COMPARATIVE DATA OBTAINED FROM DIFFERENT CHEMICAL PRETREATMENTS OF MODERN AND ANCIENT SAMPLES IN RADIOCARBON DATING STUDIES

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The complex activity of authentication of artworks is becoming increasingly important since the amount of forged works and artifacts circulating in the cultural heritage market is getting frighteningly high. In the following we describe the chemical pretreatment of a series of particular samples included in radiocarbon dating analysis at RoAMS laboratory in IFIN-HH, Bucharest, Romania. Painting canvas, leather, papyrus and clothing textiles materials were involved in authentication and archaeological studies. In the case of painting canvas, we have successfully correlated the information of elemental composition obtained via X-Ray Fluorescence (XRF) on the primers and pigments with the radiocarbon determined age of the vegetal fibers. On the same set of samples, the purification based on chloroform was compared with the purification results using the Soxhlet device and a sequence of acetone, hexane and ethanol as extracting solvents. The papyrus and leather samples, originally estimated to belong to the Roman era have proven to be recent artifacts, while one of the pieces of clothing textiles was correctly radiocarbon dated only after the complete removal of the poly(vinyl acetate) present on the sample as a restoration agent.

Keywords: radiocarbon dating of textiles, radiocarbon dating of canvas, artifact authentication

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1. Introduction

The greatest advantages of Accelerator Mass Spectrometry (AMS) radiocarbon dating over the traditional radiometric methods are the small sample size required for the analysis, the good precision and relatively short sample preparation and measurement time, thus making it the most widely used method nowadays for dating artifacts from various material, i.e. the Shroud of Turin [1], Dead Sea scrolls [2, 3] and Voynich manuscript. In order to obtain the amount of graphite required for an AMS measurement (usually 500 μg - 1 mg) the losses during different stages of chemical processing must be taken into account. In this regard, the initial sample mass should sometimes be considerably higher. Typical raw sample quantities required by AMS radiocarbon dating method range from the order of tens of milligrams for charcoals, up to 1-3 grams of bone when consider the bone collagen extraction. The mass losses in the chemical pretreatment process depends on the type of material, the representative fractions for radiocarbon dating and the percentage of contaminants present in the sample.

Sampling of the material involves the removal of a small amount from an area which is not a subsequent addition of that object and which does not include visible contaminants such as hair, soot, organic matter or synthetic substances such as resins, primers and paints. In the case where traces of restauration/consolidation substances are present in the sample, these must be totally removed since they might have an aging effect on the sample. The choice of the applied method for chemical pretreatment requires increased attention in order to obtain a good separation of the datable fraction and for obtaining a sufficient quantity of sample to be converted into solid graphite.

The year 2015 was the year of the international accreditation of RoAMS laboratory, which followed the commissioning during 2012 of the 1 MV AMS system [4, 5], built by High Voltage Engineering Europe (HVEE), The Netherlands. At RoAMS Laboratory we are currently dating organic materials such as bone collagen, charcoals, wood, vegetal remains, and inorganic materials such as water and carbonates [6]. Lately, there has been an increased need for dating of a series of new materials and in this regard several steps have been taken in order to identify the most appropriate physio-chemical treatments for separating the datable fraction as well as preserving the integrity of this fraction along the preparation process.

2. Sample types and description

In the RoAMS Laboratory organic materials such as bone collagen, charcoal, wood, vegetal remains, as well as inorganic carbonates and water samples are currently processed using the procedures described in **[6]**. The new sample materials we have analyzed within the present study are presented in Table 1**,** together with their provenience information and estimated calendar age.

Table 1

Analyzed Samples

Types	**RoAMS Code**	**Origin**	**Estimated Calendaristic Age**	**Additional information**
Canvas	298.60	“Modigliani” painting	1890-1920 AD	Part of an authentication process
	297.60	“Rembrandt” painting	1620-1669 AD	Part of an authentication process
Papyrus	256.58	Roman manuscript	1^{st} BC – 5^{th} AD centuries	Identification of forgery
Leather	257.58	Roman belt	1^{st} BC – 5^{th} AD centuries	Identification of forgery
Cloths	565.73	Mycenaean clothing textile from Greece	13^{th} century BC	Archaeological study
	625.73	Copt clothing fragment from Egypt	4^{th}-5^{th} centuries AD	Archaeological study

The canvas fragments from “Modigliani” and “Rembrandt” paintings were subject to an authentication process ordered by international art experts. The fragments were sampled by the beneficiary and sent to RoAMS laboratory for radiocarbon determinations. The papyrus and leather samples supposedly belonging to the Roman ages were subject to artefact forgery and were received under these circumstances.

