Minerals associated with artists' paintings and archaeological iron objects

M. Odlyha · D. Thickett · L. Sheldon

Abstract This article provides a short review of mineral-based pigments used in paintings with examples drawn from technical studies of selected historic paintings. Pigments such as azurite, natural ultramarine, orpiment, and clay earth pigments have been identified. Some examples will also be given of particular case studies which describe the alteration of selected pigments and consequences of these interactions. The second theme shows how use has been made of such interactions in evaluating the effects of environmental impact on paintings and reference is made to previous studies and the application of paint films as dosimeters. Accelerated ageing and site exposure studies are reported, and results provide information on pigment binder interactions. Dynamic mechanical analysis (DMA) and thermogravimetric analysis (TG) have been used to characterise the behaviour of pigments in binding media and to assist in characterising samples from wall paintings. Reference is also made to the occurrence of iron-oxide based minerals present as corrosion products in archaeological iron objects. Examples are given of objects from two archaeological sites in England, the Anglo-Saxon burial site Sutton Hoo in Suffolk, and the burial site in Wetwang, East Yorkshire. It will be shown that post excavation changes occur in the objects and this information is used to inform preventive conservation of these objects, in storage and in display.

Keywords Mineral-based pigments · Paintings · Paint dosimeters · Archaeological iron

M. Odlyha (✉)
Institute of Structural and Molecular Biology, Department of Biological Sciences Birkbeck, University of London, Malet Street, London WC1E 7HX, UK
e-mail: m.odlyha@bbk.ac.uk

D. Thickett
English Heritage, Rangers House, Chesterfield Walk, London SE10 8QX, UK

L. Sheldon
Paintings Analysis, History of Art, University College London, 20-21 Gordon Square, London WC1H OAG, UK

Introduction

Colour plays a key role in our appreciation of painted works of art. In paintings, the preparation of the paint layer and its resulting quality depends on the nature and quality and proportion of pigments used and in the different binding media. There are a number of fundamental works on mineral-based pigments, their use, and identification [1–4]. In this article, examples have been selected of studies performed on historic paintings in major European collections. In current practice some contemporary artists still prefer to use mineral-based pigments and prepare their own pigment binder mixtures. For example, the British artist Michael Price prepares pigments for his paintings from mineral sources. Azurite (basic copper carbonate) is separated into different particle sizes to reveal different hues of blue which possess superior quality in his opinion to modern-day synthetic pigments (http://www.michaelprice.info/). Other examples include use of the mineral cerussite (lead carbonate) from the deposit in Kazakhstan which is close in composition to the commonly used synthetic lead white, and hematite (iron oxide Fe_2O_3), which is currently sourced from iron ore deposits in the Kirov Rog area of Russia. A recent article on clay and iron oxide pigments provides general information about geological sources and literary evidence of the use of different forms of earth pigments in historical paintings [5]. The author, D.

Hradil, makes the point that clay-rich materials used in fine arts are not satisfactorily described with respect to their mineralogical and structural variability and origin.

Technical studies on paintings

The National Gallery Technical bulletin (London) is a specialist publication which focuses on the characterisation of the materials used in paintings in the collection of the National Gallery, London. A technical analysis of Raphael's painting "The Madonna and Child with Saint John the Baptist and Saint Nicholas of Bari (The Ansidei Madonna)" dated 1505 (cleaned and restored in 1956) has been reported. It is painted on a poplar panel which was coated with a gesso ground (calcium sulphate dihydrate) [6]. Blue pigmented areas of the sky were examined and the pigments found were the following: in the sky natural ultramarine over azurite mixed with white; the Virgin's robe also contained natural ultramarine, azurite, and in lighter regions this was mixed with lead white. In the study of the Van Dyck paintings in the National Gallery, London [7] the painting "Lady Elizabeth Thimbelby and Dorothy Andover" was included. Optical microscopy and X-ray analytical techniques performed on prepared paint cross sections revealed that the flesh tones makes use of pure lead white with small quantities of finely ground red earth, vermilion, and Cassel earth. Paint layers in the regions of the dress and sleeve showed that the darker more golden tones of the dress consisted of a deep yellow ochre in the top layer with lead white and some amount of crystalline red earth (hematite). Orange colours of the sleeve were found to contain a higher proportion of hematite. A double ground preparation layer was used and this was found to consist of a red-brown layer of earth pigment and calcium carbonate. Clay-rich grounds started to replace chalk and gesso ground layers in paintings of the sixteenth century and were predominant in the seventeenth and eighteenth centuries in all European countries. Brown, red and yellow ochres are amongst the earliest pigments used in paintings and are quite common in European paintings.

