Facultad de ciencias.

Grado en Física.

Trabajo fin de grado

Use of luminescence techniques in the analysis of archaeological sediments

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1 ABSTRACT

La búsqueda de información y datos con respecto a cómo vivían nuestros antepasados ha motivado la aplicación de distintas técnicas de estudio sobre muestras de sedimento arqueológico. La espectroscopía estudia la interacción de la radiación con la materia. Cuando esta materia reacciona emitiendo luz (luminiscencia) se puede obtener información de sus propiedades por lo que la espectroscopía es una herramienta analítica usada principalmente en Física y Química. Las técnicas basadas en luminiscencia son una gran alternativa junto a otros métodos tradicionales en el estudio de sedimentos arqueológicos pues se trata de una técnica prometedora en el ámbito de la arqueología debido fundamentalmente a su capacidad de realizar análisis sobre cualquier tipo de muestras de forma no destructiva.

En este trabajo se ha estudiado el efecto de la temperatura en distintas muestras de hueso de vaca a partir de sus propiedades luminiscentes con el fin de compararlas con restos de huesos arqueológicos e identificar si estos han sido calcinados en hogueras en asentamientos prehistóricos. Como punto de partida, se han estudiado los efectos que producen la resina y el epoxi (pegamento) usados en el proceso de fijación de las muestras arqueológicas a partir de sus espectros de emisión, excitación y hallando el tiempo de vida media de la emisión. Posteriormente, se siguió el mismo procedimiento de medidas para las distintas muestras de huesos de vaca, obteniendo su máxima emisión excitando a 375 nm, coincidiendo con el rango en que la resina y el epoxi también tienen su emisión máxima. Por último, se compararon los espectros de emisión, excitación y tiempos de vida medios obtenidos en tres de las muestras de hueso de vaca, en concreto las muestras de color blanco, con los obtenidos para la muestra de restos arqueológicos. Una vez realizadas las comparaciones a partir del carácter luminiscente de los huesos, que puede ser útil para determinar las alteraciones térmicas, se comprueba que es posible diferenciar a que temperatura han sido calentados los restos arqueológicos a pesar de estos están impregnados en resina y epoxi.

The search for information and data regarding how our ancestors lived has motivated the application of different study techniques on archaeological sediment samples. Spectroscopy studies the interaction of radiation with matter. When this matter acts by emitting light (luminescence) information on its properties can be obtained, which is why spectroscopy is an analytical tool used mainly in Physics and Chemistry. Luminescence-based techniques are a great alternative to other traditional methods in the study of archaeological sediments. It is a promising technique in the field of archaeology mainly due to its ability to perform analysis on any type of samples in a non-destructive way.

In this work we have studied the effect of temperature on different samples of cow bone from their luminescent properties in order to compare them with archaeological bone sediments and identify whether they have been burned in bonfires in prehistoric settlements. As a starting point, the effects produced by the resin and the epoxy (glue) used in the fixation process of the archaeological samples have been studied from their emission and excitation spectra and obtaining their emission lifetime. Subsequently, the same measurement procedure was followed for the different samples of cow bones, obtaining their maximum emission exciting at 375 nm, coinciding with the range in which the resin and epoxy have their maxima emission. Finally, the emission, excitation and lifetime obtained in three of the cow bones samples, specifically the white samples, were compared with those obtained for the archaeological sample. Once the comparisons were made on the basis of the luminescent character of the bones, which can be useful to determine thermal alterations, it was found that it is possible to differentiate at what temperature the archaeological remains have been heated despite they are impregnated with resin and epoxy.

2 INTRODUCTION

Los huesos son un buen reflejo de información metabólica, dietética y hormonal; permiten estimar los hábitos alimentarios a partir de elementos traza. En sentido metafórico, los huesos se pueden ¨leer¨ y utilizar como ventana al pasado [1]. La aplicación de técnicas de luminiscencia para el estudio de sedimentos arqueológicos está siendo de gran utilidad a la hora de identificar restos biológicos.

El objetivo de este trabajo es proporcionar un estudio en el cual, utilizando técnicas de luminiscencia podamos obtener información a partir de espectros de emisión y excitación sobre los huesos pertenecientes a una muestra de sedimento arqueológico. El interés, en particular, es saber si estos habían sido calentados o no. Para ello, se analizaron primero diferentes muestras de hueso de vaca calcinadas a distintas temperaturas y se compararon con los resultados (espectros) obtenidos para la muestra arqueológica. También se analizaron los efectos de la resina y el pegamento con las que se realiza el proceso de fijación de la muestra arqueológica pues estos elementos de fijado tienen una emisión muy similar a la de los huesos. Este ¨nuevo¨ método de estudio propone la necesidad de encontrar resinas menos luminiscentes, y poder seguir avanzando en el estudio de sedimentos arqueológicos a partir de técnicas no invasivas.

The bones are a good reflection of metabolic, dietary and hormonal information; allow estimating eating habits from trace elements [1]. In a metaphorical sense, bones can be "read" and used as a window into the past. The application of luminescence techniques for the study of archaeological sediments is being very useful when identifying biological remains.

The objective of this work is to provide a study in which, using luminescence techniques, we can obtain information from emission and excitation spectra of the bones belonging to an archaeological sediment sample. The interest, in particular, is to know whether these had been heated or not. For this, different samples of calcinated cow bones were first analyzed at different temperatures and compared with the results (spectra) obtained for the archaeological sample. The effects of the resin and glue with

which the process of fixing the archaeological sample is carried out were also analyzed, since these fixing elements have an emission very similar to the bones. This "new" study method proposes the need to find resins with lower luminescent, and to be able to continue advancing in the study of archaeological sediments using non-invasive techniques.

Information on the luminescent properties of thermally altered human remains is scarce. The luminescent character of the bones may be useful in identifying these thermal alterations [2].

Bones go through four stages when exposed to thermal stress. First, dehydration occurs (about 105 to 600°C), followed by decomposition of the organic matrix by pyrolysis and combustion (between 500 and 800°C). The third stage is characterized by inversion due to loss of carbonate resulting in calcination of the inorganic matrix with calcium oxide (CaO) and calcium hydroxyapatite (CHA) as solid end products. Finally, the inorganic matrix recrystallizes (about 1600ºC). These stages are associated with the generally observed changes in bone color, from ivory, white-yellow (fresh bone) to black-brown (carbonized bone) and bluish-white-gray (calcined bone) [2].

Fluorescence is currently used as a tool to detect various biological traces. By stimulating molecules with a specific wavelength, the molecules can reach higher energy states. Quickly thereafter, the molecules will lose some of the energy gained to their surroundings and subsequently return to their ground state, emitting light. This emitted light is called (photo) luminescence. Luminescence can be divided into two pathways, fluorescence and phosphorescence. The difference between these lies in the decay time associated with the excited state [3].

Studies show that fresh bone presented a main emission peak at 440 nm when it is excited at 365 nm (UV light) and two minor peaks at 590 nm and 640 nm. Both inorganic and organic components of bone (hydroxyapatite and type 1 collagen) were found to fluoresce [2].

Hydroxyapatite (HAP) is a biocrystal, consisting of calcium, phosphorus and hydrogen atoms, according to the formula Ca10(PO4)6(HO)2. HAP is present in teeth and bones and belongs to the apatite family with hexagonal structure, with the space group P63/m (see Fig. 1 [2-3]). In a bone it is always accompanied by organic structures

such as collagen. Other apatites of biological importance are fluroapatite and chlorapatite [2].

