IL NUOVO CIMENTO Vol. 36 C, N. 4 Luglio-Agosto 2013
DOI 10.1393/ncc/i2013-11556-8

Communications: SIF Congress 2012

Removal of synthetic resins through a chloroform-based pretreatment for a correct radiocarbon dating of restored artworks

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ricevuto il 19 Dicembre 2012

Summary. — In Archaeometry, the collaboration among different specialists can be very useful to solve problems of authentication and to characterize the artworks. This cooperation is also recommended in radiocarbon dating. Before dating, for example, it is important to be aware of possible restorations undergone by the artworks and, in particular, which products have been used, since they may represent a source of contamination altering the obtained date. In fact, these products are generally organic compounds, thus representing an addition of exogenous carbon, which must be completely removed. In this paper, the case of the removal of synthetic resins will be discussed. The issue of contamination by synthetic resins will be presented using two case studies: the wooden frame of a Trittico by Ambrogio Lorenzetti and a painting on canvas of the first decades of the XX century.

PACS 89.90.+n – Other topics in areas of applied and interdisciplinary physics.
PACS 29.20.Ba – Electrostatic accelerators.
PACS 89.20.Mn – Forensic science.

1. – Introduction

It is well known that sample preparation is an important and critical step in radiocarbon dating. One of its aims is the removal of contaminations that might affect the ^{14}C measurements. Indeed, since its "death", the object to be dated might have entered in contact with different natural or anthropogenic sources of carbon, that can introduce contaminations either by modern carbon or by "dead" carbon, *i.e.* nominally depleted of ^{14}C. If not removed, these contaminations would make the dated sample appearing younger or older, respectively.

Concerning the dating of samples collected from objects of art-historical interest (such as paintings on canvas or on wood), it can be quite common to analyze samples that are affected by contaminations due to restorations. Products used for restorations can be of natural (*e.g.* oil, animal or vegetal glue, and resin) or industrial (*e.g.* synthetic resins) origin. The latter are generally obtained by synthesis of hydrocarbons, *i.e.* chemical organic compounds extracted by petroleum, which is "infinitely" old from the point of view of radiocarbon dating (older than ~ 50000 years). This means that, if the synthetic resin is not completely removed from the sample to be dated, an apparent ageing is produced.

Since the synthetic resins are used especially to consolidate the artwork supports, one of their main characteristics is the great capability to penetrate into the matter. As a consequence, a simple physical pre-treatment by a scalpel is not generally sufficient to remove them: the use of chemical solvents is required. These solvents are characterized by a selective spectrum of applicability, so that it is necessary to know which products have been applied to decide the appropriate solution to adopt. In addition, in specific preservation conditions (high temperature and in the presence of natural and artificial lights), owing to polymerization processes, cross linking effects take place in the resins, with the main effect of reducing their solubility in organic solvents.

Among the synthetic resins used for consolidation purposes, the most usual products are *Paraloid B72*® (Rohm and Hass) [1] and *Gustav Berger's Original Formula*® *371* (Berger ethylene vinyl acetate, BEVA 371 in the following) [2]. Paraloid B72 is a thermoplastic acrylic resin and in particular a copolymer of EMA/MA (ethyl methacrylate/methyl acrylate), dissolved in ethyl acetate solution. BEVA 371 is a product based on ethylenvinylacetate, paraffin and ketone resin, in a solution of aliphatic and aromatic solvents. For both, the complete removal is recommended using organic solvents, in particular petroleum solvents and chlorine-based products [3-5]. In this family of chemical compounds, one of the most suitable solvents is chloroform ($CHCl_3$). Moreover, chloroform is characterized by a rapid evaporation at room temperature too, hence possible contamination effects due to residues of this product inside the treated sample to be dated is minimized.

In this paper, the issue of contamination due to synthetic resins is presented reporting the radiocarbon measurements performed on two case studies: pieces collected from the wooden frame of the Trittico of Badia a Rofeno by Ambrogio Lorenzetti and a sample collected from a painting on canvas of the first decades of the XX century.

2. – Materials and methods

All the samples to be dated were divided into two parts: one was treated only with the LABEC ABA (acid-base-acid) standard protocol [6] and the other with the new chemical pre-treatment based on the use of chloroform, followed by the ABA standard protocol. In this way, the possible apparent ageing related to an incomplete removal of synthetic resins using only the standard protocol can be checked.

According to the new chemical pre-treatment based on chloroform, all samples are firstly cut in little pieces and put in a closed tube where the solvent, *i.e.* chloroform, is added (approximately 10 ml every 5 mg of sample); afterwards, the tube is placed on a magnetic agitator to favour the solubilization of the resins. This pre-treatment lasts for two days. After the removal and the complete evaporation of the solvent under the fume hood for two days, the sample is also treated using the ABA protocol.

The first case study is represented by the wooden frame of the polyptyc "*Pala con la Vergine e il bambino, S. Michele Arcangelo e Santi*" painted by the Italian artist Ambrogio Lorenzetti (1290-1348) (fig. 1).

Fig. 1. – Polyptyc "Pala con la Vergine e il bambino, s. Michele Arcangelo e santi": (a) the picture frame (b) the painting.

