

# NEW STUDIES ON LORENZO LOTTO'S PIGMENTS: NON-INVASIVE AND MICRO-INVASIVE ANALYSES

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## Riassunto

Nell'ambito di un ampio progetto di ricerca, a margine della mostra monografica tenutasi a Roma presso le Scuderie del Quirinale, nel corso degli anni 2010-2011 sono state esaminate *in situ* mediante analisi di tipo non invasivo – spettrometria in riflettanza nel visibile (vis-RS), fluorescenza dei raggi X (ED-XRF), riflettografia IR, IR falso colore, talora RX e fluorescenza UV – oltre 50 opere dipinte da Lorenzo Lotto (Venezia, 1480 – Loreto, 1556-57) tra il 1505 e il 1556 circa, presenti sul territorio italiano, tra cui alcuni politici.

Sulla base dei risultati ottenuti dalle analisi non invasive, condotte dall'Università di Bergamo, sono state selezionate, per quattro opere sottoposte a restauri, le aree su cui svolgere microprelievi dai quali sono state successivamente realizzate sezioni stratigrafiche, studiate mediante microscopia ottica ed elettronica e microanalisi EDX dall'Università di Urbino e con micro-Raman dall'Università di Modena e Reggio Emilia.

Le analisi non invasive hanno permesso di chiarire le peculiarità tecniche di Lotto, dalla tipologia del disegno sottostante e dei ripensamenti, al tipo di pigmenti impiegati e alle loro modalità di utilizzo, ad esempio relativamente all'impiego in diverse combinazioni di lapislazzuli, azzurrite e loro mescolanze con lacche rosse. Particolarmente rilevanti risultano le alternanze, evidenziate dalle analisi vis-RS, di lacca rossa animale (tipo carminio) e vegetale (lacca di robbia) a seconda degli effetti desiderati, e l'impiego accanto al consueto giallo di piombo e stagno di un giallo di piombo e antimonio (giallo di Napoli), rilevato dalle analisi XRF

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già in suoi dipinti dei primi anni Trenta. Quest'ultimo è riferibile al “zalolin da vasarj” di cui Lotto scrive nel 1541 nel suo *Libro di spese diverse*.

Le analisi microinvasive, svolte sul polittico di San Domenico (1508) e sulla *Trasfigurazione* (1511-12) di Recanati, e su due opere realizzate a Bergamo all'inizio degli anni Venti, hanno permesso di accertare una serie di peculiarità raramente o per nulla segnalate nella letteratura sul pittore, come la presenza di litargirio (giallo di piombo) e di zafferano, l'esistenza di un giallorino ad alto tenore di stagno, l'uso di vetro trasparente macinato negli strati pittorici, la presenza di preparazioni colorate con terre e di imprimiture colorate, la ricchezza e la complessità di alcune stesure, specie nelle campiture verdi.

Parole chiave: tecnica pittorica, analisi integrate microinvasive/non-invasive, sezioni stratigrafiche, vetro, lacche rosse

### **Abstract**

In the frame of large research project, also related to the exhibition “Lorenzo Lotto” (Venezia, 1480 – Loreto, 1556-57) held at the Scuderie del Quirinale in Rome in spring 2011, more than 50 paintings of Lotto spanning from 1505 to around 1556 were studied by means of scientific examinations.

The University of Bergamo coordinated and carried out non-invasive analyses using portable instruments: IR reflectography in different bands, false colour IR, reflectance spectrometry in the visible range (vis-RS), X-ray spectrometry (EDXRF), sometimes UV-induced fluorescence and X-ray radiography. On the basis of the obtained results some areas of four paintings undergoing restoration treatments were subjected to micro-sampling in order to be mounted in cross-sections and studied by optical microscopy (OM) and SEM/EDX by the University of Urbino e by micro-Raman spectroscopy by the University of Modena and Reggio Emilia.

Non invasive exams allowed to know the evolution of Lotto's palette during all the periods of his activity, as well as his underdrawing, the nature of painting changes and his pictorial technique. Among the most interesting results, the use of lapis lazuli and azurite in different combinations, and their mixture with red lakes. About these lakes, Lotto shows a peculiar use of madder, also alternated with carmine-type lake, according to desired effects. About yellows, he uses both lead-tin and lead-antimony (Naples yellow) pigments, the latter found by XRF in works starting from 1530 to the last years: it can be related to the “zalolin da vasarj” cited by Lotto in 1541 in his account book (*Libro di spese diverse*).

Micro-invasive analyses (Raman and SEM/EDX) stated also the presence, among yellows, of litharge, of a high tin content “giallorino” (lead-tin yellow) and of saffron, as well as the use of grinded transparent glass in the pictorial layers, the existence of coloured priming and – in one case – of an iron-oxides coloured ground, the complexity of some stratifications and mixtures. This kind of analyses were carried out on a few selected samples of four works painted during different periods of Lotto’s career, from 1508 (Recanati) to 1522 (Bergamo).

Key-words: pictorial technique, micro-invasive/non-invasive integrated analyses, cross sections, glass, red lakes

## **Introduction**

Lorenzo Lotto is one of the most interesting painters of Venetian 16<sup>th</sup> century – besides Titian, Giorgione, the late Giovanni Bellini, Veronese and Tintoretto – for the elegance of his works as well as for iconographic and chromatic innovations, with a special feel for opposite colours juxtapositions and for cold and saturated hues.

His technique has been quite investigated during the last years [1-6] (an almost complete bibliography of published analyses on the painter until year 2010 can be found in [7]), but never with a comprehensive approach including non-invasive exams together with micro-invasive analyses over a broad range of works. In this project, coordinated by the University of Bergamo [8], almost all the paintings (except two) by Lotto in the Marche and Veneto regions have been studied with non invasive tools (29 works), together with 7 paintings of Bergamo and 2 fresco cycles (Credaro and Trescore Balneario), 6 paintings of Brera (Milan) and other 10 belonging to different Italian and foreign collections.

Many features of Lotto’s technique, considering literature and a first screening of new collected data (mainly non-invasive) have been recently discussed in a non-technical essay [7], while more specific results have been published on almost each single painting of Marche [9] and Veneto [10], and on three works of Bergamo [11]. In this paper we want to focus on some new technical results about pigments, emerged from non-invasive and micro-invasive exams listed below.

