Edited by

Ernst Pernicka
Günther A. Wagner

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Editors' Address:

Professor Dr. Günther A. Wagner
Dr. Ernst Pernicka
Forschungsstelle Archäometrie
Max-Planck-Institut für Kernphysik
Postfach 10 39 80
D-6900 Heidelberg/Germany

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Archaeometry '90

IN SITU ND ANALYSES OF XVI AND XVII CENTURIES ITALIAN PAINTINGS

G.E. Gigante [1], C. Maltese [2], S. Rinaldi [2] and S. Sciuti [3]

1) Dipartimento di Fisica, Universita'di Roma "La Sapienza", p.le A.Moro 5, 00185 Roma.
2) Istituto di Storia dell'arte, Universita' di Roma "La Sapienza", p.le A.Moro 5, 00185 Roma.
3) Dipartimento di Energetica, Universita' di Roma "La Sapienza", via Scarpa 14-16, 00161 Roma.

SUMMARY: Since 1983 a multi-disciplinary group composed of physicists, chemists and art historians performed a research work on ancient paintings devoted to the interconnections between elemental analyses of artists' pigments and sematometric evaluations of optical parameters such as color and luminosity.
The elemental analyses have been carried out by means of a portable X-Ray Fluorescence (XRF) spectrometer. So far 18 paintings by Caravaggio, Raffaello, Michelangelo and Veronese have been analyzed in those points considered significant after a critical inspection. More than 400 spectra have been collected and stored.
The methodology developed to correlate the elemental analyses with the historic manufacture of artists' pigments and the organization of analytical data are described.

INTRODUCTION

Fast ND (nondestructive) analyses with portable or transportable instrumentations (PI in the following), can solve diagnostic and/or research problems concerning the artistic patrimony. Nowadays different techniques and methods are feasible by means of PI; therefore a great variety of analyses can be performed directly in museums,

TABLE I: List of paintings examined "point by point" by portable XRF devices.

Author	Painting	Age	Location	Sizes (cm)	N.of points(*)
Michelangelo1)	Holy Family (Tondo Doni)	1504/6	(1)	diam.120	40
Raffaello 2)	Dama con unicorno	1506	(2)	66x51	19
Raffaello 3)	Deposizione	1507	(2)	184x176	25
Raffaello 4)	La Fornarina	1520	(3)	85.5x61.4	20
Raffaello 5)	Unknown man portrait	?	(2)	45x31	12
P.Veronese 6)	Battle of Lepanto	end XVI	(4)	169x137	36
Caravaggio 7)	Self-portrait as Bacchus	1593/94	(2)	67x53	23
Caravaggio 8)	Boy with a basket of fruit	1593/94	(2)	70x67	27
Caravaggio 9)	Gypsy Fortuneteller	1596	(5)	116x151.2	34
Caravaggio 10)	Judit beheading Holofernes	1598/99	(3)	145x195	25
Caravaggio 11)	Madonna and child with St.Anne	1605/6	(2)	292x213	13
Caravaggio 12)	St.Jerome in his study	1605/6	(2)	112x157	38
Caravaggio 13)	St.Francis in meditation	1606	(6)	123.8x93	13
Caravaggio 14)	St.Jerome writing	1607/8	(7)	117x157	29
Caravaggio 15)	David with the head of Goliah	1609/10	(2)	125.5x101	29
Caravaggio 16)	St.John the Bapstist	1609/10	(2)	152x124.5	11
Caravaggio 17)	St.Francis in meditation	?	(8)	130x98	14
Caravaggio 18)	S.Gennaro decollato	?	(9)	116.5x98	18

(*) A "point" is a selected small area of a painting (see text).
(1) Gallerie degli Uffizi, Firenze.
(2) Galleria Borghese, Roma.
(3) Galleria Nazionale di Palazzo Barberini, Roma.
(4) Gallerie dell'Accademia, Venezia.
(5) Pinacoteca Capitolina, Roma.

(6) Chiesa di S.Pietro, Carpineto Romano (Roma).
(7) Cattedrale,La Valletta (Malta).
(8) Chiesa dei Cappuccini, Roma.
(9) Chiesa di S.Antonio Abate, Palestrina (Roma).

workshops, excavations, etc. (Sciuti & Gigante,1989). As far as paintings are concerned, imaging and XRF, possibly together, can solve problems such as the optimization of a restoration program, the study of drawing, color techniques, etc. Systematical research works on ancient paintings performed by XRF energy dispersive PI have been carried out in Roma since about twenty years (Cesareo et al.,1972).

