The colors of Keith Haring: a spectroscopic study on the materials of the mural painting *Tuttomondo* and on reference contemporary outdoor paints.

Costanza Cucci[1*], Giovanni Bartolozzi[1], Marco De Vita[1], Veronica Marchiafava[1], Marcello Picollo[1], Francesca Casadio[2]

[1] Istituto di Fisica Applicata "Nello Carrara" del Consiglio Nazionale delle Ricerche (IFAC-CNR), Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy.

[2] The Art Institute of Chicago, 111 S. Michigan Ave 60603 Chicago, IL.

*corresponding author: c.cucci@ifac.cnr.it

Abstract

To date little attention has been given to the scientific investigation of modern and contemporary mural paintings. This paper reports on 1) the *in situ* spectroscopic analyses of the mural *Tuttomondo* (1989) painted by Keith Haring (1958-1990) in Pisa (Italy), and 2) the laboratory characterization of acrylic paints produced by Caparol Italy GmbH & Co., the original supplier of paint materials to the artist for the mural. Ultraviolet (UV), visible (Vis), and near-infrared (NIR) Fiber Optic Reflectance Spectroscopy (FORS) measurements were carried out *in situ*. The Caparol paint samples were characterized using benchtop instrumentation including both dispersive and Fourier Transform-Raman spectroscopy, Fourier Transform Infrared spectroscopy (FT-IR; with sample pre-treatment to remove filler interference in the fingerprint region), and UV-Vis-NIR FORS. This combined analytical approach confirmed that the materials used by Haring for the mural *Tuttomondo* have the same composition of the new Caparol acrylic paints, except for the case of the yellow pigment. This information offers valuable documentation for the materials history and for the conservation of a mural painting that is considered the last great public work by Haring.

Keywords: Keith Haring, UV-Vis-NIR spectroscopy, FORS, Raman spectroscopy, FT-IR spectroscopy, acrylic paints, *Tuttomondo* mural painting.

Introduction

Artists' paints are complex organic/inorganic systems requiring a multi-technique approach for their complete characterization. While countless scientific studies have been focused on easel paintings and on the palette of the old masters, it is only in the past two decades that the scientific study of modern art materials has been given some sustained consideration.[1] Among these investigations, exceedingly rare are the studies of modern murals.[2,3]

In this work, *in situ* non-invasive analysis with UV-Vis-NIR Fiber Optic Reflectance Spectroscopy (FORS) of Keith Haring's (1958-1990) mural *Tuttomondo* (1989, Fig.1) has been complemented with a laboratory characterization of a set of acrylic paint samples provided by Caparol Italy GmbH & Co., the original supplier of paint materials to the artist for making the mural in 1989. These laboratory analyses, based on the integrated use of FORS, FT-IR, as well as dispersive and FT-Raman, were performed on a selected set of paint samples given to the authors in 2011 by Caparol Italy GmbH & Co. under the assumption that they were identical to the ones originally supplied to the artist. The in-situ and laboratory analyses allowed to meet a dual objective: a) to identify and document the original materials of *Tuttomondo,* and b) to characterize a set of industrial products, commercially available today, which are fully compatible with the original ones, and could be used for future testing (including artificial aging) and possible conservation interventions.

Painted in June 1989, the mural entitled *Tuttomondo* is the last great public work by Haring and it is widely considered the artist's spiritual legacy.[4] Executed on the external wall of the 14th century convent annexed to the Church of Sant'Antonio Abate in the city center of Pisa, Italy, the mural covers an area of approximately 180 m^2 and includes 30 figures aimed to evoke feelings of peace and harmony for humanity.[5] Contemporary mural paintings are rarely created as long-lasting artworks, but rather carry messages that are related to their specific time: their materials are often temporary and unstable. *Tuttomondo* instead was conceived as a "permanent" mural. Haring wanted its message

to be universal and timeless, and its pictorial qualities to be in harmony with its surroundings as well as in tune with the aesthetic and cultural features of the city. For these reasons the colors of *Tuttomondo* are more subtle and mixed with greater quantities of white than those, intense and bright, typically found in the artist's previous works.

In order to guarantee the mural's long-term durability, Haring accurately chose the technique to execute its work, and all the materials, which were supplied by the company Caparol Italy GmbH & Co. Furthermore, Caparol craftsmen as well as young people from the Church of Sant'Antonio and B-boys from Pisa assisted the artist in the completion of the mural.[5,6]

A little over two decades after its creation, the mural was still in acceptable condition, although a far cry to its original appearance. The artwork showed yellowing of the white preparation layer and discoloration of the black outlines of the figures. The colored areas showed intense graying-out of the colors and their hues were uniformly lacking in saturation.[3,7,8]

In 2011 a program aimed at restoring, protecting and setting up a long-term preventive conservation strategy of one of the latest works by Haring was launched. As part of this large project it was considered important to gain knowledge of the material composition of the original colors of the mural *Tuttomondo.*[6] This information was considered crucial to support conservators in their decision making processes for the conservation treatment, which involved cleaning and a protection treatment with a hydrophobic silicone varnish.[8]

Thus, in-situ spectroscopic analysis was carried out by using UV-Vis-NIR FORS. These measurements allowed to characterize several areas of the original pictorial film of the mural painting. The acquired data provided information useful for both identification of materials and assessment of the conservation state before the conservation treatment. Moreover, FORS being non-invasive, measurements could be repeated over time on selected areas, in order to support cleaning tests and follow the conservation treatments, and to check their durability in time.

