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FTIR spectroscopy as a support for radiocarbon dating: advantages and limitations to identify possible contaminations

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***Abstract* – One of the fundamental hypotheses the radiocarbon dating technique is based on is the fact that the sample to be dated has to be considered as a close system. However, when we would like to date a finding that has been restored, that hypothesis might be called into question. Any carbon-based material used for restoration has to be completely removed from the sample before the radiocarbon measurement, in order not to alter the result. In this framework, a careful diagnostics using an independent technique to either identify the possible contaminant or its complete removal after the sample preparation is of crucial importance. Considering its capability to discriminate organic compounds, FTIR spectroscopy can be considered as a good opportunity. Here we will discuss the application of this technique as a support of radiocarbon dating, showing its positive aspects and some limitations as well.**

I. INTRODUCTION

Contamination is a fundamental issue in radiocarbon dating. Since its "death", any sample to be dated is considered as a close system. This is essential to apply the radioactive decay law and univocally express the sample age as a function of the residual ^{14}C concentration (once the initial concentration and the ^{14}C mean life are known, of course) [1].

However, in the practice, we cannot neglect that, for all the time between the "death" and the measurement, there may be external sources of carbon contaminating a sample. This can happen in the case of an archaeological find, which has remained buried underneath the earth surface for years, and also in the case of an artefact that has been restored.

Actually, during restoration, organic materials, such as glues or resins, are typically used to, for example, consolidate a work of art [2]. All these materials have to be completely removed before the radiocarbon measurement. If this does not happen, they introduce some exogenous carbon, which alters the original ^{14}C concentration, thus changing the measured radiocarbon age.

Such a problem can be overcome thanks to careful preparation procedures that are capable of removing the possible contaminants [3]. It is evident that the more information we can have about the possible materials used in a past restoration, the more accurate those procedures can be. Of course, information can be achieved by talking with the restores or by looking in the archives. However, when this is not possible, the feasibility of applying an independent technique to identify the presence of exogenous organic compounds is very important. Such a possibility can be given by Fourier Transform Infrared (FTIR) spectroscopy, which has now become a very widespread method to analyse organic compounds, in the Cultural Heritage field too [4].

Here we present our experience in using FTIR as a diagnostic tool to support radiocarbon dating in case of samples that are suspected to have been restored. In particular, we investigated the case of dating wood and bone samples, that had been previously restored by applying Paraloid B72®, one of the most widespread products used in restoration [5,6].

II. CHARACTERISTCS OF PARALOID B72®

Paraloid B72, previously also known as Acryloid B72, is an acrylic resin: a copolymer of ethyl methacrylate (70%) and methyl acrylate (30%). It is sold in the form of transparent pellets to be dissolved in a solvent such as, for example, ethanol, acetone or butyl acetate. Once the solution is ready, Paraloid can be applied by spray or brush, or by directly soaking in it the find to be restored.

It has been widely used since 1960s as a glue or a consolidating and protective agent, even though, in some cases, it has been proved that it can damage the main physical and chemical properties of the "preserved" works. This is true especially in the case of frescoes [7]. However, in the case of wooden artworks or bones,

Paraloid is still used to, respectively, consolidate the support or stick together broken parts.

Since Paraloid is a synthetic product (i.e. derived from fossil fuels materials), we expect a radiocarbon concentration that is very low, basically of some pMC (percent of Modern Carbon). If this resin is not removed from a sample to be dated, it contributes to apparently age the sample itself.

In Figure 1, the FTIR spectrum acquired on Paraloid B72 (prepared from a solution of Paraloid pellets and acetone in a ratio of 10:90) is shown.

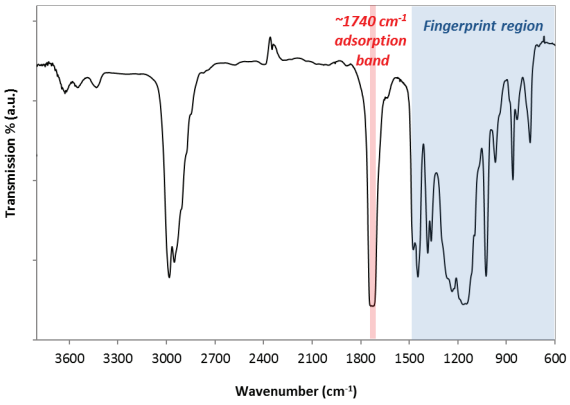

Fig. 1 FTIR spectrum of Paraloid B72. The sample was prepared by putting a drop of the Paraloid-acetone solution on a KBr plate.

