.

^{‡+}The instrument is a NRS–3100 spectrophotometer equipped with: Ar⁴ laser source with wavelengths of excitation equal at 488 or 514 nm, a diode laser emitting at 785 nm, a triple grating (800 l/mm, 1200 l/mm and 1800 l/mm), an optical microscope provided with four objectives (5×, 20×, 50× and 100×) and a charge-coupled device detector (CCD) cooled to -50° C with a Peltier cooling system. The area of interest of a sample is focused with an objective of the optical microscope and the Raman spectra are recorded adopting different values of the exposure time (generally from 5 to 15 s), of the number of accumulations (generally from 10 to 20) and of the laser power. The latter reaches a maximum value equal to 5 mW for the Ar⁺ laser and 12 mW for the diode laser.

^{§8}In Europe, cellulose pulp is more expensive than industrial fillers. For this reason, the amount of fillers in paper can be up to 25–28%, while in the United States, this is of the order of 12–18%.

total reflection $(ATR)^2$ identifying the presence of polystyrene (Figure 27.2(b)) distinguished by a series of bands between 3100 and 3000 cm⁻¹, due to the stretching vibration of the bond =C-H, and from the signals at 1600 cm⁻¹ and 690 cm⁻¹ attributable to the stretching and bending of the aromatic ring respectively. Furthermore, signals were also observed at 2918 and 2849 cm⁻¹ due to the stretching and that at 760 cm⁻¹ of the bending of one of the aliphatic C-H groups. The bands at 1725 and 1152 cm⁻¹, however, could be generated, respectively, by the carbonyl stretching C=O, and from the C-O bond of an acrylate compound.¹

These findings lead us to suppose that the resin analyzed corresponds to a copolymer styrene acrylate, a material commonly employed in the formulation of toner for photocopiers.^{8–10}

The study of the pigment in the ink has been examined by means of non-invasive techniques such as XRF and micro-Raman spectroscopy.[¶] This latter technique was used to verify the presence of a carbonaceous pigment, yet any scattering was effectively covered by an intense fluorescence. The former technique is a technique for elemental analysis and provides information on components of an inorganic nature only. The XRF analysis, in fact, showed the presence of iron with impurities of manganese, although no separation of the contribution of the paper matrix from that of the ink was possible. For this reason, microscopy SEM-EDS^{|||} has been carried out encasing the same fragment as that used for the infrared investigation in epoxy resin. As can be seen from Figure 27.2(a), the thickness of the ink layer is about 10–20 um, while that of the sheet of paper is between 30 and 40 µm. The ink consists essentially of iron with impurities of manganese, silicon, aluminium, sodium, potassium, magnesium, titanium and chlorine.¹¹ The composition of the paper, however, shows the presence of silicon, aluminium, potassium, magnesium (due to the presence of the kaolin filler); the trace amounts of calcium and chlorine likely indicate its use as a whitener.

¹¹The instrument consists of a ZEISS LEO 1525 scanning electron microscope with a GEMINI column and equipped with a field emission source and an EDX detector from Bruker. The resolution changes from 3.5 nm to 1.5 nm with the variation of the acceleration voltage of the source (0.1–30 kV). The magnification range goes from $20 \times$ to $1000k \times$.

¹¹Hydrogen-driven NMR stratigraphy was collected at 17.6 MHz with a unilateral NMR instrument from Bruker Biospin interfaced with a single-sided sensor by RWTH Aachen University, Aachen, Germany. This sensor generates a magnetic field with an extremely uniform gradient to resolve the near-surface structure of arbitrary large objects. Experiments were carried out by repositioning the single-sided sensor in steps of 30 µm to cover the desired spatial range, from the back surface of the immersing to the front surface with a resolution of 40 µm. The intensity of each experimental point in the stratigraphy was obtained as the addition of the first four echoes acquired with a CPMG sequence.



Figure 27.2 Front of drawing A53 by Stefano Arienti for the art work *Picasso*; (a) SEM image of the cross-section obtained from the micro-sample taken from A53; (b) infrared ATR spectrum of ink used in A53 compared to standard polystyrene from the IRUG database (www.irug.it).