The first of the clothing textile sample came from an excavation taken in 1985 within an archaeological site of Mycenaean origin, dating back to the 13th century BC. The sample was held in improper conditions until 2009, being found in direct contact with the soil and under severe degradation. Only a very small quantity of this material was compatible with radiocarbon dating. The second clothing textile was of Coptic origins. The piece of clothing was found after an excavation taken somewhere in Egypt during the 19th century and stored in a museum until the end of the ‘80s, washed with natural soap in the ‘90s and restored and consolidated during the ‘70s. The estimated age was 4-5th century AD.

3. Chemical pretreatment of samples

For organic materials such as charcoal, plant fibers, textiles, paper, parchment, standard acid-base-acid (ABA) chemical pretreatment is usually used [7]. This pretreatment of the organic materials starts with acid treatment, followed by a treatment with a basic solution and ends-up again with acid treatment, using intermediate washes after each step until neutral pH of the rinse water is reached. The first acid solution is planned to remove the inorganic carbonates deposited by the underground waters, the alkali solution is used to remove the humic and fulvic acids found in the soil, while the insoluble humin fraction is removed by the water washings. The last acid treatment is aiming to stop any atmospheric CO_2 sorption into the samples. At the end, the samples are dried in the vacuum oven. For the samples of the present study, before the standard ABA pretreatment protocol, specific supplementary purifying treatments were used. The application of this extra treatments is justified in the following.

3.1 Pretreatment of the painting canvas samples

Preservation conditions, temperature, humidity and their fluctuations can alter the canvas-like textiles. To the intrinsic degradation of the material during the time, there is an added influence of the chemical compounds often found on such materials. For this reason, adapted procedures for separating the pure vegetal fraction are needed in order to obtain a representative radiocarbon age.

In the pretreatment of the artwork samples treated with primers, substrates and painted afterwards, the application of the ABA pretreatment is not enough and additional purification with a sequence of solvents is often required. This process may involve a Soxhlet device where the samples washing is performed in solvents which are generally characterized by reduced evaporation times and whose succession is set in such a manner that the influence of the previous one is totally removed [8]. In the case of the present canvas samples we have used acetone, hexane and ethanol as in [9]. For comparison, the same canvas samples underwent a simpler chloroform ($CHCl_3$) treatment protocol as a less time consuming substitute.

Fig.1. RoAMS 298.60 „Modigliani" sample, at the beginning (left), after Soxhlet treatment (center) and ABA treatment (right). Brown primer layer covering the vegetal fiber of the canvas is observed at the beginning of the treatment while at the end the vegetal fibers are completely cleaned.

The canvas samples observed under the microscope before processing showed at least one support layer. In Fig. 1 and Fig. 2 are presented the

Modigliani (RoAMS 298.60) and Rembrandt (RoAMS 297.60) studied samples. These support layers are likely to be source of carbon containing different isotopic ratio than the one in the canvas fiber. Often these substances are of a synthetic origin, so they do not contain ^{14}C and thus they lead to an “aging” effect. For this reason, the canvas support material (primers, resins, etc.) must be completely removed prior to the graphitization and AMS measurement. Due to the ability of the resins and primers to penetrate the materials, only a simple scrubbing treatment with a scalpel is not enough, while the laser ablation removal would be considered too invasive. Therefore, radiocarbon dating laboratories prefer the chemical treatment involving the use of solvents.

Soxhlet extraction: The sample were treated with solvents using the Soxhlet device and N-hexane (heated at the boiling point of 68 °C), acetone (heated at the boiling point of 56 °C), ethanol (heated at the boiling point of 78 °C) at, each step of 60 minutes. The samples were washed with MilliQ ultrapure water and in the end dried in the vacuum oven for 4 hours at 60 °C.