Another specialist publication from which examples are given is the book "Examining Velázquez" [8] which reports results from the technical examination of over twenty canvas paintings by Velázquez in the collection of the Prado Museum, Madrid. In his works, brown, red, and yellow ochres are present in small amounts in virtually every colour. These coloured iron oxides often contain other minerals such as clays, mica, quartz which reflects their geological source and method of preparation. Brown ochres and umbers contain additional manganese oxides which give them their darker colour. Studies of a paint cross section from the "Bust of Philip 1V"(ca., 1620) from

the red sash showed a thin red lake glaze over a pink layer of lead white and red glaze. This was over a grey layer (lead white and charcoal black) and the red earth ground which contained large translucent grains of quartz and mica(s). The layer of size below the ground layer was found to contain some calcite and ochre. In the painting "The Forge of Vulcan" (1630), a cross section from the sky showed a thin glaze which contained some ultramarine blue and a grey layer which probably contained some smalt. This was over a thicker light grey layer of lead white which contained small scattered black particles, calcium carbonate (calcite) and some calcium-magnesium carbonate (dolomite). At the base of the section was an orange-red ground over the layer of size. In addition to red ochres, vermilion was also used. Mines at Almaden, Spain, were a major source of the mineral but by seventeenth century much of the pigment may have been the synthetic variety manufactured by the Dutch process.

Technical studies also revealed the unexpected use of orpiment (As_2S_3) in some paintings of the Flemish School in the early seventeenth century. An example is on a landscape painting attributed to Cuyp where it was used not only in the last touches of light on the skating figures but also in some of the warm brown colours of the building [9]. Figure 1 shows another example on a privately owned painting "Lot and his daughters" Orpiment was found in Lot's cloak, and the cross section shows a paint layer containing orpiment over a layer of old varnish which was itself over a layer with green copper containing pigment (Fig. 2). Technical studies revealed the presence of a painting (still life) beneath the current image. In addition to orpiment, realgar (As_2S_2) was also identified in paintings of seventeenth century Flemish school, as was the pigment lead tin yellow. The result demonstrated that the artist had ignored warnings about mixing lead tin yellow with realgar.

In addition to the identification of pigments, alterations in pigment layers were also found to occur. In the painting, "Still Life of Flowers and Fruit with Tazza and Birds" Jan Davidsz De Heem early 1670s (private collection) a yellow paint layer showed presence of bright yellow ball-shaped particles. Elemental analysis using X-ray analytical techniques also provided elemental distribution maps and this showed that the spheres consisted of arsenic and sulphur, which according to X-ray diffraction were non-crystalline amorphous compounds. An explanation for the formation of the spheres was given. If orpiment underwent oxidation with the release of hydrogen sulphide, then the process for the formation of yellow spheres on the painting would resemble the wet process used for making orpiment. This relies on hydrogen sulphide gas being passed through a solution of arsenic salts. So out of the products of decay of the old pigment, new orpiment could be formed within the

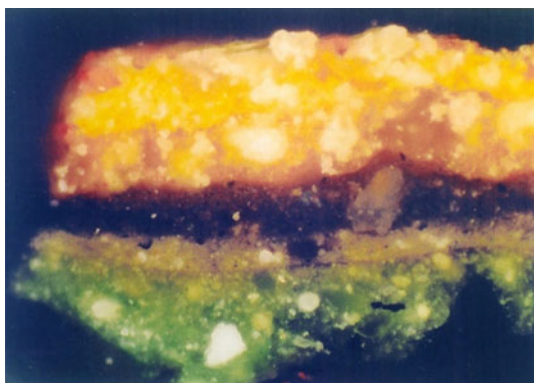Fig. 1 "Lot and his daughters" Flemish School early 17th century (private collection)

Fig. 2 Paint cross section from the painting "Lot and his daughters" from area of Lot's cloak. This shows a paint layer containing orpiment over a layer of old varnish which was itself over a layer of green copper containing pigment

paint layer, and would be produced by a peculiar self-correction process within the degradation process [9].

