

# CHEMISTRY IN CULTURAL HERITAGE AND CULTURAL HERITAGE IN CHEMISTRY. RESEARCH AND EDUCATION. PAINTER AND SCULPTOR: ALONSO CANO'S PROJECTS

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## Abstract

The starting point for this communication are two research projects funded by the Ministry of Science and Technology (Leading researcher Dr L.R. Rodriguez-Simón). These two projects are focused on the identification and characterisation of the materials used in paintings and sculptures by Alonso Cano (1601-1667), considered as one of the most original and brilliant artists from the so-called Spanish Golden Age (seventeenth century), and the founder of the baroque painting school of Granada (Spain). The full study attempts to contribute to the understanding of his artistic technique taking into account both the evolution of his painting style, as well as the reconstruction of the so called "Cano palette". Also, the study tries to establish the necessary scientific basis on which to support the confirmation or refusal of authorship in those cases of controversial attribution which remain in the current catalogue. In addition, a further goal of these projects is a proposal regarding the theory of the most suitable restoration techniques for each of the studied works. To achieve the above cited objectives about Alonso Cano's pictorial work our research team aims to undertake surface investigations (including macroscopic and microscopic examinations), infrared reflectography and x-radiography; and material characterization of the ground, pigments and organic binders. In order to characterise binding media we are working on three important topics: developing more accurate and reliable methods of analysis; aging studies in artistic materials; and probing the usefulness of using chemometric approaches as valuable tools for the investigation and characterization of painting materials. The importance of these achievements both for the restoration of works of art and for analytical chemistry has led the team of researchers, members of the aforementioned projects, to consider the transmission of knowledge through teaching: Chemistry in Cultural Heritage and Cultural Heritage in Chemistry. The course "Chemical Analysis of Cultural Heritage" has been imparted since 2001 to students in their last years of the Degree in Chemistry at the University of Granada (Spain). This approach to Cultural Heritage has provided Chemistry students with a new perspective on Analytical Chemistry and its relation to the analysis of artworks as well as aspects related to the Conservation and Restoration of Cultural Heritage. In the same way, the University Master in "Preservation and Restoration of Easel Painting. Materials and Methods", (currently 3rd edition), is imparted to Restoration students at the University of Granada (Spain). Learning Chemistry provides humanity students with a scientific knowledge which gives them a basis of skills and abilities for a more complete professional development in restoration.

Keywords: Cultural Heritage, Chemical Analysis, Imaging, Education, Research Project.

## 1. PROJECTS ABOUT ALONSO CANO

A interdisciplinary group of colleagues to the University of Granada (Spain) from department of Painting and Restoration and Analytical Chemistry, to the University of Jaén (Spain) from department of Historical Heritage, some researchers from Centre for Scientific Instrumentation (CIC) of the University of Granada (Spain) and some relevant specialist in Conservation and Restoration from Technical Documentation Department of Prado Museum's in Madrid (Spain) are participating since 2003 in the multi-disciplinary research Projects about the painter Alonso Cano [1].

The key point of the Alonso Cano Project is the promotion and reinforcement of the cooperation between the chemical sciences and the art historical and Cultural Heritage. Therefore our team works researching with an interdisciplinary approach that would be plural in its interests and in its scientific methods. This study combines the wishes and knowledge of the specialists attached to different scientific fields and the Conservation and Restoration of Cultural Heritage.

### 1.1. Alonso Cano

Alonso Cano (Granada, 1601-1667), is considered as one of the most original and brilliant artists from the so-called Spanish Golden Age (seventeenth century), and the founder of the baroque painting school of Granada (Spain). Cano was distinguished as a painter, sculptor and architect. He was a contemporary and friend of Velázquez, and during his stay in Seville and later at court in Madrid, coincided with him. In 1638 he left for Madrid where he was named painter and gentleman of the bedchamber to the count-duke Olivares and where he met Velázquez again. It was a period of great activity for the painter when he produced paintings as important as the Budapest "*Noli me tangere*" and the Prado "*Milagro del pozo de San Isidro*". He returned to Granada in 1652 where he undertook one of the most important groups of cycles of great paintings in the whole of Spanish art. An example is the series the "*Vida de la Virgen*" painted for the Capilla Mayor of the Cathedral of Granada, which is currently the object of studies within our investigations.

### 1.2. Research Projects. Objectives.

Our research into the paintings of Alonso Cano begins with the awarding of the first research project in 2003 and the following project, three years later, in 2006 [1]. The starting point of our research project is the historiographic review of the artist, carried out on the occasion of the celebration of the fourth centenary of his birth. Nevertheless, apart from the obvious progress in the understanding of Alonso Cano, the historiographic reality of the artist from Granada suffers from a catalogue compromised by ambiguous attributions and insufficient knowledge of his plastic resources. This latter aspect is essential for the understanding of the artistic personality of Alonso Cano and for making a diagnosis which allows for the optimal preservation and/or restoration of his works.

