Talanta 79 (2009) 419–428

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Identification of reaction compounds in micrometric layers from gothic paintings using combined SR-XRD and SR-FTIR

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ARTICLE INFO

Article history:
Received 11 December 2008
Received in revised form 27 March 2009
Accepted 1 April 2009
Available online 10 April 2009

Keywords:
Synchrotron radiation
XRD
FTIR
Metal carboxylates
Oxalates
Gothic paintings
Artwork

ABSTRACT

Synchrotron radiation X-ray diffraction (μ-SR-XRD) and Fourier transform infrared spectroscopy (μ-SR-FTIR) are used in the non-destructive identification of reaction and aging compounds from micrometric ancient painting layers. The combination of the micrometer size and non-destructive nature of the techniques together with the high resolution and brilliance of the synchrotron radiation has proved to be a procedure most advantageous for the study of reaction, aging and degradation processes. Copper, lead and calcium carboxylates and oxalates are determined in the chromatic, preparation and alteration layers from 15th century egg tempera and oil paintings. Their nature and crystallinity have been assessed. Some hypothesis about the mechanisms of development of both carboxylates and oxalates are presented.

1. Introduction

The identification of aged binders [1] and of the reaction compounds formed by the interaction between the binding media and the pigments is a subject of the highest interest in the chemical stability and conservation of ancient paintings. However, the identification of pigments, binders, reaction and alteration compounds presents great technical difficulties since most of them appear in extremely small amounts. In addition most of these substances lack a good crystallographic order since some of them are soluble in the binders and the solid state reactions and aging processes involved are kinetically controlled. The art works studied correspond to 15th century Catalan Gothic paintings. In this period, oil-based binders started being used and coexisted with the preceding tempera techniques that used egg yolk and animal glue. Sometimes different binders were used in the same paint and due to the micrometer size layered structure of the paint this makes the study more interesting but at the same time more difficult.

The samples extracted from an artwork are necessarily small; a few hundred micrometers surface area, which gives a measurable volume of only 10^{-3} mm^3. The identification of the organic fraction when present in very small proportion can be obtained by chemical separation techniques after a process of dissolution of the sample [2,3]. However, using this methodology information the exact location of the different compounds is lost. The use of spatially resolved low level detection non-destructive techniques is a good option, although the sensitivity is moderate. Thus a special and careful preparation of the samples is required. Analytical techniques sensitive down to the 10 μm level must be used. High resolution X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) techniques are non-destructive and a good combination for the identification of compounds present in the painting layers. Synchrotron radiation has a clear advantage with respect to conventional radiation sources because it has a high brilliance, low noise and tuneable monochromatic and highly collimated light with footprints down to the micrometers size [4–6]. In this study we demonstrate the capability and potentiality of combined μ-SR-FTIR and μ-SR-XRD techniques in the detection and identification of those compounds in micrometric painting layers. When μ-SR-FTIR is used, separation of the compounds can only be achieved by first a previous mechanical separation of

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doi:10.1016/j.talanta.2009.04.005

layers under the stereomicroscope, followed by the thinning out of small fragments taken from each layer in a diamond cell. When the technique employed is μ-SR-XRD thin cross-sections are prepared and measurement points are focused with a video microscope. The combination of μ-FTIR and μ-XRD allows for the identification of compounds and information to be gathered on the distribution of these highly heterogeneous samples.

The drying oils used in the 15th century are either linseed or walnut oils. They include two poly-unsaturated fatty acids containing 18 carbon atoms, linoleic and linolenic acids, as well as, the mono-unsaturated oleic acid. They contain also about 8% of saturated acids, palmitic and stearic (C16 and C18 straight-chain monocarboxylic fatty acids) [7–9]. The drying and aging process results in a polymerization by uptake of oxygen that free fatty acids may be produced [2,7,8,10–12].