In addition to the in-situ campaign, an in-depth spectroscopic analysis on modern samples of Caparol paints was performed. This was driven by the desire to confirm their similarity to the original paints

supplied to Haring, so as to serve as expendable samples on which to perform cleaning and other conservation tests, as well as to assess the original, intended color of the paints used by the American artist.

Besides its usefulness to gain insight on the artwork *Tuttomondo,* the acquisition of compositional data on paints not originally intended for artists' use enriches the body of literature of interest for the practice of modern and contemporary artists who have used industrial acrylic paints[1], and may be relevant for the forensic field. The research also allowed an extensive comparative analysis of the relative merits of various spectroscopic methods with respect to the characterization of acrylic paint systems that are complex organic/inorganic materials.

Materials and methods

The Caparol materialss

All the materials used by Keith Haring were supplied at the time of the creation of *Tuttomondo* by the local company Caparol Italy GmbH & Co. Beside the industrial paints colors, the artist commissioned Caparol to prepare a special exterior insulation and finishing system (EIFS) to be used as support of the painting: This avoided the direct application of the pictorial film to the building wall so as to prevent deterioration phenomena due to humidity, thermal excursions, etc.. Technically, EIFS is a type of building wall cladding that provides exterior walls with an insulated finished surface and waterproofing in an integrated composite material system. It consists of insulating boards of polystyrene foam, coated with a white primer containing quartz and calcite with a styrene-acrylic resin as the binding medium.

In the present work a new set of samples of modern industrial paints and support materials supplied byCaparol were analyzed. These included seven samples of paint, namely white, red, yellow, orange, blue, and violet, a sample of Capatect-Putz 622 Silacryl substrate, and a facsimile of the EIFS. These

materials were provided to the authors under the premises that they were the same as those provided several years earlier to Haring.

Painted mock-ups were prepared on glass microscope slides and on the EIFS sample, using the paints as supplied by the producer. The paints were analyzed after being left to cure at room temperature for three months (Fig. 2).

Analytical methods and experimental setup

FORS

FORS measurements in the 350–2200 nm range were performed using two single-beam Zeiss spectroanalyzers, model MC601 (190–1015 nm range) and model MC611 NIR 2.2WR (910–2200 nm range), housed together in a compact and portable chassis for *in situ* analyses. The data acquisition step was 0.8 nm/pixel for the 1024-element silicon photodiode array detector (MCS601), and 6.0 nm/pixel for the 256-element InGaAs diode array detector (MCS611 NIR 2.2 WR). The radiation between 320 nm and 2700 nm, which was provided by a voltage-stabilized 20W tungsten-halogen lamp (model CLH600), was conveyed to the sample by means of a quartz optical fiber bundle which also collected the reflected radiation. This was connected to a probe-head designed for reflectance analysis with 8°/8° geometry: a circle-shaped area with a 2 mm diameter was investigated. Calibration was performed by means of a 99% *Labsphere Spectralon*® diffuse reflectance standard. Each spectrum was collected as the average of three acquisitions so as to increase the signal/noise ratio and processed by means of Aspect Plus® 1.80 software. The same equipment and set-up were used for both *in situ* and on paint samples analyses.

Raman Microspectroscopy

A Jobin Yvon Horiba Labram 300 confocal Raman microscope was used, equipped with Andor multichannel Peltier cooled open electrode charge-coupled device (CCD) detector (Andor DV420-OE322; 1024x256), BXFM open microscope frame (Olympus), holographic notch filter, and a

dispersive grating with 1800 grooves/mm. The excitation line of a solid state diode laser (λ_0=785.7 nm), was focused through a 100x objective on to the samples and Raman scattering was back collected through the same microscope objective. Power at the samples was kept very low (about 0.2 mW) by a series of neutral density filters in order to avoid any thermal damage.

FT-Raman Spectroscopy

A Bruker high resolution (0.4 cm^{-1}) Fourier Transform Infrared Spectrometer (VERTEX 70-BS) coupled with a Ramscope III FT-Raman Microscope was used. The instrument is equipped with a (D418-T/R) high-sensitivity Ge detector and Nd3+/YAG laser, with excitation wavelength at 1064 nm. The nominal laser power used was 100mW (corresponding to approximately 40 mW at the sample), and a microscope objective of 10x was employed.

FT-IR Spectroscopy

FT-IR spectra were recorded in transmittance mode on paint samples dispersed in KBr matrix (13-mm diameter KBr pellet, 64 scans, 4 cm^{-1} resolution, 4000–400 cm^{-1} range), using a purged Thermo Scientific Nicolet Protégé 460 E.S.P. Fourier transform spectrometer equipped with a DTGS detector. In most cases, due to the extremely low percentage of pigment in the formulation of the paints, the FT-IR spectra allowed to identify only the fillers and gave some information about the binder when analysis was carried out without pre-treatment. In order to maximize the pigment content of the analyzed samples, the paints were diluted with distilled water and acidified till slightly acidic (pH 4-5) with diluted HCl (0.5-1%) in order to remove some inorganic fillers (such as calcite). After filtration the insoluble materials were washed with ethyl acetate in order to solubilize as much as possible the organic resin and the residue was analyzed again as KBr pellet after drying.