27.2.2 Sandra Vásquez de la Horra: Paper Impregnated with Wax and Drawing *Mi Marioneta*

The graphic work by Sandra Vásquez de la Horra is easily recognized not only for the poetic universe, and sensual and provocative representations, but also for her material peculiarities: the artist creates, in fact, graphite drawings and watercolor on paper, which are then immersed in hot wax. The works are directly hung on the wall with the aid of pins at the four corners without a frame.

The drawings are realized in pencil, the forms are often filled, almost colored by the graphite, which is sometimes smudged or highlighted by eraser marks. The graphite drawings are rarely retouched by yellow, orange or red watercolored areas. Since 1997, Sandra Vásquez de la Horra has been plunging her drawings into hot wax. The immersion almost totally impregnates the paper; the wax fills the spaces between the fibers of cellulose, it changes the refractive index to the point of making it translucent, and finishes it with a skin. The wax traps the drawn figures and highlights, by saturation, the colors of the different papers.

The design chosen for analysis is *Mi Marioneta*. It is made of a sheet of paper on which there is already a written text with an iron gall type ink. To these existing subscriptions, the artist has added a drawing in pencil, an extension of thought and body, as a form that floats, beyond any space-time dimension. Her drawings are similar to fingerprints, from furtive thoughts, to daydreams. With the design *Mi Marioneta* Sandra Vásquez de la Horra traces the colonized Chilean past in which individual liberty was suspended, confused and programmed. Thanks to her concerns, the artist gives form to ghosts, fears and desires that recall the collective memory conferring it a universal and a political dimension.

27.2.2.1 Diagnostic Investigations: Infrared Spectroscopy (FTIR) and Unilateral NMR Profilometry. The drawing Mi Marioneta by Sandra Vásquez de la Horra was analyzed by non-invasive infrared spectroscopy, with the main objective to assess the sensitivity and specificity of instrumentation in the identification of the materials constituting this specific work. The results obtained, reported in Figure 27.3(a), have allowed us to detect the presence of wax due to signals of stretching (2910, 2855 cm⁻¹) and bending (1472 cm⁻¹) of the methylene C-H,¹² as well as their combination bands that fall at 4330 ($v_a + \delta$) and 4261 cm⁻¹ ($v_s + \delta$).¹³ Moreover, the band at 1740 cm⁻¹, attributable to the stretching of the carbonyl C=O, allowed the identification of the beeswax.

In order to evaluate the penetration of wax inside the paper, a micro-sample obtained by a mock-up, realised following the artist's procedure (paper, graphite and wax), was embedded in epoxy resin and than analysed by micro-infrared spectroscopy.*** The results show that the penetration of the wax in the paper is about $20-30 \ \mu m$ in both sides of the sheet. This evidence indicates the absence of a shielding behaviour by the graphite.

^{***}The instrument is a Jasco Fourier transform infrared (FT-IR) 4100 spectrophotometer equipped with a ceramic light source, a Michelson interferometer and a DLATGS detector. This instrument can be employed for infrared measurements working in transmission mode in a KBr pellet. All powdered samples are prepared with finely ground KBr using a manual hydraulic press. The background was collected on a KBr pellet. In addition, the spectrophotometer is coupled to a Jasco IMV 4000 optical microscope provided with three objectives (Cassegrain 16X, Cassegrain 32X and ATR) and two liquid-nitrogen-cooled detectors, a midband MCT (mercury cadmium telluride) and a Linear Array 16X MCT to perform microinfrared measurements. These measurements can be performed in transmittance geometry using a diamond cell or in reflection mode.



Figure 27.3 Drawing entitled *Mi Marioneta* by Sandra Vásquez de la Horra. The highlighted squares indicate the areas measured by NMR profilometry and the numerical values indicated within refer to the thickness of each area as reported in the histogram (Figure 27.3(b)); (a) reflection infrared spectrum of an area of the drawing compared to standard beeswax and cellulose.

NMR^{†††} profilometry was applied to this work to evaluate the thickness and homogeneity of the wax film that entirely covers the drawing. What is evident from the 15 measurements is that the thickness of the wax varies from a minimum of 150 to a maximum of 380 μ m, see Figure 27.3(b). Considering the execution technique, which consists of completely immersing the drawing in hot wax and then hanging it to dry,^{‡‡‡} the trend of variable thickness follows this behavior quite well (shown in Figure 27.3 by dashed arrows) where in particular, hanging the drawing by corner E1 and leaving the still not completely cooled wax to drip by gravity. In fact, the thickest area is side 3, that is, opposite the corner that was hung, with a particular accummulation in the central area. The only exception is corner A3,

^{‡‡‡}Supplied by the artist during a visit to his studio in Rio de Janeiro.