Micro-invasive analyses were carried out on a few selected samples of the polyptych of the church of St. Dominic (1508) (**figure 1**) and on the *Transfiguration of Christ* (1511-12) (**figure 2**), both in Recanati (Museo Civico, Villa Colloredo Mels), as well as on two works painted in Bergamo: the altarpiece of the church of St. Bernardino (1521) (**figure 3**) and the polyptych of Ponteranica (1522) (**figure 4**).

The context of this contribution allows us to restrict the field of view to micro-analyses and to the most interesting data emerged from XRF and vis-RS examinations.



Figure 1 – Lorenzo Lotto, *Polyptych of San Domenico* (1508), Recanati, Museo Civico.



Figure 2 – Lorenzo Lotto, *Transfiguration of Christ* (1511-12), Recanati, Museo Civico.



Figure 3 – Lorenzo Lotto, *San Bernardino altarpiece* (1521), Bergamo, Church of San Bernardino.



Figure 4 – Lorenzo Lotto, *Ponteranica polyptych* (1522), Ponteranica, Parish church of Santi Vincenzo and Alesandro.

### **Materials and methods**

Limiting this paper to non invasive analyses useful to detect pigments, we carried out XRF and vis-RS on field, using handheld instruments. Points of measure were chosen on the basis of infrared and visible (macro) images, in order to investigate the palette and also the cause of chromatic alterations.

XRF analysis was carried out using two Bruker Tracer III SD energy dispersive spectrometers, both operating at 40 kV, with X-Flash SDD detector and 4 mm diameter spot, one with an Ag target X-ray tube operating at 22  $\mu$ A, the other with a Rh tube at 11  $\mu$ A, with Al-Ti-Cu filter. They both are particularly sensitive to Sn and Sb K-lines.

Diffused reflectance spectrometry (vis-RS) and colorimetry were performed using Minolta CM-2600d, with range 360-740 nm, 10 nm acquisition step, d/8 geometry, SPIN/SPEX.

In the two paintings of Recanati, micro-samples (< 1 mm) were made on the basis of the results obtained by non invasive exams, while in the two painting of Bergamo, samples are micro-fragments incidentally detached during the restorations, so small that it was impossible to reattach them.

The micro samples collected were prepared as cross sections and observed in visible light optical microscopy (Nikon TK-1270E), then they were studied by environmental scanning electron microscope (Philips Quanta FEI 200), equipped with a energy dispersive spectrometer (EDX: 30 KeV, lifetime 60 s). ESEM samples were metallized using gold vapour in vacuum (50 Å of gold cover).

Micro-Raman spectra were recorded with a Labram instrument from the Jobin Yvon-Horiba, equipped with a red 633 nm laser, a Peltier-cooled (-70°C) CCD detector with 1024 x 256 pixels; spectral resolution 1  $\text{cm}^{-1}$ , spatial resolution 1  $\mu\text{m}$ . According to the intrinsic intensity of the spectrum recorded, the scanning time varied from 5 to 20 s and the number of scans from 5 to 20 with the laser power (5 mW) attenuated to about 1/10. Olympus long-distance objectives with 50 and 100 enlargements were used. Raman analyses were performed on some of the cross sections as well as on non-embedded micro-fragments of the same samples.

## Results

We discuss here the main features emerged about ground layers and pigments, organized by colour. A detailed synthesis obtained by integrated analyses carried out on some of the studied micro-samples are illustrated in **tables 1a-7a** and related images (**figures 5-14**), with the linked non invasive exams (**tables 1b-7b**). We underline that the high focalization of Raman analyses allowed to study only the grains of pigment which colour and shape appeared to be different at light optical microscopy view (OM); therefore some particles/compounds remain unstudied.

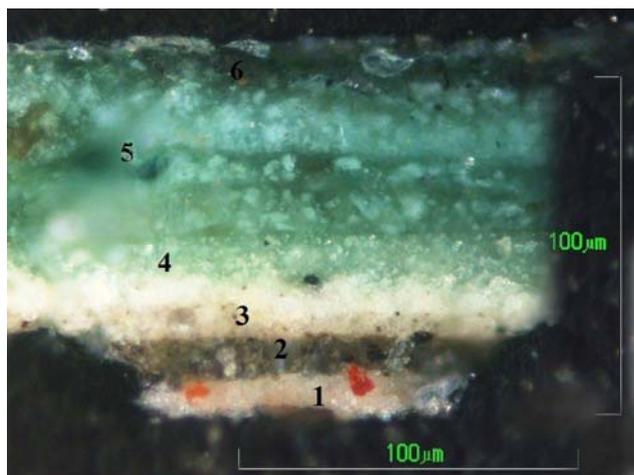


Figure 5 – *Polyptych of San Domenico* (1508), Recanati. Cross section of the green of St. Gregory's cope (sample PR1)

layers	maximum thickness (μm)	typology	colour	EDX, detected elements	stratigraphic identification (OM+SEM/EDX)
6	15	painting layers	green	Pb, Cu, Sn, Si, Al, Na, Ca	Cu-based green, lead-tin yellow in glassy matrix
5	15		green	Cu, Si	Cu-based green, silica
4	50		pale green	Pb, Cu, Si, Sn, Ca	lead-tin yellow, Cu-based green, calcium carbonate
3	20		hazel	Pb, Sn, Si, Ca, Al, Na	lead white, lead-tin yellow in glassy matrix
2	10		dark green	Pb, Cu, Si	lead white, Cu-based green, silica
1	15	priming	pink	Pb, Sn, Ca, Al, Si, Na	lead white, lead-tin yellow, glassy particles, red lead
0	20	ground layer	white	Ca, S	calcium sulphate

Table 1a – Pigments detected by micro-analyses in the cross-section PR1 (fig. 5).

vis-RS spectra characteristics (nm)	vis-RS identification	XRF, detected elements	XRF identification (except ground layer)
560M, 700m	prob. copper acetate (verdigris)	Ca, Fe, Cu <sup>^</sup> , (Hg), Pb, Sr, Sn <sup>^</sup>	Cu-based pigment, lead-tin yellow

Table 1b – Pigments detected by non-invasive analyses in the green area of PR1. Vis-RS characteristics refer to reflectance spectra (M=max., m=absorption band, s=shoulder, w=weak). <sup>^</sup> indicates higher amounts, (...) stand for very low counts; "prob" for probably.