We subscribed proposals that had already been investigated and were points of reference, such as the proposals made by the Prado Museum's Technical Documentation Section on the figure of Velázquez, with excellent results increasing our knowledge of the artistic technique of this brilliant painter. Therefore, our study proposal is based on historical and artistic studies, optical examination and scientific analysis that demonstrates a knowledge of the material composition and artist technique used by the artist.

Among the objectives of a historic and artistic study of the paintings of Alonso Cano in this Project are those summarised in Table 1 (see also figure 1). These objectives are aimed at making an in-depth study of the artistic personality of Alonso Cano and at the normalization of the catalogue of his work by confirming or rejection questionable attributions.

**Table 1. Objectives of the Alonso Cano Project (n: 1-7). Study of historical and artistic paintings by Alonso Cano**

1. To make an iconographic and iconological study of the composition of the paintings and sculptures of Alonso Cano, based on a review of his engraving repertoires and other plastic sources; of the painter's familiarity with literary sources evidenced by the inventory of his library; and, finally, to place his artwork within the political, social, ideological and spiritual context of the period in which he lived.
2. To discover and make evident the plastic resources adopted by Cano, possible changes in composition and modifications made by the artist in the course of creating each of his works, and the changes introduced by others at later dates due to changes in taste or poor conservation.
3. To distinguish between original materials and materials added during subsequent periods, in order to determine the specific features of each work. X-radiography and Infrared Reflectography can expose the artist's preliminary workings beneath the paint surface, which often reveals his early thinking.
4. To establish the concrete period to which each work belongs within the author's development as an artist.
5. To make a diagnosis of the changes and deteriorations affecting the paintings and sculptures of Cano, and to determine their causes. Also, to prescribe the remedies that should be adopted regarding the conservation/restoration of Cano's work.
6. To delimit the best conditions for establishing the key properties of the works, with a view to preventive conservation.
7. To elucidate unknown factors and unresolved issues at the historiographic level, paying special attention to detecting possible forgeries and incorrect attributions.



Figure 1. Optical and electronic microphotography, imaging study and SEM-EDX microanalysis. Painting: "La Visitación" by Alonso Cano

Advancing the objectives of this project, modern scientific methods are always important aids when a painting is being closely studied, or undergoing conservation treatment. Usually the artistic materials used are heterogeneous or are involved in their degradation, and that often leads to complex composition materials that require the use of scientific and technical examination. Powerful microscopes and chemical analysis of micro-samples of paint, give information about pigments and media used to create a painting and the layer structures involved. The scientific team from this Project wish to contribute to the understanding of Cano's technique taking into account both the evolution of his painting style, as well as the reconstruction of the so called "Cano palette". Thus, the main objective of the scientific study of this Project (objective n.9) is double, as can be seen in Table 2.

**Table 2. Objectives of the Alonso Cano Project (n: 9). Chemical Analysis of paintings.**

9.1.- Application of analytical techniques for the characterization and identification of the organic compounds used by the artist as binders and the pigments used based on colors in the painting. Development of new analytical methodologies for its application to real samples belonging to the artwork of Alonso Cano.

9.2.- Study of the evolution processes of aging from the organic binders.

The scientific group investigate developing new analytical methodologies to be applied to the analysis of organic binders used in painting and the correlations between analysis data and multivariate analytical approach. This research that aimed to characterize lipidic and proteinaceous binders in artistic painting are based on two foundations:

- Selection of advanced analytical techniques with a high sensitivity that requires a minimum amount of sample and the application of these techniques to identify artistic components. Proposal of new analytical methodologies to be applied to the analysis of organic artistic substances (drying oils and proteins).
- Search profiles of amino acids or fatty acids respectively, or relations between them that are specific to proteinaceous material or drying oil. Multivariate technique of data analysis enable the characterization of protein binders and drying oils, respectively.