Results

FORS Analysis on Tuttomondo

In situ FORS measurements were carried out on 67 small areas of the mural on the first level of the scaffolding mounted during the conservation campaign of 2011. The mural was painted with nine different hues (burgundy, red, pink, yellow, orange, green, blue, violet, black) on a white background. All the different painted areas and the background were analyzed.

The spectra collected on the background support showed the presence of a white pigment identifiable as titanium dioxide (TiO_2) in the rutile crystalline form. The presence of this pigment is revealed by a strong absorption band in the region between UV and visible, with an inflection point at about 400 nm, due to an energy band transition, since the band gap between valence and conduction band is around 3.0 eV in rutile.[9,10]

The absorption of rutile was also detected in all the spectra of the painted areas, used by the artist in mixture with pure colors. Another common feature of all the spectra recorded on painted areas were two absorption bands in the NIR region, at 1394 nm and 1414 nm, assigned to the first overtone of the hydroxyl stretching mode of kaolinite ($Al_2Si_2O_5(OH)_4$), used in the paints as filler. Other bands that were found in all the spectra recorded occur around 1140 nm, 1200 nm and 1950 nm and are attributable to the presence of adsorbed water, as well as bands between 1680 nm and 1770 nm that can be attributed to the acrylic binder.[11,12]

The reflectance spectra acquired on the burgundy areas showed two absorption bands at about 530 nm and 865 nm, with a shoulder at 660 nm and a reflectance maximum at 750 nm. All these spectral features are due to charge-transfer transitions and *d-d* Fe(III) transitions characteristic of iron oxides (hematite α-Fe_2O_3).[13,14]

The spectra collected on the red and pink areas presented the typical spectral shape of red synthetic pigments. In the red paint two absorption bands around 517 nm and 555 nm were observed, which can be likely attributed to the presence of a compound of the class of Quinacridones by comparison to published references, and are due to π-π^* electronic transitions in the aromatic rings.[15,16] In the pink areas the spectra showed two bands at 498 nm and 535 nm attributed to the presence of another

organic compound, maybe a synthetic orange pigment, which was not identified due to lack of available reference spectra.

The measurements acquired on the yellow areas resulted in S-shaped spectra, with inflection point at around 500-510 nm, likely due to the presence of a Hansa® Yellow pigment. Hansa® Yellows are a class of synthetic monoazo compounds obtained by coupling of a substituted aniline with derivatives of acatoacetanilide, and there are several different pigments belonging to this family of compounds which show very similar reflectance spectra in the UV-Vis range, only differing in the position of the inflection point.[17,18] Because of the presence of white and the overall discoloration the inflection point was not well-defined, so it was not possible to identify the specific pigment of the Hansa® Yellow class.

With regards to the orange areas, the reflectance spectra exhibited an intense absorption band in the UVa, at approximately 360 nm, with other two absorption bands at 640 nm and 910 nm, with a reflectance maximum around 760 nm, and two shoulders at around 420 nm and 480 nm. These features can be attributed to charge-transfer and *d*-*d* transitions of iron oxide/hydroxide (goethite α-FeO(OH)).[9,13,14]

The green and blue areas showed the characteristic spectral features of copper phthalocyanine pigments. The green area showed absorption bands at 650 nm, 730 nm and 780 nm, which are attributable to a phthalo green pigment. The presence of a phthalo blue pigment in the blue areas was confirmed by two absorption bands at 620 nm and 715 nm, with a shoulder around 430 nm, due to π-π* transitions, and by two other bands at about 910 nm and 1100 nm, the latter probably due to the second stretching overtone of the C-H bond.[19]

Lastly, the FORS spectra acquired on the violet areas showed three absorption bands at around 535 nm, 563 nm and 625 nm, indicating a polycyclic pigment, most likely of the dioxazine family. Based on comparison with published references it was possible to infer the presence of carbazole dioxazine violet PV23.[15]

UV-Vis-NIR reflectance spectra recorded on black lines did not provide any specific information on the chemical composition of the pigments used by the artist. This was due to the presence of a strong absorption band that covered the entire spectral range investigated.

Analyses on the Caparol samples

EIFS samples

Analysis on the EIFS samples (bare EIFS and paint layers applied over it) was conducted only with FORS, to replicate the *in situ* measurements. The spectral features recorded were similar to the ones collected on the background of the mural, although the spectra acquired *in situ* exhibit a lower average reflectance between 400 nm and 600 nm due to the yellowing of the white background.

Red paint

FORS measurements matched the spectral curves recorded on the mural, hence the presence of a pigment of the Quinacridone Red class was identified. The spectra of the pure paints, compared with the ones collected on *Tuttomondo*, showed a higher reflectance especially in the visible region due to yellowing of the substrate and accumulation of dirt and grime on the actual mural. They also showed the absorption bands of kaolinite (1394 nm and 1414 nm) used as filler. Moreover, spectra collected on the reference paint lacked the absorption band below 400 nm observed *in situ*, because, unlike the pure reference materials, the colors of the mural were all mixed with white (a rutile-based paint). All these features were observed for all types of colors and therefore will not be repeated in the following sections.

