Macro X-ray fluorescence scanning (MA-XRF) as tool in the authentication of paintings

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ABSTRACT

Scanning macro X-ray fluorescence (MA-XRF) was evaluated as a means for the non-invasive study of two paintings to investigate their authenticity. The first painting, a still-life attributed to the 17th century Spanish painter Francisco de Zurbarán, was analysed both with point XRF analyses and MA-XRF. MA-XRF analyses facilitated the interpretation of the results, revealed a hidden painting and gave a clear answer on the question of authenticity. The second painting, attributed to the workshop or school of Pieter Paul Rubens, was investigated by MA-XRF alone. This revealed a hidden stamp of a canvas manufactory, which situated the painting a few hundred years later than originally supposed. In this last case MA-XRF results were supported by X-radiography and infrared reflectography (IRR). A brief comparison was made between MA-XRF and these traditional scientific imaging techniques, which were not able to detect the stamp. Moreover, it is suggested that in certain cases where for budgetary reasons X-radiographs cannot be made, MA-XRF images can sometimes suffice.

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1. Introduction

Copies and forgeries have been around since the art market came into existence. The idea of making money - the main reason for the production of falsifications - by producing art in the style of a well-known artist has always been attractive to criminal minds. Although art works of all kinds have been falsified or copied [1–3], the emphasis in this paper is on paintings. Over the last decades the buying of art as a long-term investment has boomed, and the art market is therefore increasingly attractive to fraudsters. It has witnessed many scandals [4, 5], and although cases of fraud have been known since the Renaissance – even Michelangelo supposedly forged a classical sculpture by artificially aging it [3] – the most notorious cases date from after the Second World War. One of the most famous is the Van Meegeren affair, when Dutch artist Han van Meegeren falsified old Master paintings, including paintings by Johannes Vermeer [6,7]. One of these paintings ended up in the collection of *Reichsmarschall* Hermann Göring during the Nazi occupation of the Netherlands. After the Second World War, Van Meegeren was accused of collaboration for having sold Dutch art to the enemy and in order to avoid a death sentence, he confessed that the painting was in fact a fake. During the trial, a team of scientists led by Paul Coremans, the later founder of the Royal Institute for Cultural Heritage, proved by chemical analysis that the painting contained 20th century

paint hardeners, hence ruling out the attribution to Vermeer [8]. This is also one of the first cases where exact science could prove a painting to be a later copy. In the following decades the art market was disrupted by forgeries on a large scale. Well-known cases include forgeries by Elmyr de Hory [9], John Myatt [10], Wolfgang Beltracchi [11–13] and Pei-Shen Qian [14]. Besides these great scandals, many other lesser-known forgeries have come onto the market [15–18]. These can lead to a crisis of confidence in the art market, as the value of a painting largely depends on its attribution to a known artist. For art historians forgeries are also problematic, as they falsify history, especially when they are not (yet) exposed as being fake.

In authenticity matters, the opinion of the expert or connoisseur has long been the only source on which the final verdict is based [19]. Comparison of the style and technique of the painting under investigation with that of known and well-established paintings by the master to whom the painting is attributed lead to a judgement on authenticity. Provenance studies, in which the history of the painting is traced back to the artist himself, can sometimes support the opinion of the expert. Since the 20th century, and especially since the second half of the 20th century, exact science has played an increasingly important role in these kinds of studies. Although analyses alone cannot prove the authenticity of a painting, it can sometimes disprove an early dating or strengthen the case for authenticity. In the aforementioned Beltracchi case, it was the finding of one anachronistic pigment - titanium white - in a falsified painting that triggered further research and exposed the scandal [13,20]. This does not imply that the eye of the expert is less

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important than before. Indeed, it is only through the synergy of connoisseurship, provenance studies and exact science that real progress can be made in the battle against forgeries.

The arsenal of analytical techniques is ever expanding as science develops. Well-established techniques include scientific imagery methods like X-radiography [21] and infrared reflectography [22], which reveal underlayers and underdrawings respectively and give important art historical and technological information on the works examined [1]. However, scientific analysis of materials paintings are made of is playing an increasingly key role in the investigation of possible forgeries, especially in the identification of anachronistic materials. Both a painting's support and its painting materials can be analysed. In terms of the support, dating methods are often of crucial importance, namely ^{14}C-dating and dendrochronology [1]. Painting materials are investigated by a large range of scientific methods such as scanning electron microscopy (SEM), X-ray fluorescence (XRF), micro-Raman spectroscopy (MRS), pyrolysis gas chromatography mass spectrometry (Py-GCMS) and high-performance liquid chromatography (HPLC) to name only the most commonly used ones [23]. The development of new analytical techniques and applications has helped advance the fight against counterfeiting. Although micro-Raman spectroscopy has been used for the identification of pigments in artworks since the late 1990s, the potential of the technique for the identification of synthetic organic pigments was only fully exploited a decade later [24–27] and has since played an important role in the characterisation of the palettes of modern and contemporary artists [28,29] and in the exposure of many artworks as fakes [16–18,30].

