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The issue of contamination by synthetic resins in radiocarbon dating: the case of a painting by Ambrogio Lorenzetti

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Abstract

Nowadays, the most common products used in restoration are of synthetic origin. Being these resins obtained from fossil oil, they are devoid of ^{14}C. Therefore, a not complete removal from the sample to be dated can be the cause of a consistent apparent ageing of the dated artworks. A chemical pre-treatment is required in order to clean the samples before the measurements. At INFN-LABEC laboratory in Florence, a new procedure based on the use of an extraction with chloroform as solvent was tested. In this paper, the radiocarbon measurements made on a restored polyptyc by Ambrogio Lorenzetti are presented.

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Keywords: radiocarbon, contamination, synthetic resin, Paraloid B72, FT-IR

1. Introduction

Radiocarbon dating can be a very useful instrument to determine the age of an artwork. In the field of Cultural Heritage, common dated materials are wood, paper, textile and papyrus. It is well known that these materials might be subjected to restoration in order to preserve artworks. In particular, since 1960s, these operations have been often performed using synthetic resins, because they are characterized by a better stability over time with respect to the natural remedies. These synthetic resins are usually produced by polymerization processes of fossil

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oil and/or its by-products. Since hydrocarbons are devoid of ^{14}C, they can represent a source of contamination by "dead" carbon, so a not complete removal of these products may be the cause of an apparent ageing of the radiocarbon dated sample. Actually, the term dead carbon is typically used to refer to those materials containing a ^{14}C concentration that is well below the sensitivity limit of the measurement technique, thus, in a radiocarbon measurement, they appear as infinitively old. As a consequence, if a percentage of this contamination is present in the measured sample, the radiocarbon age will appear older than the true age. The relevance of the contamination depends on the quantity of the contaminant present in the samples (see Figure 1).

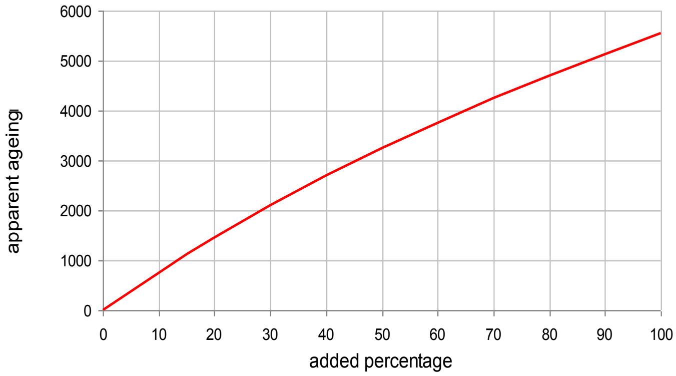

Fig. 1. Apparent ageing as function of the percentage of contaminant present in the sample.

To remove all the possible contaminations that can affect the measured age, each organic sample undergoes a physical-chemical pre-treatment before dating. In particular, in case the artwork to be dated was preserved, the pre-treatment has to remove the substances added during restoration. Concerning the physical-chemical properties of synthetic resins and in particular of the products used to consolidate the artistic supports, they are characterized by a good capability to penetrate in the matter. In addition, their solubility decreases as a consequence of the natural ageing and the cross linking effect. This means that, for their removal, the simple use of mechanical treatment with different tools (e.g. scalpel) cannot be sufficient and the application of organic solvents is usually recommended.

As far as the sample preparation is concerned, the most widespread procedure in the radiocarbon community used to remove contaminations by synthetic resins is based on the use of the Soxhlet extraction system [1] where the sample come into contact with different organic solvents (each solvent is able to remove the traces of the previous agent in order to avoid any contamination effects). Finally, the so-called ABA standard protocol [2], based on the use of acid and basic solutions (HCl 1M and NaOH 0.1M, in our laboratory) is applied in order to remove the "natural" contaminations such as carbonates and humic acids. As an alternative to the Soxhlet method, which can be very time consuming, we have tested a new chemical pre-treatment procedure, which can be easily operated. The new procedure is based on the use of a simple extraction with only one organic solvent. In this case, the chosen organic solvent was chloroform ($CHCl_3$).