In principle, the most characteristic bands pattern in a FTIR spectrum is represented by the so-called fingerprint region (about 1500-500 cm^{-1}), which is really peculiar of any organic compound. However, adsorption bands in this area can be strongly modified by the interference of other compounds in the same sample. This is actually what we expect in our application. In case we would like to use FTIR as a diagnostic tool before radiocarbon dating, we expect to measure samples that do not consist only in the pure resin, but in a mixture of Paraloid and a substrate, either wood or bone.

Thus, our proposal is to use another band as a reference for the presence of Paraloid: the band at about 1740 cm^{-1}, due to the C=O stretching bond of the ester group of monomeric units derived from methyl acrylate and methyl methacrylate, which Paraloid is composed of.

III. MATERIALS AND METHODS

A. *Wooden samples*

We prepared samples by cutting thin slices from the outer ring of a poplar tree fell in 2009. The expected radiocarbon concentration is thus the atmospheric concentration in 2009, clearly above 100 pMC [8]. One of the slices was not treated (this is the poplar sample used as reference); the others were "contaminated" by injecting a fixed volume of Paraloid (0.15, 0.30 and 0.50 ml). The samples were artificially aged in a climatic chamber (CO.FO.ME.GRA Solarbox3000e) to simulate the typical degradation of the applied Paraloid when exposed to natural lights and atmospheric agents.

B. *Bone samples*

Two bones, an ulna and an humerus collected from the archaeological site of Portico d'Ottavia in Rome, were chosen for this study. These bones had been restored using Paraloid as a glue. Three samples were collected from each of the bones: two of them from the break resin-glued (clearly expected to be contaminated) and the other from one of the bone extremes, far from the break (expected to be not contaminated and thus used as reference).

Fig. 2 The humerus bone chosen for this study: the green circle indicates the clean area where the sample used as reference was collected; the red circle indicates the restored area where the collected samples are expected to be contaminated by the applied Paraloid.

C. *^{14}C-AMS measurements*

Radiocarbon measurements were performed by Accelerator Mass Spectrometry (AMS) at the 3 MV tandem accelerator installed at INFN-LABEC in Florence [9].

Before the AMS measurement, samples were treated to remove possible contaminants (both natural and Paraloid-due) and to convert their carbon content to pure graphite.

Wood samples underwent the so-called ABA (Acid-Base-Acid) pre-treatment, which is characterized by a succession of baths in, alternatively, acidic and basic solutions, to remove especially carbonates and humic substances.

The other fractions of the wooden slices suspected to be contaminated by Paraloid were also treated according to a new procedure set-up at LABEC [3]. This procedure is based on the use of chloroform ($CHCl_3$). Samples are put in a close tube in a chloroform bath; up to four extractions are performed (every time the solvent is removed and changed). Afterwards, samples are dried

under a fume hood for a maximum of 48 hours and finally treated according to the ABA procedure, described above.

Bone samples were treated to achieve complete demineralization and to eventually extract collagen as gelatine. One of the two samples collected from the restored break in each of the studied bones were also treated in chloroform. In this case, the $CHCl_3$ treatment was applied on the bone powder, before the demineralization process.

After chemical pre-treatment, both wood and collagen samples were combusted through elemental analyser (Thermo Flash EA 1112) to extract carbon as gaseous CO_2. Finally, CO_2 was converted to graphite by reaction with hydrogen, in the presence of fine powdered iron as catalyst and at high temperature, about 600 °C [10]. This graphite constitutes the sample to be inserted into the accelerator source for the AMS measurement.

Samples prepared from NIST Oxalic Acid II (SRM 4990C, certified ^{14}C concentration 134.06 pMC) were used as primary standards; samples of IAEA C7 (certified ^{14}C concentration 49.53 pMC) were used as secondary standards, to check the accuracy of the measurement.