Chloroform extraction: The samples were immersed in chloroform and placed on a magnetic stirrer for 8 hours while changing the chloroform at every 2 hours to increase the extraction rate between the chloroform and material. This was followed by washing with MilliQ ultrapure water and again washed with a mix of ultrapure water: acetone (1:1) in the ultrasonic bath in order to remove unwanted organic contaminants such as adhesives **[**10**]**. The sample was then washed again with ultrapure water and dried in the vacuum oven for 4 hours.

Fig. 2. RoAMS 297.60 („Rembrandt”) sample at various stages of the pretreatment: beginning of the chemical treatment (left); after Soxhlet treatment (center); pure canvas fiber obtained at the end, after ABA treatment (right).

At the end of both protocols, the canvas samples were treated using the ABA treatment according to the following procedure: 0.5 M HCl at 60 °C for 30 minutes; 0.2 M NaOH at 60 °C for 30 minutes; 0.5 M HCl at 60 °C for 1 hour and MilliQ ultrapure water washes after each step. In the end the samples were dried in the vacuum oven for 4 hours.

3.2 Pretreatment of textiles samples from clothing

Depending on their nature, origin and degree of preservation, these types of samples may contain contaminants such as pigments, plant or animal oils, waxes, even soot, which may lead to an erroneous dating. In textiles pretreatment, the main purpose is to isolate the original protein fraction and to completely remove all other substances which were added at the time of the manufacture or later through restoration or preservation.

The first sample on which we focused our attention was a small quantity of Mycenaean textile (RoAMS 563.73), consisting of a carbonized material. This was found under severe degradation conditions as seen in Fig. 3. For dating this sample, we intended to extract the fibers that were still unbroken after partial combustion and the influence of the improper conservation conditions. Since almost all the sample was converted into ash, and a consistent amount of calcium carbonate (limestone) was also present, it was very difficult to choose and physically separate the sample fraction to be subject of a subsequent chemical treatment. The separation was carefully done using an optical microscope.

Knowing the fact that the sample did not suffered a restoration process and did not showed any impregnated synthetic substances, we proceeded to the faster chloroform treatment followed by the standard ABA treatment using lower concentration of hydrochloric acid (0.2M) due to the fragility of the sample. The chloroform treatment consisted in washing with chloroform for 1h, washing with MilliQ ultrapure water and drying in the vacuum oven for 1hour at 60°C.

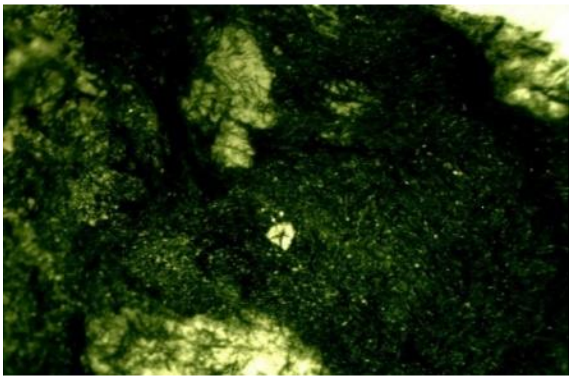

Fig. 3. Mycenaean origin sample before chemical pretreatment; it was found in severe degradation conditions. The presence of $CaCO_3$ in the sample can also be observed.

For the second textile sample (RoAMS 625.73), we highlighted the need for solvents purification of the samples impregnated with adhesives and synthetic resins using two pretreatments: (1) a simple ABA pretreatment and (2) a treatment involving sample washing with a solution of distilled water and acetone (1:1) in the ultrasonic bath [10], in order to remove the poly(vinyl acetate), followed by the ABA process. Between the acetone treatment and ABA sequence, the sample was washed and dried in the vacuum oven for 4 hours at 60 °C.

1. For the simple ABA pretreatment, the following steps were applied: 0.5 M HCl for 30 minutes at 60 °C; 0.2 M NaOH for 30 minutes at 60 °C; 0.2 M HCl for 30 minutes at 60 °C; drying in the vacuum oven for 1 hour at 60 °C.