In another painting that of The Erythraean Sibyl' Maerten van Heemskerk from 1564 and which is in the Rijksmuseum Amsterdam, orpiment was found in the drapery. Previously some scholars had assumed that the painting was unfinished because the underdrawing was visible to the eye. Light induced oxidation can convert realgar into orpiment which can be further oxidised to arsenic oxide The closeness of refractive indices between the newly formed arsenolite (As_2O_3) and the oil binding medium was possibly responsible for the transparency of the orpiment paint [9].

In this article, results will be presented of selected thermoanalytical studies on samples prepared according to traditional recipes which were then exposed as dosimeters in various museums and galleries or used to assist in characterisation of binding media in samples removed during the restoration of wall paintings (sixteenth century) in the dome of S. Maria del Fiore in Florence executed by the artists Federico Zuccari and Giorgio Vasari.

Technical studies on archaeological iron objects

Technical studies performed on archaeological iron objects have shown that the main corrosion products present on excavated objects are Goethite (α-FeOOH) magnetite (Fe_3O_4), lepidocrite (γ-FeOOH), and akaganéite (β-FeO-OH) [10]. Deterioration after excavation of archaeological iron objects presents serious problems for their preservation and so knowledge of optimum storage conditions are important. Figure 3 shows a representative object from the Sutton Hoo archaeological site (seventh century AD) which was excavated in 2000, together with the characterised corrosion products. This and other objects from both Sutton Hoo and Wetwang sites are discussed in the Ph.D thesis "Post excavation Changes and Preventive Conservation of Archaeological Iron" (D.Thickett, in preparation). Figure 4 shows a terret from a chariot from the Wetwang site. This is one of the few chariot burial sites found in the UK. The object was displayed in a showcase with RH values ranging between 35 and 52% and within 6 weeks deterioration was observed with the formation of akaganéite crystals. A similar object stored in dry silica gel showed no visible
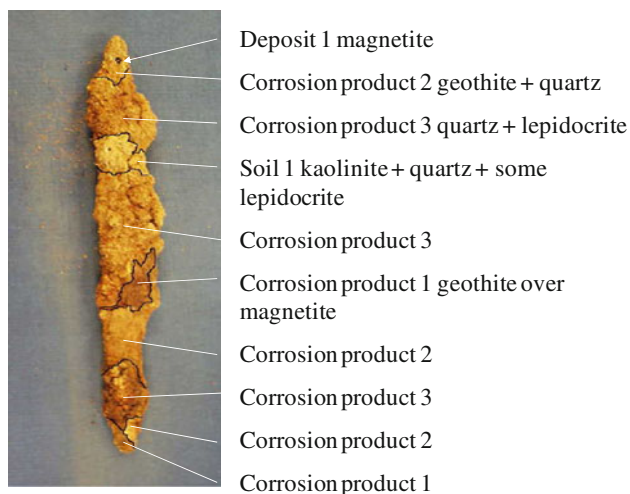
Deposit 1 magnetite

Corrosion product 2 geothite + quartz

Corrosion product 3 quartz + lepidocrite

Soil 1 kaolinite + quartz + some lepidocrite

Corrosion product 3

Corrosion product 1 geothite over magnetite

Corrosion product 2

Corrosion product 3

Corrosion product 2

Corrosion product 1

Fig. 3 A representative object from the Sutton Hoo archaeological site (seventh century A.D.) which was excavated in the year 2000 together with the characterised corrosion products

