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Cyrielle Messenger, Lucile Beck, Laurence de Viguerie, Maguy Jaber. Thermal analysis of carbonate pigments and linseed oil to optimize CO₂ extraction for radiocarbon dating of lead white paintings. *Microchemical Journal*, 2020, 154, pp.104637. 10.1016/j.microc.2020.104637. hal-02969265

HAL Id: hal-02969265

<https://hal.science/hal-02969265v1>

Submitted on 8 Jan 2021

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Thermal analysis of carbonate pigments and linseed oil to optimize CO₂ extraction for radiocarbon dating of lead white paintings

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Abstract

Lead white was a white pigment extensively used in paintings from Antiquity until the beginning of the 20th century. It is composed of hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) and cerussite (PbCO_3). Historical recipes report metallic lead, vinegar and horse manure as ingredients to produce the two lead carbonates. The incorporation of organic CO₂ carrying ¹⁴C representative of the time of manufacture of lead white allows radiocarbon dating of this pigment. One possible protocol for lead white paint preparation for dating is based on the extraction of carbon from lead carbonates by thermal decomposition.

Since lead white paints are mixed with a binder and other pigments, a thermogravimetric study was implemented to study the extraction of each component. The measurements were carried out on samples of modern paints prepared with lead white (lead carbonate), Meudon white (calcium carbonate) and linseed oil.

The results show that it is possible to separate the carbon of interest (carrying the ¹⁴C signature: lead white and linseed oil) from the dead carbon coming from geological carbonates (containing no radiocarbon: Meudon white) by heating the paint sample at 400°C. This study provides a better understanding of the thermal behavior of these three paint constituents and confirms the validity of the thermal protocol for the preparation of lead white paints for radiocarbon dating.

Keywords: thermogravimetry, lead white, calcite, linseed oil, radiocarbon dating

1. Introduction

Lead white is the only inorganic pigment used in cosmetics and paints that can now be dated by the radiocarbon method [1, 2, 3]. Indeed, most of the historical recipes for the synthesis of lead white report vinegar and horse manure as ingredients, thus providing the organic carbon necessary for the dating of this pigment. Two lead carbonates are produced by this process, hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) and cerussite (PbCO_3), in different proportions depending on the synthesis conditions [4]. In order to date this pigment, our laboratory has developed an experimental protocol for extracting carbon from lead carbonates based on the thermal decomposition of the components [3, 5, 6]. This protocol has been successfully tested on Greek and Egyptian cosmetics [1] and we aim to extend it to the more complex case of paintings.

Lead white was used to paint stelae in Antiquity and works of art and was also used as house-paint until the very beginning of the 20th century. Various grades of lead white were produced [7]. Painters bought it pure or mixed with an extender, in different proportions [8, 9, 10]. Painting manuals from different periods provide information on the manufacture, use and marketing of lead white. The adulteration of lead white by the addition of another white had been known since the end of the 16th century [7, 8, 9]. In the 17th century, T. de Mayerne (1573-1655) defined common ceruse as a mixture of “a portion of chalk and a portion of lead white” [7]. In the 18th-19th century, J-N. Paillot de Montabert in *Traité complet de la peinture* [8] gave details about the quantities of each compound, quoting Watin’s (1728-?) *L’Art du Peintre, Doreur, Vernisseur* published in Paris in 1772: “Ceruse” says Watin, “is lead white crushed with chalk or marl in equal proportions or in the proportion of ten to sixteen; that is to say, ten ounces of marl are incorporated into six ounces of lead white.” Perego in the *Dictionnaire des matériaux du peintre* [10], reports the addition of 20 % to 50 % of chalk to lead white over different historical periods. Different qualities of lead white were sold to painters under different names and it is difficult to predict the mixture used by painters as they could create their own recipe according to the desired shade and optical and rheological properties [11].

White paints can thus be constituted of a mixture of lead and calcium carbonates in a binder which, depending on the period and the technique, may be of animal, plant or synthetic origin. Some of these materials contain carbon derived from organic matter carrying ^{14}C contemporaneous of the time of their manufacture, while others come from geological sources depleted in ^{14}C . These geological materials must be eliminated in order to obtain accurate paint radiocarbon dating.