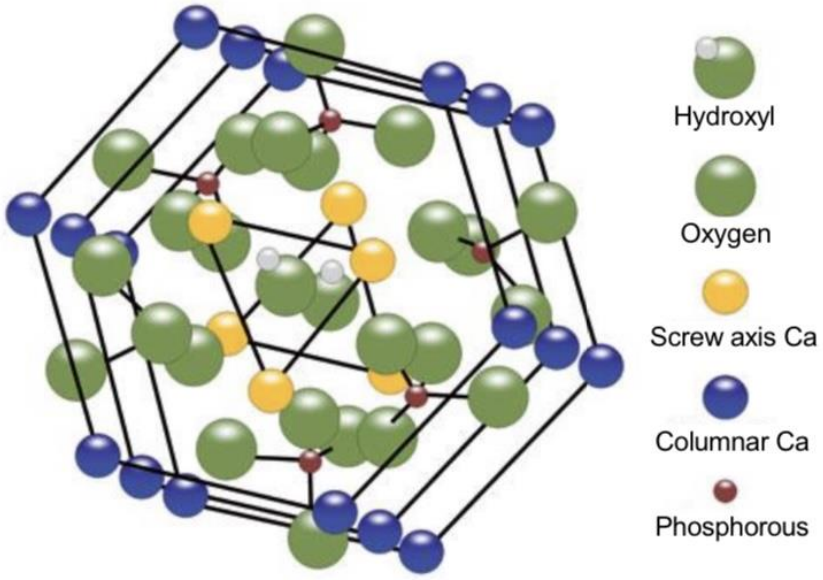

Fig. 1. *Atomic arrangement in the hexagonal unit cell of hydroxyapatite, showing the atomic positions of Ca, P, O and H within the unit cell.*

The study of the thermal behavior of HAP using spectroscopic techniques and chemical analysis provides insight into the behavior of this dynamic crystal. By analyzing the thermal treatment of bone tissue, aging can be determined, since the size of the crystals is dependent on both thermal treatment and age. From 600°C onwards the crystallinity of the bone mineral increases resulting in a better characterization of HAP by X-ray studies. There is also a partial decomposition of hydroxyapatite to calcium oxide (CaO) and beta tricalcium phosphate (β-TCP) [3]. It has been suggested that chemical conversion of CHA to β-TCP occurs in (non-human) bones heated to temperatures of 600°C [2].

The major obstacle encountered in the application of luminescence techniques when studying sediments is that the method of fixing these samples (thin films) uses fluorescent resins and glues.

The thin films of archaeological sediments are a source of information because of their content in archaeological microrests; they also allow us to observe the relationship between these microrests and the sediments affected by the use of fire [4].

The samples are obtained undisturbed in the field in the form of monoliths (blocks) due to their fragility and unconsolidated state. In the laboratory they are hardened with resins, cut into blocks and polished with a grinding machine to acquire flatness on a glass slide with a standardized thickness of 25-30 µm. Initially the samples are dried at 60º C for several days. Once dried, the blocks are placed in unsaturated resin, styrene and hardener where they remain for several days until they reach the necessary hardness to be cut into 7x4x1 cm^3 plates and finally mounted on a glass slide and polished to a thickness of 30 µm.

3 OBJECTIVES

El objetivo principal de este trabajo es caracterizar una muestra de sedimento arqueológico aplicando técnicas de luminiscencia. Para ello, se estudian y comparan los espectros de emisión, excitación y tiempos de vida de la muestra de sedimento arqueológico con los de distintas muestras de hueso de vaca previamente calcinadas a distintas temperaturas.

The main objective of this work is the characterization of archaeological samples through the application of luminescence techniques.

In order to achieve this objective, the following steps were covered:

a) To study the emission, excitation and lifetime of the resin and glue with which the samples were fixed.

b) To measure different emission spectra of the cow bone samples treated at different temperatures.

c) Analyze and compare the emission spectra of cow bone samples previously heated at different temperatures.

d) Analyze and compare emission spectra, excitation and lifetimes of the archaeological sample with those of the cow bone samples.

4 METHODOLOGY

En este trabajo se analizan distintas muestras de hueso de vaca y muestras arqueológicas. Estas últimas, están fijadas con resina y epoxi, con lo cual se estudiaron los efectos que estos producen en la luminiscencia de la muestra. Se obtuvieron sus espectros de emisión, excitación y tiempos de vida. A continuación, se analizaron las muestras de hueso de vaca con el objetivo de observar sus espectros de emisión para explorar los efectos de la temperatura en las propiedades de fluorescencia de los huesos.

In this work, different samples of cow bones and archaeological samples are analyzed. The last ones were fixed with resin and epoxy, so the effects that these produce in the luminosity of the sample were studied. Their emission, excitation and lifetime spectra were obtained. Next, the cow bone samples were analyzed in order to obtain their emission spectra and to explore the effects of temperature on the fluorescence properties of the bones.

The samples belong to cow bone (tibia), where one of them, the reference sample, is unheated and the rest have been heated at different temperatures (100º C, 200º C, 300º C, 400º C, 500º C, 600º C and 700º C). The emission spectra of these samples were analyzed by exciting them with different wavelengths, thus obtaining the maximum emission for each of them, and then the spectra of the samples with similar colors were compared. Finally, the archaeological sample was analyzed at different points, measuring their emission spectra, excitation and lifetimes, which were compared with those obtained for the cow bone samples.

4.1 EXPERIMENTAL PROCEDURES

4.1.1 Samples

Different types of samples were studied in this work:

Epoxy and resin: The archaeological sediment sample has been fixed with resin and epoxy. This fixation method produces fluorescence in the same range in which the samples emit. Resins and epoxy were used in composite applications in applications from 1950's. Moreover, they possess good physical, mechanical and electrical properties. Other notable characteristics of epoxy resins are their relatively high resistance to humid environments and high temperatures, as well as their resistance to attack by chemical reagents, their dimensional stability, ease of processing and low cost [5]. The emission and excitation spectra of the epoxy and resin used in the preparation of sediment were measured to quantify their contributions in the emission spectra on the samples.

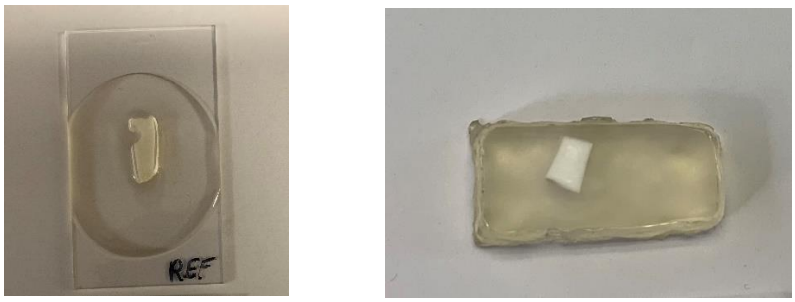

Fig. 2. *Different samples used to obtain the emission spectra of the epoxy (reference with epoxy) left and of the resin (sample heated at 700ºC with resin) right.*

Cow bone (tibia): eight cow bone samples are available. One of them was a reference sample (unheated), and the rest were previously heated at different temperatures for one hour (100º C, 200º C, 300º C, 400º C, 500º C, 600º C and 700º C). The picture of these samples is shown in Fig. 3. All the samples were polished on the side where the emission and excitation spectra would be studied to check the effects of temperature on

the bones in order to compare with unknown samples. This process will let know if the sample had been heated or not and at what temperature.

Fig. 3*. Cow bone samples without thermal treatment (reference) and heated at different temperatures.*

Cow bone (tibia) with epoxy and cow bone (tibia) with resin: As part of the experimental method, emission and excitation spectra of some samples fixed with epoxy and resin were performed to determine the effect of these fixing methods on the emission of the samples (Fig. 4).

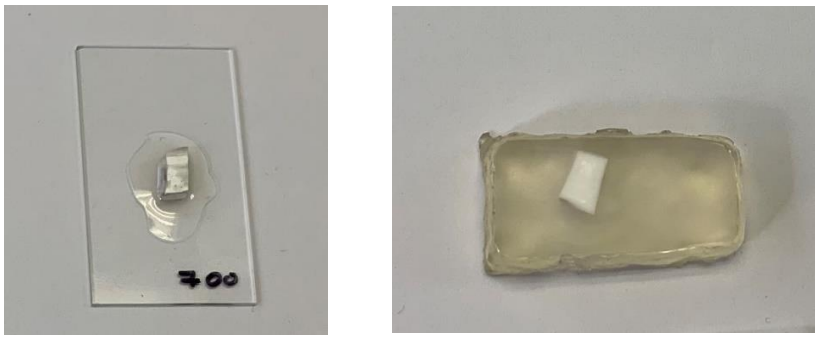

Fig. 4*. Cow bone with epoxy heated at 700ºC (left) and cow bone with resin heated at 700ºC (right).*

Archeological sample: We have a thin sheet of archaeological sediment from which we have obtained emission, excitation, and lifetime spectra at different points, in order to later compare the results obtained with those of the cow bone samples and thus be able to identify whether this sediment has been heated or not (Fig. 5). This study has been focused in a position in the archeological samples of white color which is expected to be a bone (see Fig. 5).