FT-IR spectra of a chip of the red paint *as is* were dominated by the bands of the fillers and the medium. Specifically absorption bands of calcite, barite and kaolinite (Table I) were identified.[20-25] Bands suggesting an acrylic resin were also observed (Table I), in agreement with what declared by Caparol, but the exact nature of the polymer could not be inferred from the FT-IR data alone.[26]

Previous GC/MS analysis of the binder for the paints of the mural actually identified a styrene/n-butylacrilate copolymer.[8]

For what concerns the red pigment, before the chemical treatment of the sample, the only bands that were clearly visible in the FT-IR spectrum were three bands at 3266 cm^{-1}, 3227 cm^{-1}, and 3165 cm^{-1}. However, after acidic treatment and solvent rinse, more bands related to the pigment became visible (Table II), allowing its unambiguous identification as Quinacridone Red PR122 (Fig. 3).[27]

The dispersive Raman spectra of the red paint (not shown) were characterized by a significant sloping fluorescence baseline, and were dominated by the bands of calcite. The peaks of the pigment were very weak, and only the most intense bands centered at 1597 cm^{-1}, 1568 cm^{-1} and 1311 cm^{-1} were barely visible. On the other hand, the FT-Raman spectrum clearly showed the bands due to the Quinacridone Red pigment (PR122) (Fig. 4) as well as the bands due to the calcite and barite fillers.[23,27-29] The FT-Raman spectrum also contains some peaks that allowed to identify the general class of the binder: a weak band at 1733 cm^{-1}, and a peak at 1451 cm^{-1} are indicative of the acrylic binder and the bands at 2927 cm^{-1} and 3061 cm^{-1} as well as the sharp band at 1002 cm^{-1} are characteristic of the styrene moiety.

Because the Raman bands for the binding medium, calcite and barite fillers were observed in all the spectra recorded for the colored paints, these spectral contributions are not further discussed in the following sections.

Orange paint

FORS spectra confirmed the presence of an orange pigment, which was at first identified as tetracene, according to the information given by Caparol.[30] FT-IR spectra were dominated by the spectral features of the fillers (kaolinite, barite and calcite) and the binding medium, and even after chemical treatment the identity of the orange pigment was not determined.

Both the dispersive Raman spectrum and the FT-Raman spectrum clearly showed bands attributable to the pigment Pyrazoloquinazolone PO67 (Table II), with different intensities due to the different laser excitation wavelengths (Fig. 5a).[31,32] Furthermore, in the dispersive Raman spectrum the peaks due to calcite are the most intense (Fig. 5b).

Interestingly, FORS spectra taken of a mixture of the new Caparol orange paint and the white paint showed the same spectral features as those measured on the pink areas of the mural, where a synthetic pigment was originally detected, but not identified. Because the mixture of the Caparol orange and white paint produced a pink color very similar to the pink areas of the mural, the similarity of the FORS spectra and the unambiguous Raman identification of PO67 allowed to put forth the hypothesis that the pink areas of the mural were painted with the Pyrazoloquinazolone pigment (Fig. 6).

Yellow paint

The FORS spectra obtained on the yellow paint showed an inflection point at a lower wavelength (493 nm) than the ones collected in the yellow areas of the mural. This difference was initially attributed to the fact that the paint applied on the mural was mixed with white, or alternatively to the presence of a different pigment in the recent formulations.

The FT-IR spectra of the yellow paint were comparable to those obtained on the orange paint, which was again dominated by the absorption bands of the fillers and binder, thus making impossible the identification of the yellow pigment even after acidic pre-treatment.

The Raman spectra obtained, on the other hand, allowed to confirm the presence of a different pigment in the paint supplied by Caparol with respect to the one in the mural, revealing the presence of bismuth vanadate ($BiVO_4$) PY184. Both the dispersive Raman (Fig. 7a) and FT-Raman (Fig. 7b) spectra showed the characteristic bands of this pigment (Table II), which were clearly distinguished from those of the binder and extenders.[33,34] To support this identification, elemental analysis was conducted of this paint only with XRF with Mo excitation, confirming the presence of Bi, Ba, V, Sr, Ca, and a little Fe. To the best of the authors' knowledge this is the first time that the Raman spectrum

of bismuth vanadate has been published in the context of the examination of paints of relevance for the creation of contemporary works of art.

Blue paint

FORS analysis of the blue paint confirmed the presence of phthalocyanine blue (Fig. 8). Although the FT-IR spectrum of the blue paint *as is* was identical to that of the yellow and orange paint, showing only the bands of the binder and fillers, the chemical pretreatment successfully brought to light the bands of the pigment. The absorption bands reported in Table II, together with the absence of a band at 1190 cm^{-1}, allowed to more precisely confirm the presence of the β-polymorph of phthalocyanine blue PB15:3.[35,36]

Because blue pigments tend to absorb in the near infrared region of the spectrum, it was not possible to record a good FT-Raman spectrum of the blue paint, due to localized heating and high fluorescence. On the other hand, dispersive Raman analysis with 785 nm excitation showed an excellent spectrum in which the bands of phthalocyanine blue were clearly visible.[28,32,37] The peak position of the pyrrole C=C stretching at 1530 cm^{-1} and relative intensity of the 747 cm^{-1} and 680 cm^{-1} bands allowed to confirm the β-polymorph of copper phthalocyanine, the blue pigment PB15:3 (Fig. 9).[28,32]