This study aimed to determine the heating temperature to be applied to prepare lead white based samples for radiocarbon dating. In order to assess the selectivity of our experimental protocol based on thermal decomposition for extracting carbon from lead carbonate [3], thermogravimetric analysis on modern lead white paints was conducted. This study focuses on the mixing of lead white with its main extender, geological calcium carbonate, and its main binder, linseed oil. The thermogravimetric profiles of linseed oil and lead white paint with linseed oil have already been studied by several authors [12,13,14] to characterize binding media in old paintings, to understand the oil hardening process and the effect of lead white on the ageing of the oil binder. Some studies have also been carried out on mortar and calcite structures [15, 16]. Thus, although thermogravimetry is used for cultural heritage applications, to our knowledge, more complex paints composed of mixtures of lead white, calcium carbonate and linseed oil have not as yet been investigated.

2. Materials and methods

2.1. Paint sample materials

Paint samples were made from modern commercial materials produced according to ancient recipes or known to have been used in the past. Lead white, Meudon white and linseed oil were purchased from Master Pigments (USA), Laverdure (France) and Winsor & Newton (UK), respectively. According to the supplier, the lead white was synthesized from lead and CO₂ produced by the activation of yeast. Meudon white is the name of the pigment produced from geological calcium carbonate extracted from the calcareous basin of Meudon, in the southern part of the Parisian basin. These samples were previously characterized by Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) [3, 11]. Lead white pigment contains mainly cerussite (PbCO₃) and Meudon white is made from naturally occurring calcium carbonate (CaCO₃). The granulometry of the two powders was 0-10 µm for lead white and 0-20 µm for Meudon white.

The paints were made in accordance with the respective oil absorption value of lead white and Meudon white, i.e. the minimum amount of binder to be used with the pigment powder to form a paint. For lead white, between 8 to 11 % of linseed oil is mixed with 89 % to 92 % of pigment [17, 18]. For Meudon white, it is necessary to use 13 % to 36 % of binder for 64 % and 87 % of pigment [10]. Paints were then spread with an 30 µm applicator "Erichsen" on a glass slide. The samples were dried open to the air at room temperature for 2 months.

Table 1 summarizes the proportions of pigments and binder in the samples prepared in the laboratory. The amounts of each component were based on historical recipes. For one sample (LW + MW (2)), the amount of Meudon white was overestimated to better study its effect. All samples presented in the table 1 were analyzed by thermogravimetry except sample LW + MW (3).

Table 1: Mass percentages of lead white, Meudon white and linseed oil for each sample

Sample label	Sample description	% wt Lead White	% wt Meudon White	% wt Linseed Oil
O	Pure dried linseed oil			100
LW	Pure lead white	100		
MW	Pure Meudon white (calcite)		100	
LW + MW (1)	Mixture of lead white and Meudon white	50	50	
LW + MW (2)	Mixture of lead white and Meudon white	20	80	
LW + MW (3)	Mixture of lead white and Meudon white	70	30	
LW + O	Paint with lead white	90		10
MW + O	Paint with Meudon white		80	20
LW + MW + O	Paint with lead white and Meudon white	45	45	10

2.2. Implementation of the thermogravimetric study

The thermogravimetric study was carried out using an SDT Q600 V20.9 Build 20 TA device. Around 10 mg of paint were introduced in an alumina crucible. Each measurement was carried out over a temperature range between 20°C and 1000°C in a nitrogen atmosphere. The acquisition ramp of the measurements was 5°C/minute to allow differentiation of each decomposition step. The relative uncertainty on weight measurements is about 5 %.

2.3. Carbon extraction protocol for radiocarbon dating of lead white paint samples

Between 20 and 30 mg of mixture of pigment or lead white based paint were introduced in a quartz tube and were heated at 400°C on a dedicated CO₂ collection line under vacuum. This temperature was determined from the thermal analysis results (see Section 3). The extracted CO₂ was trapped using a liquid nitrogen trap (−196°C). The CO₂ pressure was measured with a pressure gauge and then converted into a mass of carbon.

