A multi-analytical approach for the characterization of wall painting materials on contemporary buildings

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ABSTRACT

Samples from Keith Haring's wall painting of the *Necker Children Hospital* in Paris were studied by a multi-analytical protocol. X-ray fluorescence (XRF), powder X-ray diffraction (XRDP), Electron microscope (SEM-EDS), Infrared and Raman spectroscopy (μ-FT-IR and μ-Raman) measurements were performed in order to characterize the materials and to identify the art technique used to produce this contemporary work.
Materials from the mural suffered from severe detachments of materials and several fragments were found on the ground beneath. Some of these fragments, which were representative of the whole palette and stratigraphic sequence, were collected and studied. The fragments were sufficiently large to enable non-invasive measurements to be performed in order to characterize the materials. A comparison of the data of the techniques applied revealed that Haring's palette was composed of organic pigments such as Naphtol red, phthalocyanine blue and green and Hansa yellow, in accordance with those used previously by the artist in other painted murals.

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1. Introduction

Since many years, knowledge and conservation of the materials of contemporary art is an active research field among curators, scientists and conservators worldwide. Modern and contemporary paintings present a variety of new challenges. Artists nowadays can choose from among a huge variety of products. The paint materials are made up of polymeric binders, colorants and inorganic fillers. Titanium dioxide, alumina, gypsum or barite can be added in order to adjust the hiding power. The manufacturer blends pigments and dyes in order to obtain the desired hue. Conservation scientists are thus faced with the challenge of identifying the composition of the materials used. This entails a different approach to the characterization of a classical palette on canvas or easel paintings. Contemporary artists choose the materials available on the market not based on the chemical composition, but only on final colouring effect.

The chemical composition of a painting material affects the state of conservation of the paint layers thus lead to fading or discoloration. However neither the long-term aging behaviour of these materials nor

the safe conservation methods for most of them are known. In addition, no data are available to record the history of suppliers for a specific artist, and consequently fakes and imitations are frequent.

A comprehensive understanding of both the chemical composition and physical characterization of materials is a central consideration in planning the correct conservation treatments for modern artworks. This diagnostic campaign was thus planned to support the mural restoration performed by Antonio Rava and Will Shank, who benefited from a charity auction promoted by the Jérôme de Noirmont and the Keith Haring Foundation in New York [1,2].

The charity auction was part of an important project of architectural refurbishment which included a fire escape staircase being transformed into a monumental sculpture: a 90-ft totem in the centre of a two-and-a-half acre garden inside the new hospital complex [3].

The mural painting (Fig. 1) was created in 1987, in typical Haring style, with large areas painted with primary colors and characters outlined with the hallmark black [2].

This monumental work of art was painted on the outer walls of a grey concrete fire exit but due to the weather and the passage of time, the structure is deteriorating. The concrete on which the paint was applied is crumbling and cracking, endangering the work's long-term survival. A number of black lines have deteriorated, and some have sunk into the concrete.

Fragments were collected from the ground below the mural painting. These samples were assumed to be representative of the whole

Fig. 1. The Necker Hospital mural in Paris painted by Keith Haring in 1987. Credits: Keith Haring art © Keith Haring Foundation.

palette and stratigraphic sequence. The samples were sufficiently large to enable non-invasive and micro-invasive analyses to be performed in order to characterize the materials and verify the state of conservation.

This work contributes to the identification of contemporary art painting materials, highlighting some of the problems ensuing when painting layers are applied to building material substrates. It also enhances the knowledge of the products used by Keith Haring in one of his famous mural paintings, and provides an insight into his artistic technique. This approach offers useful information not only for planning future conservation works, but also for increasing our knowledge of similar works by the author.

2. Material and methods

XRF spectra were recorded on the micro-fragment surfaces using a handheld *TraCer III-SD* spectrometer by *Bruker* equipped with a Rhodium X-Ray tube and an SDD detector. Spectra were recorded under vacuum conditions for 60 s at a voltage of 40 kV and 12 μA of current using the *S1PXRF* dedicated software.

Fragments were sampled with a lancet in order to isolate single materials.

X-ray diffraction analyses were carried out to identify the presence of crystalline phases in the samples using an X-ray diffractometer X' Pert PRO (PANalytical) for powders (XRDP), anticathode Cu (λ = 1.54 Å, investigated 2θ 3–70°, step size 0.017°, time per step 50 s), equipped with an X'Celerator multidetector. Data were processed using *HighScore* software and an ICDD database. The powders were analysed in zero background sample stages, and powders belonging to different layers were selected under a stereomicroscope.