XRF has long been an established technique for the study of painting materials owing to its non-invasiveness, speed of analysis, good spatial resolution and the fact that information from both the surface and underlayers can be obtained in one measurement. However, some of these features are also drawbacks. Pigments (or other inorganic materials) in different layers all produce secondary X-rays, complicating the interpretation of results. Furthermore, due to the limited number of spots that can be analysed in a feasible amount of time, only local point information is obtained, which is not necessarily representative of the whole painting. The recent introduction of macro X-ray fluorescence (MA-XRF) deals effectively with some of these drawbacks [31–35]. In MA-XRF the X-ray beam scans areas or even the whole painting, producing thousands and sometimes millions of data points. Results can be plotted as elemental distribution maps. These images can make interpretation more straightforward and since the points analysed cover a wide surface area, they are more representative of the whole painting. Moreover, discussing images instead of raw spectra with conservators, art-historians and other non-XRF experts is infinitely more conducive to useful exchanges during multidisciplinary projects.

This paper discusses the benefits of MA-XRF for the authentication of paintings [32,36,37] in comparison with classic point XRF measurements and scientific imagery (mainly X-radiography). Two case studies

are presented, a still-life painting attributed to the Spanish painter Francisco de Zurbarán and a Portrait of Jan Brant, attributed to the workshop or school of Rubens.

2. Experimental

2.1. Paintings under investigation

2.1.1. Still-life painting attributed to Francisco de Zurbarán (1598–1664), private collection

The work investigated (Fig. 1a) is a still-life painted in oil on canvas (104.5 × 146.5 cm). Stylistically, it recalls Spanish painting from the second third of the 17th century. The painting arrived at the Royal Institute for Cultural Heritage with an attribution to the Sevillian painter Francisco de Zurbarán (1598–1664). A thorough stylistic study showed that certain elements are indeed similar to still-lifes carried out by Zurbarán, but the style of the composition is more characteristic of Sevillian and Madrilenian still-lifes from the 1630s. The neutral dark background and the arrangement of the objects on a stone shelf are characteristic of Spanish still-lifes of this period, especially those originating from Madrid. The arrangement of the fruit on a metal tray, probably pewter or silver, is often seen in other still-lifes by Zurbarán, but also features in many Spanish still-lifes of the period, especially from Madrid, as in the work of Juan Van der Hamen y León (1596–1631) and Antonio Ponce (1608–1677).

The painting does include motifs, however, that do not fit with the period in question. The typology of the metal jug on the left, for example, does not correspond to that of contemporary Spanish silverware. Its decoration is atypical for the Baroque period, suggesting instead a 19th century origin. It could be an element added at a later date. Moreover, the lobster at the foot of the jug also raises doubts, as to the best of our knowledge no other Spanish still-life paintings of the period are known to depict lobsters. Finally, the vase with lilies is not painted with the finesse of brushwork seen in the flowers and plate with grapes, suggesting possible repainting.

On the basis of artistic style, it was concluded that the painting might have originated in 17th century Spain, possibly modified in the 19th or 20th century by the addition of elements such as the lobster, metal jug and vase with flowers. The style of the older motifs situates the painting in the context of still-life painters of the school of Madrid active in the middle of the 17th century, such as Antonio Ponce and Francisco Barrera. Attribution to Francisco de Zurbarán seems unlikely.

2.1.2. Portrait of Jan Brant attributed to the workshop or school of Pieter Paul Rubens (1577–1640), private collection

The second painting (Fig. 2a) studied with MA-XRF is also painted in oil on canvas (65.5 × 56.5 cm). It is a faithful copy of Rubens's Portrait of Jan Brant in the Alte Pinakothek in Munich [38]. Jan Brant was Rubens's father-in-law as well as an important Antwerp humanist, lawyer,

Fig. 1. Still-life painting, formerly attributed to Francisco de Zurbarán (1598–1664), oil on canvas (104.5 × 146.5 cm), private collection, under a) normal light and b) UV-light illumination.