3. Results and discussion

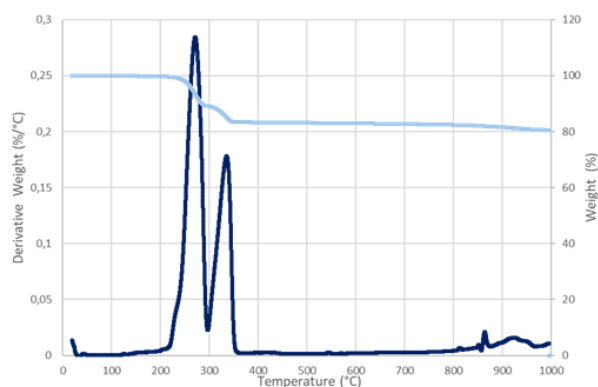
3.1. Thermogravimetric study

3.1.1. Pigments without binder

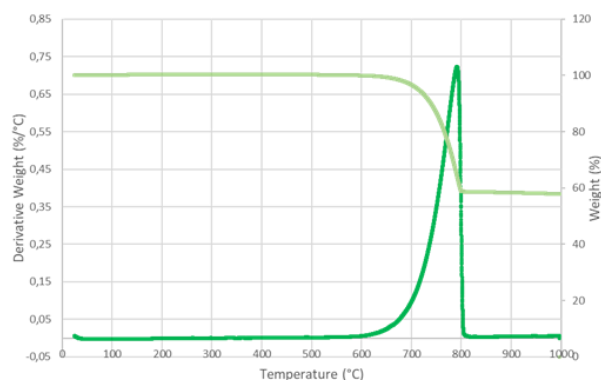
The thermogravimetric reference profiles of lead white (LW) and Meudon White (MW) are presented in Figures 1a and 1b. The lead white differential thermogram (DTG) is characterized by a double decomposition peak in the 200-350°C temperature range and other events in the 800-1000°C temperature range: the first peaks at around 271 °C and 336 °C correspond to CO₂ loss. The percentage of weight loss (16.7 %) is in agreement with the theoretical percentage of CO₂ in PbCO₃ (16.5 %). Therefore, at 400 °C, cerussite is fully decomposed into CO₂ and PbO and the total amount of carbon present in the sample is thus collected. Above 800 °C, the lead oxide residue melts [5,6]. The thermogravimetric profile of Meudon white indicates a single decomposition peak from 550 °C to 800°C. The weight loss is 41.4 %, indicating that this peak corresponds to the total loss of CO₂ present in the sample (44%). At 800 °C, Meudon white is fully decomposed into CO₂ and CaO [5].

When lead white is mixed with Meudon white in different proportions (LW+MW(1) and LW+MW(2)) and without a binder, the thermogravimetric profiles are the result of the two carbonate contributions (Figure 1c). No change in temperature decomposition is observed for lead white. Calcium carbonates decompose from 550°C but a shift in temperature as a function of CaCO₃ content is noticed. This shift can be due to the sample size effect as also observed by Gallagher et al. [19]. Gallagher et al. demonstrated that, for a given acquisition ramp temperature, the decomposition of calcium carbonates varies according to the sample mass. However, due to the large gap between the decomposition temperatures of the two carbonates, CO₂ release from lead white and Meudon white can be easily separated thermally.