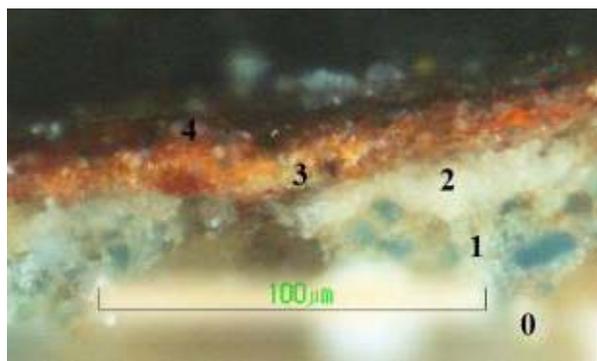


Figure 6 – *Polyptych of San Domenico* (1508), Recanati.. Cross section of Saint Lucia's robe (sample PR2).

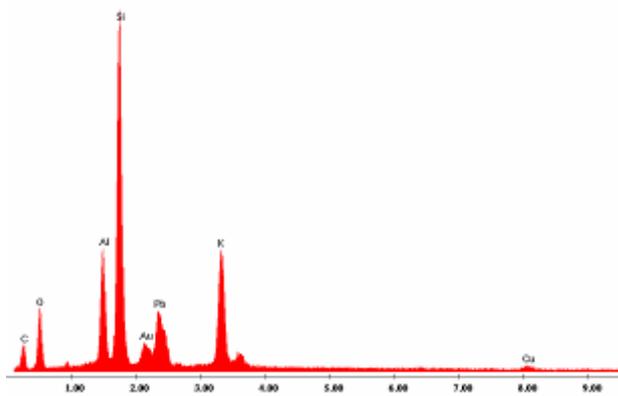
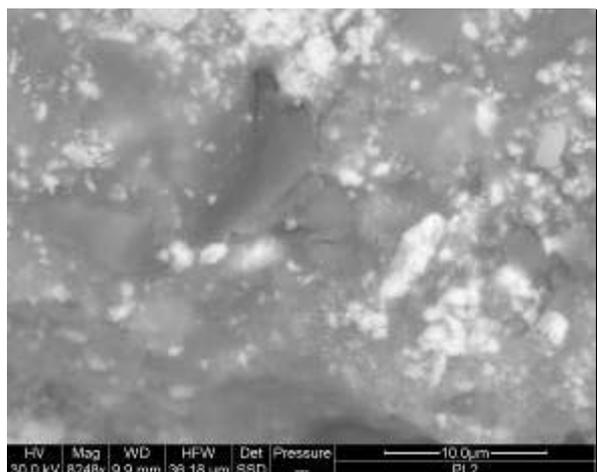


Figure 7a-b – SEM micrograph of glass fragment in layer 1 of sample PR2 (a) and its EDX spectrum (b).

layers	maximum thickness (µm)	tipology	colour	EDX, detected elements	stratigraphic identification (OM+SEM/EDX)	Raman
4	10	painting layers	brown	Pb, Si, As, S, Ca, Fe, Zn, Cu, K, Mn, Al	arsenic sulphides (orpiment/ realgar), red ochre, red lead, raw umber, Zn containing pigment	realgar and orpiment, red compound with a large band at 300 cm <sup>-1</sup> , lead white
3	15		orange-red	Pb, As, S, Si, Ca, K, Fe, Zn, Cu, Al	arsenic sulphides (orpiment/ realgar), red ochre, Pb- based pigments, Zn containing pigment	
2	10		white	Pb, Ca	lead white, calcium carbonate	lead white
1	35		light blue	Pb, Sn, As, S, Cu, Si, Al, K, Ca	lead white, azurite, lead-tin yellow, glass particles, orpiment	azurite, litharge, lead white, goethite
0	200	ground layer	white	Ca, S, Si	calcium sulphate, silica	n.a.

Table 2a. Pigments detected by micro-analyses in the cross-section PR2 (fig. 6). n.a. means not analysed.

vis-RS spectra characteristics (nm)	vis-RS identification	XRF, detected elements	XRF identification (except ground layer)
<420m, 390sw, 590s/M, 640mw	azurite, yellow pigment, traces of Zn-oxide (or Ti-oxide?)	Ca, Fe, Cu <sup>^</sup> , Zn?, As, Pb, Sr, Sn	Cu-based pigment, lead-tin yellow, As-based pigment

Table 2b. Pigments detected by non-invasive analyses in a blue area close to the sample PR2. Vis-RS characteristics refer to reflectance spectra (M=max., m=absorption band, s=shoulder, w=weak). ^ indicates higher amounts.

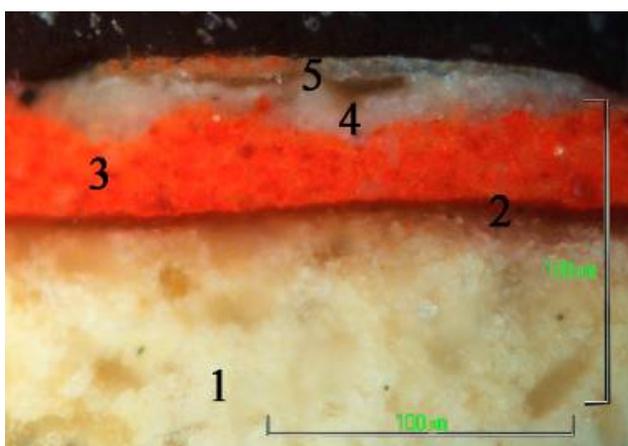


Figure 8 – *Transfiguration of Christ* (1511-12), Recanati. Cross section of the red of St. John's robe, light, with white-yellow decorated border (sample TR1).

layers	maximum thickness (μm)	typology	colour	EDX, detected elements	stratigraphic identification (OM+SEM/EDX)	Raman
5	50	painting layers	red	Pb, Hg, S, Si, Al, Ca	lead white, vermilion, lake	n. a.
4	20		white	Pb, Si, Sn, Al, Ca	lead white, lead-tin yellow in glassy matrix	n. a.
3	45		red	Hg, S, Si	vermilion, silica	vermilion, particles of lead white
2	5		dark	Pb, Al, Si	red lead, silica	litharge, a few indigo
1	110	priming	white	Pb, Si, Sn, Ca, Fe	lead white, lead-tin yellow, glassy particles, calcium carbonate	lead-tin yellow type I, litharge, saffron, gamboge?, particles of calcite