^{†††}Information regarding the execution technique has been given directly by the artist.

which was very thinly covered; this may have been the corner by which the artist removed the once cooled design from the wall.

27.2.3 Beatriz Milhazes and the Collage Manjary

Milhazes's unique painting technique is reminiscent of the decalcomania. She applies paint to transparent plastic foil and mounts the paint on canvas by pulling off the foil. Used again and again, the pieces of foil retain traces which may then reappear in the same or other works. Each painting is thus marked by the flux of time, like a palimpsest. The result is a perfectly smooth surface without the slightest brush trace.

In the collage, Beatriz Milhazes works with any type of material, some of daily use, some recycled such as packaging of sweets, chocolates and nougat, and some plastic, fluorescent, holographic or monochrome, as in the collage *Manjary* (see Figure 27.4) whose title suggests and evokes the cocoa native of Madagascar. Everything gives an impression of color, joy, distraction and brings us closer to the inevitable physical geography, human and social development of her country Brazil. Each work presents a constant search for new materials and new forms. Substrates are glued onto pieces of paper and then cut out and assembled on a single support following the project of the artist.

27.2.3.1 Plastics. The collage Manjary by Beatriz Milhazes is made from various kinds of materials, including colored paper, plastic sheets and aluminium packaging. Some waste fragments of these materials^{§§§} have been analyzed by various analytical techniques such as scanning electron microscopy (SEM), X-ray fluorescence, infrared and Raman spectroscopy.

The four plastic sheets analyzed are characterized by different holographic prints, and are indicated with the letters: A (gold), B (green), C (silver) and D (silver with "windmill" design), see Figure 27.4.

To understand the stratigraphy, some micro-samples were firstly embedded in epoxy resin and observed by optical microscopy.^{¶¶¶} The magnifications achieved did not allow a detailed observation of all the

^{***}The optical microscope used is a Leica DMRX. Optical images have been captured with a Leica DC 300 digital camera in reflection mode using polarized visible light and at several different magnifications (5×, 10× and 40×).

Surface enhanced Raman spectroscopic examinations (SERS) were acquired through the use of citrate reduced silver colloids showing an absorption maximum at 425 nm with a FWHM of 110 nm. Measurements were carried out by adding a 10 µl drop of sulfate aggregated colloid directly onto the sample where spectra could be obtained between 2 and 10 minutes with Raman laser excitation that remained of constant quality until evaporation of the liquid.



b) SEM mapping of an area of Figure 27.4(a); (c) distribution of chlorine; (d) distribution of aluminium; (e) distribution of calcium; (f) transmission infrared spectra of plastic from samples C and D; (g) Raman spectra of plastic from samples C Collage Manjary by Beatriz Milhazes: (a) SEM stratigraphy of a sample of plastic with an indication of the various layers; and D; (h) OM image of stratigraphy of sample E; (i) ATR spectra of the two sides of sample E compared with standard cellulose nitrate and acrocryl (www.irug.it), an acrylic compound similar to that identified in the sample. Figure 27.4

layers present, which can instead be seen with a scanning microscope, see Figure 27.4(a). The samples are composed of four layers: the first is the plastic film with a thickness of about 100 μ m, see Figure 27.4(a), followed by an aluminium layer of about 10 μ m, see Figure 27.4(d), then an adhesive layer of variable thickness between 20 and 30 μ m, and finally the paper that forms the support showing a thickness estimated at around 300 μ m, see Figure 27.4(e). The mapping of elements such as chlorine and aluminium, reported in Figure 27.4(c)–(d), shows the presence of stacked layers. The elemental composition of the two plastics allows two groups to be distinguished: the first (A, B, and C) is characterized by the presence of chlorine, see Figure 27.4(c), while the second does not show the characteristic elements (D), thus is essentially composed of carbon and oxygen.

