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Analyzing Works of Art

Revealing the *sfumato* Technique of Leonardo da Vinci by X-Ray Fluorescence Spectroscopy**

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The perfection of Leonardo da Vinci's painting technique has always been fascinating. The gradation of tones or colors from light to dark is barely perceptible. Neither brushstroke nor contour is visible: lights and shades are blended in the manner of smoke. Understanding this technique, usually called *sfumato*, remains one of the challenges still unaddressed in art history. Herein we show that quantitative X-ray fluorescence spectroscopy performed directly on the works of art makes it possible to access the description of the paint layers used in the flesh tones. We determined the composition and the thickness of the paint layers of nine faces, painted by Leonardo (or attributed to him) over 40 years of his activity. The results shed new light on his constant research to improve the visual aspects of his works of art. In his later paintings, he was able to apply translucent layers (glazes), which were mainly composed of an organic medium in very thin films, down to a micrometer scale.

How did Leonardo da Vinci obtain such impressive naturalistic effects in his paintings? The description of the master's *sfumato* technique is the subject of active discussion in art history.[1,2] Above all, the way the flesh is rendered gives rise to many comments because of its crucial role in the fascination exerted by Leonardo's portraits.[3] Such subtly softened transitions were pioneering work in Italy at the end of the 15th century and have to be linked to the master's creativity and his research to obtain new paint formulations and artistic effects. To date, it had not been possible to carry out a technical study on the faces because of the preciousness of these works of arts. Information was obtained on such points as the preliminary drawing and the list of pigments,[4–6] but not on the flesh tones. Museum laboratories usually develop studies based on the characterization of minute cross-section samples to discover three key elements of the painter's technique: the nature of pigments, of the binders, and the thickness of the paint layers. However, the exact composition of the organic binders cannot be determined without taking samples. Because sampling the faces is obviously not conceivable, we used a non-invasive analytical approach to gain information on the binder concentration, the inorganic composition of the pigments (even if they are at low concentration in the glazes), and the thickness of the layers.

X-ray fluorescence spectrometry (XRF) provides a non-invasive characterization of the pigments based on their elemental inorganic compositions.[7] Until now, the analysis had remained qualitative, because all the pigments layers were considered simultaneously.[8,9] With advances in XRF, it is now possible to obtain in-depth information by taking into account X-ray absorption through the different paint layers.[10] We have recently shown that new developments of the software PyMca[11] give quantitative access to the composition and to the thickness of the different layers using appropriate hypotheses on the multilayered material. It is no longer necessary to take samples from the paintings to describe the stacking of paint layers as we can obtain virtual cross-sections using this non-destructive technique. Moreover, the development of new systems with high-resolution energy-dispersive X-ray detectors enables higher quality measurements.

Herein we use this analytical technique to study seven paintings (with emphasis on the faces of the figures) that have been attributed to Leonardo da Vinci and preserved in the Louvre museum (Supporting Information, Table S1). Direct optical microscopy examinations and sample characterizations on various paintings from the same period showed that the flesh tones were usually obtained by superimposing four layers: 1) the priming layer made of lead white, 2) a pink layer based on a mixture of lead white, vermilion, and earth, 3) a shadow layer made with a translucent glaze or an opaque paint (with dark pigments), and 4) varnish. The thickness for each colored layer ranges from 10–50 μm.[4] Layers (1), (2), and (3) were identified on a cross-section taken from the feet of Saint Anne in the Leonardo painting *Saint Anne, the Virgin and the Child*. Unfortunately, in this area, Leonardo did not apply any shadows. The nature of the layer (3) (shadows) is still a topic of discussion: art historians[3,12,13] suggested that Leonardo drew his inspiration from the Flemish technique of glazes to create shadow effects on the faces. This technique is based on the superimposition of translucent paint layers rich in organic medium with low pigment content. Optical methods confirmed the presence of glazes on the *Mona Lisa* painting,[4,14] but they gave no information about their composition and thickness.