Table 3a. Pigments detected by micro-analyses in the cross-section TR1 (fig. 8).

vis-RS spectra characteristics (nm)	vis-RS identification	XRF, detected elements	XRF identification (except ground layer)
460Mw, <570m, 620-630s	vermilion, traces of red carmine-type lake (clearly detected in the shadow)	Ca, Fe, (Cu), Hg <sup>^</sup> , Pb <sup>^</sup> , Sr, Sn <sup>^</sup>	Cu-based pigment, lead-tin yellow, lead white

Table 3b. Pigments detected by non-invasive analyses in the red area of the sample TR1. Vis-RS characteristics refer to reflectance spectra (M=max., m=absorption band, s=shoulder, w=weak). ^ indicates higher amounts, (...) stands for very low counts.

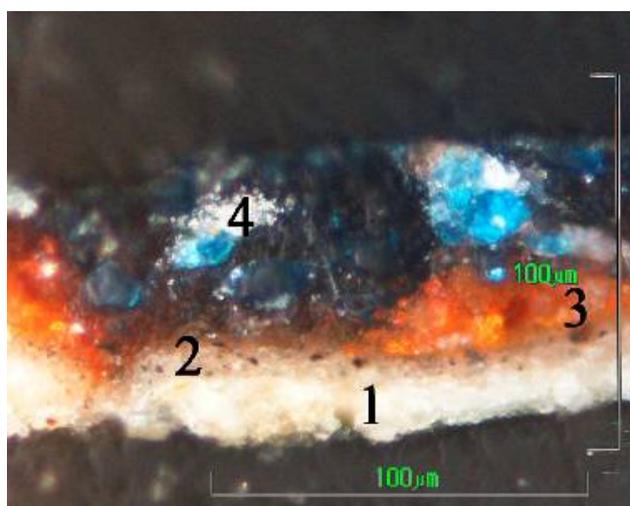


Figure 9 – *Transfiguration of Christ* (1511-12), Recanati. Cross section of the blue of St. Peter's robe, along the border, over his orange cloak (sample TR2).

layers	maximum thickness (μm)	typology	colour	EDX, detected elements	stratigraphic identification (OM+SEM/EDX)
4	55	painting layers	blue	Cu, Si	azurite, silica
3	25		orange-red	Pb, As, S, Hg, Ca, Al, Si, Fe, K	arsenic sulphide (orpiment/realgar), Pb-based pigments, red lake, vermilion, red ochre
2	10	drawing	grey		carbon black
1	30	priming	white	Pb, Si, Ca, Sn	lead white, lead-tin yellow in glassy matrix

Table 4a. Pigments detected by micro-analyses in the cross-section TR2 (fig. 9).

vis-RS spectra characteristics (nm)	vis-RS identification	XRF, detected elements	XRF identification (except ground layer)
490M, 560m, 640m	azurite, small amounts of red carmine-type lake	Ca, Fe, Cu <sup>^</sup> , Pb <sup>^</sup> , Sr, Sn <sup>^</sup>	Cu-based pigment, lead-tin yellow, lead white

Table 4b. Pigments detected by non-invasive analyses in the blue area near TR2 (without orange sub-layer). Vis-RS characteristics refer to reflectance spectra (M=max., m=absorption band, s=shoulder, w=weak). <sup>^</sup> indicates higher amounts, (...) stands for very low counts.

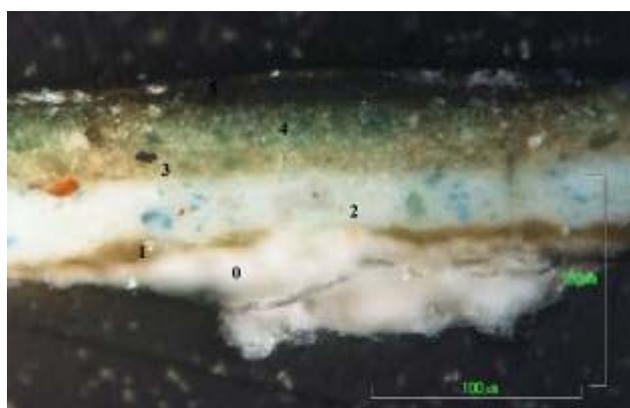


Figure 10 – *Transfiguration of Christ* (1511-12), Recanati. Cross section of Elia's iridescent green-pink robe, in the green shadow (sample TR4).

layers	maximum thickness (µm)	tipology	colour	EDX, detected elements	stratigraphic identification (OM+SEM/EDX)
5	10	painting layers	dark green	Cu	Cu-based green
4	40		green	Pb, Cu, Al, Sn, Si, Ca	Cu-based green, lead-tin yellow in glassy matrix
3	15		hazel	Si, Pb, Ca, Al, Mg, K	lead white, silicates
2	30		light blue	Pb, Cu, Si, Fe	lead white, azurite, hematite
1	10	priming	hazel	C	(organic compounds)
0	50	ground layer	white	S, Ca, Al, Si	calcium sulphate, Si/Al based particles

Table 5a. Pigments detected by micro-analyses in the cross-section TR4 (fig. 10).

vis-RS spectra characteristics (nm)	vis-RS identification	XRF, detected elements	XRF identification (except ground layer)
590M, 700m	prob. copper acetate (verdigris)	Ca, Fe, Cu <sup>^</sup> , (Hg), Pb <sup>^</sup> , Sr, Sn	Cu-based pigment, lead-tin yellow, lead white