a) Lead white



b) Meudon white



c) Mixtures of lead white and Meudon white

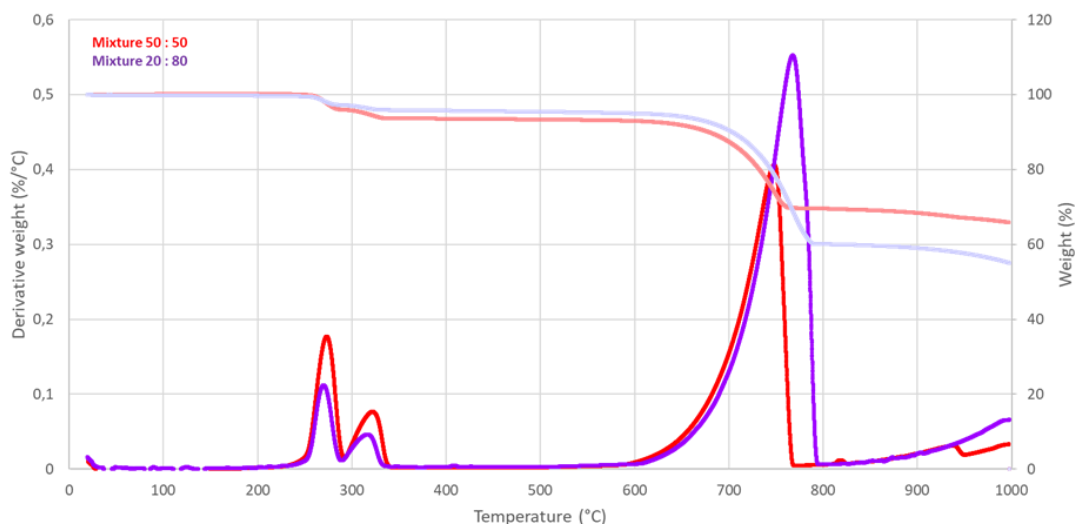


Figure 1: Thermogravimetric profiles in weight loss and their derivatives (DTG) of: a) lead white (LW), b) Meudon white (MW) and c) mixtures of lead white and Meudon white without binder in different mass proportions: in red, 50:50 (LW+MW(1)), in purple, 20:80 (LW+MW(2)).

3.1.2 Linseed oil and pigments with binder

Linseed oil thermogravimetric profiles are presented in Figure 2. Linseed oil begins to decompose slowly from 100°C and then sharply from 300°C to 550°C. The linseed oil weight loss corresponds to dehydration and decomposition [14].

Linseed oil was then mixed with lead white (LW+O) or with Meudon white (MW+O) to produce white paints. Thermogravimetric analyses are presented in Figures 2 and 3, respectively. In comparison with pure lead white, an increase is observed in the weight loss indicating that the decomposition of lead white is accompanied by the decomposition of a small proportion of the linseed oil (Figure 2a).

The thermogravimetric profile of LW+O (Figure 2b) can be interpreted thanks to previous studies on lead white paints: according to Bonaduce et al. [13,14], the peak at 230 °C corresponds to free fatty

acids of oil and the shoulder at 350 °C corresponds to carboxylates. The small peak at 420 °C can be ascribed to degradation compounds of linseed oil (tripalmitines and dipalmitines) or to the decomposition of lead white soaps (lead palmitate). In addition, the two peaks at 271 °C and 336 °C, corresponding to CO₂ loss in the lead white thermograms seems to be displaced to 315 °C and ca. 350 °C, probably due to interactions with oil. The intense peak at 315 °C was barely visible in Bonaduce et al., partly hidden in the 250 – 400 °C broad massif. This discrepancy can be explained by the ageing of the samples: the sample analyzed by Bonaduce et al. was 11 years old, whereas our experimentation is based on a sample dried for 2 months. After drying and ageing, interactions with oil and formation of lead soaps affect the thermal decomposition behavior of the paint but should not modify the total carbon extraction yield as carbon remains in the paint layer.