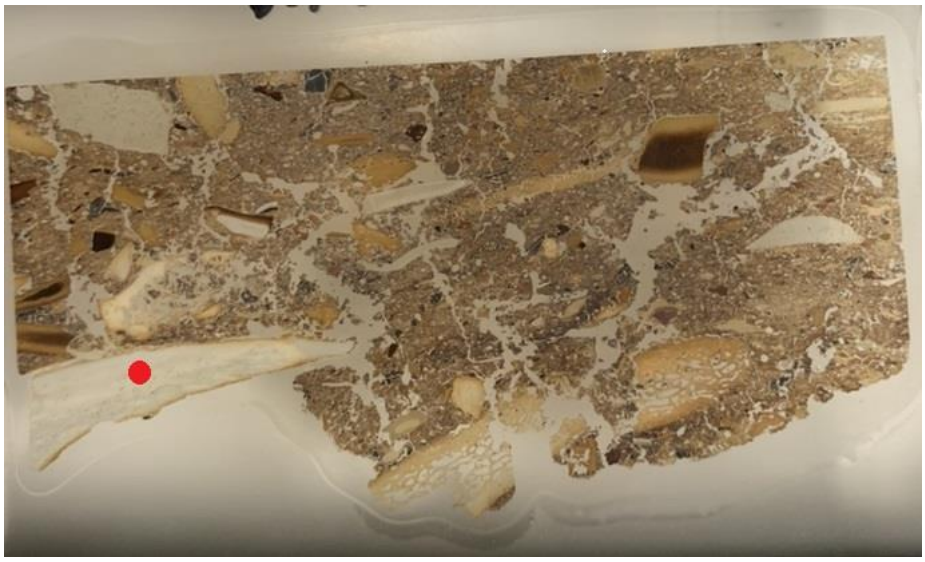

Figure 5. *Thin sheet of an archaeological sediment (the red point indicates the studied zone in the sample M1).*

4.1.2 Emission and excitation spectra

The emission spectra of the different samples were obtained using the experimental setup shown in Fig. 6. Luminescent spectra were obtained exciting the samples using a 400W Xe arc lamp passed through a 0.25m Spex 1680 double monochromator. A chopper (source modulator) and a 51124 filter (UV bandpass filter) are placed at its output. The light converges with a lens to excite a surface of few mm^2 of the sample. The fluorescence emission from the sample is then passed through a converging lens and a LP400 filter (long pass filter at 400 nm) to avoid diffuse light from the lamp. This fluorescence was detected using a 0.25m Spex 1681

monochromator with a photomultiplier. The signal was amplified using a lock-in amplifier and registered by an analog-digital converter controlled by a computer.

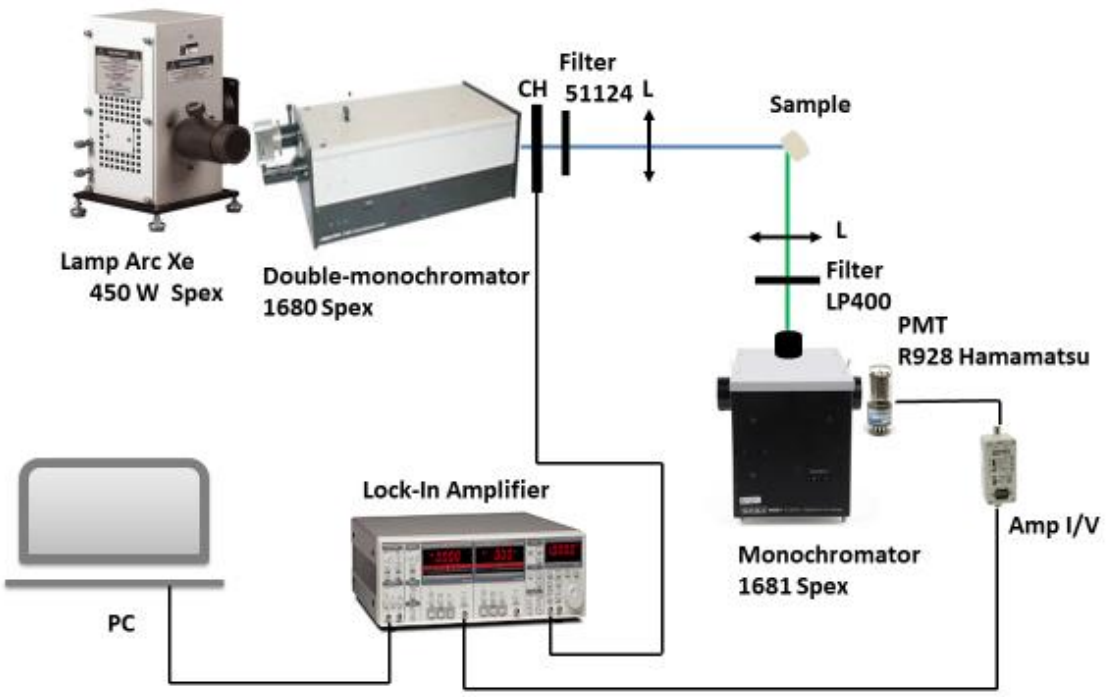

Figure 6. *Experimental setup. Lamp Arc Xe 450W Spex, Double-monochromator 1680 Spex, CH chopper, Filter 51124, L lens, Sample, Filter LP 400 nm Long Pass Filter, PMT R928 Hamamatsu, Amp I/V, Lock-in Amplifier, PC.*

To obtain the excitation spectra we used the same setup as for emission spectra shown Fig. 6, but in this case the light coming from the double monochromator passes through a 51122 filter (UV bandpass filter) and the fluorescence coming from the sample passes through a LP455 filter (long pass filter at 455 nm).

4.1.3 Time Resolved Measurements

In order to find significant differences in the emission of the resin, epoxy, cow bone and archeological sample, time-resolved spectroscopy was used. Time-resolved fluorescence spectroscopy investigates the change in fluorescence over time of a sample when it is irradiated with pulse UV, Visible or Near Infrared light. The decay curves in the fluorescence can be measured over a wide time interval: from picoseconds the milliseconds and beyond.

The obtained decay curves were in the range of ns, therefore these ones were obtained using an Edinburgh Instruments LifeSpec II fluorescence spectrometer (shown in Fig. 7). The samples were excited at λ = 375 nm with an Edinburgh Instruments EPL-375 picosecond pulsed diode laser working in the MHz repetition range (temporal pulse width at half maximum about 90 ps) and using the Edinburg Instruments F900 acquisition software.

Fig. 7*. Edinburgh Instruments LifeSpec II fluorescence spectrometer. Experimental setup for measuring lifetimes in the range of ns.*

If the decay curves shown a non-exponential character is useful to give a mean fluorescence lifetime value defined as:

$$< \tau >= \frac{\int_0^\infty I(t)dt}{I(0)} \qquad \text{Eq. (1)}$$

where I(t) is the intensity of luminescence after the laser pulse at t=0 s.

5 RESULTS

5.1 EPOXY AND RESIN EFFECT

5.1.1 Emission and excitation spectra of the epoxy and the resin

In this section, emissions from the epoxy and resin that may remain in the sample during its preparation were analyzed. The emission spectra were obtained using experimental setup shown in Fig. 6.

The following graph (Fig. 8) shows the emission spectra of the resin and epoxy excited at 375 nm.