2. For the acetone solution + ABA pretreatment, we performed the following steps: acetone treatment: ultrapure water (1:1) for 1 hour at 35 °C; washing with ultrapure water and continued with the following chemical treatment: 0.5 M HCl for 30 minutes at 60 °C; 0.2 M NaOH for 30 minutes at 60 °C; 0.2 M HCl for 30 minutes at 60 °C; washing with ultrapure water and drying in the vacuum oven for 4 hours at 60 °C.

3.3 Pretreatment of codex/papyrus and leather samples

For the pretreatment of the papyrus and leather samples, the Soxhlet purification was used (hexane, acetone, ethanol) after which the leather sample lost a certain gloss given by the substances used for the surface treatment. In the end the ABA cleaning method was used.

3.4 Graphitization

Following the chemical pretreatment, all the samples were subject to the graphitization process, which was handled by the Automated Graphitization Equipment (AGE) III installation (IonPlus, Switzerland) [11] coupled to an elemental analyzer (EA), (Elementar, Germany), where samples were combusted at 900 °C. The resulting carbon dioxide was further converted to graphite in hydrogen atmosphere using an iron powder catalyst (Alfa Aesar - 325 mesh iron, 99% purity).

4. Results and discussion

The results obtained after are summarized in Table 2. The concentration of carbon and nitrogen, as well as the C/N ratio are automatically recorded after the combustion in the elemental analyzer. $\delta^{13}C$ parameter is measured within the AMS system and represents the isotopic fraction between ^{13}C and ^{12}C normalized to the international reference material Vienna Pee-Dee Belemnite (VPDB). This quantity is used for radiocarbon age corrections. The radiocarbon ages are reported as BP years (years before present, considered as 1950 AD). Negative radiocarbon ages represent the enrichment in the radiocarbon concentration started with the year 1950 AD, the period when the first nuclear tests in the atmosphere began [12].

Table 2.

Experimental results obtained on the analyzed samples for different pretreatment methods

Sample/ RoAMS code	Special pre-treatment	C (%)	N (%)	C/N (mass ratio)	$\delta^{13}C$	Age ^{14}C BP (1σ)
Modigliani 298.60	Soxhlet	47.97	0.07	685.28	-25.8	115 (29)
	Chloroform	47.03	0.07	650.34	-24.5	121 (28)
Rembrandt 297.60	Soxhlet	47.43	0.02	1936.56	-25.4	-1726 (29)
	Chloroform	48.85	0.02	2263.76	-23.3	-1690 (25)
Codice 256.58	Soxhlet ABA soft	47.78	0.04	1196.10	-14.3	-214 (25)
Belt 257.58	Soxhlet ABA	45.16	11.98	3.77	-19.1	-339 (26)
Mycenaean Fragment 565.73	Chloroform ABA soft	59.57	5.22	11.41	-0.3	3090 (35)
Fragment from Egyptian museum 625.73	ABA	58.01	0.06	1053.50	-29.9	3169 (30)
	Acetone+ABA	38.77	0.15	256.5353	-30.3	1527 (41)

4.1 Painting canvas

4.1.1 XRF analysis

In order to establish the authenticity of a painting, often both the canvas and the pigments have to be analyzed. Counterfeiters often choose to use old pigments receipts and different aging techniques. Since the appearance of the radiocarbon dating by AMS method, which determines the age of the canvas with great precision, falsifiers resort to paint a canvas of an unknown painter contemporary with the original artist after removing the pigments [13].

Thus, to give a proof of authentication, small pigment fragments of the studied canvas were subject to a XRF analysis using the X-MET 3000TX spectrometer, produced by Oxford Instruments, England. The obtained spectrum presented in Fig. 4 for the “Modigliani” painting shows the three X lines corresponding to lead (Pb), while for the "Rembrandt" the spectrum shows the titanium (Ti) X lines.