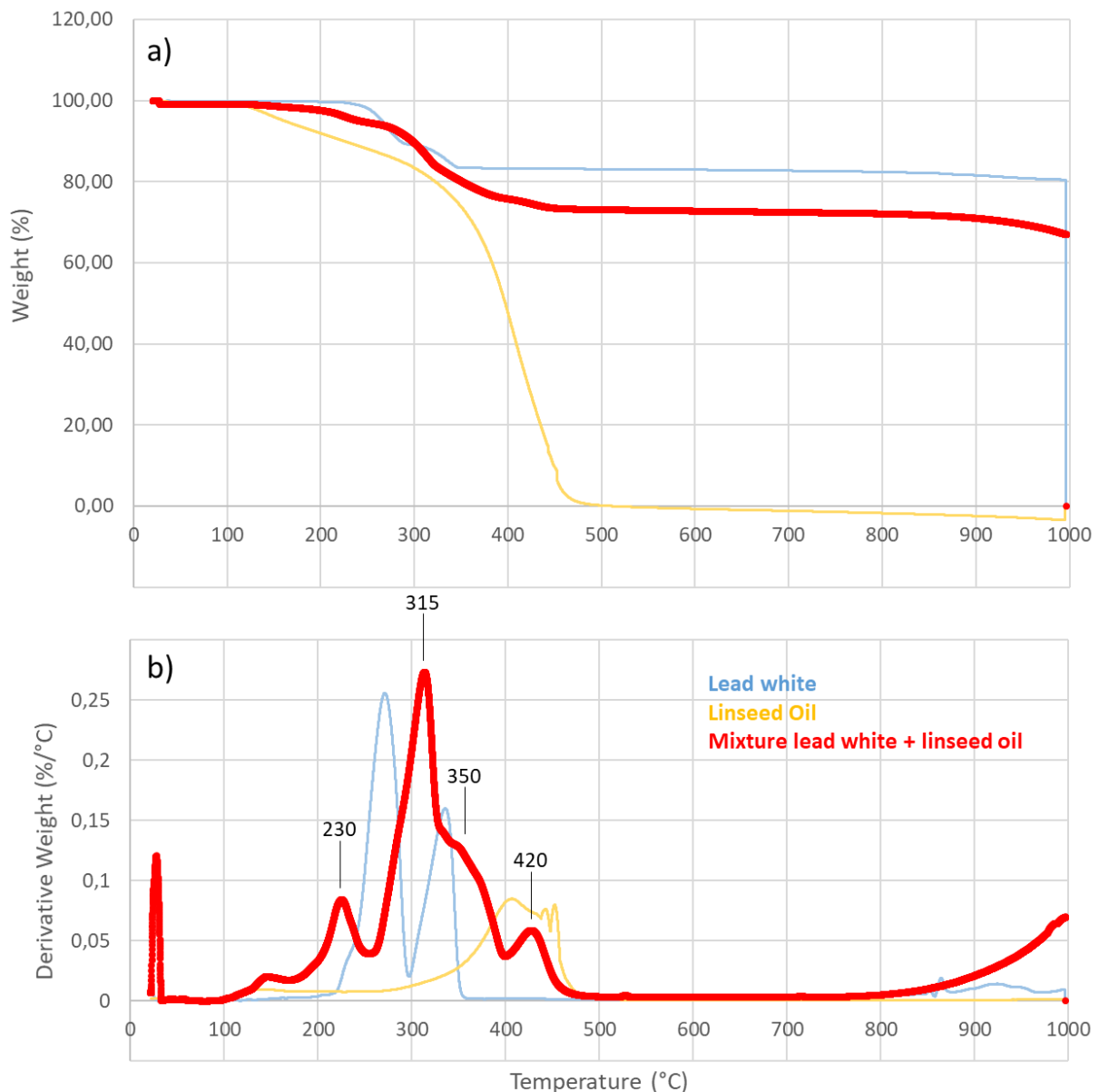


Figure 2: Comparison of a) Thermogravimetric profiles and b) their derivatives (DTG) of the mixture of lead white and linseed oil LW+O (thick red), pure lead white LW (blue), linseed oil O (yellow).

The thermogravimetric profile of the mixture MW+O (Figure 3b) shows three peaks. A two-step decomposition process is observed in the same temperature range as for pure linseed oil. The drying process is less advanced than for the lead white paint because Meudon white has lower drying properties. At a higher temperature, around 600°C, calcium carbonates start to decompose by losing CO₂ and forming lime (calcium oxide). A shift in the decomposition temperature is observed, probably due to the presence of the linseed oil or to the sample size effect.