In relation to this we have made progress in the following topics that have to be published in papers collected from the Science Citation Index and proceedings in Congress, described as follows and quoted in brackets:

- Chromatographic analysis of the characterization of pictorial technique of "Spanish Golden Age". GC/MS characterization of drying oil in painting represents an important advance in technical knowledge, material and aesthetic, of the paintings by Alonso Cano [2]. Chromatographic procedure (HPLC-UV) for the determination of amino acid as phenylthiocarbonyl derivatives (PTC) in proteinaceous binders are a topic that is performed. The proposed method was applied to chromatographic separation, identification and quantitative determination of amino acids present in samples from Cultural Heritage with good results [3,4].
- Pattern Recognition strategy (SIMCA) in classification of old proteinaceous binders. The data from an amino acidic profile of proteinaceous binders coming from a sample collection prepared by us using old recipes were processed using several strategies to classify the binders by origin. We chose the SIMCA pattern recognition technique, characterising the models in terms of sensitivity, specificity, classification capacity and prediction capacity. The technique was applied to eleven samples coming from Cultural Heritage selected such as mural and easel painting, manuscript and polychrome sculptures from the 15th-18th centuries. The results obtained are compared with results using classical strategies [5,6,7].
- The characterization of binder and pigment materials and their interactions has been carried out through Diffused Reflection Spectroscopy (DRIFTS) analysis. The discussion is mainly focused on the practical benefits of using this technique joined to Principal Component Analysis, a powerful

multivariate analysis tool. Also comparative results of direct spectra and multivariate analysis using Transmittance-FTIR spectroscopy are discussed. In particular the effects of a UV-accelerated ageing test on model samples of azurite glue tempera, pure azurite and pure rabbit glue, all elaborated according to medieval recipes, were studied [8-10]. Raman spectroscopic discrimination of pigments and tempera paint model samples by Principal Component Analysis. Multivariate approach on Raman Spectroscopic data to investigate protein-pigment interaction in tempera paintings [11-13].

- Multivariate statistical analysis applied to processes of aging in binders. Artificial ageing of binder material, in a UV accelerated test chamber (figure 2). Study of Ageing Process of Dry Oil in Replicate Paintings Under UV Light by FT-IR and Principal Component Analysis. Study of UV ageing process of proteinaceous paint binder by FT-IR and Principal Component Analysis [14,15]. These studies use FTIR Spectrometry as alteration criterion, and establish a relation between the degradation of proteinaceous and drying oil material and its capacity of classification through pattern recognition techniques.



- Non-destructive techniques. Raman Microspectroscopy to binders analysis [16]. In the field of Conservation and Restoration, the current criteria for preservation of artworks, and especially of paintings, requires the application of procedures that do not damage the works, so that its originality is respected. In figure 3 shown  $\mu$ -Raman Spectroscopy “in situ” analyzed over some area of the painting.

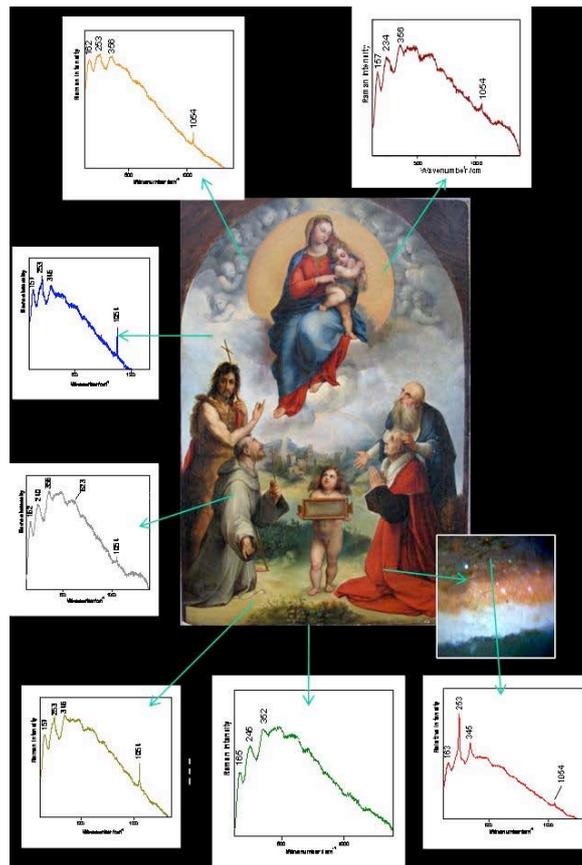


Figure 3. Application of non-destructive analytical techniques. Micro-Raman analysis “in situ”.

### 1.3. Benefits of the Research Project

In the field of History of Art the main benefit is the progress in research on painting and sculpture techniques in the 17th century in Spain to allow confirmation of the way that the artists in Granada, and concretely Alonso Cano, followed the artistic techniques written in the principal treatise of the time.

Additionally, the scientific and methodological advances made would respond to the demand raised by the professionals involved in pictorial heritage preservation, as they are effective, practical and less costly methods of analysis of the pictorial materials and can be used routinely. Moreover, this multidisciplinary study will provide the necessary data to adopt guidelines to follow for preventive preservation of paintings.

In addition, the project proposes the development and validation of diverse methodologies based on the use of different complementary and innovative analytical techniques for the specific characterization of certain pictorial components and interactions between them, the precise study of which is often unresolved in the bibliography.