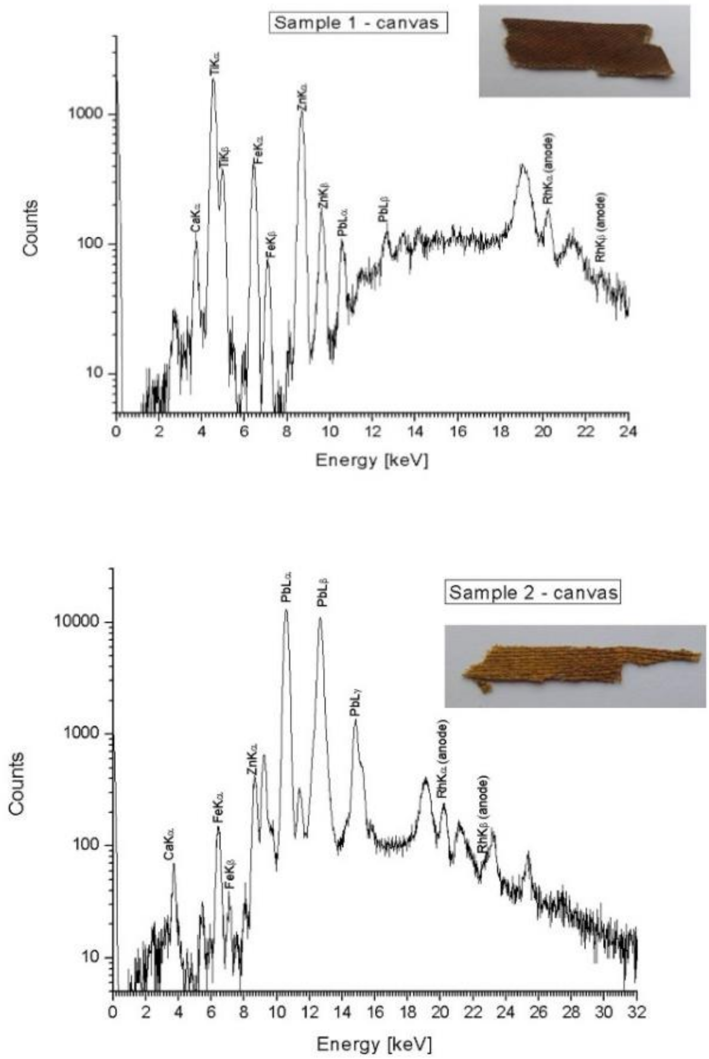

Fig. 4. XRF spectra for the two studied canvas samples: "Rembrandt" sample (left),"Modigliani" sample (right).In the "Rembrandt" sample the presence of titanium dioxide was observed, while for the "Modigliani" sample we observed the presence of the white lead.

These X lines suggest the presence of *lead white* ($2PbCO_3{\cdot}Pb(OH)_2$) in the „Modigliani" painting and the titanium dioxide (TiO_2) in the "Rembrandt". Both compounds are white colored and were easily visible. Considering that the *lead white* has been used since antiquity in the art of painting, being the main white pigment in the European oil painting [14], it may be suggested that the painting might have been from the time period of Amadeo Clemente Modigliani (1884-1920). On the other hand, for the "Rembrandt" painting we can certainly say that it was not realized during his lifetime (1606-1669), since the use of the titanium dioxide pigment started only after 1916 [14].

4.1.2 Radiocarbon dating

For the radiocarbon dating we have used the chemical pretreatment protocols described in Section 3. Observing the carbon and nitrogen composition from Table 2, one can say that the "Rembrandt" sample contains a very small quantity of nitrogen, suggesting the canvas used in this case might of natural vegetal origin, this fact being also confirmed by the very large C/N ratio. In the case of the "Modigliani" sample, the C/N ratio shows that the canvas is of the natural type [9]. $\delta^{13}C$ value for both, the "Modigliani" and the "Rembrandt" samples suggests that the canvas of the two paintings contains natural fibers [15].

The radiocarbon ages obtained after the AMS analysis in case of the "Modigliani" sample treated with Soxhlet and chloroform are (115±29) BP and (121±26) BP, respectively. The calibration of these ages, using the IntCal13 [16] curve of the OxCal 4.3 online program (https://c14.arch.ox.ac.uk/oxcal.html), presented in Fig. 5a**,** leads to the conclusion that the age of the canvas of this painting is between 1680–1940 with a probability of 95.4% for both types of treatments. The obtained age shows a canvas contemporary with the painter lifetime period (Amedeo Clemente Modigliani: 1884 – 1920). Unfortunately, the period between 1700-1950 AD known as "Stradivarius gap", has been remarked in rapid excursions of 14C levels in the atmosphere due to large quantities of fossil fuels burnings. In this regard, the radiocarbon age calibration largely spreads the calendar ages on this large intervals, Fig. 5a**.**