Table 5b. Pigments detected by non-invasive analyses in the green area of the sample TR4 (fig. 10). Vis-RS characteristics refer to reflectance spectra (M=max., m=absorption band, s=shoulder, w=weak). ^ indicates higher amounts, (...) stands for very low counts; “prob” for probably

layers	maximum thickness (µm)	typology	colour	EDX, detected elements	stratigraphic identification (OM+SEM/EDX)	Raman
6	20	varnish?	white	-	-	-
5	20	painting layers	green	Cu, Pb, Ca, Si, Sn	Cu-based green, lead-tin yellow in glassy matrix	azurite, lead-tin yellow type I, lead white, particles of litharge, traces of phtalocyanine (restoration, at surface)
4	45		green	Cu, Pb, Ca, Si, Sn, Cl, K	Cu-based green, lead-tin yellow in glassy matrix, Cl/K-based particles	n.a.
3	40		light green	Pb, Cu, Sn, Si, Ca, Fe	lead-tin yellow in glassy matrix, lead white, Cu-based green	n.a.
2	35		green/brown	Cu, Pb, Si, Sn, Ca, Al	Cu-based green, azurite, lead-tin yellow in glassy matrix, lead white	litharge
1	25	priming?	white	Pb, Si, Ca, Al, Mg, K, Fe	lead white, calcium carbonate, silicates	n.a.
0	95	ground layer	light brown/hazel	Ca, S, Si, K, Fe, Mg, Al	calcium sulphate, green earth	calcium sulphate

Table 6a. Pigments detected by micro-analyses in the cross-section PSB (fig. 11). n.a. means not analysed.

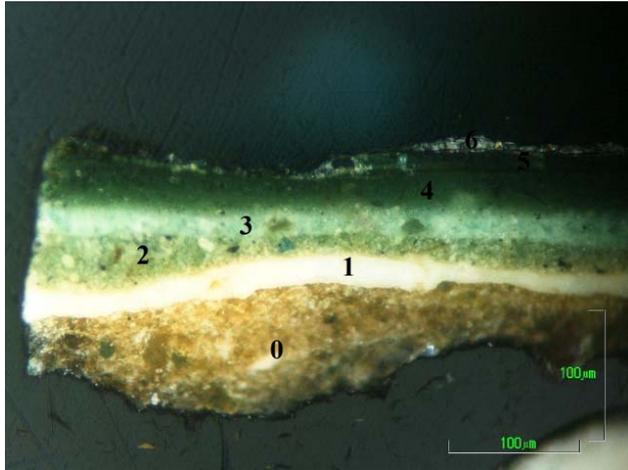


Figure 11 – *San Bernardino altarpiece* (1521), Bergamo. Cross section of the green of the tent, shadow (sample PSB).

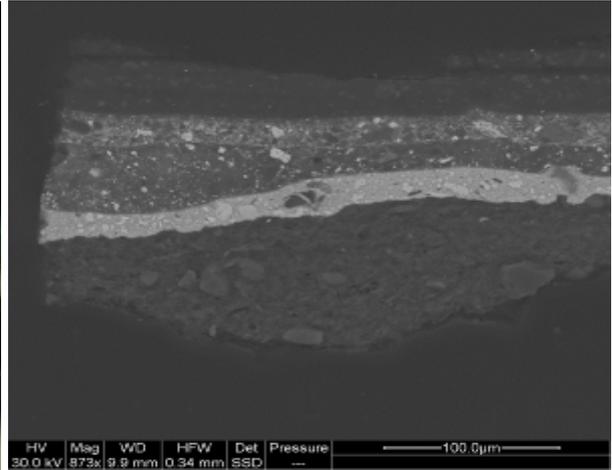


Figure 12 – SEM micrograph of sample PSB.

vis-RS spectra characteristics (nm)	vis-RS identification	XRF, detected elements	XRF identification (except ground layer)
560M, 700-710m	copper acetate (verdigris)	Ca, Fe, Cu <sup>^</sup> , Pb, Sr, Sn	Cu-based pigment, lead-tin yellow, lead white

Table 6b. Pigments detected by non-invasive analyses in the green area of the sample PSB (fig. 11). Vis-RS characteristics refer to reflectance spectra (M=max., m=absorption band). ^ indicates higher amounts.

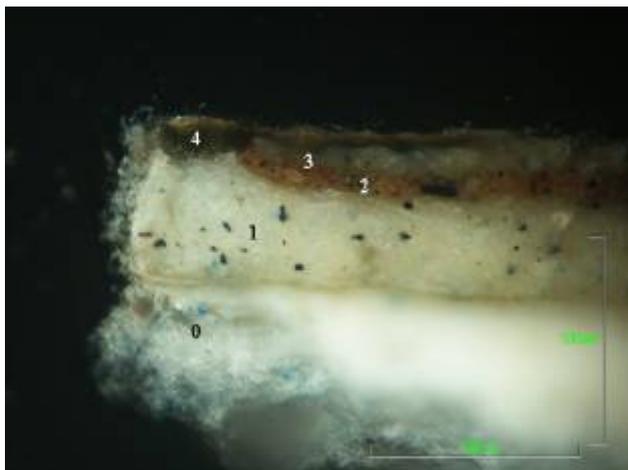


Figure 13 – *Polyptych of Pontenatica* (1522), Pontenatica (BG). Cross section of the brown-greenish reading desk of the Virgin's panel (sample PPB).

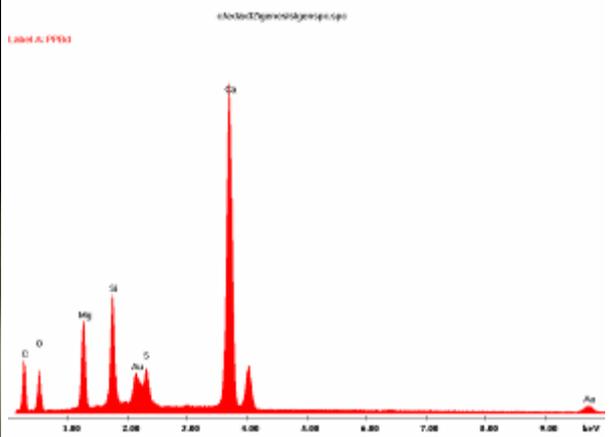


Figure 14 – EDX spectrum of a Mg-containing particle (magnesium carbonate) in the ground layer of sample PPB.

layers	maximum thickness (µm)	typology		EDX, detected elements	stratigraphic identification (OM+SEM/EDX)	Raman
4	20	painting layers	dark hazel	Pb, C, Ca, Si, Fe, K	varnish and parts of layer 3	copper phthalocyanine*
3	25		hazel	Pb, Si, Fe, Ca, K, Cu, Sn, Al	lead-tin yellow, azurite, red ochre	lead-tin yellow type I (strong band at 132 cm <sup>-1</sup> ), azurite, lead white
2	30		brown-red	Fe, Al, Si, K, Hg, S, Ca	iron oxides, carbon black, vermilion	hematite, carbon black
1	95	priming ?	light hazel	Pb, Si, C, Ca, Al, Mg, K, Fe	lead white, carbon black, silicates	carbon black, lead white
0	275	ground layer	white	Ca, S, Si, Mg, Fe, Mn	calcium sulphate, calcium and magnesium carbonate, iron oxides (raw umber)	calcium sulphate