In this paper, the issue of contamination by the products used during the restorations is presented in reference to a case study, i.e. a polyptic by Ambrogio Lorenzetti (1290-1348), an Italian painter who worked especially in Tuscany. In particular, the radiocarbon measurements were performed on two wood samples collected from the wooden picture frame previously consolidated with a synthetic resin, Paraloid B72®, a copolymer produced by Rohm and Haas (USA) and composed by two monomers methyl acrylate and ethyl methacrylate [3].

This study was performed at INFN-LABEC (Laboratorio di tecniche nucleari per l'Ambiente e i BEni Culturali) in Florence, where a 3MV Tandem Accelerator and a sample preparation laboratory are installed [4].

The relative abundances of the radioactive isotope ^{14}C and of the other two stable isotopes of carbon (^{12}C and ^{13}C) were measured by the Accelerator Mass Spectrometry (AMS) technique [5].

In the following, the basic principles of radiocarbon dating are discussed in brief. Then, the new chloroform based pre-treatment method and measurement results on the samples collected from the polyptyc are presented.

2. Radiocarbon dating

Radiocarbon is the only natural unstable isotope of carbon. ^{14}C is produced in the upper layers of the atmosphere by interaction of thermal neutrons (secondary products of cosmic rays) and nuclei of nitrogen (^{14}N). It is only a very small fraction (about $1.2 \cdot 10^{-12}$) with respect to the other two natural stable isotopes of carbon (^{12}C~98.9% and ^{13}C ~1.1%). Radiocarbon decays via beta emission to ^{14}N with a half life of 5730±40 years. In the atmosphere, the ^{14}C atoms rapidly combine with oxygen to form carbon dioxide (CO_2). Then the CO_2 spreads over the atmosphere, dissolves into the oceans and also enters in the biosphere via several paths such as photosynthesis, respiration and nutrition. Considering the radiocarbon half life and its fast production rate, the decayed radiocarbon is promptly compensated by natural continuous production; hence the same ^{14}C concentration is present in all living organisms and in the different carbon reservoirs (such as atmosphere and oceans).

When an organism dies, if we can considerer it as a close system and considering the radiocarbon concentration in the formerly living organism as known and constant in the past, the residual radiocarbon concentration $^{14}R(t)$ after a period t from the death is in agreement with the radioactive law:

$$t_{RC} = \tau \cdot \ln\left[\frac{^{14}R_0}{^{14}R(t)}\right] \tag{1}$$

Assuming the ^{14}C mean life τ of 8033 years and the ^{14}C concentration $^{14}R_0$ at the moment of the death of about 10^{-12} (i.e. the ^{14}C concentration in atmosphere measured in a reference year, 1950), we can obtain the so-called conventional radiocarbon age which is expressed in years Before Present (years BP), where present is 1950. Then, the distribution of probability for the true age of the sample can be obtained thanks to the calibration of the conventional radiocarbon age.

3. Materials and methods

The new chemical pre-treatment tested at LABEC consists in a series of extractions with chloroform ($CHCl_3$). In particular, the sample, cut in little pieces, is inserted in a Pyrex tube where the solvent is added (about 10 ml of $CHCl_3$ per 20 mg of sample). The tube is placed on a magnetic agitator at room temperature; soaking in chloroform lasts for two days (the time can depend on the state of polymerization of the synthetic resin) during which the chloroform is periodically changed in order to promote a better reaction between the sample and the solution. Finally, the sample is removed from the solution and dried in fume hood at room temperature for two days at least. Afterwards, the sample is treated using the ABA standard protocol.

A fraction of the collected wood samples is also treated using only the ABA standard protocol; in this way, the possibility to estimate the real apparent ageing due to the synthetic resins can be also checked.