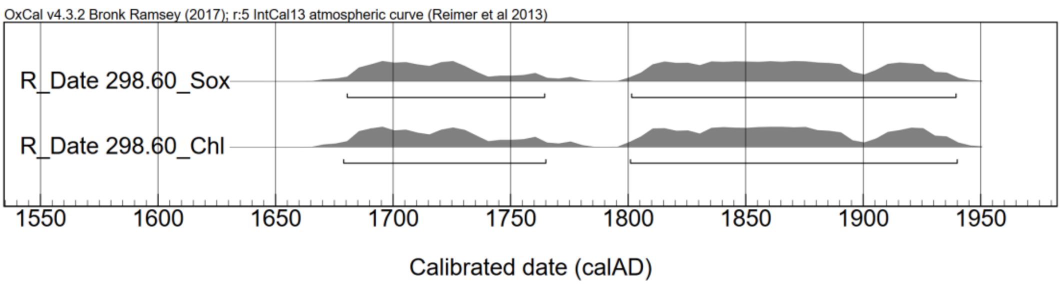

Fig. 5a. Calibration of radiocarbon ages for the „Modigliani" sample, which resulted an age in the interval [1680-1764, 1801-1940 AD]. The sample is contemporary with Modigliani lifetime period (1884-1920 AD).

In case of “Rembrandt” sample, the obtained ages for the two types of treatment, with chloroform and Soxhlet, are (-1690±25) BP and (-1726±29) BP, respectively. The calibration of these ages using the Bomb13 NH1 [12] curve in Oxcal 4.3 online, as seen in Fig. 5b shows with a probability of 95.4% that for both treatments, the age of the canvas of this painting is between (1959–1983), much more recent than the lifetime of the great painter (Rembrandt Harmenszoon van Rijn 1606–1669).

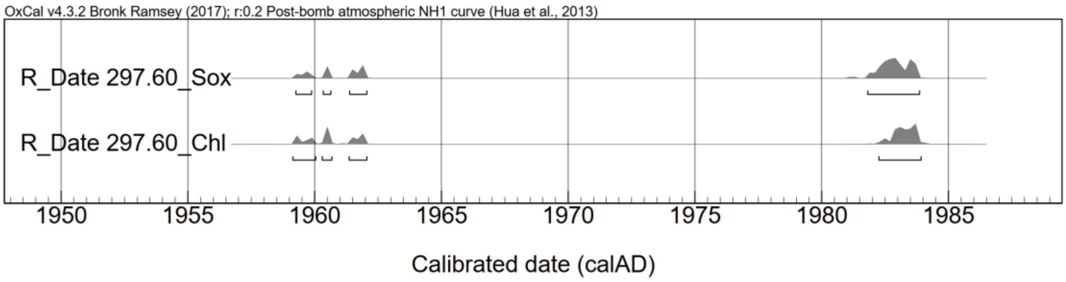

Fig. 5b. Calibration of radiocarbon ages for the „Rembrandt” sample. This sample proved to be a 20th century sample, probably a copy or a fake artwork.

In case of “Rembrandt” sample, the obtained ages for the two types of treatment, with chloroform and Soxhlet, are (-1690±25) BP and (-1726±29) BP, respectively. The calibration of these ages using the Bomb13 NH1 [12] curve in Oxcal 4.3 online, as seen in Fig. 5b shows with a probability of 95.4% that for both treatments, the age of the canvas of this painting is between (1959–1983), much more recent than the lifetime of the great painter (Rembrandt Harmenszoon van Rijn 1606–1669).

Contrary to the “Modigliani” painting which can be presumed to be an old artwork, the “Rembrandt” appears to be a copy or a fake, being painted on a contemporary canvas by using recent discovered pigments.

Since the obtained radiocarbon ages for two canvases, in both cases, chloroform pretreatment and Soxhlet solvent pretreatment, are almost identical, it suggests that regardless of the used protocol, no old or contemporary carbon was added throughout the chemical pretreatments and the removal of the synthetic substances was successfully done. This is also proved by the close carbon values and C/N ratios for both pretreatments. Further, it can be concluded that the use of the purification with chloroform method can be used as an alternative method for the more laborious Soxhlet (hexane-acetone-ethanol) in cases of white lead and titanium dioxide removal.