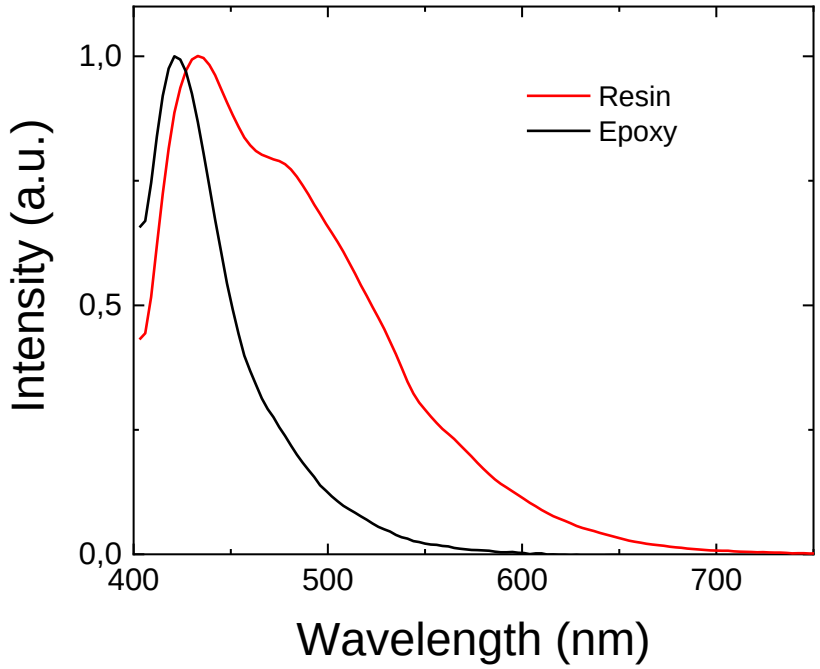

***Fig. 8**. Emission spectra for resin (red) and epoxy (black) obtained exciting at 375 nm.*

The emission spectra shown in Fig. 8 shows for the epoxy a maximum emission peak at 421 nm and a rapid decrease in the emission intensity up to 550 nm. In the case

of the resin, a maximum is observed at 433 nm with a slower decrease in the emission intensity up to 700 nm.

For the excitation spectra, the emission was fixed at 480 nm and excited in the range from 250 nm to 450 nm. The excitation spectra of these two products have been plotted in Fig. 9.

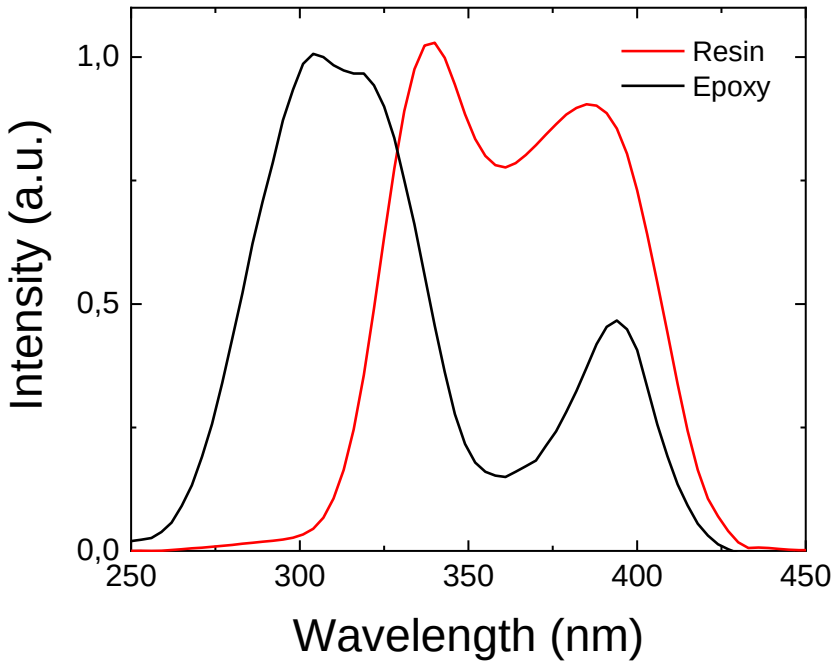

Fig. 9*. Excitation spectra for resin (red) and epoxy (black).*

As can see in Fig. 9, both epoxy and resin have intense UV excitation peaks. For the epoxy appears a maximum peak of excitation at 304 nm and a second peak at 394 nm, while for the resin appear a peak at 340 nm and a lower peak at 385 nm.

The difference in the fluorescence of the two types of fixation can be clearly observed. However, the presence of these peaks (due to these fixation products) in the excitation spectra obtained from archaeological samples could make its analysis complicated.

5.1.2 Lifetimes obtained in the epoxy and resin

Lifetimes were studied in order to analyze the differences between the two fixation methods. The decay curves of the different samples were obtained by exciting with a picosecond laser exciting at 375 nm and detecting at 440 nm. Clear differences in the decay curves of the resin and epoxy can be seen in Fig. 10.

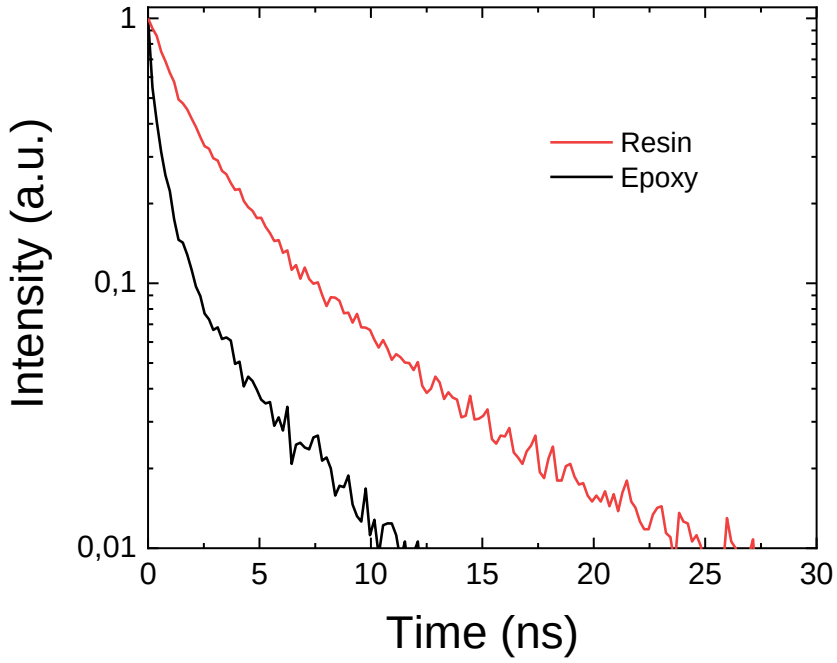

Fig. 10. *Decay curves of the resin (red) and epoxy (black) samples represented in logarithmic scale.*

The mean lifetime of the epoxy and resin were obtained using Eq. (1). As can be seen in Table I the resin has a longer lifetime than the epoxy. Probably this longer mean lifetime indicate that the resin has les non-radiative losses and for this reason produced higher emission intensity.

SAMPLES	<τ> (ns)
Resin	3,0
Epoxy	0,9

Table 1*. Mean lifetime of the resin and epoxy obtained exciting at 375 nm and detecting at 440 nm.*

5.2 EXPERIMENTAL RESULTS OBTAINED ON COW BONE SAMPLES

5.2.1 Emission spectra at different wavelengths

In the experimental section it was indicated that 8 samples of cow bone were prepared, 7 of these samples were heated at different temperatures. The analysis of these samples begins by studying the emission spectra. Firstly, emission and excitation spectra were carried out on the sample without heat treatment (reference sample).

- **Comparison of emission spectra of the reference sample and the sample heated to 700º C.**

Fig. 11 shows the emission spectra obtained with the reference sample (unheated) and for the sample heated to 700º C in order to analyze the possible differences in their spectra since these two samples have a similar same color. These measurements were made by exciting at different wavelengths (350 nm, 360 nm, 370 nm and 375 nm) using again the experimental equipment shown in Fig. 6. These spectra were normalized to their maximum values.