Fig. 4 A terret from a chariot from the Wetwang site. This is one of the few chariot burial sites found in the UK
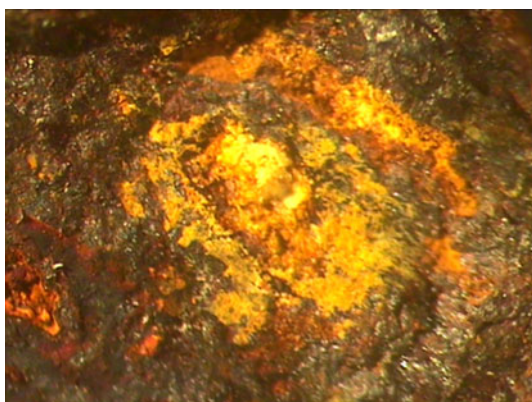

Fig. 5 Detail of changes in the terret reveal the presence of Goethite yellow (ca., 1 μm) on top and the formation of akaganéite β-FeOOH beneath. FTIR spectra of the orange areas provided evidence for the presence of the latter [11]

deterioration. Detail of changes in the terret (Fig. 5) reveal the presence of Goethite yellow (ca., 1 μm) on top and the formation of akaganéite β-FeOOH beneath. FTIR spectra of the orange areas provided evidence for the presence of akaganéite and Goethite [11]. Iron, oxygen and chlorine were detected in the orange brown areas, whereas a much lower chlorine concentration was detected in the yellow areas. Local high concentrations of chloride combined with low pH have been found to favour the formation of akaganéite. Most archaeological iron in moist-aerated burial conditions will contain chloride ions which promote electrolytic corrosion [10]. On excavation solid ferrous chloride can form and this under certain conditions in contact with iron can cause it to corrode. Total desiccation can prevent this process, however, such an environment is difficult to maintain [12]. Turgoose proposed a post-excavation model based on oxidation of Fe^{++} to produce ferric oxyhydroxide (FeOOH) and acid. This occurs in the presence of large quantities of chloride and the β-FeOOH polymorph (akaganéite) is expected to form along with the stable α-FeOOH (Goethite) [13]. The formation of akaganéite on archaeological iron has been studied in situ and through experiments using infra-red and Raman spectroscopies [11]. In this article, the results of tests to simulate the formation of akaganéite are reported. This is part of the work performed within the Ph.D thesis "Post excavation Changes and Preventive Conservation of Archaeological Iron" (D.Thickett, in preparation).

Experimental

Dynamic mechanical analysis was performed using a Rheometric Scientific Mark 3 DMA analyser. The heating rate was 3 °C/min from −100 to 300 °C at 1 Hz. The paint films were prepared on a Melinex support and measured on the support in tension. Thermogravimetric analyses of the paint were carried out using the PE TGA 7. Measurements were made at 10 °C/min in an atmosphere of O_2 (flow rate 60 cm^3/min). Sample size of paint ranged from 0.25 to 2 mg and measurements were made in open Pt crucibles up to 800 °C.

To simulate conditions for formation of iron corrosion products mixtures (1:1) mixtures of iron (II) chloride and iron powder were exposed to different relative humidity environments generated above water/glycerol solutions. After, 2 years' exposure to the selected RH values, the corrosion products were analysed. Samples were measured in sealed aluminium crucibles with 30 μm hole in the lid in a Shimadzu TGA50 analyser in N_2 (60 cm^3/min). Initially they were heated from 25 to 110 °C at 20 °C/min and held at 110 °C for 1 h. They were then heated to 500 °C at 20 °C/min.