4.2 Textile from clothing

The AMS analysis of the Mycenaean sample (RoAMS 565.73) showed a radiocarbon age of 3090±35 years BP. Following the calibration of this value on the IntCal13 curve, showed in Fig. 6**,** the obtained calendar age with a probability of 95.4% was ranging between 1431 and 1264 BC, which confirms the estimated age of the beneficiary. This fact proves that although the sample was much degraded, the chemical treatment was fit for the sample condition.

For the second textile piece (RoAMS 625.73), treated with the simple ABA pretreatment, the radiocarbon age of 3169±30 years BP was obtained, which by calibration on the IntCal13 curve [16] resulted a calendar age between 1504-1396 BC, far older than the estimated age of 4^{th} – 5^{th} century AD. For the same sample treated supplementary with acetone, a radiocarbon age of 1525±41 years BP was obtained, leading to calendar age ranging within 424-611 AD (95.4%) after calibration on the IntCal13 curve. This last age corresponds to the estimation of the beneficiary concluding the fact that acetone treatment was effective in removing the poly(vinyl acetate) from the textile fibers, as already proved in the case of the wool [17].

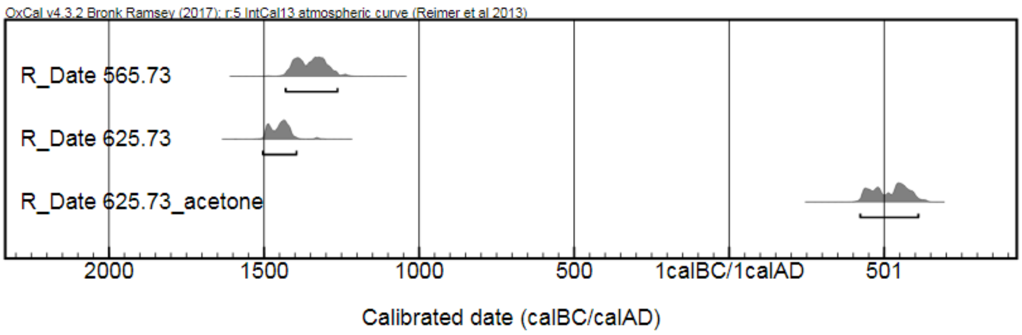

Fig. 6. Calibration results for Mycenaean (565.73) sample and Coptic sample (625.73) pretreated twice via simple ABA and ABA + acetone. The remove of the poly(vinyl acetate) leaded to a calibrated age shift of approximate 2000 years.

4.3 Codex and roman leather belt

The result of the carbon dating proves the recent origin of these samples. For the papyrus sample, the uncalibrated radiocarbon age was -214 years BP, while after calibration the calendar age proved to be between 1955 and 1956. In the case of the leather sample, the uncalibrated age of -339 years BP led to a calibrated calendar age between 1956-1957 with a probability of 41.2% and also a probability of 54.2% to an age included within 2007-2009. Both calendar ages were associated to the 95.4% (2σ) confidence interval. Due to the negative radiocarbon ages, for both samples the Bomb13 NH1 calibration curve was used.

C/N and $\delta^{13}C$ values obtained for the codex are typical for plant parchment (papyrus) [15] and those for the leather belt specific for the animal collagen [18], this suggesting that the two samples suffered a proper pretreatment adapted to their fragility and contamination degree.

5. Conclusions

The chemical pretreatments of the canvas, leather, papyrus and textiles samples, through material-specific procedures adapted to the sample fragility and degree of contamination, provided enough carbon (*graphite*) for AMS analysis. The use of the Soxhlet extraction as well as the simple chloroform extraction in the case of the canvas dating showed the possibility of substituting the Soxhlet method by the chloroform one for the white lead and titanium dioxide primers. Acetone has proven to be very effective in completely removing the poly(vinyl acetate) from the natural fabrics.

Synthetic substances were completely removed from the papyrus and leather samples. In all these cases the AMS measurements of the radiocarbon content were performed under the best conditions, leading to essential information concerning the origin and also the nature of the studied samples.

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