Violet paint

FORS analysis of the violet paint confirmed the pigment carbazole dioxazine violet (PV23) with a spectrum matching the one recorded *in situ* on Haring's mural (adjusting for the aging and condition effects that are affecting the *in situ* measurements as a whole, as already mentioned before) (Fig. 10). While the FT-IR spectra again were similar to those recorded in the yellow and orange paint even after acid chemical treatment, bearing only the vibrational signatures of binder and extenders, both the dispersive (Fig. 11a) and FT-Raman spectra (Fig. 11b) allowed the precise identification of the pigment. Although the quality of the dispersive data was higher than that of the FT-Raman data, due

to the fluorescence background affecting the latter, by comparison with published references the bands observed in the spectra confirmed the presence of carbazole dioxazine violet PV23.[28,31]

Discussion

FORS analyses of the paints, both in the mural painting *Tuttomondo* and in the new Caparol reference samples, confirmed this method as a powerful non-invasive *in situ* spectroscopic technique to obtain preliminary information on the composition of the materials. This result is also significant from a methodological point of view since it indicates the suitability of the FORS to investigate contemporary works of art. In the case under analysis, FORS made it possible to identify some of the pigments used (rutile, red and yellow ochre, carbazole dioxazine violet), and to reveal the presence of kaolinite as filler. However, for most of the synthetic organic pigments it was possible to identify only the general chemical class, but not the specific pigments (Quinacridone Red, Hansa® Yellow, copper phthalocyanines). Furthermore, FORS analyses in the 350-2200 nm range, gave no information about the binder. For the yellow and orange pigments of the new Caparol paints no reference spectra were available in literature. Their FORS spectra showed the distinctive features of organic pigments that could be attributed only after the unambiguous identification of the chromophore with complementary Raman spectroscopic analysis.

FT-IR analysis of the new Caparol paint samples provided the most comprehensive identification of the fillers present in the formulations: calcite, barite, and kaolinite, while Raman (both dispersive and FT) only identified calcite and barite, but not kaolinite. Furthermore, both Raman and FT-IR analysis uncovered useful information on the binding medium, with the detection of bands that unambiguously attributed it to the class of acrylic/styrene co-polymers, even though the specific type of polymer could not be identified.

For what concerns the identification of the pigments used in the paints, FT-IR spectroscopy tended to suffer from the interference of intense absorptions due to the fillers and binders, which in general

dominate the spectra also after chemical pre-treatment with acidic and solvent rinses. Only the red (PR 122) and blue pigment (PB 15:3) were correctly identified with this technique.

With Raman spectroscopy, the main difficulty using a dispersive system with 785 nm excitation laid in the fact that often a significant fluorescence background was still present, leading to sloping baselines that rendered automatic database searches very difficult. Because several hundred new synthetic pigments were introduced from the late 19th century to the present day, the ability to identify these synthetic pigments is highly dependent on available reference spectra and on efficient search algorithms, given that a manual search through several hundred spectra is impractical and time consuming. FT-Raman analysis, on the other hand, offered a very versatile option, as both the signals for the pigment, binder and fillers were evident on a low or non-existent fluorescence background. However, kaolinite was not detected in this modality and blue and violet pigments occasionally showed fluorescence that hindered the correct observation of diagnostic peaks for the pigment. In general though both Raman approaches proved valuable, with FT Raman spectra of the synthetic pigments analyzed in this work showing enhanced intensity for the bands above 1200 cm^{-1}, while dispersive Raman spectra enhanced those below 800 cm^{-1}.

Although the new Caparol paints were mostly confirmed to have the same composition as the ones provided approximately 20 years earlier to the artist, two main differences were observed. The first was that the new set did not include any shades containing iron oxides, contrary to what detected *in situ* on the mural. The second difference was that instead of a Hansa® Yellow pigment the new yellow paint was re-formulated with bismuth vanadate. Hansa® Yellows are reported to have high lightfastness in full shades, but much lower stability in tints, and they are relatively highly soluble in organic solvents.[18] Bismuth vanadate, on the other hand, is reported as more stable in terms of lightfastness and solvent resistance, and it is less expensive than organic pigments, which may be the reason for the observed change in the formulation of the yellow paints.[33,34]

Conclusions

In this work the complementary techniques FORS, FT-IR, dispersive and FT-Raman spectroscopies were applied to the study of a set of contemporary art materials including the paints used by Keith Haring for his mural *Tuttomondo* (1989), and some recent reference samples provided by the artist's paint supplier at the time, the Caparol firm. Although only FORS was available for in-situ measurements, the combined spectroscopic approach allowed to completely characterize the paints, including fillers and white (barite, kaolinite and calcite, as well as titanium white in the rutile form, used only for the original hues of the mural), binding medium (an acrylic/styrene copolymer) and pigments. Specifically, the following pigments were detected: rutile, Quinacridone Red (PR122), red and yellow ochre, Hansa® Yellow, bismuth vanadate (PY184), copper phthalocyanine green and phthalocyanine blue (PB15:3), carbazole dioxazine violet (PV23), and Pyrazoloquinazolone orange (PO67). Analysis revealed that most of the new paints supplied by Caparol in 2011 had the same compositions as the ones used by Haring in 1989. The formulation changes found were the absence of ochre pigments in the new samples, the use of PO67 for the orange tone and a change in the yellows from the Hansa® Yellow used for *Tuttomondo* to the bismuth vanadate pigment (PY184) used in the new formulations. Analysis of the new reference Caparol paints also allowed to hypothesize the presence of the orange pigment pyrazoloquinazolone (PO67) in the pink areas of the mural, in mixture with white.