Results

Paint samples as dosimeters

The preparation of paint dosimeters was performed within the framework of the EU project ERA (Environmental Research for Art Conservation) and has been described elsewhere [14, 15]. The rationale for the use of paint tempera as dosimeters was that they would integrate the damage resulting from the synergistic action of relative humidity, temperature, light and pollutants and would provide an early warning of adverse environmental conditions in museums and galleries. The binding medium used was egg tempera, and commonly used pigments lead white and azurite were among those selected in the preparations. After curing some samples were exposed to accelerated ageing and others to natural ageing in various art galleries and historic castles [14, 15]. Figure 6 shows the DMA measurements: tan delta curves for lead white and azurite tempera paint samples exposed at Tate Britain (London, UK) for 9 months are shown together with the control samples. In the case of azurite tempera, the tan delta peak moves to a higher temperature which is indicative of oxidative crosslinking whereas in the case of lead white tempera there is a change in peak shape. Mass spectrometric data with discriminant analysis indicated that hydrolytic processes were dominant in lead white tempera and oxidative processes dominated changes in azurite tempera [16]. This could account for observed differences in behaviour on exposure under the same conditions. In addition, in lead tempera paint, formation of lead soaps has been reported and this pigment binder interaction could also be a contributing factor to the observed difference [16].
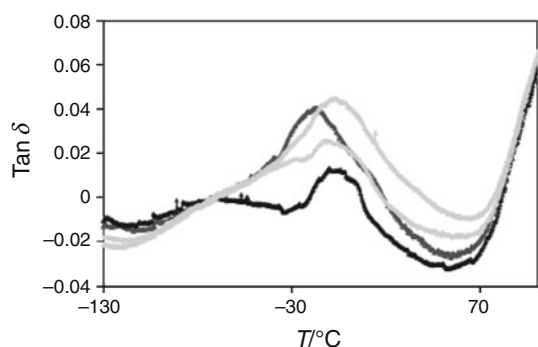

Fig. 6 Tan delta versus temperature (°C) for lead white (*black*) and azurite (*grey*) tempera paint samples exposed at Tate Britain (London, UK) together with the control samples. The azurite exposed sample shows a shift to higher temperature whereas the lead white exposed sample shows a decrease in the intensity and change in peak shape of the tan delta peak
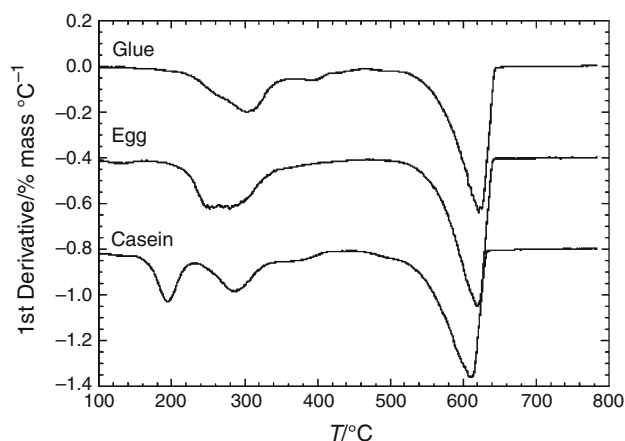

Fig. 7 The first derivative of the TG curves of various binders with the pigment Bianco di San Giovanni

Thermoanalytical studies performed on samples from wall paintings

Paint samples were obtained during the restoration and cleaning of Giorgio Vasari's frescoes in Brunelleschi's dome, S. Maria del Fiore, Florence of the *Last Judgment* (1572–1579). These were designed by Vasari and painted together with his student Frederico Zuccari. To assist in the characterisation of the materials, used samples were prepared according to traditional recipes by the restorers at the Opificio Pietre Dure in Florence. Figure 7 shows the first derivative of the TG curves of various binders with the pigment Bianco di San Giovanni. This is a pigment of natural mineral origin from limestone (calcium carbonate) deposits and was used at that time for fresco painting. The name of the natural mineral is portlandite. In Fig. 7, differences can be seen due to the binder and these occur in the temperature region (150–500 °C). The final peak corresponds to the degradation of the pigment. Figure 8 shows TG curves of samples from Vasari (15/1/97-9) and Zuccari (4/6/38-3). The numbers refer to the level, sector, and quadrant from which the sampling occurred in the dome and the last number is the sample number. Samples were coloured pink (red ochre) and yellow (yellow ochre), respectively. The TG curves show a difference due to the binder and by comparison with Fig. 8 it can be seen that the sample from Vasari is similar to casein and that of Zuccari has closer similarity to glue or egg or their mixture. This points to a difference in painting technique which is also reported elsewhere [17, 18].