D. FTIR measurements

FTIR spectra were acquired both on wood and bone materials before and after any treatment. Spectra were also acquired on the liquid extracts collected during the chloroform-based chemical pre-treatment. These measurements were performed using a Shimadzu FTIR-8400S spectrometer with a resolution of 2.0 cm^{-1} and 16 scans per sample.

Wooden and collagen samples were prepared by mixing either wooden small chips or gelatine small fragments with KBr powder. The liquid extracts collected during the chloroform extractions were first dried in a rotary evaporator to let the solvent evaporating, and eventually the residues were deposited on KBr plates.

IV. EXPERIMENTAL RESULTS

A. Wooden samples

Figure 3 shows the comparison of the FTIR spectra acquired on the raw poplar sample (measured ^{14}C concentration 104.31±0.45 pMC) and on one of the Paraloid-contaminated sample (measured ^{14}C concentration in the fraction contaminated with 0.15 ml Paraloid 90.55±0.88 pMC).

The first thing that can be observed is that FTIR spectra are not so easy to read. This is a direct consequence of the difficulties to prepare the KBr pellets for the analysis. As mentioned above, pellets were prepared by cutting the samples in fragments as smallest as possible. The difficulty is represented by the fact that we are working with samples as small as 1 mg and thus we cannot use any typical tools to powder them (as e.g. usual wood grinders). On the contrary, we typically prepared our chips by scalpel. Thus, it is very difficult to obtain an homogeneous pellet when mixing with KBr in the mortar: it is highly probable to obtain a sample where the IR adsorption is not homogeneous all over the whole surface. In addition, it is probable to have a sample which is too thick so that the IR absorption is too much (as one can infer by looking at the not so enhanced fingerprint region in Figure 3).

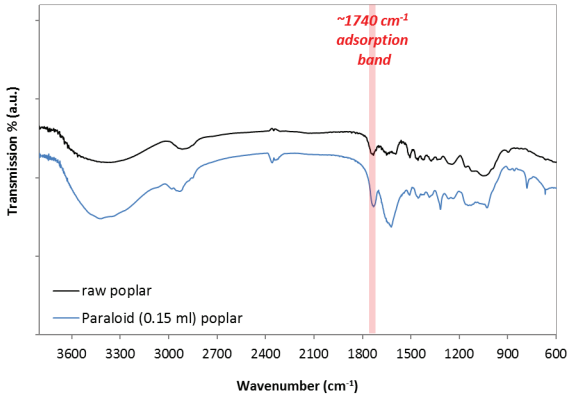

Fig. 3 FTIR spectra acquired on the raw poplar and the Paraloid-contaminated sample (0.15 ml of Paraloid added).

Another interesting thing to observe in Figure 3 is the presence of the band at about 1740 cm^{-1} in the raw poplar sample itself, even though it is characterized by a low intensity. Actually, this band can be due to wood itself [11]: this is just associated to the presence of ester groups like those forming when lignin is linked to carbohydrate compound and in particular with some hemicelluloses, or those due to fats and waxes, present in the wood extractive components. However, the comparison in Figure 3 shows that in the contaminated sample this band is more evident, suggesting the presence of an additional material containing esters, i.e. Paraloid.

A greater effect is also visible in the samples contaminated with 0.30 ml and 0.50 ml of Paraloid, as one can expect, even though a linear dependence of the band intensity with respect to the amount of added contaminant cannot be drawn.

However, FTIR spectra suggest that Paraloid is removed when samples are treated according to the $CHCl_3$-based procedure. For example, the ^{14}C concentration in the fraction contaminated with 0.15 ml of Paraloid and treated in chloroform has been measured as 103.27 ± 0.47 pMC.

The FTIR spectra acquired on the liquid extracts collected during the four extractions in chloroform are also interesting and can be read as a sort of negative proof of the radiocarbon analysis on wood pieces.