Table 7a. Pigments detected by micro-analyses in the cross-section PPB. \* means that some blue particles on the surfaces are due to copper phthalocyanine: its presence can be ascribed to traces of a previous restoration or to unwanted touch with blue modern materials. Really the strength of Raman scattering of this kind of compound is high and it allows its identification also in small amounts.

vis-RS spectra characteristics (nm)	vis-RS identification	XRF, detected elements	XRF identification (except ground layer)
450sw, 570s, 460mw	yellow-brown ochre, small amounts of blue/green pigment (azurite?)	Ca, Fe <sup>^</sup> , Cu <sup>^</sup> , Pb <sup>^</sup> , Sr, Sn <sup>^</sup>	Cu-based pigment, lead-tin yellow, lead white, iron oxide (ochre/earth)

Table 7b. Pigments detected by non-invasive analyses in the light brown-greenish area near the sample PPB. Vis-RS characteristics refer to reflectance spectra (m=absorption band, s=shoulder, w=weak). ^ indicates higher amounts.

### Ground layers

The typical Lotto's preparation of the canvas or wood panel is commonly made of calcium sulphate ("gesso") and animal glue [2, 3, 4, 5, 7]. In our samples, Ca, S are well identified by EDX, while, at the excitation energy we used, XRF detects Ca, Sr (a substitute of Ca in some of its compounds, or due to impurities of celestine) and some amounts of Fe, sometimes present at impurity level. As known, in XRF the S line is hidden by Pb M-line, and can be seen only in lacunas where priming and upper layers are absent.

Sometimes a priming – white or coloured, depending on the area and desired effect – is added over it, at least locally. In earlier works a pink or reddish priming can be seen – like in the *Santa Cristina* altarpiece (1504-1506), with lead white, vermilion, ochres, carbon black, calcium carbonate – very seldom reappearing in later paintings – like Lotto's *Madonna delle rose* of Jesi (1526), with lead white and red ochre. After 1506, XRF data, showing amounts of Pb and Sn in almost all the measured points of many paintings from 1508 to the 1530s, let us suppose the presence of a priming containing lead-tin yellow and lead white.

In particular, the polyptych of *St. Domenico* and the *Transfiguration of Christ* are characterized by a priming of lead white and lead tin yellow (type I) in glassy matrix; in the previous painting – as in the *Annunciation* of Jesi (about 1526) – also minium is detected.

Exceptionally, the ground of *San Bernardino* altarpiece is a light brown one, containing green earth and probably other iron oxides together with calcium sulphate (**table 6a**).

The presence of Mg and Ca in the calcium sulphate matrix in the polyptych of *Ponteranica*, (**figure 14**) can be attributed to calcium and magnesium carbonate (**table 7a**). Silica is sometimes due to transparent glass (**figures 7a-b**), mixed in order to accelerate oil drying, as happened to other artists [12]; also lead-tin yellow (in glassy matrix) is perhaps used in the ground layers for the same goal [13]. At least in one case, the presence of saffron and perhaps gamboge (sample TR1, **table 3a**) suggests that also the yellow tone of the priming was needed to reach special effects, while only lead-tin yellows and lead white gave a pale yellow layer.

### ***Blue pigments***

Lotto uses or lapis lazuli (vis-RS abs. band around 600 nm) or azurite (vis-RS abs. band around 640 nm), also in the same work, both of them characterized by a very good quality depending on desired tone and on the economy of the painting (**figure 15**). In many cases the precious ultramarine blue, usually dedicated to the Virgin's cloaks and sometimes to the sky, is used above a layer of azurite.

As vis-RS shows, small amounts of red lakes can be added to the blue pigment (i.e. **table 4b**) to reach the desired blue tone. If larger amounts of lakes are used a violet tone is obtained, both using azurite or lapis lazuli (**figure 15**). The blue Cu-carbonate, mixed with yellow, is also rarely used to obtain some specific dark green or blue-grey shades (**figure 16**, curves 17, 69-70).

Smalt blue seems to be used only in mural paintings by Lotto, but in Trescore azurite is widely employed. Indigo is detected by Raman spectroscopy in an inner layer (**figure 17**), but it was never found with vis-RS in external layers, except for the predella of the late Mogliano altarpiece

(1548) attributed to a collaborator of Lotto (vis-RS is a very suitable tool to detect indigotin, also in small amounts, because of its strong absorbance band at about 670 nm).

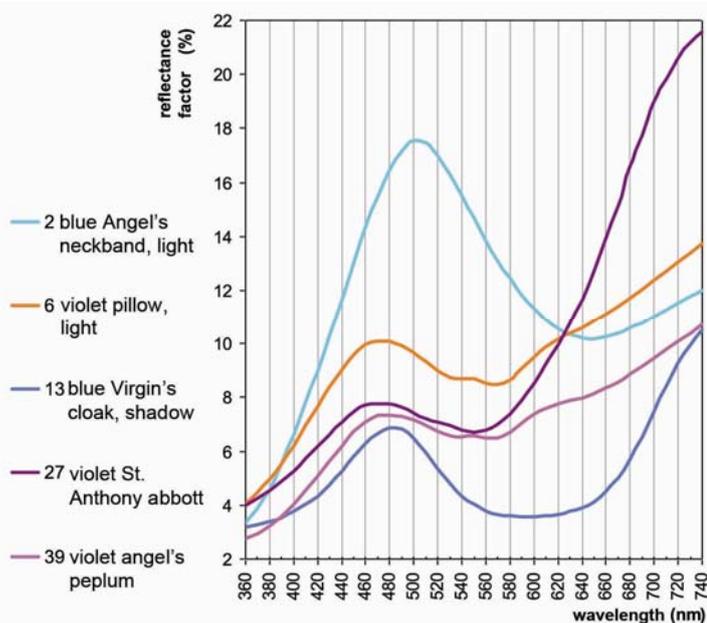


Figure 15 – Vis-RS spectra of blue and violet colours from the polyptych of Ponteranica. Identified pigments: 2=azurite; 13=lapis lazuli; 27=lapis lazuli and madder red lake; 6, 39=azurite and red carmine type lake.