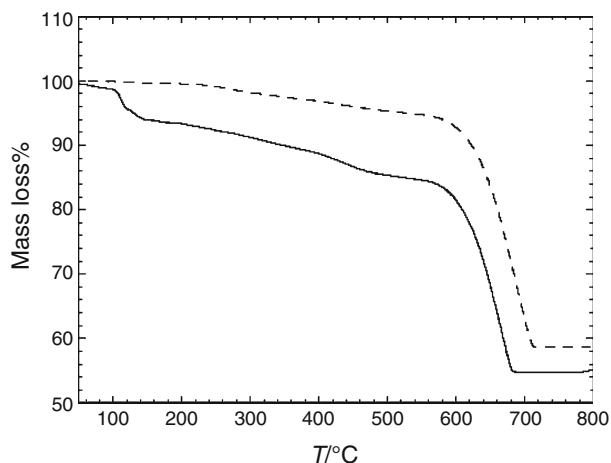The pigment Bianco di San Giovanni is present in both as seen in the final mass loss.

Fig. 8 TG curves of samples from Vasari (15/1/97-9) and Zuccari (4/6/38-3). The numbers refer to the level, sector, and quadrant from which the sampling occurred in the dome and the last number is the sample number. Samples were coloured pink (*red ochre*) and yellow (*yellow ochre*), respectively
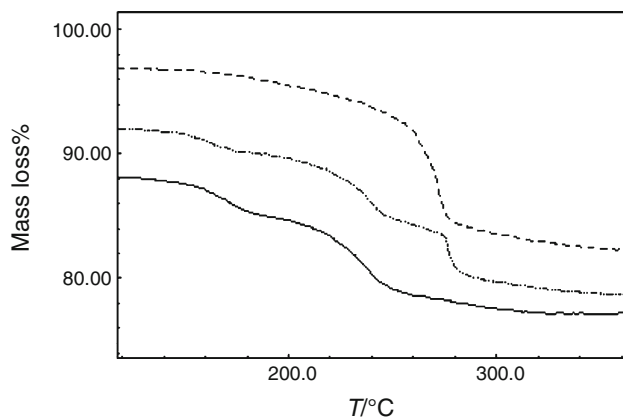

Fig. 9 TG curves of iron corrosion products from mixtures (1:1) of iron (II) chloride and iron powder exposed to 15, 30, and 70% RH (from bottom to top) environments for 2 years. The lowest curve (15%RH) shows no weight loss in the temperature region used for akaganéite characterisation

Accelerated ageing studies performed to simulate iron corrosion

Results from thermogravimetric analysis of iron corrosion products from mixtures (1:1) of iron (II) chloride and iron powder exposed to 15, 30, and 70% RH environments are shown in Fig. 9. The initial mass loss with an onset just above 200 °C is due to iron (II) chloride remaining in the sample. The sample exposed to 15% has the most residual Fe(II)Cl and this reduces in the RH 30% exposed sample and is completely absent in the 50 and 70%RH exposed samples. The amount of akaganéite was calculated from the mass loss between 260 and 285 °C. Complementary quantification of the akaganéite formed in the samples was

also carried out with FTIR [11]. The experiments show that no akaganéite was formed at 15% and a small amount formed already at 20% and is present in the 30%RH exposed sample (Fig. 9). This provides the rationale for displaying and storing archaeological iron at less than 20% RH in order to retard akaganéite formation and associated deterioration of the objects with loss of the archaeological information contained within them.

Although there is general agreement on the corrosion products formed, the exact role of chloride and the exact structure of chloride containing corrosion products is still under discussion. Corrosion layer is typically built up by a magnetite layer near the metal core, covered by a layer of ferric oxide, typically goethite, cemented with soil particles (Fig. 3). Formation of ferric oxyhydroxides is associated with volume expansion which causes cracks and exfoliation of the corrosion layers or the whole artefact, which may accelerate the deterioriation. At the position of fracture, an orange powder can be observed which on several artefacts has been identified as β-FeOOH, akaganéite). This study provides the rationale for displaying and storing archaeological iron at less than 20% RH in order to retard akaganéite formation and associated deterioration of the objects with loss of the archaeological information contained within them.