It is interesting to note that the entire palette (with the exception of the iron oxide reds and yellows detected *in situ* and the bismuth vanadate in the modern Caparol paints) is based on synthetic organic pigments that are typically less photostable than inorganic paints. This choice would seem counterintuitive for paints that were intended to be used outdoors and durable, but may conform to the artist's aesthetic of using bright hues, although extensively mixed with white in *Tuttomondo*. Actually, the paints were expressly designed for outdoor exposure and the wall cladding system prevented the pictorial layer from direct contact with the plaster. All this explains the fairly good state of conservation of the mural. Although it is likely that the colors have faded a little with respect to the originals, the majority of the discoloration observed *in situ* was attributed to the formation of a

whitish patina of recrystallized calcite, and colorimetric measurements performed after the recent conservation treatment did not show any significant color variation in a 30-month period after treatment.[30] Comparison of the results obtained with FORS on the Caparol reference samples with the other laboratory spectroscopic techniques demonstrated, from a methodological point of view, that FORS is a valuable technique to characterize contemporary artworks *in situ.* Because of its wide applicability and fast and reliable results, the technique was also demonstrated suitable to monitor the effects of treatment *in situ.*

Overall, this research demonstrates the validity of combining different spectroscopic techniques to successfully address the complex composition and predominant use of modern synthetic pigments in contemporary paints. By tailoring the analytical methodology to offset each individual technique's limitations, this spectroscopic approach allows a deeper understanding of the materials used in the creation of contemporary artworks and helps make informed conservation choices for complex and fragile artworks such as outdoor murals.

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Captions for Figures

Fig. 1: View of the mural *Tuttomondo* (1989) on the external wall of the 14th century convent annexed to the Church of Sant'Antonio Abate in the city center of Pisa.

Fig. 2: Samples of the paints supplied by Caparol and mockups prepared on glass and on the EIFS.

Fig. 3: Comparison of FT-IR spectra of the chemically treated (A) and not treated (B) Caparol red paint.

Fig. 4: FT-Raman spectrum of the Caparol Red paint, (pigment identified as Quinacridone Red PR122, spectrum shown after multipoint baseline subtraction and smoothing)

Fig. 5: Caparol orange paint, pigment identified as Pyrazoloquinazolone PO67: a) dispersive Raman spectrum (after multipoint baseline subtraction and smoothing); b) FT-Raman spectrum (after smoothing)

Fig. 6: Comparison of FORS spectra of a pink area of the mural (straight line) and of a mockup made with a mix of white and orange Caparol paints (dot line). A' stands for apparent absorption

Fig. 7: Caparol yellow paint, pigment identified as bismuth vanadate ($BiVO_4$) PY184: a) dispersive Raman spectrum; b) FT-Raman spectrum

Fig. 8: Comparison of FORS spectra of a blue area of the mural (straight line) and of a mockup made with a mix of white and blue Caparol paints (dot line).

Fig. 9: Caparol blue paint, pigment identified as phthalocyanine blue PB15:3: dispersive Raman spectrum (after multipoint baseline subtraction and smoothing)

Fig. 10: Comparison of FORS spectra of a violet area of the mural (straight line) and of a mockup made with a mix of white and violet Caparol paints (dot line). A' stands for apparent absorption

Fig. 11: Caparol Violet paint, pigment identified as carbazole dioxazine violet PV23: a) dispersive Raman spectrum (after multipoint baseline subtraction and smoothing); b) FT-Raman spectrum (after smoothing)

Tables

Table I - FT-IR absorption bands and Raman bands (cm^{-1}) of fillers and binder of the new Caparol paints. Band assignments are given when available from the literature (ν: stretching, δ: bending, ρ: rocking, s: symmetric, a: asymmetric, ar: aromatic, es: ester, al: aliphatic).

		FT-IR	**Raman**
fillers	kaolinite	3700 3653 3624 (ν OH) 1032 1009 (ν Si-O) 913 (δ OH) 540 (ν Si-O-Al) 470 (δ Si-O-Si)	-
	calcite	2515 ($\nu_s + \nu_a$ CO_3^{2-}) 1795 ($\nu_s + \delta$ CO_3^{2-}) 1435 (ν_a CO_3^{2-}) 875 (δ_{op} CO_3^{2-}) 712 (δ_{ip} CO_3^{2-})	1086 (ν_s CO_3^{2-}) 282 157
	barite	1200-1050 (ν_a SO_4^{2-}) 987 (ν_s SO_4^{2-}) 632 613 (δ_{op} SO_4^{2-})	988 (ν_s SO_4^{2-}) 622 (δ SO_4^{2-}) 461
binder	styrene/n-butylacrilate	3100-3000 (ν CH_{ar}) 1735 (ν $C{=}O_{es}$) 1453 (δ CH_{al}) 1166 (ν C-C(=O)-O) 1032 (ν O-C-C) 700 (ρ CH_2)	3061 2927 (ν CH_{ar}) 1733 (ν C=O) 1451 1002

Table II - FT-IR absorption bands and Raman bands (cm^{-1}) of pigments and dyes of the new Caparol paints. Band assignments are given when available from the literature (ν: stretching, δ: bending, s: symmetric, a: asymmetric, ip: in-plane, op: out-of-plane, ar: aromatic).