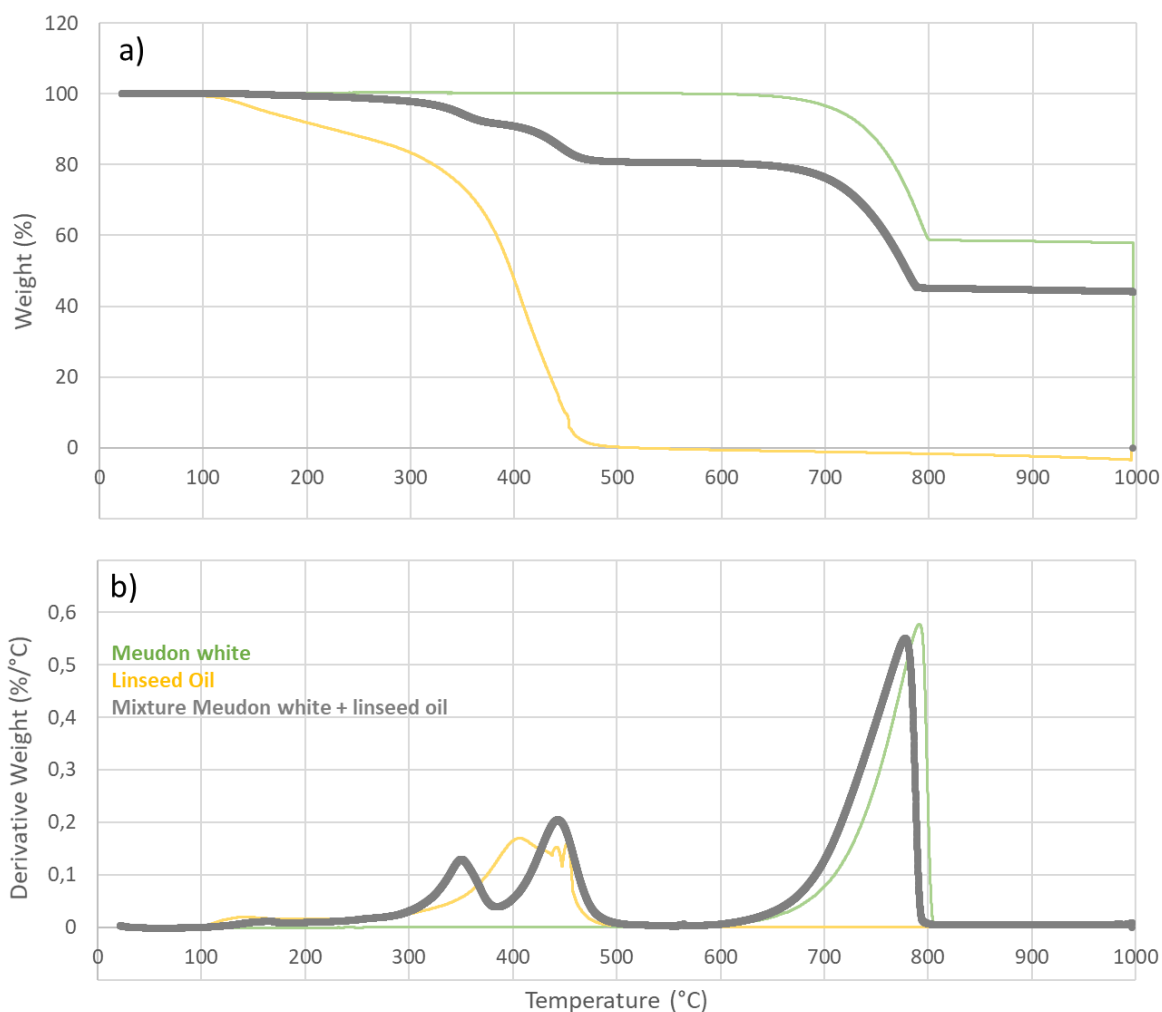


Figure 3: Comparison of a) Thermogravimetric profiles and b) their derivatives (DTG) of the mixture of Meudon white and linseed oil MW+O (thick grey), pure Meudon white MW (green), linseed oil O (yellow).

3.1.3. Reproduction of old white paint: mixture of lead white, Meudon white and linseed oil

The thermal behavior of a paint containing lead white, Meudon white and linseed oil (LW+MW+O) is presented in Figure 4. As observed for the LW+O sample, several peaks from 100 °C to 500 °C correspond to the decomposition of lead white, linseed oil and lead-linseed oil compounds. At 800

°C, the complete decomposition of the paint occurs with the decomposition of Meudon white. A smaller gap than for mixtures of lead white and Meudon white is observed between the decomposition temperatures of the two carbonates due to the presence of linseed oil. Nonetheless, this gap appears to be large enough to allow the separation of the organic carbon carrying the ^{14}C signature of the paint (CO_2 from lead white and linseed oil) from the geological Meudon white by heating the sample up to 600°C. However, previous studies have shown that the decomposition temperature of calcium carbonates can be lower than this value, depending on the composition, crystallinity, sample size and presence of oil [20, 21, 21, 23, 24, 25]. In order to safely date lead white painting samples by the radiocarbon method, it is very important to prevent the addition of any dead carbon contamination. By reducing the heating temperature to 400°C, the potential contamination by geological sources is obviated and the majority of carbon originating from lead white is collected.