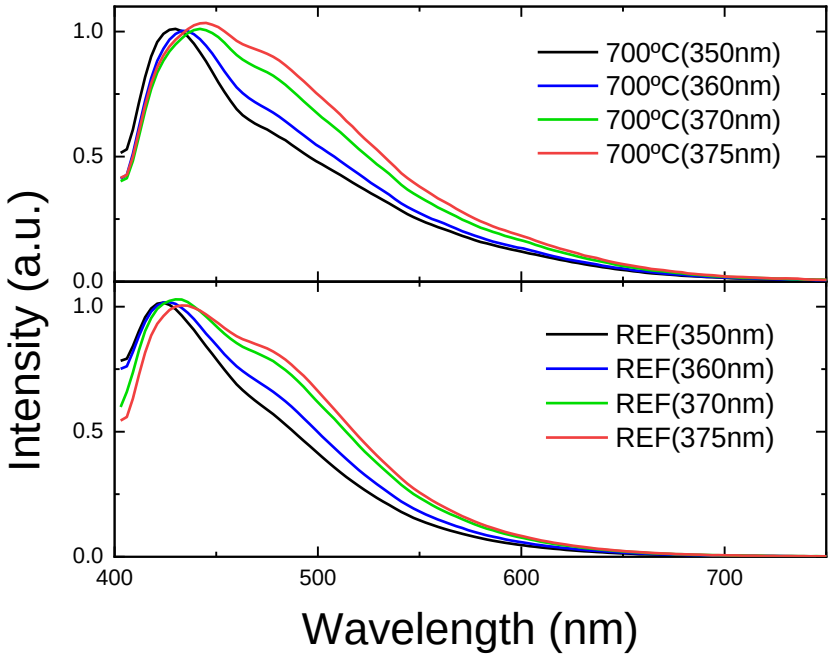

Fig. 11*. Emission spectra obtained from unheated (REF) and 700°C heated cow bone samples excited at different wavelengths. The curves are normalized to their maximum intensity.*

As shown in Fig. 11, there are differences in the emission spectra when the excitation wavelength is changed. Differences are also observed when comparing the results obtained between the reference sample and the heated sample. As the objective is to select a wavelength at which these differences are more important, the spectra of both samples at each excitation wavelength are shown in Fig. 12.

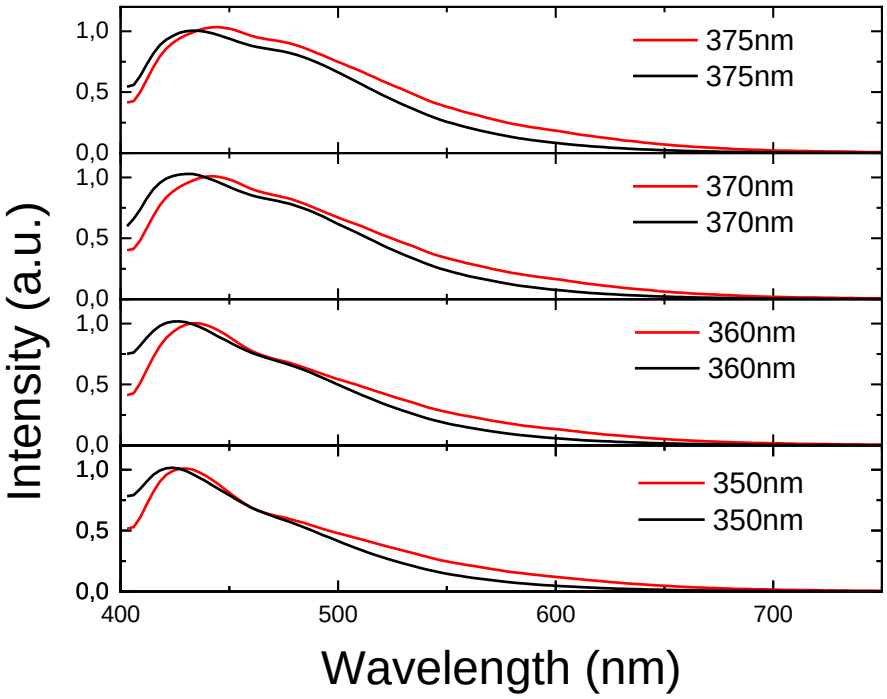

***Fig. 12**. Comparison of emission spectra obtained from reference (black) and 700°C heated (red) cow bone samples excited at different wavelengths. The curves are normalized to their maximum.*

As can be seen in Fig. 12, the most notable differences are obtained with the excitation at 375 nm. Although these changes are important cannot be observed directly by the naked eye.

- **Comparison of emission spectra obtained at different points of the reference sample.**

In order to check if the emission spectra depend of the position of the sample which is excited, then different emission spectra were obtained for different points of the reference sample under excitation at 375 nm excitation. The experimental setup of Fig. 6 was again used, and excited at different points in the sample to check whether the location at which it is excited affects the emission.

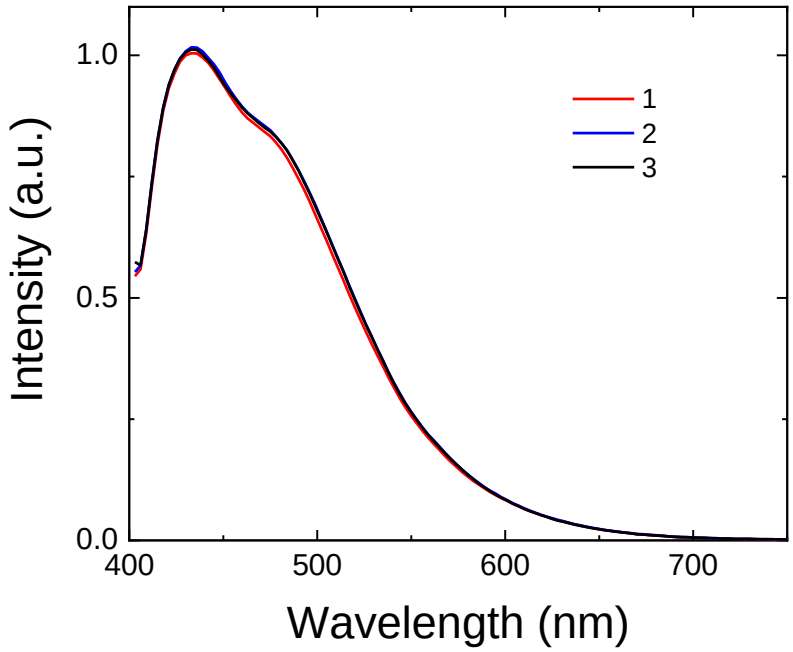

***Fig. 13**. Emission spectra obtained at three different points in the reference sample excited at 375 nm.*

As can be seen in Fig. 13 the same spectra in the reference sample are obtained independently of the excitation position.

5.2.2 Emission spectra of cow bones at different temperatures.

Cow bone emission spectra were obtained for the different samples, for the reference sample (unheated) and for the rest of the samples previously heated to different temperatures (see Fig. 14). These measurements were made by exciting at 375 nm using the experimental equipment shown in Fig. 6.