FTIR spectra were recorded using a *Perkin Elmer, System 2000* in transmission mode using KBr pellets in the range of 400–4000 cm^{-1} at a resolution of 2 cm^{-1} over 16 scans and ATR-FTIR spectra were recorded by an Agilent Technologies Cary 660 Series Spectrometer coupled with a microscope in the range of 400–4000 cm^{-1} at a resolution of 2 cm^{-1} over 64 scans.

Polished cross sections were prepared by embedding the sample in a bi-component epoxy resin (*Epofix, Struers DK*).

The cross sections were then observed with an optical microscope, and analysed by SEM-EDS and micro-Raman spectroscopy.

Preliminary observations of the micro-fragments and of the polished cross sections were performed with a *Nikon Eclipse E600* microscope, equipped with a halogen lamp and a mercury lamp (OSRAM HBO, 200 W), to carry out optical observations under visible and UV light.

The cross sections were analysed using an *ESEM Quanta200* (*FEI/ Philips Electron Optics*) electron microscope equipped with an X-ray spectrometer. Observations were carried out using backscattered electrons (BS). The specimen chamber was maintained in a low vacuum (1 Torr), thus avoiding metallization, and the accelerating voltage was 25 keV at 1–3 × 10^{-7} A.

μ-Raman analyses were carried out on polished cross sections using a *Senterra* dispersive micro-Raman spectrometer (Bruker) with a 1200 grooves/mm grating and coupled to an *Olympus* BX51 microscope equipped with 20×, 50× and 100× objectives. The laser excitation wavelength was 785 nm with a power of ~1 mW. The Raman spectra were acquired using a Peltier cooled CCD detector (1024 × 256) and an overall acquisition time ranging from 100 to 300 s (5 accumulations with 20 to 60 s each).

From sample KH_ 08 a thin section was also obtained (thickness 30 μm) in order to perform petrographic observations of the preparation layers. A ZEISS Axio Scope.A1 polarized microscope equipped with a 5 Megapixel camera resolution and dedicated Axio Vision image analysis software was used.

3. Results and discussion

The analyses performed enabled most of the materials used by Keith Haring in his famous French wall painting to be identified. Data resulting from different techniques were compared to obtain a final characterization. The samples analysed and the results obtained are summarized in Table 1.

3.1. Support

Not all the samples showed the complete stratigraphy. In some cases only the painting layers were present. However, it was possible to identify the whole stratigraphic sequence of the support, which was visible in a few samples. Our findings revealed that the support is structured in several layers. There is concrete at the inner layer, then a thin white ground layer, and the external coating covered with one or more painting layers.

The sample KH_01, reported in Fig. 2, can be considered as representative of the complete stratigraphic sequence of the support.

Starting from the innermost layer, the concrete contains a matrix where several crystals are embedded. They have various sizes ranging from 10 to 300 μm. This concrete layer shows a standard composition [5,6] based on the presence of calcite ($CaCO_3$), quartz (SiO_2), gypsum ($CaSO_4 \cdot 2H_2O$) and calcium silicates, as highlighted by XRDP. Traces of iron and aluminium are due to the presence of the corresponding oxides. On the top of this layer, a white ground is visible. It has a non-homogeneous thickness ranging from 30 to 400 μm. XRDP analysis identified calcite ($CaCO_3$) and gypsum ($CaSO_4 \cdot 2H_2O$). Titanium is also present in the crystalline form of rutile mineral (TiO_2) (Fig. 3). Traces of an organic binder were also found by FT-IR and Py-GC–MS [7,8]. This layer might be a kind of plaster used as a 'priming' layer. It covers the substrate thus obtaining a flat and homogeneous surface, which also provides protection and prevents the support from decaying.

The upper coating layer of the support is a white matrix with some grey and white grains. XRF measurements highlighted high amounts of both calcium (Ca = K$_\alpha$ at 3.691 keV, K$_\beta$ at 4.012 keV) and iron (Fe = K$_\alpha$ at 6.403 keV, K$_\beta$ at 7.057 keV). XRDP and FT-IR revealed the presence of calcite ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$) with some traces of magnetite (Fe_3O_4) and aluminous silicates [9].

Preliminary FTIR analysis of the binder of the coating, showed the presence of a vinyl resin. In order to confirm the identification and to obtain a more reliable evaluation of the molecular composition of the paint samples, pyrolysis analysis was performed. VeoVa™ and butyl phthalate, which are plasticizers used during the synthesis of commonly used vinyl resins and paints, were detected [4].