Dried egg yolk contains two thirds of lipids and one third of proteins, resulting in different drying and aging processes from those that work with oil. The lipids are made up of one third phospholipids and two thirds triglycerides. These triglycerides contain two thirds unsaturated acids (~60% oleic, ~25% linoleic) and one third saturated acids, such as stearic and palmitic acids. Aging of the lipids in the egg yolk is the same as in the drying oil; an oxidative polymerization and, consequently, similar reaction compounds are formed [7,13]. Consequently, drying and aging will produce similar free fatty acids in the egg yolk and in the drying oil.

The simultaneous presence of free fatty acids in the binders and metals, such as lead, calcium, copper or tin from the pigments and ground layers makes the formation of metal soaps predictable. In fact they are part of the drying process of the paint and therefore, they are always expected to form. In some cases those compounds affect the artwork to a large extend (formation of protrusions), and it is in these cases that they have been identified [10,11,14–16]. However, in most of the cases, and in particular, when they are not aggregated, their presence is hard to detect [17]. In this study we identify the lead, calcium and copper carboxylates formed in different paint and ground layers from both 15th century paintings both with egg yolk and oil-based binders. The presence of metal carboxylates has been reported in other studies, in particular in oil painting [2,10,14–16,18], in this study they have been non-destructively identified and isolated in ancient egg yolk paintings. Moreover, it is the first time that these compounds have been identified by means of micro-XRD directly on ancient painting layers.

Oxalates are a type of salts usually found on the surfaces of artworks [18–20]. However, their relationship to the degradation/weathering processes, although suspected, is still unknown. In this study, we determine the nature of the oxalates formed, in particular of lead, calcium and copper oxalates and their distribution in the different chromatic, preparation and alteration layers. This is the first step necessary in order to ascertain origin of their oxalates and to establish the mechanisms responsible for their development and to relate their presence to specific degradation processes.

2. Experimental

2.1. Samples and reference materials

The samples analysed belong to altarpieces painted by the most important masters of the Crown of Aragó: *Sant Vicenç de Menàrguens* dated 1438–1440 by Bernat Martorell (1400?–1452), *Sant Vicenç de Sarrià* dated between 1455 and 1460 and *El Conestable* dated 1464 both by Jaume Huguet (141?–1492), *La Mare de Déu dels Consellers* dated 1443–1445 by Lluís Dalmau's (1428–1461) and *L'aparició de la Mare de Déu a Sant Francesc a la Porciúncula* by Mestre de la Porciúncula dated around 1450. They are on exhibit at the Museu Nacional d'Art de Catalunya in Barcelona [21]. Finally, the

Fig. 1. Detail of the scene of the Crucifixion in the altarpiece of the Conestable from the chapel of Saint Àgata in Barcelona by the painter Jaume Huguet, 15th century. Photo: Carles Aymerich, Centre de Restauració de Bens Mobles de Catalunya (CRBMC).

altarpiece *El Conestable* dated 1464 by Jaume Huguet is placed in the chapel of Santa Àgata in Barcelona (Fig. 1).

The paints were applied over a ground preparation, mixing the pigments with an organic binder, either egg yolk or animal glue and water (tempera technique) or a drying oil (oil technique). The ground preparation was made of several layers of gypsum mixed with animal glue and applied over the wood surface. The paintings are formed by a sequence of layers including a ground layer (few millimetres), several paint layers (between 10 and 100 μm thick each) and superficial layers of alteration of varnishes and contamination (less than 2 μm thick).

Organic binders and pigments react and age, therefore some naturally aged materials are also analysed. Egg yolk (chicken), drying oils (linseed oil) and some pigments mixed with the binders applied over a glass slide and allowed to age naturally in the laboratory for at least 8–10 years are also studied.

The mixtures were prepared blending binding media with pigments or gypsum in a weight proportion of 25–30% binding media and applying it over a glass slide in layers of between 60 and 150 μm in thickness.

2.2. Specific sample preparation

The samples taken were small in size (surface area of a few hundred micrometers side), from which two preparations are made, fresh-fractured fragments and polished cross-sections. For