Summary

Technical studies of paintings have provided evidence for the use of mineral-based pigments and examples of the unusual use of orpiment in Flemish seventeenth century paintings. There is also evidence for alterations which occur within the layered structure of paintings and which alter their appearance. Preparation of paint samples according to traditional recipes has shown to be useful in understanding interactions between pigment and binding medium and in assisting characterisation of samples from wall paintings. Thermoanalytical techniques have demonstrated differences in behaviour of azurite and lead tempera paint, and indicated differences in painting techniques used by Vasari and Zuccari. In the case of iron corrosion studies, it was possible to determine threshold levels of RH at which akaganéite did not form. Recent article highlights the use of thermoanalytical techniques in the preservation of cultural heritage [19].

References

1. Harley RD. Artists' pigments c 1600–1835. London: Butterworths Scientific; 1982.

2. Feller RL, editor. Artists' pigments, vol. 1. London: Cambridge University Press; 1986.
3. Roy A, editor. Artists' pigments, vol. 2. New York: Oxford University Press; 1993.
4. Fitzhugh EW, editor. Artists' pigments, vol. 3. New York: Oxford University Press; 1997.
5. Hradil D, Grygar T, Hradilova J, Bezdicka P. Clay and iron oxide pigments in the history of paintings. Appl Clay Sci. 2003;22: 223–36.
6. Roy A, Spring M, Piazotta C. Raphael's early work in the National Gallery paintings before Rome. Natl Gallery Tech Bull. 2004;25:62–72.
7. Roy A. The National Gallery Van Dycks: technique and development. Natl Gallery Tech Bull. 1999;20:5–83.
8. McKim-Smith G, Anderson-Bergdoll G, Newman R. Examining Velázquez. New Haven: Yale University Press; 1988. ISBN 0-300-03615-9.
9. Sheldon L, Woodcock S, Wallert A. Orpiment overlooked: expect the unexpected in 17th century workshop practice. In: Preprints ICOM Committee for Conservation, vol. 1. 14th Triennial Meeting, The Hague, 12–16 September 2005, p. 529.
10. Selwyn L. Overview of archaeological iron: the corrosion problems, key factors affecting treatment, and gaps in current knowledge. In: Proceedings of metal 2004, National Museum of Australia ACT, 4–8 October 2004, p. 294–306.
11. Thickett D. The use of infra-red and Raman spectroscopies for iron corrosion products. In; Postprints 6th Infrared Users' Group, Florence, Prato, Padua 2005, p. 86–93.
12. Watkinson D, Lewis MT. Desiccated storage of chloride-contaminated archaeaological iron objects. Stud Conserv. 2005;50: 241–52.
13. Turgoose S. Post excavation changes in iron antiquities. Stud Conserv. 1982;27:92–101.
14. Cohen NS, Odlyha M, Campana R, Foster GM. Dosimetry of Paintings:determination of the degree of chemical change in museum exposed test paintings(lead white tempera) by thermal analysis and infrared spectroscopy. Thermochim Acta. 2000;365: 45–52.
15. Odlyha M, Cohen NS, Foster GM, West RM. Dosimetry of paintings: determination of the degree of chemical change in museum exposed test paintings (azurite tempera) by thermal and spectroscopic analysis. Thermochim Acta. 2000;365:53–65.
16. van den Brink O. Molecular changes in egg tempera paint dosimeters as tools to monitor the museum environment. Ph.D thesis, University of Amsterdam, 2001. http://www.amolf.nl/.
17. Musumarrra G, Fichera M. Chemometrics and cultural heritage. Chemom Intell Lab Syst. 1998;44:363–72.
18. Colombini MP, Modugno F, Giacomelli A. Two procedures for suppressing interference from inorganic pigments in the analysis by gas chromatography-mass spectrometry of proteinaceous binders in paintings. J Chromatogr A. 1999;846:101–11.
19. Odlyha M. Introduction to the preservation of cultural heritage. J Therm Anal Calorim. 2011;104:399–403.