One of our research team’s projects is to continue studying the figure of Alonso Cano until we have completed all of his paintings and sculptures. This will allow us to make a catalogue that will include many of the aspects provided by a multidisciplinary team.

### 1.4. Deliverables

Finally, we emphasize the learning benefits from the existence of an active research group at the University. Among others, these benefits are associated with creating a specific bibliography, training

researchers and the production of Doctoral and Master theses. Doctoral theses and Master theses that already have been defended, are:

- Title of Master thesis: "Effect of some pigment on the UV-photostabilisation of proteinaeous binders: a spectroscopic and principal component analysis investigation in paint reconstructions" [8].

- Title of PhD thesis "Identificación de aglutinantes proteicos pictóricos mediante cromatografía líquida y técnicas de reconocimiento de pautas" [3].

- Provisional title of Master thesis which will be defended in this course: "CG-MS (Q) and HPLC-MS (QqQ) analysis of drying oil binder".

As a consequence of the two previous studies a new line of investigation based on the application of high resolution digital photography, by the incorporation of a new member of our team, from Department of Informatics Languages and Systems, of University of Granada. At the same time the team is planning another very innovative line of investigation based on the application of the principles of Archaeological stratigraphy to the study of heritage assets.

- Provisional title of PhD Thesis: "Documentation of pictorial stratigraphic as a tool in the scientific cleaning of polychrome surfaces, from the interpretation of stratigraphic units and diagrams elaborated from transversal sections of the pictures. Application to the works by Alonso Cano"

## 1.5. Future plans

Research studies will be continued and some papers will be written and published. In the reference lists some of the published scientific articles are cited [2-16].

The Study and Documentation of Alonso Cano's Paintings by means of multispectral images that offers restorers a non destructive tool for identifying "in situ" the materials used by the artist together with their spatial distribution. This information will help to understand the artistic technique, document accurately the state of conservation of the work and the selection of pigments used.

Further comparative studies of paint samples by Raman spectrometry will take place in collaboration with other projects team members.

Artificial ageing experiments controlled on the organic binders will be continued. Priority will be given to the effects of ageing on untreated and pigmented oil paints. Photo ageing studies of tempera painting by MALDI-TOF-MS and multivariate analytical approaches is being researched.

Contribution of the Gas Chromatographic-mass spectrometry (GC/MS) and Liquid chromatography-mass spectrometry (LC-MS) to study of oil binding media. Pictorial technique in paintings from the "Spanish Golden Age".

## 2. TEACHING

The importance of these achievements both for the restoration of works of art and for analytical chemistry has led the team of researchers, members of the aforementioned projects, to consider the transmission of knowledge through teaching: Chemistry in Cultural Heritage and Cultural Heritage in Chemistry.

The Course "*Chemical Analysis of Cultural Heritage*" has been imparted since 2001 to students in their last years of the Degree in Chemistry at the University of Granada (Spain), who do not have any particular experience of studying art. This approach to Cultural Heritage has provided Chemistry students with a new perspective on Analytical Chemistry and its relation to the analysis of artworks as well as aspects related to the Conservation and Restoration of Cultural Heritage [17,18].

In the same way, the University Master in "*Preservation and Restoration of Easel Painting. Materials and Methods*", (currently 3<sup>rd</sup> edition), is imparted to Restoration students at the University of Granada (Spain) ([www.ugr.es/local/restauracionpintura](http://www.ugr.es/local/restauracionpintura)). Recently, its Homologation has been approved by the Andalusian Institute of Public Administrations of the Junta de Andalucía. Learning Chemistry provides humanity students with a scientific knowledge which gives them a basis of skills and abilities for a more complete professional development in restoration. This Master teaches an education derived from in-house investigation developed by our research team. In the Classroom workshops for the

Restoration of easel painting, located in the Centre for Restoration "Palace of the Admiral" of the University of Granada, we are teaching lessons about the theory and the practice on some intervention procedure of restoration. The constituent materials are canvas, board, copper, glass or leather. The goal of these lessons is to introduce to students knowledge of the restoration treatments applied in easel painting, regarding the causes and agents that cause deterioration and the preventive conservation to arrest its alteration.

Before restoration activities, it's necessary to document the conservation state of the original works by testing and using the means that science has put into the service of art. The studies with radiation ultraviolet, infrared, and X-ray techniques, are resources available in the workshops to Restoration (figure 4). In addition the technical images can serve students learning from Fine Arts, Restoration o Chemistry.



Figure 4. "The Encarnación" by Alonso Cano.  
Left: Photograph with visible light of "The Encarnación"  
Centre: X-ray radiography of painting  
Right: Photograph with Ultraviolet light.

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