Infrared and Raman analyses proved fundamental for the identification of the different polymeric materials. The micro-Raman investigations were conducted directly on the samples. For the samples A, B and C (Figure 27.4(g)), only the bands assignable to the C-Cl bond around 650 cm^{-1} can be observed¹⁴ suggesting the possible presence of PVC. To test this hypothesis, it was considered appropriate to perform a micro-sampling of the material, with a dispersion in a disc with potassium bromide (KBr), and analyzing it in transmission mode with a benchtop FTIR spectrophotometer. The results from these analyses have allowed us to identify polyvinyl chloride (PVC). Indeed, in the infrared spectra acquired for the cards A, B and C (Figure 27.4(f)), in fact, the characteristic signals of PVC can be seen at 690 cm⁻¹ (stretching C-Cl), 1200, 1250 and 1330 cm⁻¹ (bending C-H), 1427 (CH₂ bending), 2854 and 2919 cm⁻¹ (CH₂ stretching).¹⁵ The band at 1735 cm⁻¹, however, could be related to the stretching of a carbonyl group C=O of a plasticiser used in the process of production of PVC.¹ Such a plasticiser, with signals also at 1386 cm⁻¹ (CH₃ bending) and 1198 cm^{-1,16} may belong to the phthalate family.17

Regarding the identification of the plastic film D, both the infrared and micro-Raman analyses (Figure 27.4(f)–(g)), show the characteristic bands of polyester, in particular the assignment of the respective bands suggest the presence of polyethylene terephthalate (PET). The main infrared characteristic bands assigned to PET (Figure 27.4(f)) can be observed at: 1714 cm⁻¹ (v C=O), 1410 cm⁻¹ (δ_{as} C–H), 1017 cm⁻¹ ($\delta_{in-plane}$ =C–H) and at 727 cm⁻¹ ($\delta_{wagging}$ =C–H).¹⁸

Concerning the micro-Raman spectrum in Figure 27.4(g), the band at 1730 cm⁻¹ indicates a stretching of a carbonyl group, the band at 1616 cm⁻¹ indicates stretching modes of C-C/C=C, 1094 cm⁻¹

attributed to modes of the phenyl ring around 1000 cm⁻¹ is a signal of the *trans* configuration of ethylene and finally the band at 860 cm⁻¹ is given to the bending of the ester group C(O)-O or C-C bond.¹⁹

Finally, micro-Raman spectroscopy was decisive for the identification of the dyes used for coloring plastics A and B. In fact, for plastic A, which shows a gold-yellow color, it was possible to identify the dye as the diarylide PY55,²⁰ while the green (plastic B) appears to be a mixture of the same PY55 along with the phthalocyanine PG7²¹ as hinted by XRF, which gave evidence of the presence of copper.

27.2.3.2 Wrapping Papers. The only aluminium packaging analyzed was the red paper of a chocolate sweet, shown in Figure 27.4 by the letter E. Optical microscopy has allowed a very thin layer of color to be distinguished from an underlying layer, see Figure 27.4(h). SEM-EDS investigations indicated that the color layer is between 2 and 5 μ m and the aluminium foil below is between 20 and 30 μ m.

The infrared spectra, as observed in Figure 27.4(i), were acquired in reflection mode, but due to the high reflectivity of the surfaces of the sample, these are characterised by a transflection $effect^{22,23}$ and therefore seem to be similar spectra recorded in trasmission.

In the spectrum of the external red layer, see Figure 27.4(i), signals are observed corresponding to those of cellulose nitrate which fall at 1657 and 1278 cm⁻¹ (the asymmetric and symmetric stretching of the NO₂ group, respectively), 837 cm⁻¹ (N–O stretching) and 752 and 694 cm⁻¹ (bending NO₂).²⁴ At the back of the same paper (silver color), however, by infrared analysis, see Figure 27.4(i), it was possible to identify an acrylic compound characterized by characteristic signals at 1730 cm⁻¹ (C=O stretching), 1240 cm⁻¹ and 1152 cm⁻¹ (C–O stretching).²⁵ The red dye, however, was identified by SERS^{¶¶¶} spectroscopy and found to be PR 57:1 from the family of monoazo lake BON.²¹