In the present work we describe a recent archaeometric campaign set up in the last decade by physicists, chemists and art historians of Roma University "La Sapienza". In Table I the paintings examined by us in the last five years employing energy dispersive XRF spectrometers (Fig.1) are listed (Gigante et al., 1983; Maltese et al.,1984; Maltese et al.,1985; Sciuti & Gigante, 1986). Our final aim is to find a new "integrated methodology", using a computer assisted XRF PI, able to supply an exhaustive description of the artistic and technical capabilities of a painter during the entire period of his production.

MATERIALS AND METHODS

Artists' pigments can be identified through the ND analysis of their characteristic elements such as those listed in Table II.

The analyses were carried out by examining in each painting (Table I) particular areas (points) according to chromatic and artistic criteria.

Spectrometers: For the present investigation two different portable XRF spectrometers have been designed and assembled. In the first radioactive Am-241 "point" sources were employed, while in the second a small X-ray tube was used (Sciuti,1987).

The X-ray detector used in all the arrangements was a hyperpure Ge semiconductor (200 eV at 6 keV). The electronic chain was that depicted in Fig.1. The data collection and analyses were performed initially

with computer codes specially developed by one of the study group (G.E.G) and later with the software supplied with the "The Nucleus" multichannel card. In all measurements the counting rate was kept below 10^3 counts/s in order to avoid spectrum distortions.

TABLE II: XRF Detectable Element(s) Characterizing Pigments

Pigment	Elements	Chemical composition
WHITE		
W.Lead	Pb	$2PbCO_3Pb(OH)_2$
YELLOW		
Lead-Tin Y.	Pb,Sn	Pb_2SnO_4; $PbSn_2SiO_7$
Y. Ochre	Fe	$Fe(OH)_3$
Y.of Sb	Pb,Sb	$Pb_3(SbO_4)_2$
RED		
R. Ochre	Fe	Fe_2O_3
Vermilion	Hg	HgS
Realgar	As	As_2S_2
BROWN		
B. Ochre	Fe	$Fe(OH)_3$
Umber	Mn	$Fe(OH)_3 + MnO_2$
GREEN		
Copper resinate	Cu	$Cu(C_{18}H_{29}COO)_2$
Verdigris	Cu	$Cu(CH_3COO)_2$
G. Earth	Fe	K & Fe silicate
BLUE		
Azurite	Cu	$Cu_3(CO_3)(OH)_2$
Smaltino	Ba,Cu,Fe,Mg	K & Ba, Cu,..oxides

The detector-source assembly was mounted in both cases on movable television-type tripods equipped with x,y,z gross and micro-adjustments which allow one to point the device in any direction. The majority of the XRF measurements we carried out were performed by the spectrometer of the first type.

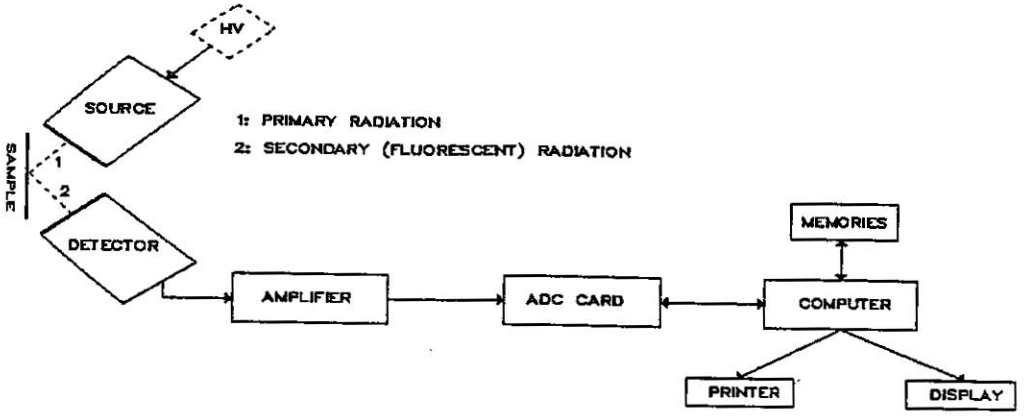

Fig.1 : Scheme of a X-ray fluorescence spectrometer

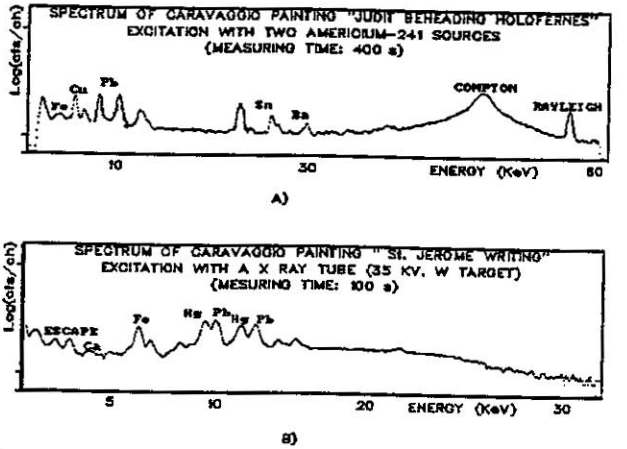

Fig.2: Two typical spectra as obtained (A) with the spectrometer using the Americium-241 sources, an (B) with the direct radiation coming from a X-ray tube.