As reported in technical reports [7], the painting was restored several times to consolidate the frame using the synthetic resin Paraloid B72. Several samples were collected from different parts of the left pillar and from the altar step of the frame in order to perform radiocarbon dating. The aim of these measurements was at verifying whether the present wood frame was obtained using timbers of a possible original frame or using new wood.

The second case study is a sample collected from the rear edge of a painting on canvas of the first decades of the XX century (signed in 1918). The goal of the measurement was just to prove the effectiveness of the new chloroform-based treatment in removing a restoration product different with respect to Paraloid on a different support.

The painting was recently restored using an acrylic resin, namely BEVA 371, to consolidate the painting support and the painted layers. Residues of this treatment are evident since the "rigid" consistency of the canvas and the darker brown colour in several spots (see fig. 2).

Fig. 2. – Canvas sample under optical microscope: a darker brownish area is visible.

The radiocarbon measurements were performed using Accelerator Mass Spectrometry (AMS) at INFN-LABEC (Laboratorio per l'Ambiente e i BEni Culturali) in Florence, where a 3 MV Tandem accelerator and a sample preparation laboratory have been installed since 2004 [8]. Concerning the AMS measurements, at LABEC, both $^{14}C/^{12}C$ and $^{13}C/^{12}C$ isotopic ratios are measured during the same run in the accelerator. $^{13}C/^{12}C$ ratios are used to correct the measured radiocarbon abundance for isotopic fractionation; radiocarbon concentrations of unknown samples are calculated from the corrected $^{14}C/^{12}C$ ratios by eventually subtracting the background (obtained measuring blank samples, *i.e.* with nominally no ^{14}C) and normalizing to the ratios measured for a set of standard samples (in this case, NIST Oxalic Acid II [9]). The software used to calibrate the conventional radiocarbon age is OxCal version 4.1 [10] and the reference calibration curve is IntCal09 [11].

3. – Results

Radiocarbon measurements concerning the wooden frame are summarized in table I.

As is possible to notice in table I, the radiocarbon concentrations measured in the samples treated using only the ABA standard protocol are not consistent between each other, and largely inconsistent with both the period in which Lorenzetti lived and the later period which the wooden frame was attributed to on the base of its style (XVI century). We can reasonably explain this result considering that the Paraloid B72 contamination was different in the two samples and that it was not removed (or only partially removed) using this protocol, as it might have been expected.

In the case of the samples treated using the new chloroform-based procedure, the radiocarbon concentrations and the corresponding radiocarbon ages are instead consistent between each other. This suggests that the procedure is effective in completely removing the contamination. The calibrated age comes out to be compatible only with the XVI century, therefore indicating that it was not made using again wood from a previous original frame. This result was important for the restorers and the museum curators, who then decided to display the original painting in the museum separated from the framework.

Table I. – *Measured radiocarbon concentrations, corresponding radiocarbon ages and calibrated ages of the wooden samples treated using the ABA standard protocol and the new chloroform-based procedure.*

Sample	^{14}C concentration (pMC)	Radiocarbon age years BP	Calibrated age years AD
OPD 5_ABA	77.9 ± 0.5	2005 ± 55	170 BC–85 AD
OPD 5_Chl	95.5 ± 0.5	370 ± 40	1445–1635 AD
OPD 7_ABA	86 ± 1	1160 ± 110	650–1045 AD
OPD 7_Chl	96.1 ± 0.4	320 ± 35	1480–1645 AD

TABLE II. – *Measured radiocarbon concentrations, corresponding radiocarbon ages and calibrated ages for the fragment of the canvas sample treated either with or without chloroform.*

Sample	^{14}C concentration (pMC)	Radiocarbon age years BP	Calibrated age years AD
Can1918_ABA	79.3 ± 0.3	1860 ± 30	55–255 AD
Can1918_Chl	97.8 ± 0.3	180 ± 30	modern

Concerning the canvas sample, the results are shown in table II.

As we can notice in table II, the experimental results show a large discrepancy between the concentration measured for the ABA-treated fragment and for the chloroform-treated sample. In particular, the sample prepared following the ABA protocol only, appears to be much older than any reasonable expectation, which shows that it is contaminated by a fraction of dead carbon. Even in this case, the ABA protocol is clearly insufficient to remove the acrylic resin. On the contrary, the radiocarbon concentration measured in the fragment treated with the new procedure is in agreement with the expected value. The radiocarbon age of 180 ± 30 years BP corresponds to the period during which a sample can be just classified as modern (1650 – 1950 AD). This result is thus in agreement with the date on the painting (1918).

4. – Conclusions

The measurements presented in this paper point out that radiocarbon dating can be very useful to confirm the presence of parts added at later times with respect to the period in which the artwork was made, and to help in problems of authentication. In addition, these measurements show how important is knowing which kind of restorations have been performed in order to select the areas where the samples have to be collected from the artworks, and the chemical pre-treatment to be used prior to radiocarbon dating. Concerning the new pre-treatment based on the use of chloroform, we checked that it can get rid of problems related to the presence of residues that may be the cause of an apparent ageing of the dated samples. The effectiveness of the new procedure was verified on two different materials and with different synthetic resins, thus suggesting a broad spectrum of applicability.

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