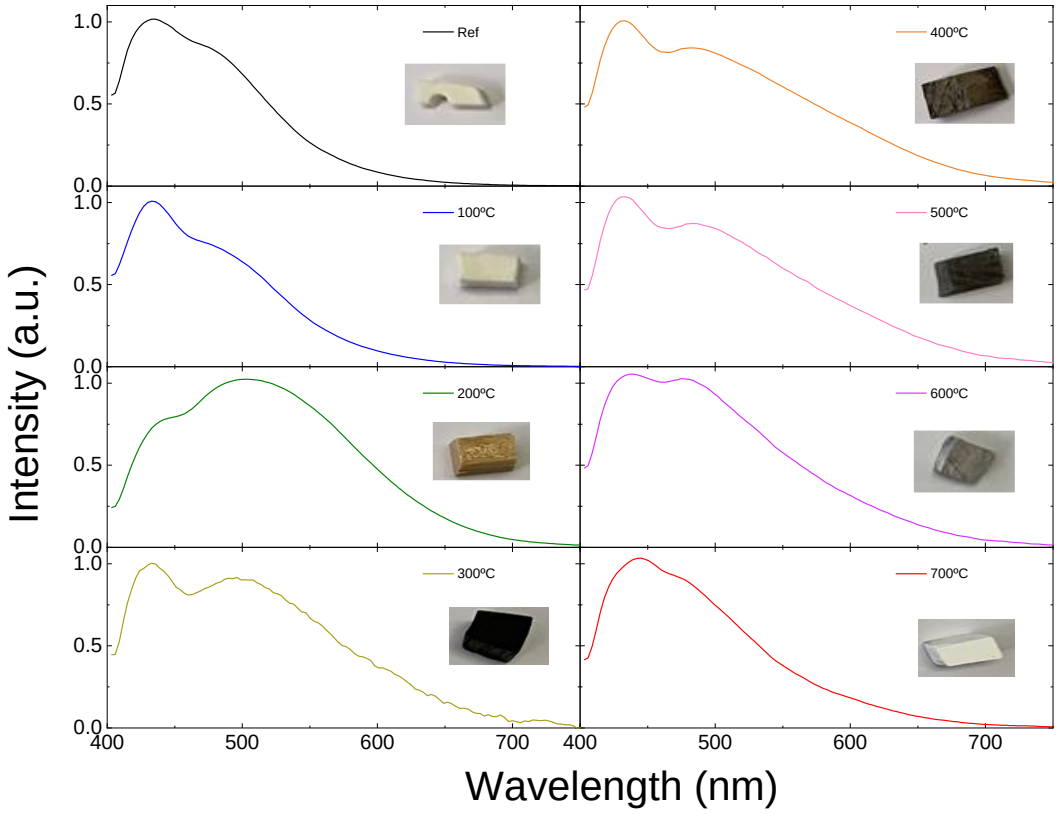

***Fig. 14**. Emission spectra obtained from reference and heated cow bone samples excited at 375 nm. The curves are normalized to their maximum intensity.*

The emission spectrum of the reference sample shows a main emission peak at 436 nm when it is excited at 375 nm and a minor peak at 478 nm. Therefore, it is proved that the components of the bone (hydroxyapatite and collagen) are fluorescent.

For the sample heated to 100º C, sample that is of the same color as the reference sample, presents a sharp peak at 433 nm and a smaller peak at 478 nm can be appreciated.

In the case of the sample heated to 200º C, in which a clear change in color is observed, it shows a shift of the emission maximum to larger wavelength presenting a maximum peak at 442 nm and a lower peak at 502 nm. At this point it can be appreciated a greater change in the intensity of luminescence.

For the sample heated to 300º C it can be seen a maximum emission at 433 nm and a lower peak at 500 nm.

The spectra of the samples heated to 400ºC and 500ºC show a similar behavior, having their maximum emission peaks at 433 nm and 430 nm, respectively. Increasing the luminescence intensity with respect to the previous sample (300ºC).

In the case of the 600ºC sample it is detected a maximum peak of emission at 439 nm and a peak at 475 nm. It is detected an increase of the luminescence.

Finally, the emission spectrum of the sample heated to 700ºC shows that it has regained a white color similar to that of the reference sample, with a maximum peak at 440 nm. The sample heated to this temperature produces an increase in luminescence intensity.

5.2.3 Lifetimes obtained in the samples.

In this part of the experiment, the different lifetimes were measured for each one of the samples, the reference sample and those heated to different temperatures. In Fig. 15 are shown the luminescence decays obtained for the different bone samples excited at 375 nm and detecting the emission at 440 nm. Therefore, in order to compare the different decays have been obtained the mean lifetimes using the Eq. (1) and the values are given in Table 2.

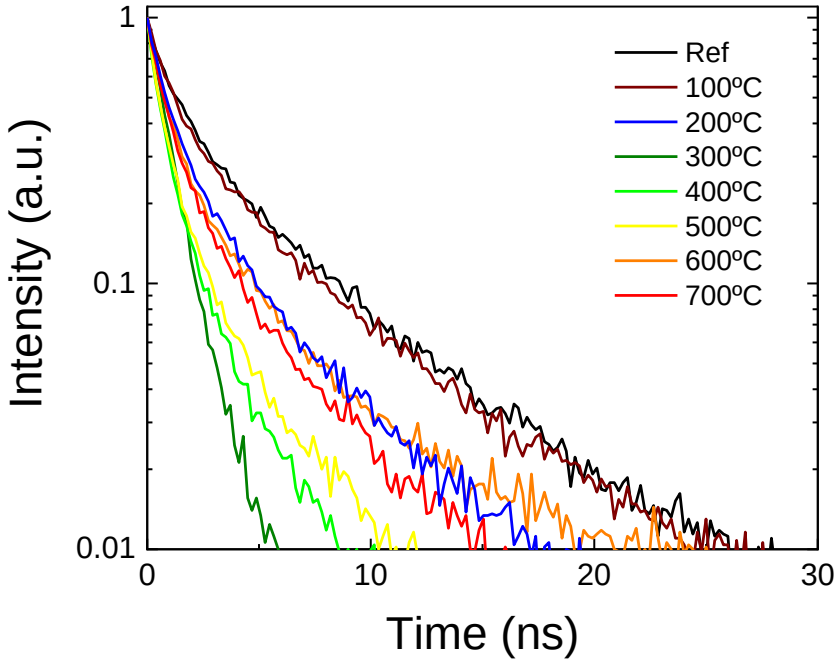

Fig. 15*. Decay curves of cow bone samples plotted in logarithmic scale.*

In Fig. 15 it can be seen that the reference sample and the 100ºC sample have a longer lifetime (see Table 2). When the heat treatment is increased the lifetime decreases, but after the sample is heated at 400 ºC the lifetime begins to increase.

In our case, the difference between the reference sample and the one heated to 700º C is of special interest. Both samples have similar colours and their emission spectra (exciting at 375 nm) show few differences, however analyzing the mean lifetimes it can be seen that there is a clear difference between these two samples (see Table 2).

SAMPLES	<τ> (ns)
Resin	3,0
Epoxy	0,9
Reference	3,1
100º C	2,9
200º C	2,0
300º C	1,0
400º C	1,1
500º C	1,2
600º C	1,9
700º C	1,7
M1	1,9

***Table 2**. Mean lifetimes of the resin, epoxy, cow bone samples (reference and heated) and archaeological sample (M1) obtained exciting at 375 nm and detecting at 440 nm.*

5.2.4 Emission spectra in epoxy and resin samples.

Emission spectra are obtained for two samples of cow bone heated to 100°C, one impregnated with epoxy and the other with resin (see Fig. 16), in order to see how these fixation methods affect the luminescence intensity of the samples. The same comparison was made with cow bones heated at 700 ºC and the results are shown in Fig. 17.