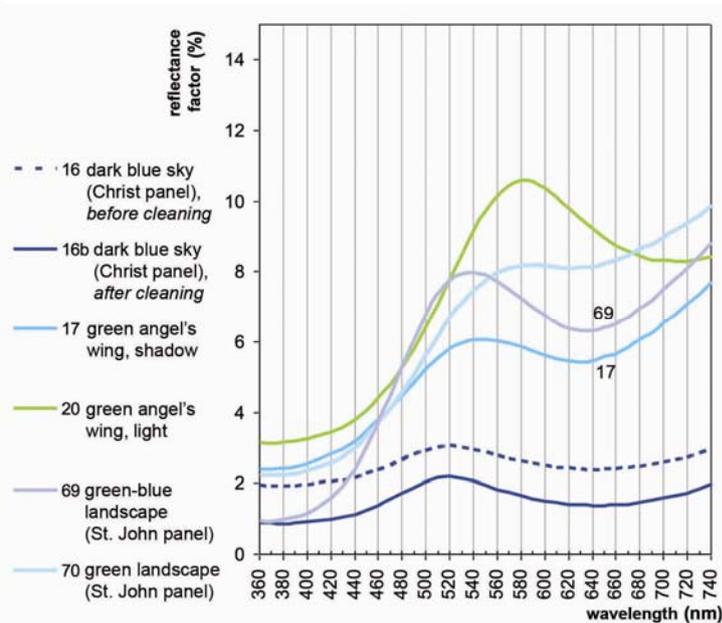


Figure 16 – Vis-RS spectra of blue and green colours from the polyptych of Ponteranica. Identified pigments: 16-16b=azurite; 17, 69, 70=azurite (and yellow pigment); 20=probably copper acetate (verdigris)

### Green pigments

Vis-RS band around 700-720 nm (**figure 16**, curve 20) is frequently found where copper acetate is mixed with yellows (like lead-tin one) or sometimes with lead white, as many comparative analyses (vis-RS and cross sections) show. The abs. broad band of verdigris alone is commonly in the range 700-750 nm, and its reflectance peak, generally around 520 nm when pure, is shifted to a higher wavelength (about 580 nm) as a typical effect of aged pigment mixture, where possible alterations of binder (oil?), varnish, or pigment itself may have occurred. For malachite, the reflectance peak is around 540 nm, and in old paintings also some shift can occur. So, the position of the peak can't be considered a good criterion to distinguish between the most common Cu-containing greens, while the absorption band is generally a good one, because malachite broad absorption band falls in the range 750-900 nm, far ahead in respect to verdigris. This pigment seems to be the most used green by Lotto, as well as from the majority of XVI century Italian painters, allowing translucent glazes made of many thin brushstrokes. Not detected by Raman on the sample PSB, probably because of binder high content, verdigris is very finely grinded and usually painted in many overlying layers (**figures 5, 10-11**). Malachite

has been only seldom identified in Lotto's works [3, 7, 10]. Rare is green earth, used apparently only in mixtures, as in **table 6a**.

### ***Yellow and orange pigments***

Lead-tin yellow type I is commonly present in yellow and green areas, as well as in priming, as told, well detected by XRF, EDX and Raman (**figure 19**). As XRF analyses show, in some works, starting from 1530 to the last years of the century, also lead-antimony (Naples yellow) pigments, can be found, together with the previous yellow or almost alone: they can be related to the “zalolin da vasarj” cited by Lotto in 1541 in his account book (*Libro di spese diverse*). This yellow appears to be a little darker, intense, than the lead-tin yellow, which exhibits a pale colour.

Some yellow particles found in many studied layers are referable to litharge, being the main peak at about  $142\text{ cm}^{-1}$ . This can be interpreted with the use of some lead compounds that are not always stoichiometric ones or that come out from the preparation procedure of the lead compounds.

Of course, some Pb compounds like Pb oxides (minium and litharge) cannot be identified by XRF. But the presence of minium is certified by vis-RS (absorption band  $< 540\text{ nm}$ , shoulder at about  $580\text{ nm}$ ) where it belongs to the surface layer, as happens only in two paintings we studied, the *Deposition* of Jesi and the *Sedrina* altarpiece.

Saffron identification seems quite interesting (**figure 18**) because never noted with other techniques and thought not to be used anymore in painting at that age.

Orpiment and/or realgar are detected in orange areas, usually shaded with iron oxides.

### ***Red pigments***

Along with vermilion, used for bright layers, Lotto uses (at least) two types of red lakes, a carmine-type and a madder (from *Rubia tinctorum*), that can be distinguished by vis-RS for the bands at about  $510\text{ nm}$  and  $550\text{ nm}$ , and at  $520\text{-}530\text{ nm}$  and  $560\text{-}570\text{ nm}$ , respectively [14] (**figure 20**). Sometimes these two lakes are used in different areas of a painting or in alternate layers of the same area, and together with glass [15].

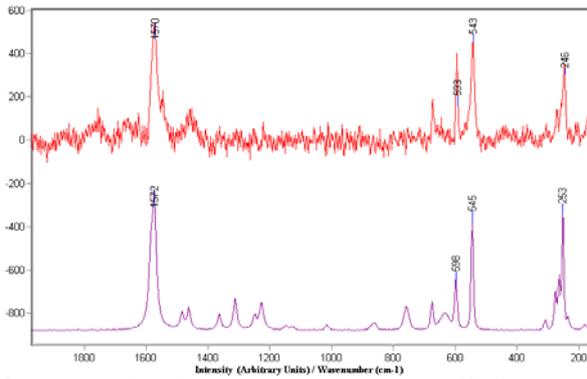


Figure 17 – Micro-Raman measured spectrum of indigo (top) on sample TR1, layer 2, compared to Clark database (bottom).