materials	FT-IR	Raman
Quinacridone Red PR122	3266 3227 3165 (ν NH) 3100-3000 (ν CH_{ar}) 1635 (ν $_a$ C=O) 1604 (ν C=C) 1579 1554 (δ NH) 1340 (ν C-C + δ $_{op}$ CH) 808 792 (δ $_{op}$ C-C-C)	1650 (ν $_s$ C=O) 1598 (ν C=C + ν C=O) 1568 1512 (ν C=C) 1312 (δ CH_{ar} + δ $_{ip}$ C-C-C + ν NH) 1201 (δ CH_{ar}) 721 541 459 (δ $_{ip}$ C-C-C)
Pyrazoloquinazolone PO67	-	1602 1575 1557 1531 1411 1374 1339 1297 1255 1153 1011 737 627 537
Bismuth vanadate PY184	-	821 (ν $_s$ V-O) 713 (ν $_a$ V-O) 365 337 (δ VO_4^{3-})
Phthalocyanine blue PB15:3	1508 (ν C=N) 1422 1335 (ν C-C isoindole) 1288 (ν C-N=) 1166 (δ $_{ip}$ C-N=) 1120 1090 1072 (δ $_{ip}$C-H) 754 724 (δ $_{op}$C-H)	1529 (ν pyrrole C=C) 747 (isoindole deformation) 681 (macrocyclic ring breathing) 483
Carbazole dioxazine violet PV23	-	1591 1432 1393 1347 1207 670 591 527 317

References

[1] J. Crook, T. Learner. The impact of modern paints. New York: Watson-Guptill, 2000.

[2] A. Thorn. "Another Red Haring?". In: J. Bridgland, C. Antomarchi, editors. ICOM-CC: 16th triennial conference, Lisbon, 19-23 September 2011: Preprints. Paris: ICOM-CC, 2011. Pp. 1-7.

[3] A. Rava, O. Chiantore. “Outdoor Painted Surfaces in Contemporary Art”. In: A. Sgamellotti, B. G. Brunetti, C. Miliani, editors. Science and Art: The Painted Surface. London: Royal Society of Chemistry, 2014. Chap. 26, Pp. 542-561.

[4] A. Kolossa. “The finale”. In: A Kolossa, editor. Keith Haring 1958-1990 A life for art. Köln: Taschen, 2009. Pp. 85-90.

[5] A. Soldani. “Tuttomondo”. (film) Italy. 1989. http://ondavideo.arte.unipi.it/o.produzioni-soldani.html. [accessed Sept. 30 2015].

[6] K. Haring. Diari. Amadasi G., Picco G. (trad.). Milan, Italy: Arnoldo Mondadori Editore, 2012.

[7] M.P. Colombini, F. Modugno, F. Di Girolamo, J. La Nasa, C. Duce, L. Ghezzi, V. Barone, V. Palleschi, E. Bramanti, S. Legnaioli, G. Lorenzetti, L. Pardini, M. Picollo, A. Ballerini, G. Bartolozzi, S.Carlesi, C. Cucci, M. De Vita, V. Marchiafava. “Preventive Conservation of Contemporary Art (COPAC): a new Italian research project”. In: T. Berchtold, editor. Future Talks 011: The Conservation of modern materials in applied arts and design. Munich: Die Neue Sammlung, 2013. Pp. 195-199.

[8] M.P. Colombini, F. Modugno, F. Di Girolamo, J. La Nasa, C. Duce, L. Ghezzi, V. Barone, V. Palleschi, E. Bramanti, S. Legnaioli, G. Lorenzetti, L. Pardini, E. Grifoni, L. Marras, M. Picollo, G. Bartolozzi, C. Cucci, M. De Vita, V. Marchiafava, A. Rava, W. Shank. “Keith Haring and the city of the Leaning Tower: preservation of the mural Tuttomondo”. In: M. Sanchéz Pons, W. Shank, L. Fuster López, editors. Conservation Issues in Modern and Contemporary Murals. Cambridge: Scholars Publishing, 2015.

[9] G.R. Hunt, J.W. Salisbury, C.J Lenhoff. “Visible and near-infrared spectra of minerals and rocks: III. Oxides and Hydroxides”. Modern Geology. 1971. 2: 195-205.

[10] M. Bacci, M. Picollo, G. Trumpy, M. Tsukada, D. Kunzelman. “Non-invasive identification of white pigments on 20th century oil paintings by using Fiber optic reflectance spectroscopy”. J. Am. Inst. Conserv. 2007. 46: 27-37.

[11] M. Bacci, D. Magrini, M. Picollo, M. Vervat. “A study of the blue colors used by Telemaco Signorini (1835–1901)”. J. Cult. Herit. 2009. 10(2): 275-280.

[12] G.R. Hunt, J.W. Salisbury. “Visible and near-infrared spectra of minerals and rocks: I. Silicate Minerals”. Modern Geology. 1970. 1: 283-300.

[13] M. Bacci. “UV-VIS-NIR, FT-IR, and FORS spectroscopies”. In: E. Ciliberto, G. Spoto, editors. Modern analytical methods in art and archaeology. Chemical analysis series. New York: John Wiley & Sons, 2000. Vol.155, Pp. 321-361.

[14] K. Helvig, “Iron Oxide Pigments". In: B.H. Berry, editor. Artists’ pigments. A Handbook of Their History and Characteristics. London: National Gallery of Arts (Washington) and Archetype Publications, 2007. Vol.4, Pp. 39-109.