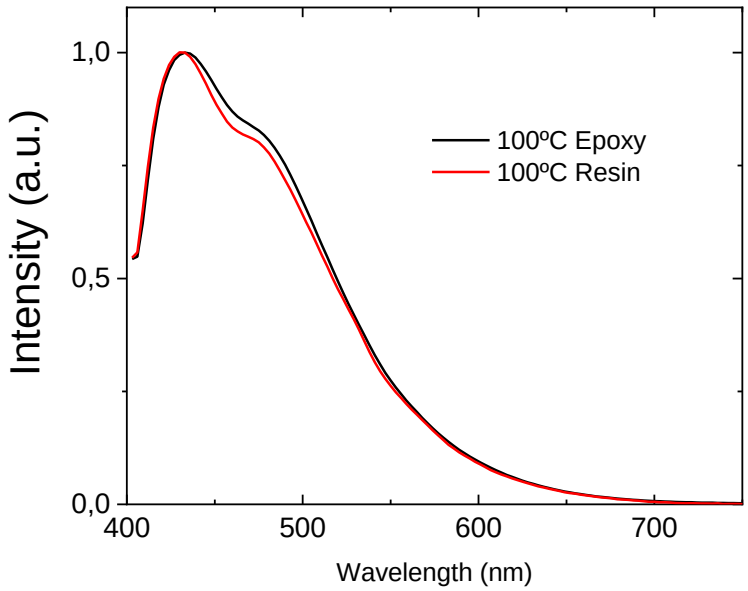

***Fig. 16**. Comparison of emission spectra of the sample heated at 100º C with epoxy (black) and with resin (red) obtained exciting at 375 nm.*

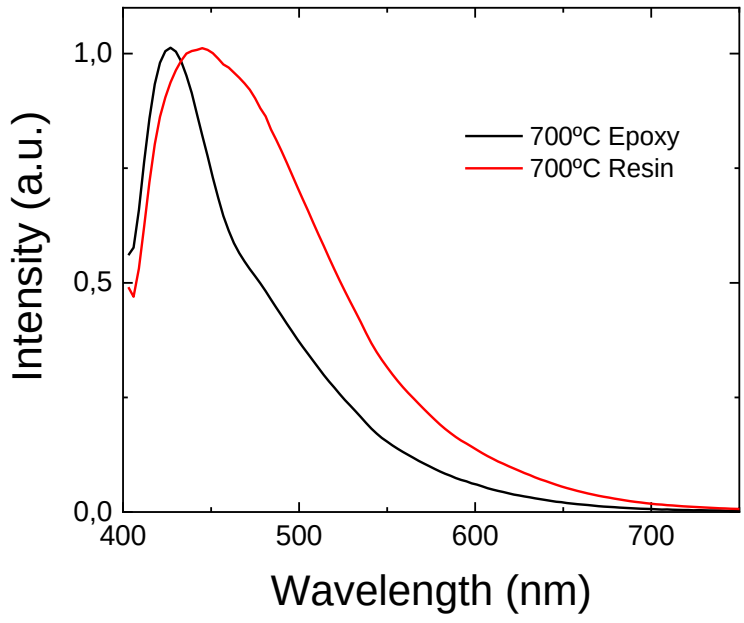

***Fig. 17**. Comparison of emission spectra of the sample heated at 700º C with epoxy (black) and with resin (red) obtained exciting at 375 nm.*

As can be seen in these figures, depending of the method used to fit the samples the emission obtained could be very different.

5.3 EXPERIMENTAL RESULTS IN THE ARCHAEOLOGICAL SAMPLE

As the spectra obtained can be sum of the epoxy, resin and sample contributions, we have performed emission and excitation spectra and lifetime measurements in the different samples in order to identify the different contributions in the final spectra that can be obtained from the archaeological samples.

5.3.1 Study of the emission and excitation spectra in the archaeological sample

In this study we have analyzed the spectra obtained in the archeological sample in the position indicated in the Fig. 5. This position shows that the archeological sediment has white color. For this reason, we started comparing the emission spectra of the archeological sample (M1) with the samples heated at 100º C and 700ºC of cow bone (see Fig. 18).

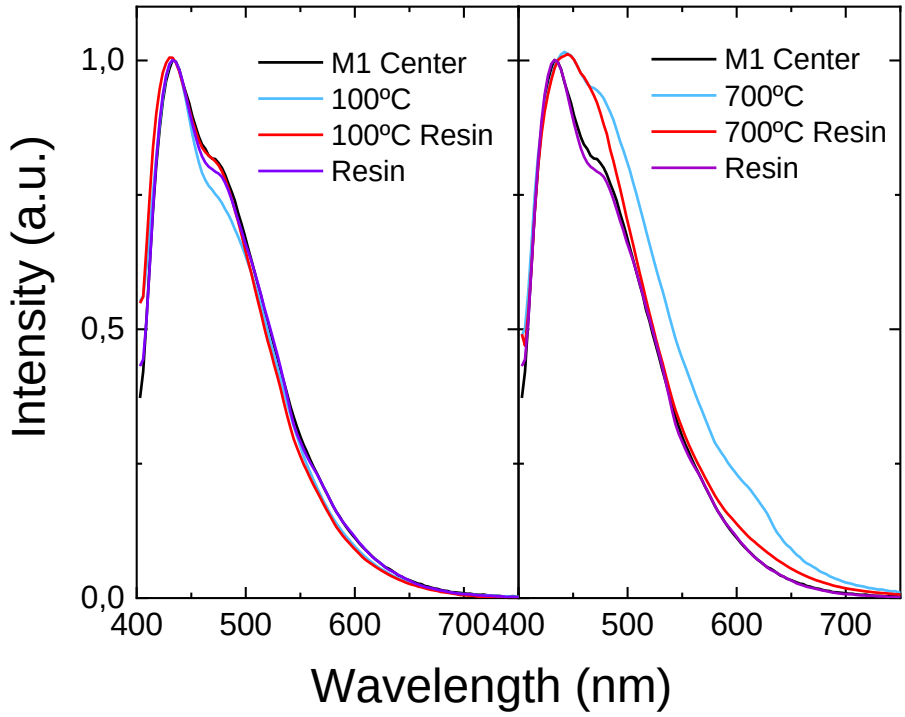

Fig. 18*. Comparison of emission spectra of M1 (black) and 100ºC sample (with resin and without resin) and pure resin and comparison of emission spectra of M1 and 700ºC samples (with and without resin) and pure resin.*

Comparing the emission spectra of the treated 100ºC and 700ºC cow bone samples with those treated with resin and with the M1 sample, it is observed that the spectrum of the archeological sample is much more similar to that of the 100ºC sample with resin.

However, we must to take into account that the contribution to the emission spectra from M1 sample can depend of the percentage of epoxy or resin in each position of the sample. Therefore, in Fig. 19 are shown the emission spectra of the archeological sediment sample obtained in different points. As can be seen in this figure, the emission spectrum for the M1 sample obtained in the center (similar to the spectra shown in Fig. 18) can be obtained as contribution of the resin spectrum. However, when the emission spectrum for the M1 sample is obtained in other position of the sample (Right) this spectrum is different and can be simulated with contributions of the emission spectra of the resin (about 26%) and the sample at 700 ºC (about 74%).

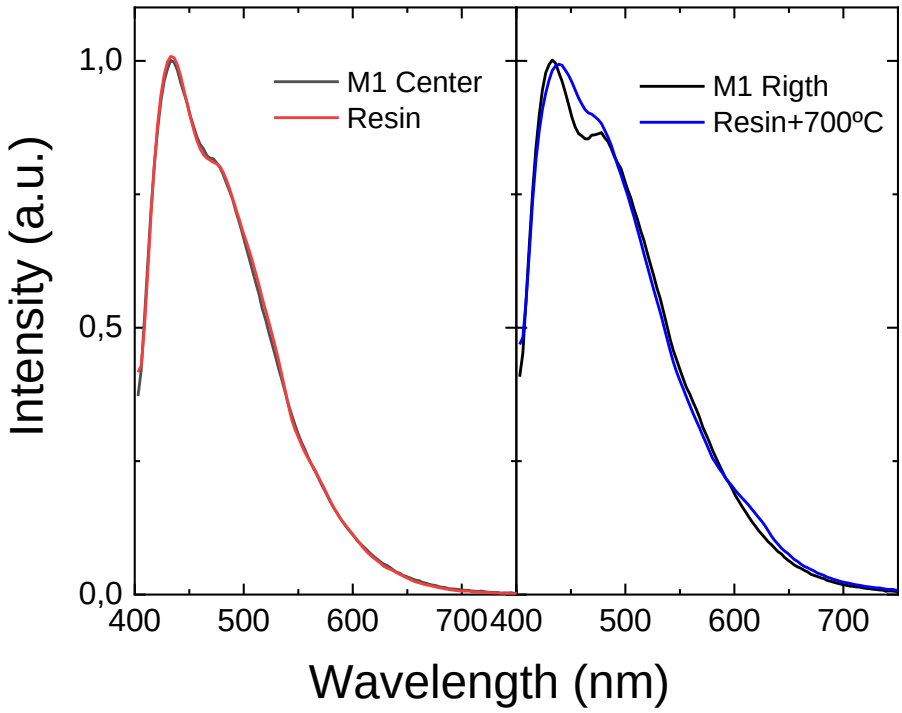

Fig. 19*. A) Emission spectrum of M1 in the center of the sample (black) and emission spectrum of the resin (red) and spectrum obtained as contributions of emission spectra (blue) of resin (about 26%) and sample at 700ºC (about 74 %).*

As conclusion, from emission spectra is difficult to conclude if the archeological sample has been heated at 100 or 700 ºC.