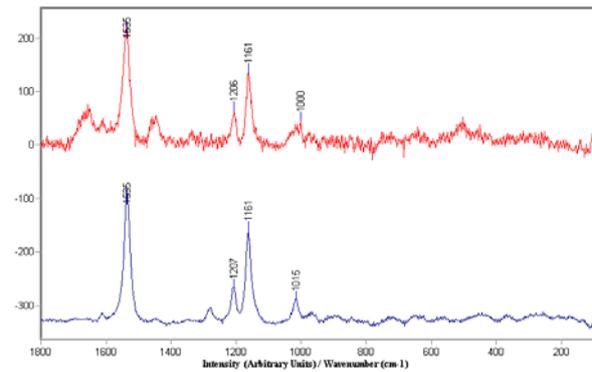


Figure 18 – Micro-Raman spectrum of saffron (top) on sample TR1, layer 1, compared to standard.

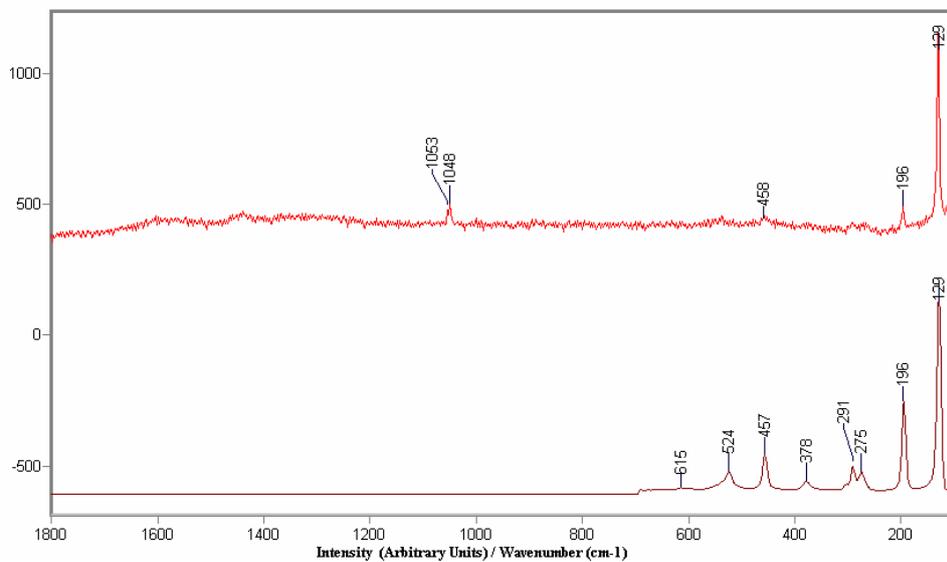


Figure 19 – Micro-Raman spectrum (top) of sample PSB2, layer 5, compared (bottom) to a standard of lead-tin yellow type I. Lead-tin yellow type I, lead white (cerussite and hydrocerussite) can be detected.

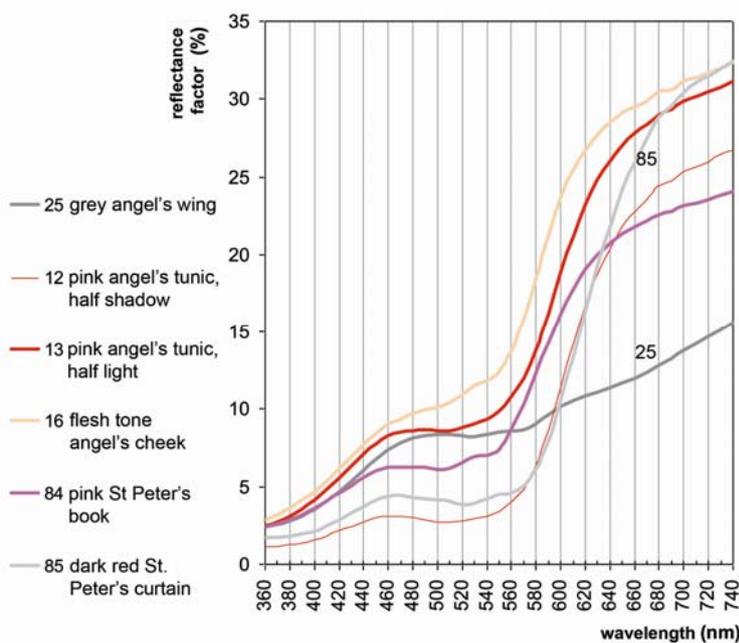


Figure 20 – Vis-RS spectra of red colours from the San Bernardino altarpiece. Grey curves (25 and 85) show the presence of a carmine type lake (bands at 520-530 nm and 570 nm); red and pink curves (12, 13, 16, 84) can be related to madder lake (bands at ab. 510 and 550 nm).

Particles of hematite are also found mixed with vermilion in some layers (**Table 7a**). A red compound with a large band at  $300\text{ cm}^{-1}$  ( $\text{HgO?}$ ) was detected by micro-Raman in sample PR2.

### ***Other pigments***

The only detected black is carbon black. Different iron oxides are used by Lotto, some of them are Mn-rich (umber). Only in some paintings also Zn-rich brown earths can be found [9, 11, 16-18], with Zn/Fe ratio usually lower than 0.2. In the *San Domenico* altarpiece, Zn amounts are detected by XRF where Fe content is greater, and according to vis-RS spectra, zinc white appears to be absent. This can indicate a Zn-rich earth, also if a strong Fe-Zn correlation is absent (Zn/Fe ratio varies from 10 to 50%). In the sample PR2 (**figure 6, table 2a**), in the layers 3-4 containing orpiment/realgar the amount of Zn and Fe is the same. Here, zinc could be related to galena (blenda-sfalerite) or to the presence of zinc white used in old restoration treatments. The presence of orpiment/realgar would suggest us to exclude the layers are not original, but their presence in other areas – surely not original – of the same polyptych (central panel, St. Gregory arms), lead us to suspect they were introduced perhaps in a 18<sup>th</sup> or 19<sup>th</sup> century intervention. Further studies are ongoing.

Lead white is found almost everywhere in the painting layers, but in lower amounts where arsenic sulphides are present. Lead white exhibits a double Raman peak at  $1054$  and  $1046\text{ cm}^{-1}$ , being a mixture of cerussite and hydrocerussite. The second one undergoes a slow carbonatation with time and this is a testimony of the ageing of lead white.

Calcium carbonate is frequently employed (as a filler or extender) inside the layers.

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