Analytical procedures: In Fig. 2 a typical spectrum as obtained with the monochromatic Am-241 source (59.6 keV) and with an X-ray white radiation are given. The monochromatic radiation gives rise to the response function that consists of the XRF spectrum of elements with atomic number Z > 16 and of the two backscattered components, namely the Rayleigh line and the Compton peak. Information emerging simultaneously from the scattered intensities and from XRF spectra

constitute an excellent probe for the ND analysis of artistic objects according to the methodology developed in the recent years (Gigante & Sciuti, 1984).

All the measured spectra are stored on floppy disks in a common format (ASCII) that allows access to the data by application packages.

RESULTS

The 18 examined paintings belonging to quite different periods and artists constitute a very exhaustive test on the adopted methodology.

Limits of the method: XRF analyses are particularly suitable when the painting to be studied does not allow any kind of sampling. In this case the method turns out to be very useful even if the following limitations occur : 1) The pigment identification must be done only after a careful visual inspection of the colors (white, red, flesh tone, etc.) possibly together with other techniques providing complementary informations. 2) The interpretation of a pictorial technique can be difficult when glazings are present. In some of Caravaggios' paintings characterized by a glazing made by copper green color on a red pigment the interpretation is easy because Cu if mixed with the other pigment would give a color different from the red. 3) Lake pigments cannot be identified by XRF because of their very light composition. In this case the visual definition of the color together with the absence of a XRF detectable element characteristic of that color constitutes a very reliable test in favour of lake. 4) The XRF analyses of paintings are qualitative because the paintings are inhomogeneous samples. Therefore very complex physical and geometrical measurements would have to be done in each analyzed point in order to have quantitative evaluations. Fortunately comparisons can be carried out between points of one painting or between points of different paintings having similar structure and main composition.

XVI century painters: The above mentioned group of XVI century artists will be discussed in more detail as soon as a greater number of their

paintings will have been analyzed. The characteristic elements identified so far are many and correspond to a great variety of pigments. In some case the identification of a pigment was doubtful due to the presence of a mixture and to the lack of sufficient literature on chemical composition of pigments. For example, antimony was identified in all paintings examined and at a first glance it could be associated with Naples yellow cited in documentary sources such as Andrea Pozzo's treatise (1692-1700). Such an identification must be considered with care, because the historical notes on the use of yellow lead antimoniate in paintings are rather doubtful (Feller,1986; Rinaldi,1986). Actually, it seems more consistent to consider antimony an impurity of lead in lead-tin yellow pigment because in our analyses it is always found in presence of tin and in low quantity. Another example of doubtful identification is barium, generally considered a restoration material, having been identified as an element rather recently (1774). We have found barium practically in all paintings and in different color points. Attempts to associate it with some pigment, such as white lead, to constitute white pigments ready for use was unsatisfactory (Feller,1986; Rinaldi,1986). Considering that natural baryte (Ba sulphate) is inert like calcium sulphate mineral, and that for this reason (before its identification) it could be employed as gypsum, we can conclude that its presence is due to ground layers. A similar hypothesis can be made also for strontium. We found this element in all paintings except in those of Caravaggio. Natural strontium sulphate mineral, known as celestina, was probably used in ground layers mixed to gypsum or other earth pigments.

Caravaggio : In Table III the pigments identified in Caravaggio's paintings are reported.The absence of blue in all the 12 examined paintings, except for some details of fruit painted with grayish compound of white lead and black (charcoal black presumably) is noteworthy. Also violets do not appear except in particular red ochre-based mixtures.

Through the recognition of pigments it is possible to deduce information on grounds' composition. In all the examined points lead white appears constantly. Further we found that the bright grounds of

TABLE III: Pigments identified on paintings by Caravaggio

PIGMENT	7	8	9	10	11	12	13	14	15	16	17	18
WHITES												
white lead	*	*	*	*	*	*	*	*	*	*	*	*
YELLOWS												
lead-tin y.	*	*	*	*	*	*	*	*	*	*	*	*
yellow ochre	?	?	-	-	-	-	-	-	-	-	-	-
REDS												
red ochre	-	*	-	tr	*	*	-	*	*	*	-	*
vermilion	-	-	*	*	*	*	*	*	*	*	-	-
lake	-	-	-	-	-	?	-	-	-	-	-	-
BROWNS												
brown ochre	*	*	*	*	*	*	*	*	*	*	*	*
umber	*	-	-	-	-	*	-	*	*	*	-	*
GREENS												
green based on copper	tr	-	*	*	*	*	*	*	*	*	*	*
green earth	-	*	-	-	-	-	-	-	-	-	-	-
BLACKS	?	?	-	-	-	-	-	-	-	-	-	?