Next, we repeat a similar study but using the excitation spectra. The excitation spectra of the archeological sample is compared with those obtained with the sample heated at 100ºC and those obtained with the sample heated at 700ºC. In both spectra have been taking into account a possible contribution of the glue and the epoxy (see Fig. 20).

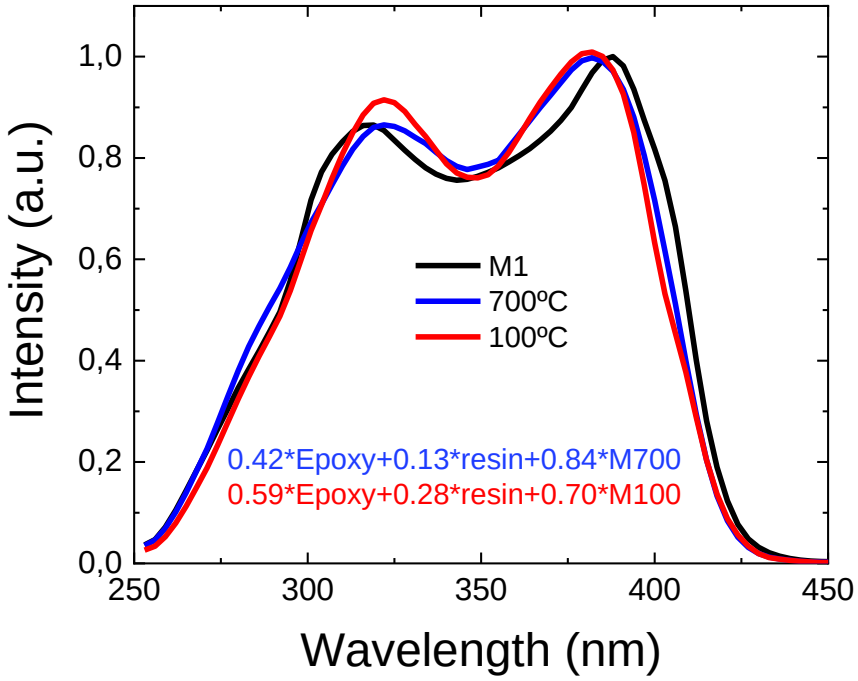

Fig. 20*. Comparison of the excitation spectrum of sample M1 with the excitation spectra obtained from the 100ºC and 700ºC samples taking into account possible contributions of the emission coming from the glue and the epoxy.*

As can be seen in Fig. 20, similar spectra are obtained using the samples heated at 100 ºC or at 700 ºC taken into account variable contributions of the emission coming from the epoxy and the resin. Therefore, it is not possible to conclude the temperature to which the archeological sample has been heated.

5.3.2 Lifetimes of the archaeological sample.

Finally, we used the time resolved experiments in order to identify the thermal treatment of the archeological sample. To obtain the lifetimes we used the same procedure described in the previous section, exciting at 375 nm and detecting the emission at 440 nm.

In Fig. 20 are compared the lifetime of the M1 sample with those ones obtained for the resin and for the 700ºC sample. As it can be seen, the lifetime for the M1 sample is similar to the 700°C sample. The lifetime values (included in Table 2) for the archaeological sample, the samples heated at 100 ºC and 700 ºC and resin are 1.9, 2.9,

1.7 and 3.0 ns, respectively. As conclusion, the archeological sample studied has been heated about 700 ºC because the lifetimes for the sample at 100 ºC and for the resin have higher values.

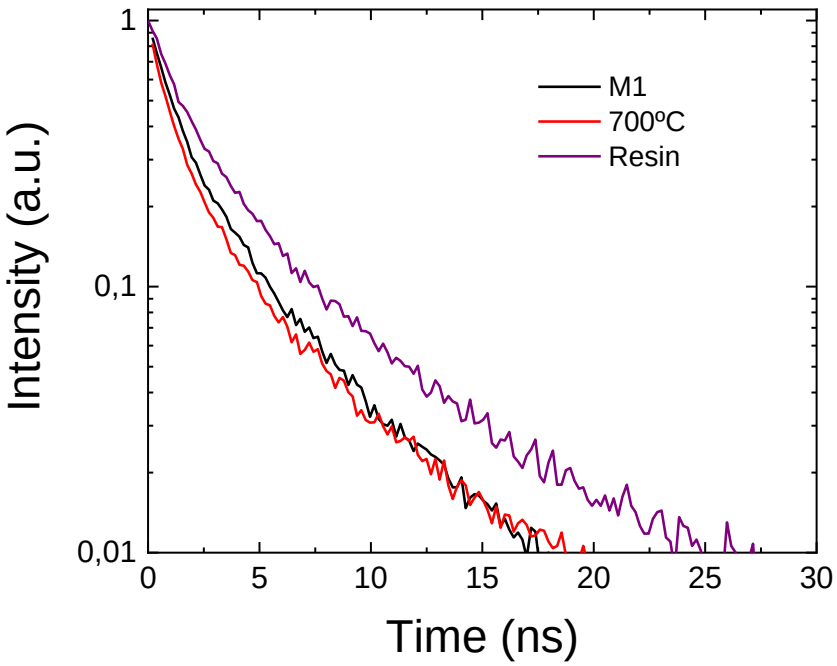

Fig. 20*. Decay curves of samples M1 (black), 700º C (red) and resin (violet) represented in logarithmic scale.*

6 CONCLUSIONS

El estudio de los espectros de emisión y excitación de las muestras de hueso, tanto las calcinadas como la de referencia y de las muestras de resina y epoxi, presentan distribuciones de intensidad de luminiscencia parecidas a huesos arqueológicos con colores similares, teniendo estas un máximo de emisión en torno a los 430 nm cuando son excitadas a 375 nm. Las muestras de resina y epoxi presentan también su máxima emisión en torno a los 430 nm excitando en 375 nm, dificultando así el análisis y comparación de la muestra arqueológica impregnada con resina y epoxi. No obstante, el estudio de tiempos de vida aporta mayor información en cuanto a diferenciación entre las muestras de hueso, las muestras de sedimento arqueológico y la resina y el epoxi.

The analysis of the emission spectra of the cow bone samples subjected to thermal treatment suggests that the luminescent characteristics observed are strongly related to the color of the samples where a decrease in luminescence intensity is observed for samples heated to 200, 300, 400, 500ºC (darker samples) and a subsequent increase in the emission intensity for samples heated to 600 and 700ºC. These spectra present a similar distribution, with a maximum around 430 nm exciting at 375nm.

On the other hand, the study of the emission and excitation spectra of the epoxy and the resin clearly shows a maximum in emission at 430 nm for the epoxy and a maximum at 450 nm for the resin excited at 375nm.

From the study of the emission and excitation spectra of the cow bone samples, the resin and epoxy samples and the archaeological sediment sample, complemented with the analysis of the lifetimes, suggests that the method of preparation of the samples where these are impregnated with resin and epoxy makes it difficult to differentiate between the luminescence coming from the bone or the epoxy and the resin. However, the observations of the lifetimes for the archaeological sample and the 700ºC sample are quite similar. As conclusion, time resolved luminescence experiments are a good

technical in order to identify if the archeological samples have received a thermal treatment.

The importance of this research lies in the fact that the method is not very invasive, so that analyses can be performed on any type of sample in a non-destructive manner. Therefore, as a future perspective, the study of different types of resins or glues that do not have the same emission range as bones is proposed.

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