[15] R. Johnston-Feller. Color Science in the Examination of Museum Objects. Nondestructive Procedures. Los Angeles: Getty Conservation Institute, 2001. Chap. 4, Pp. 62-158.

[16] E.F. Paulus, F.J.J. Leusen, M.U. Schmidt. “Crystal structures of quinacridones”. Cryst. Eng. Comm, 2007. 9: 131-143.

[17] R.P. Schunck, K. Hunger. “Hansa® Yellows and Oranges”. In: P.A. Lewis, editor. Pigment handbook. New York: Whiley-Interscience, 1988. Vol.1, Pp. 535-546.

[18] S. Lake, S.Q. Lomax. “Arylide (Hansa) Yellow Pigments”. In: B.H. Berry, editor. Artists’ pigments. A Handbook of Their History and Characteristics. London: National Gallery of Art (Washington) and Archetype Publications, 2007. Vol.4, Pp. 179-222.

[19] M. Tomàs Rubio. UV-VIS-NIR Spectroscopic characterization of two modern blue pigments: Blue Phthalocyanine and Blue Indanhtrene, [M.S. 1st Level Thesis in Materials and diagnostics techniques for Cultural Heritage]. Pisa: Pisa University, Chemistry and Industrial Chemistry Department, 2006.

[20] R.A. Nyquist, R.O. Kagel. Infrared Spectra of Inorganic Compounds. San Diego: Academic Press Inc., 1971.

[21] M.R. Derrick, D.C. Stulik, J.M. Landry. Infrared Spectroscopy in Conservation Science. Los Angeles: Getty Conservation Institute, 1999. Chap. 5, Pp. 114-120.

[22] J.A. Gadsden. Infrared Spectra of Minerals and Related Inorganic Compounds. London: Butterworths & Co. Ltd, 1975.

[23] D. Bougeard, "Vibrational spectroscopy of different classes and states of compounds; Crystals". In: B. Schrader, editor. Infrared and Raman Spectroscopy Methods and Applications. Weinheim (Germany): VCH, 1995. Pp. 314-323.

[24] B. J. Saikia, G. Parthasarathy. "Fourier Transform Infrared Spectroscopic Characterization of Kaolinite from Assam and Meghalaya, Northeastern India". J. Mod. Phys. 2010. 1: 206-210.

[25] V. Ramaswamy, R.M. Vimalathithan, V. Ponnusamy, "Synthesis and characterization of BaSO4 nano particles using micro emulsion technique". Adv. Appl. Sci. Res. 2010. 1(3): 197-204.

[26] R.M. Silverstein, F.X. Webster. Spectrometric Identification of Organic Compounds. New York: John Wiley & Sons, 1997.

[27] E. del Puerto, C. Domingo, J.V. Garcia Ramos, S. Sanchez-Cortes. "Adsorption study and Detection of the High Performance Organic Pigments Quinacridone and 2,9-Dimethylquinacridone on Ag Nanoparticles By Surface-Enhanced Optical Spectroscopy". Langmuir. 2014. 30: 753−761.

[28] N. C. Scherrer, S. Zumbuehl, F. Delavy, A. Fritsch, R. Kuehnen. "Synthetic organic pigments of the 20th and 21st century relevant to artist's paints: Raman spectra reference collection". Spectrochim. Acta, Part A. 2007. 39: 505–524.

[29] Y.H. Chen, E. Huang, S.C. Yu. "High-pressure Raman study on the BaSO4-SrSO4 series". Solid State Commun. 2009. 149: 2050-2052.

[30] V. Marchiafava, G. Bartolozzi, C. Cucci, M. De Vita, M. Picollo. "Colour measurements for monitoring the conservation of contemporary artworks". Journal of the International Colour Association. 2014. 13: 36-42.

[31] Royal Institute for Cultural Heritage (KIK/IRPA). "Modern and Contemporary Art in the laboratory". http://modern.kikirpa.be/index.php. [accessed Sept. 29 2015]

[32] W. Fremout, S. Saverwyns. "Identification of synthetic organic pigments: the role of a comprehensive digital Raman spectral library". J. Raman Spectrosc. 2012. 43: 1536-1544.

[33] M. Gotic, S. Music, M. Ivanda, M. Šoufek, S. Popovic. "Synthesis and characterisation of bismuth(III) vanadate". Journal of Molecular Structure. 2005. 744: 535-540.

[34] W. Ostertag, H. Weinand. "Bismuth Vanadate/Molybdate Yellow". In: P.A. Lewis, editor. Pigment handbook. New York: Whiley-Interscience, 1988. Vol.1, Pp. 409-411.

[35] B.N. Achar, K.S. Lokesh. "Studies on polymorphic modifications of copper phthalocyanine". J. Solid State Chem. 2004. 177: 1987-1993.

[36] D. Verma, R. Dash, K. S. Katti, D. L. Schulz, A. N. Caruso. "Role of coordinated metal ions on the orientation of phthalocyanine based coatings". Spectrochim. Acta, Part A. 2008. 70: 1180-1186

[37] M.A. Shaibat, L.B. Casabianca, D.Y. Siberio-Pérez, A.J. Matzger, Y. Ishii. "Distinguishing Polymorphs of the Semiconducting Pigment Copper Phthalocyanine by Solid-State NMR and Raman Spectroscopy". J. Phys. Chem. B. 2010. 114(13): 4400–4406.