During the different steps of the chemical pre-treatment, fragments of the treated samples are collected and analyzed using the FT-IR (*Fourier Transform Infrared Spectroscopy*) technique to verify the effectiveness of the applied procedures. FT-IR spectra were acquired with a Shimadzu FT-IR-8400S model and elaborated with software IR Solution. Spectra of solid samples were recorded as KBr pellets.

Before the ^{14}C-AMS measurements, in order to isolate only carbon, the sample is then combusted in an elemental analyzer (Thermo Flash EA 1112) and then graphitized according to the well known Bosch reaction [6]. In this way, the graphite sample is then obtained and can be inserted in the source of the accelerator.

Concerning the AMS measurements, both $^{14}C/^{12}C$ and $^{13}C/^{12}C$ isotopic ratios are measured in the accelerator beam line. $^{13}C/^{12}C$ ratios are used to correct for isotopic fractionation; eventually radiocarbon concentrations of unknown samples are calculated from the corrected $^{14}C/^{12}C$ ratios by subtracting the background (obtained measuring samples with nominally no ^{14}C) and normalizing to the isotopic $^{14}C/^{12}C$ ratios measured for a set of standard samples (in this case, NIST Oxalic Acid II [7]). The program used to calibrate the conventional radiocarbon age is OxCal version 4.1 [8] and the reference calibration curve is IntCal09 [9].

4. The case study

The polyptyc "*Pala con la Vergine e il bambino, S. Michele Arcangelo e santi*" (Figure 2) was realized by Ambrogio Lorenzetti.

(a) (b)

Fig. 2. Polyptyc "*Pala con la Vergine e il bambino, s. Michele Arcangelo e santi*": (a) painting; (b) picture frame

According to its artistic style, the wooden frame cannot be attributed to the painter himself, but it can be clearly dated to a following period, the XVI century. The goal of radiocarbon dating was verifying whether the wood frame was obtained using timbers of a possible original frame or using new wood. For the radiocarbon measurements, two wood samples were collected, one from the left pillar and the other from the altar step of the picture frame. In Table 1, radiocarbon results are reported.

Table 1. Radiocarbon concentrations (expressed in percent of Modern Carbon, pMC), the corresponding radiocarbon ages and the calibrated ages of the wooden samples treated with the new chloroform procedure and the ABA standard protocol. The experimental uncertainty is reported as 1 sigma. The calibrated ages are quoted at a 95%.probability level.

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

As it is possible to notice in the table, the radiocarbon concentrations measured in the samples treated with the two different methods are not consistent between them. In particular, the radiocarbon ages relative to the two samples subjected only to the ABA protocol are not compatible and are much older than the expected value. This result cannot be explained even considering the well known old wood problem [10], but it is the effect of the apparent ageing due to the presence of Paraloid B72 that was not completely removed with this pre-treatment. In addition, the two samples present two completely different ages and this also suggest the fact that the quantity of contaminant in the samples is not the same. On the contrary, the measured radiocarbon concentrations and the corresponding radiocarbon ages of the two samples treated with the new procedure are consistent between them. Furthermore, they are specifically in agreement with the artistic style of the picture frame. Therefore, this suggests that the frame was rebuilt at a later time without reuse timbers of the original wooden frame. Another important result that can be inferred from these measurements is that the chloroform solvent, which is also derived from hydrocarbons, completely evaporated during the sample preparation and thus it itself does not represent a new source of contamination.

In the following, the FT-IR spectra recorded on the samples treated with both procedures are reported.