27.2.3.3 Cards. Specifically, two colored cards were examined: one orange and the other purple (Figure 27.5). The observation by optical microscope (Figure 27.5(a)) clearly shows that the first paper is dyed (orange), while the second is colored only on one face (purple). SEM-EDS permitted the thicknesses of the different cards to be measured (Figure 27.5(b)); the first is between 100–150 μ m and the second between 50 and 100 μ m. The two cards contain inserts that are rich in aluminium, silicon and alkali metals, whilst only the purple card presents further calcium-rich inserts. Furthermore, the purple card, on the colored side only, presents a finishing layer of about 10 μ m, which is particularly rich in titanium, aluminium, silicon and calcium (Figure 27.5(d)–(g)).



ported in Figure 27.5(a); (c) SEM mapping of area of interest highlighted in Figure 27.5(b); (d) distribution of aluminium; (e) distribution of silicon; (f) distribution of calcium; (g) distribution of titanium; (h) reflection infrared spectra of the two cards compared with standard cellulose with kaolin (K) and calcium carbonate (C) indicated, respectively; (i) OM image of Sample made up of an orange and a purple card; (a) OM stratigraphic image; (b) SEM stratigraphy of cross-section rethe purple card indicating constituent red and blue colorants. Figure 27.5

From the infrared spectra obtained with the portable instrumentation for these two cards, see Figure 27.5(h), a different composition may be noted. In addition to signals from the cellulose and those from kaolin, which can be traced in both, in the purple card, in fact, combination bands of calcium carbonate at 2515 cm⁻¹ ($v_1 + v_3$) and 1798 cm⁻¹ ($v_1 + v_4$) are also observed.¹² Moreover, the purple card is distinguished from the orange card by the presence of an intense signal at 1730 cm⁻¹, which can be related to one of the carbonyl C=O stretching bands of the ester groups present in the hemicellulose and/or lignin.²

The purple card, therefore, differs from the orange one since it is not formed from pure cellulose, yet it also presents residues of hemicellulose and/or lignin.

Regarding the colorants used, with the advanced Raman technique SERS, it was possible to recognize the orange as Acid Orange 10, a pigment of the diazo class.²⁶ The microscopic analysis of the purple card has revealed the presence of a mixture of two dyes—one red and one blue—as seen in Figure 27.5(i). Micro-Raman and SERS have permitted the red component to be identified as PR81 (rhodamine 6G of the xanthene family)²⁷ and the blue component to be identified as metal–organic dye PB15, *i.e.*, a phthalocyanine,²¹ given the confirmation of the presence of copper by XRF.

27.2.3.4 Adhesives. The plastics that Beatriz Milhazes used in this collage show two layers of adhesive: one already present on the plastic because the sheet is commercially sold with a layer of adhesive, the other was added by the artist to afford a better overall adhesion to the collage.

The adhesives on the back of some of the plastics examined (A, B and D) were analyzed in a non-invasive manner with the infrared spectrophotometer. The spectra obtained are very similar to each other; they were then compared with that acquired for the adhesive spray used by the artist, and to which, however, a full correspondence has not been found, due to the presence of acrylic component that characterized the adhesive already present on the back of the plastic foil. Finally, the spectral features of the sum of the two adhesives show a good correlation with the infrared spectrum acquired for the brand Scotch[®].

27.3 CONCLUSIONS

The purpose of the present research was to apply standard testing methods, *e.g.* microscopic and spectroscopic techniques and image analysis, in order to identify the chemical, physical and colorimetric properties of the support and medium used in some contemporary

drawings. According to the results, it is possible to characterize and categorize constituent materials and techniques even when those materials and techniques are not common plastic arts, such as the use of heated lemon juice by Stefano Arienti, paper dipped in hot wax by Sandra Vásquez de la Horra and confectionery packaging materials by Beatriz Milhazes.

All were identified through a combination of analysis and both historical and scientific investigations.

Specifically, the drawings, which present rather exceptional features, make scientific invasive or micro-destructive tests an exception. For this reason, it is essential to determine the sensitivity and specificity of the non-invasive techniques for the characterization of the supports, the materials used, as well as of the state of conservation of the drawings and their possibility to be manipulated.

In all three cases, contact with the artists turned out to be a privileged moment of understanding of the artistic universe, for the exchange of ideas which was indispensable for the comprehension of the work. The possibility to have access to samples of the materials to study when invasive tests became necessary served to strengthen the interpretation of results. This dialogue between science and art permits the contemporary drawings to be fully appreciated by an understanding of the employed materials and conceptual aspects, emblems of the never ending discussion on the *nature* of the work and on the *intention* of the artist.

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