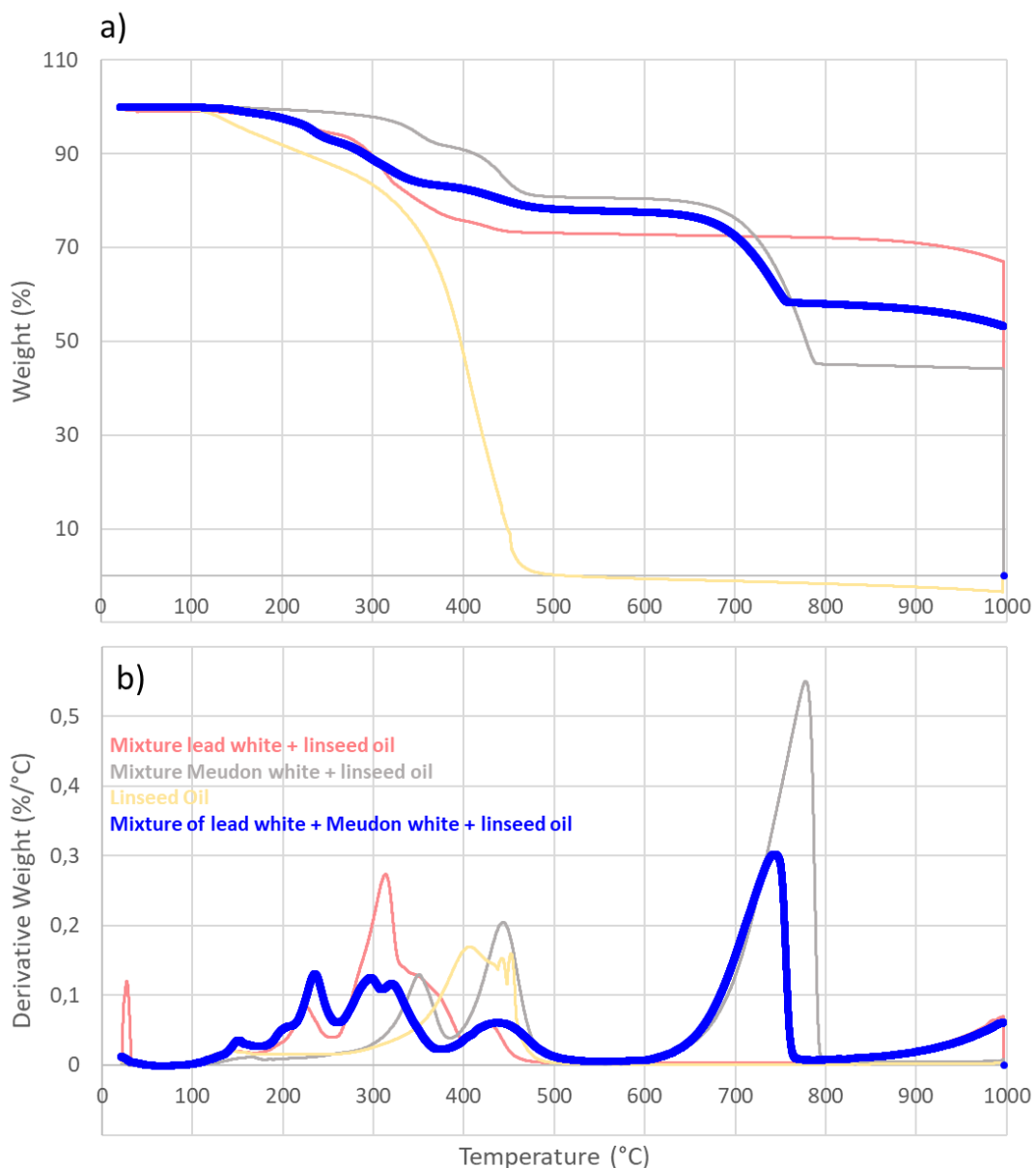


Figure 4: Comparison of a) Thermogravimetric profiles and b) their derivatives (DTG) of LW+MW+O (thick blue), LW+O (red), MW+O (grey), O (yellow).

3.2. Thermal decomposition as preparation procedure for the radiocarbon dating of lead white painting samples

Two pigments and two paint samples (LW, LW + MW (3), LW + O and LW + MW + O) were subjected to thermal decomposition at 400 °C in order to extract carbon for radiocarbon dating. Lead white decomposes to CO₂ and PbO when heated at this temperature [3,5,6]. The mass of carbon obtained after heating is calculated from the CO₂ pressure and converted into percentage of carbon extracted (Table 2). The experiment on sample LW was reproduced 10 times to estimate the uncertainty on the percentage of carbon extracted.

Table 2: Percentage of extracted carbon at 400°C for pure lead white (LW), mixture of lead white and Meudon white (70 %wt LW + 30 %wt MW), lead white paint (LW + O) and mixture of lead white and Meudon white paint (LW + MW + O).