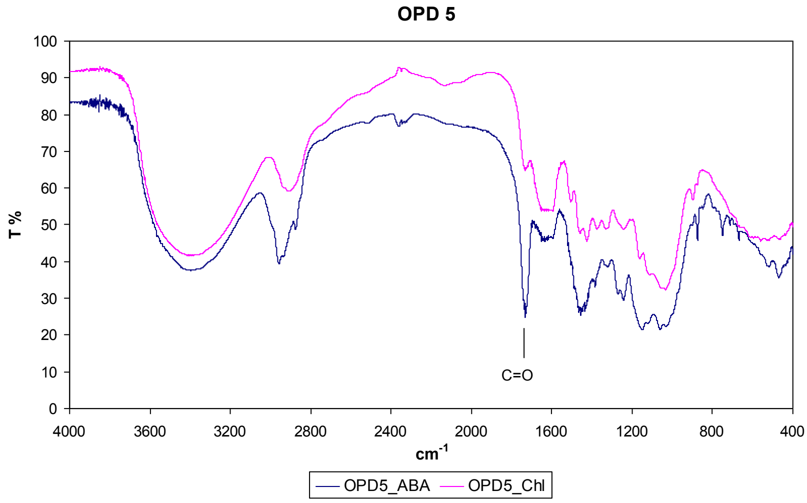

Fig. 3. FT-IR spectra of the OPD 5 samples: in blue after the ABA protocol; in pink after the chloroform-based protocol. The C=O stretching band is indicated.

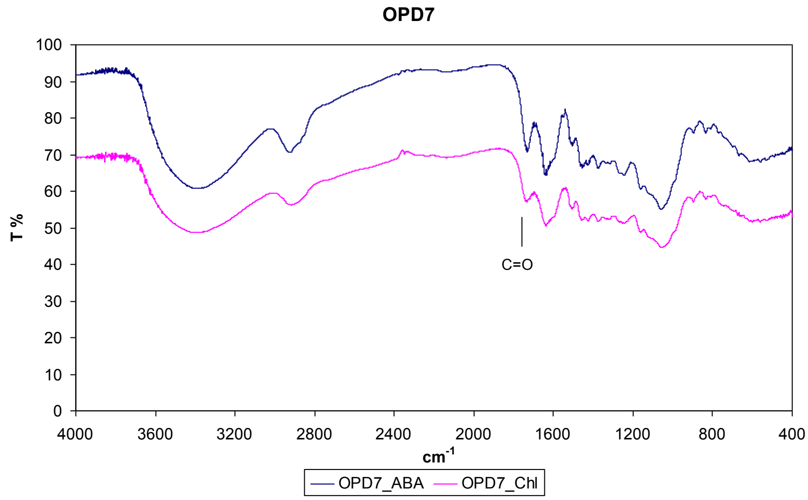

Fig. 4. FT-IR spectra of the OPD 7 samples: in blue after the ABA protocol; in pink after the chloroform-based protocol. The C=O stretching band is indicated

As we can notice in the FT-IR spectra, in both cases (OPD 5 and OPD 7) the peak at 1740 cm^{-1} [11], corresponding to the stretching bond of the ester groups and characteristic of Paraloid B72, is more intense in the samples treated only with the ABA standard protocol. This result confirms the presence of Paraloid B72 in the samples and it is in agreement with the radiocarbon measurements. On the contrary, the same peak at 1740 cm^{-1} is strongly suppressed in the spectra obtained from the samples treated with the new chloroform based pre-treatment, proving the removal of the resin and so the effectiveness of the new procedure.

5. Conclusions

In this paper the importance of the removal of synthetic resins from the object to be dated has been discussed. The effectiveness of the new chloroform-based procedure and so the real removal of synthetic resins during the different steps of the pre-treatment was checked using a complementary technique, i.e. FT-IR measurements.

The results of radiocarbon measurements performed on the picture frame of the painting by Ambrogio Lorenzetti have been useful for the work of the restorers as well. Indeed, these measurements have confirmed that the frame is not contemporary of Lorenzetti and cannot be considered a "true" and original part of the polyptyc, so that, according to the present restoration theory, the restorers have decided to exhibit the restored painting in the museum separated from the XVI century frame.

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