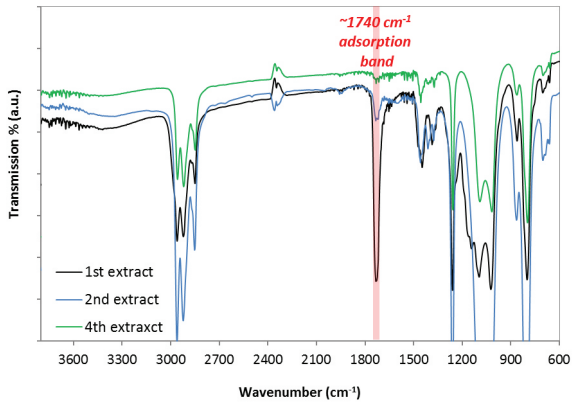

Fig. 4 FTIR spectra acquired on the liquid extracts collected after, respectively, the first, the second and the fourth extractions in $CHCl_3$ (wood sample contaminated with 0.30 ml of Paraloid). The apparently strange behaviour of the FTIR spectra in the fingerprint region is due to some silicone oils present in the syringes, which were used to collect the extracts and were actually dissolved by chloroform.

Figure 4 shows that most of the contamination is removed in the first extraction in chloroform. A very weak peak is also visible after the fourth extraction suggesting that a small contamination may still be present at the end of the procedure (a fifth extraction would have been necessary to check for this hypothesis). Nevertheless, the comparison of radiocarbon data is satisfying, as can be seen in Table 1. If a contamination is still present, it is however within the experimental uncertainty of the measured radiocarbon concentration.

Table 1. ^{14}C-AMS measurements on the wooden sample contaminated with 0.30 ml of Paraloid and treated using the simple ABA procedure (see the suffix ABA) and after the $CHCl_3$ extractions.

Sample	^{14}C concentration (pMC)
Raw poplar	104.31±0.45
0.30Paraloid-ABA	74.1±1.4
0.30Paraloid-1st extr.	102.83±0.54
0.30Paraloid-2nd extr.	102.84±0.37
0.30Paraloid-4th extr.	103.29±0.42

B. Bone samples

Figure 5 shows the FTIR spectra acquired on the collagen extracted from the ulna sample considered as reference and one of the Paraloid-contaminated ulna samples. The band at about 1740 cm-1 is not so visible in the contaminated sample, as, on the contrary, one might have expected. This can be explained by considering the strong interference of the high-intensity band at about 1650 cm^{-1} due to amide I, one of the characteristic collagen bands. Another possible explanation can be the non-homogeneous contamination in the analysed sample: the fraction collected for FTIR analysis is not the same fraction combusted and graphitised for the ^{14}C-AMS measurements.

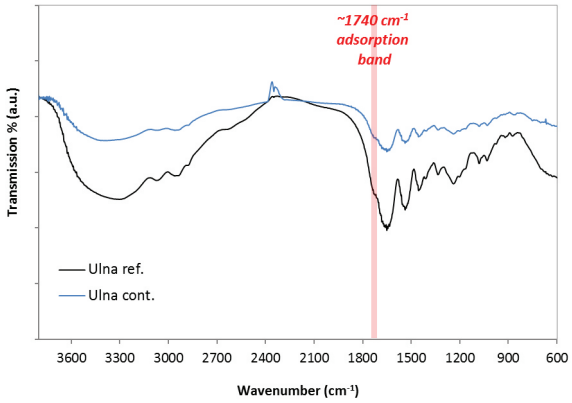

Fig. 5 FTIR spectra acquired on the collagen extracted from the ulna sample considered as reference and one of the Paraloid-contaminated ulna samples.

FTIR spectra on the liquid extracts basically confirm what already discussed in the case of wood samples: more than one extraction is needed to remove the contaminating Paraloid. A procedure based on four extractions is reasonable as the comparison of the radiocarbon data also supports (see Table 2).

Table 2. ^{14}C-AMS measurements on bone sample.

	Ulna	Humerus
Sample	^{14}C concentration (pMC)	^{14}C concentration (pMC)
Reference	87.60±0.45	88.25±0.40
Contaminated	56.55±0.44	82.95±0.54
Contaminated &$CHCl_3$-treated.	87.5±0.4	87.9±0.5

V. CONCLUSIONS

As discussed on the basis of the experimental results, the information we can get from FTIR spectra is basically only qualitative. This is essentially due to several factors: the possible presence of strong interfering bands (indeed, we are not analysing a pure resin but a resin on a substrate), the difficulty of preparing very homogeneous KBr pellets, due to typical small masses of treated samples, the non-homogeneous distribution of the

contamination in the samples themselves.

Nevertheless, there is also a positive aspect: our measurements clearly show that FTIR spectroscopy can indeed be used to verify whether the sample pre-treatment for radiocarbon has been successful.

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