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We carried out series of XRF analyses on the paintings (spot of 1.5 mm in diameter) along lines going from the lightest area to the darkest area and following the evolution of all X-ray lines for each chemical element. From a qualitative point of view, the XRF spectra on the *Mona Lisa* painting show that the low energy Pb M lines emitted by layers (1) and (2) decrease in the shadows, whereas the Fe and Mn lines that originate from layer (3) increase (Figure 1 a,b). This is linked to the growing thickness of the glaze layer in the darker areas. Fe and Mn are characteristic of the pigments used in the glaze. The low-energy Pb M lines (at about 2.3 keV) are strongly absorbed by the upper organic layers; that is, varnish and glaze layers. The Pb L lines of high energy (around 10.5 keV) are almost constant, indicating that the lead content in the painting is constant; that is, the thicknesses of the layers containing lead white do not change. However, no evolution of Pb M lines can be observed in the *Belle Ferronnière* painting: we deduce that Leonardo probably used opaque paint (dark pigments and a classical oil technique) instead of translucent glazes for the shadow effects (Figure 1 c).

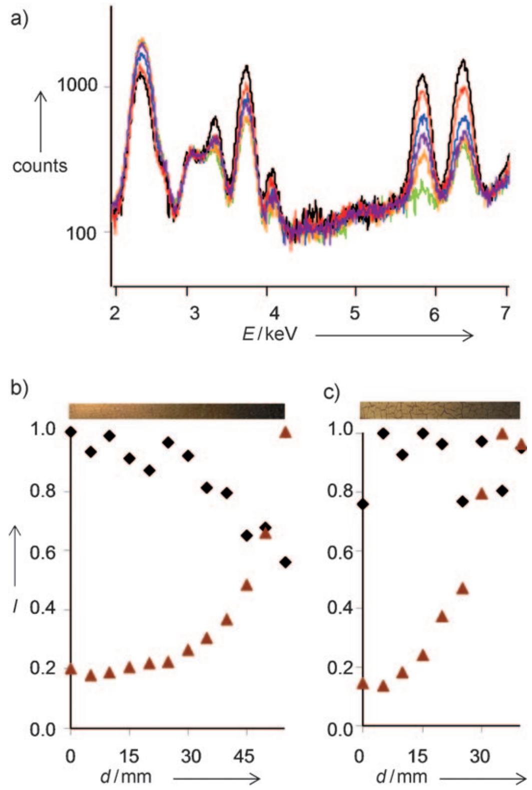

Figure 1. a) XRF spectra obtained on the face of *Mona Lisa* from the lightest zone to the shadow close to the hair. Mn, Fe and Ca K lines present in glazes increase, whereas the Pb M lines at about 2.3 keV decrease because of an increasing glaze thickness. b,c) Evolution of the Fe K signal (▲) and Pb M/Pb L ratio (◆) along the face from a light area to the darkest area: b) face of *Mona Lisa*, c) face of *La Belle Ferronniere*. The intensity is normalized to the maximum value.

To reach quantitative chemical and structural results, we have to make assumptions about glaze and paint formulations. Indeed, the XRF spectra simulation requires a description of each paint layer. Hypotheses on the density and on the composition are based on previous research on paint recipes[15,16] and on the physical properties of varnish and glaze films (Supporting Information).[17] The glaze pigment concentration is then deduced by XRF data treatment as along with the thicknesses of the layers. This is possible because we have more measurements than unknown parameters in the calculations. We have tested several models corresponding to different hypotheses to find the most accurate solution; that is, the best solution to simulate all the XRF spectra obtained from a single face, assuming that the varnish thickness and the glaze composition are almost constant. The uncertainty in the thicknesses is mainly due to possible errors in the layer model, and has been estimated to be less than 30 % (Supporting Information, Figure S1).

The presence of glazes appears clearly in four paintings: *Mona Lisa*, *Saint John the Baptist*, *Bacchus* (originally Saint John the Baptist), and the three faces in *Saint Anne, the Virgin and the Child*. Apart from the *Bacchus*, which is likely to be a work of Leonardo's studio, the others were entirely painted by the master himself over a long period during the last 15 years of his life.