"*" yes; "-" no; "?" doubtful; "tr" traces. See Table I for the name of paintings.

early Caravaggio paintings prepared with a priming of lead white, are progressively substituted by dark grounds. The latter, characterized by iron in the first paintings and by manganese in the others, have priming based on red ochre and umber earth respectively. For example, in Judith beheading Holofernes and Madonna and Child with St.Anne, iron and lead always occur, while in David with the head of Goliah and St.John the Baptist, manganese and lead appear constantly together.

Intermediate cases are St.Francis in meditation (Carpineto Romano) and St.Jerome in his study . In the first the Saint's cowl is characterized by manganese and iron, while in the second, these

elements are found in many points. Considering that iron and manganese can be associated with the ochre and umber earth respectively, one can deduce that the two paintings represent a transition in Caravaggio's production.

As far as blacks are concerned we found that early paintings do not exhibit elemental characteristics detectable with XRF analysis (lampblack or charcoal black have been probably employed). On the contrary in David with the head of Goliah the black color is obtained by mixing lead-tin yellow, umber earth, white lead, perhaps glazed with a black pigment.

In some paintings with dark ground a bright coating of lead white can be present under flesh tones. The above statement can be deduced from the fact that such a mild color can be obtained only with a layer of bright priming, as clearly shown by the higher Pb counting rate found in examining faces, hands, etc.

From these evaluations on grounds and pigments a chronological sequence for the paintings of Caravaggio can be deduced from XRF results. Tone of ground can be infact used as the main distinction between the 12 paintings. The bright priming based on lead white occurs in three paintings dated from Caravaggio's early stay in Rome, i.e. Self-portrait as Bacchus , Boy with a basket of fruit and Gypsy Fortuneteller.

The dark priming is found in the other paintings, according to the following three groups :

a) pictures painted with a rich palette, including expensive pigments like vermilion and generally making use of large amount of material (Judith beheading Holofernes and Madonna with Child and St.Anne) as deduced from the quite high count rate in the Hg L peak;

b) pictures painted with a smaller amount of material, but still including expensive pigments (St.Jerome in his study, St.Jerome writing, St.Francis in meditation from Carpineto);

c) pictures painted using very little pigment (David with the head of Goliah, St.John the Baptist).

The remaining two paintings (St.Francis in meditation, Chiesa dei Cappuccini, Roma, and St.Gennaro decollato , Palestrina) cannot be compared with others because of their profound incoherence. We

therefore assume that they could not have been painted by the same artist.

DISCUSSION

The above reported XRF results on pigment, if used together with other complementary ND techniques (radiography, IR reflectometry imaging, etc.) open new paths to the art historian as far as the painter style and technique are concerned. Further, elemental analyses performed point by point represent a powerful tool for the preparation of restoration programs.

Interesting conclusions can be drawn by comparing couples of paintings of the same subject as the two paintings of St.Francis and the two of St.Jerome all attributed to Caravaggio. The results so far obtained encourage us to further develop the system. With this aim we are assembling a new transportable work-station in which on line imaging devices (working also in X ray region), XRF and Raman microprobe are employed to study paintings and their structure and to analyze low, medium and heavy elements (Sciuti & Gigante,1989).

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REFERENCES

Cesareo, R., Frazzoli, F.V., et al.(1972) Archaeometry14, 1, 65-78.
Feller, R.L.(ed.)(1986),Artists' pigments, Univ. Press, Cambridge.
Gigante, G.E., Maltese, C. and Sciuti, S. (1983) In: RAPHAEL URBINAS.Il mito della Fornarina, Electa, Roma, pp.34-40;74-77.
Gigante, G.E. and Sciuti, S. (1984), Int.J.Appl.Radiat.Isot.35, 481.
Maltese, C., Gigante, G.E. and Sciuti, S. (1984) In : Raffaello nelle raccolte Borghese (S. Staccioli ed.), Arno e Tevere,Roma.
Maltese, C., Sciuti, S. and Gigante, G.E. (1985), In: Il Tondo Doni di Michelangelo e il suo restauro (Gallerie degli Uffizi ed.), Centro Di, Firenze.
Rinaldi, S.(ed.) (1986), La fabbrica dei colori, Il Bagatto, Roma.
Sciuti, S. (1987) Fisica e Tecnologia,X, 3, 207.
Sciuti, S. and Gigante, G.E. (1986) Chimica Oggi, 65-68.
Sciuti, S. and Gigante, G.E. (1989),Su alcune tecniche acheometriche di recente impiego, Il Bagatto, Roma.