Sample label	Expected carbon content extracted from lead white (%)	Mass of the sample (± 0.01 mg)	Mass of carbon extracted (± 0.04 mg)	% of carbon extracted (± 0.05 %)
LW	4.46	25.10	1.10	4.39
70%wt LW + 30%wt MW (3)	3.12	35.86	1.10	3.07
90%wt LW + O	≥ 4	19.39	0.91	4.69
45%wt LW + 45%wt MW + O	≥ 2	18.94	0.50	2.66

The percentage of carbon extracted from lead carbonates (4.39 %) is in accordance with the theoretical percentage of carbon contained in PbCO₃ (4.46 %). The decomposition of pure lead white is fully achieved at this temperature as also observed in thermogravimetry. The same result is obtained for a mixture of 70 %wt of lead white and 30 %wt of Meudon white without binder. The percentage of carbon extracted (3.07 %) is very close to the theoretical value (3.12 %) and reflects the total decomposition of the 70 % of lead white present in the mixture. This result also shows that Meudon white is not decomposed, confirming that the separation between the two sources of carbon is effectively obtained at 400 °C.

For the paint sample containing 90 % of lead white and 10 % of linseed oil, the percentage of extracted carbon increases to 4.69 %. This value is higher than the expected value of 4 % corresponding to the percentage of carbon coming from lead white. A similar result is obtained for the paint sample containing 45 % of lead white, 45 % of Meudon white and 10 % of linseed oil. These results indicate that linseed oil is partially decomposed at 400 °C and are in agreement with the thermogravimetry analysis (see section 1c). The proportions of carbon from the linseed oil in the total extracted amount of carbon are 16 % and 25 %, respectively. The carbon possibly coming from lead soaps decomposing at 420°C is not taken into account in the estimation.

The proportion of linseed oil extracted during the thermal preparation contributes to the radiocarbon dating of the paint together with lead white. The amount of ¹⁴C present in the oil corresponds to the harvest date of the flax. In the context of ancient paintings, it is very likely that

the production of lead white and the harvesting of the plants occurred close in time. In that case, the extraction of the binder does not alter the date obtained from lead white. In the case of acrylic-based paints, however, where synthetic binders are based on a petroleum component, the small quantity of CO₂ extracted will give an erroneous older date. Absolute dating of such modern paints is thus difficult.

The thermal extraction protocol proposed in this article deals with the standard sample quantities for routine AMS measurements (about 1 mg of carbon). In view of its application to historical paint samples the sample size reduction has to be considered. For easel paintings, it seems realistic to take 1 to 2 mg of pure lead white from the paint layer (or from the ground layer accessible at the edge of the stretcher for example), which corresponds to about 0.07 mg of extracted carbon. However, the analysis of microsamples requires appropriate facilities and adapted data processing [2, 26, 27].

4. Conclusion

To guarantee the reliability of radiocarbon dating of lead white paints, it is necessary to ensure the elimination of dead carbon contamination from calcium carbonates and to estimate the contribution of the oil.

The thermogravimetric analysis has identified the origin of the carbon extracted during the thermal decomposition of lead white based paints. The results show that by heating a paint sample at 400 °C most of the carbon from lead white is extracted while a partial amount of linseed oil is decomposed. The decomposition of Meudon white seems to be totally avoided due to the gap between the decomposition temperatures of lead carbonate and calcium carbonate. We are therefore confident that any dead carbon contamination that could alter the ¹⁴C dating of lead white paintings has been eliminated.

The small portion of carbon extracted from linseed oil will not alter the radiocarbon dating if the flax plants were harvested at the same time as the lead white was produced. As long as the binder is derived from living organisms and is contemporaneous of the lead white production, the extraction of carbon from the binder is not an obstacle to radiocarbon dating. However, further care must be taken to date more recent synthetic resin or acrylic-based paints which contain no radiocarbon.

In conclusion, these results validate the experimental protocol recently proposed to date lead carbonate paints. This study confirms that lead white based paints can be absolutely dated using a thermal decomposition process to prepare samples for the radiocarbon measurement. Dating lead white based paint will provide a new and reliable tool for authenticating paintings.

Acknowledgement

The authors thank E. Foy (LAPA-IRAMAT, NIMBE, CEA, CNRS) for DRX experiments, LMC14 colleagues for assistance in the preparation of the samples and Helen Granville for reading the manuscript. The authors are grateful to the reviewers for their comments that have improved the manuscript. This is LSCE contribution no. 6724.

Declarations of interest: none.

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