The chronology concerning these artworks is quite difficult to establish.[18] For two earlier works, Leonardo did not use the glaze technique but instead applied paint containing dark pigments: on the Virgin from the *Annonciation* panel to which the young painter may have contributed in Verrocchio's studio, and on the *Belle Ferronnière*. Analyses were also performed on the *Virgin of the Rocks*, but the interpretation turns out to be problematic because cracks and paint diffusion have occurred during the transfer of the painting, which is a drastic operation consisting of removing the paint layers from the original wood panel to another support, a canvas in this case.[19]

Figure 2 shows the calculated models of the four paintings, with glazes presented as virtual cross-sections of paint layers. The glaze thickness increases progressively from a few micrometers in the light areas to 30–55 μm in the dark areas. The whole paint thickness (apart from the varnish layer, which may not be original) is never larger than 80 μm. It is less than 50 μm for the *Saint John the Baptist*. Leonardo chose to limit not only the range of tones and hues to obtain an overall pictorial unity, but he used also the paint matter with an exceptional scarcity, as previously described after observations of samples from different paintings.[4,20] It should be stressed that it is not possible with this analysis to distinguish the priming layer (made of lead white) from the pink layer, which is also based on lead white.

We also obtained information on the pigment concentration of the glaze. For example, the estimated inorganic glaze composition of the Child in *Saint Anne, the Virgin and the Child* is Fe_2O_3 2 %, MnO_2 0.04 %, K_2O 0.4 %, CaO 1–1.4 %. This corresponds to less than 8 % of an earth pigment[21] (aluminosilicates with 25–65 % of Fe_2O_3) diluted in an organic matrix. An addition of bone black (mainly calcium phosphates) is possible and would explain the calcium content. Carbon black may also have been added, but it cannot be detected with X-ray fluorescence. Black and

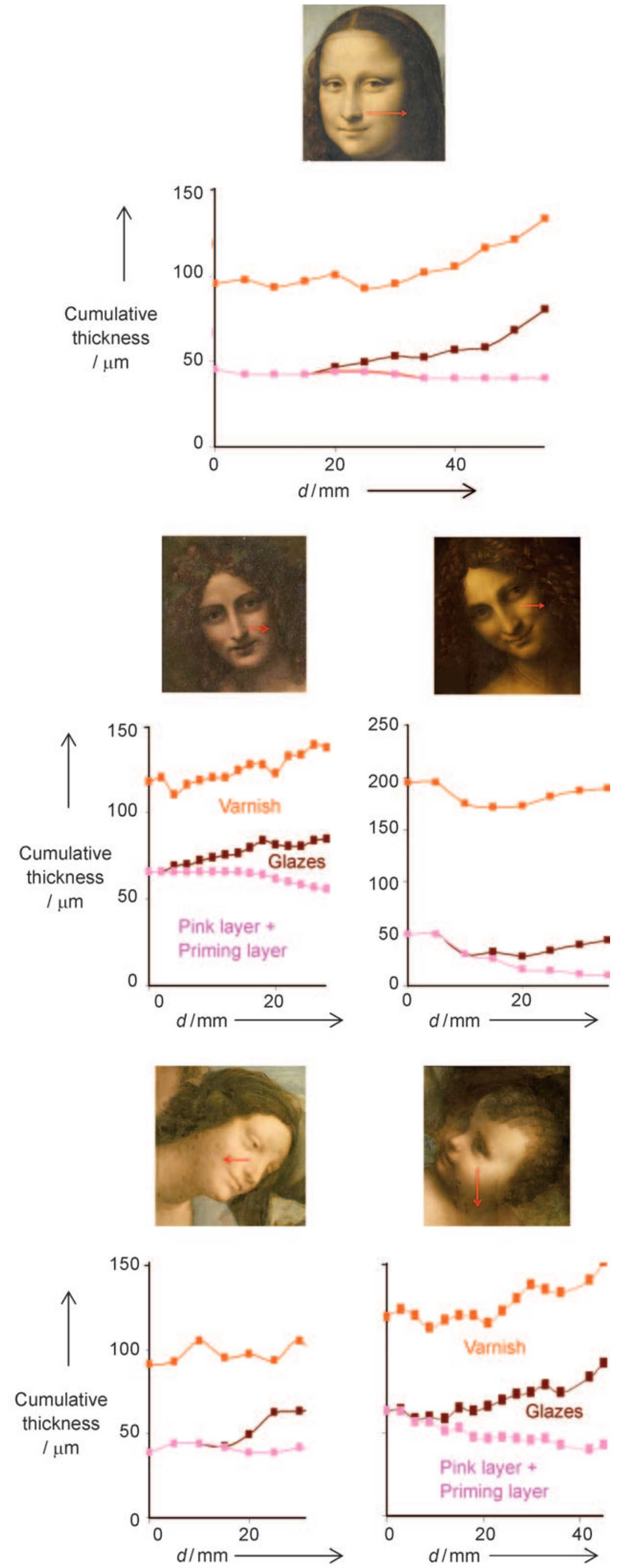

Figure 2. Virtual cross-sections obtained from faces. Top: *Mona Lisa*; center: *Bacchus* (left), *Saint John the Baptist* (right); bottom: the virgin (left), and the child (right) in *The Virgin, Saint Anne and The Child*. The interface between the pink layer and the glaze is indicated by ■, that between the glaze and varnish by ■, and the air–varnish interface by ■. The data are shown as cumulative thickness versus measurement positions on the painting surface.

red grains are extremely thin and barely perceptible by light microscopy.[4]

We have observed an unusual high concentration of manganese oxide in the glazes of the *Mona Lisa* (MnO_2 1.4%, Fe_2O_3 ca. 1%) and the *Saint John the Baptist* paintings (MnO_2 ca. 3%, Fe_2O_3 ca. 2.3%). An addition of copper in the dark color was detected in the *Virgin of the Rocks* (Supporting Information, Figure S2). It is interesting to note that the same practice was observed by XRF on the flesh tones in one of the earliest Leonardo's paintings, the *Madonna of the Carnation* (painted in ca. 1475) on display at the Alte Pinakothek (Munich, Germany)[20].

These quantitative data characterizing the glazes describe in concrete terms the practices used to realize the faces. They shed new light on other studies made by art historians. As early as 1584, in his treatise on the art of painting,[22] G. P. Lomazzo described Leonardo's talent in superimposing dark veils to model the shadows. More recently, extensive research has pointed out that "*Using a technique of almost indescribable delicacy and refinement, he has built up the head from a series of translucent membranes, microtome thin and infinitely subtle in tonal gradation*." [2] Indeed the thinness of the glaze layers (a layer of 2–5 µm is detected, see Figure 2) must be underlined: it confirms the dexterity of the painter to apply such thin layers. This technique was well-known by Flemish painters and other Italian painters, but the various practices that we have observed that were used by Leonardo to darken the flesh tones (Table 1) allow us to gain new insights on his in-depth experimental research and his mastering of the different techniques. Moreover, the measured slow and regular evolution of the thickness of the glaze layer implies that numerous layers (up to 20 or 30) have to be applied to obtain the darkest shadows. As a certain drying time has to be allowed between each application (from several days to several months, depending on the glaze content in resin and oil), another of Vasari's comments[1] on the creation time of the *Mona Lisa* painting can be easily understood: "*After toiling over it for four years, he left it unfinished*." Even today, Leonardo's realization of such thin layers still remains an amazing feat.

Table 1: Technical characteristics of the dark paint used for the face shadows.[a]

Specific characteristics	Paintings
Thin layer of oil paint (large content of pigment), no glaze	*Annonciation* *Belle Ferronnière*
Addition of a copper compound (Glaze or thin paint layer)	*Virgin of the Rocks* *Madonna of the Carnation* (from [20])
Glaze with addition of a manganese compound	*Mona Lisa* *Saint John the Baptist*
Glazes without manganese or copper	*Saint Anne, the Virgin, and the Child* *Bacchus* (originally *Saint John the Baptist*)

[a] The *Madonna of the Carnation* is preserved in the Alte Pinakothek from Munich; the other paintings analyzed for this study are from the Louvre Museum, Paris.

Experimental Section

XRF spectra were acquired with a portable system designed for this study and constructed in the C2RMF laboratory. The system is equipped with a silver anode X-ray tube (Moxtek Bullet tube) and a Si(Li) AXAS-V detector from Ketek (SDD) cooled by the Peltier effect and reaching an energy resolution (FWHM) of about 136 eV at 5.9 keV at the working temperature. The operating conditions of the tube were 35 kV and 95 μA. The distance from the sample to the detector was 2.5 cm, the beam impact angle 45°, and the detection angle 90°. Helium flowing out of the detector (flow rate 1.5 $L\,min^{-1}$) allowed the detection of low-energy X-ray radiation, which are very important for the data quantification.

The spectra were processed by the dedicated software PyMca (version 4.3.0), using the fundamental parameter method.

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