FRANCISCO PIZARRO'S BANNER OF ARMS: AN ANALYTICAL WORK CONTRIBUTING TO LATIN AMERICA´S HISTORY

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FRANCISCO PIZARRO'S BANNER OF ARMS: AN ANALYTICAL WORK CONTRIBUTING TO LATIN AMERICA´S HISTORY

Diego Armando Badillo Sánchez m34313

Cristina Barrocas Dias, University of Évora
Nicola Schiavon, University of Évora
Ana Manhita, University of Évora

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Presented by: Diego Armando Badillo Sánchez

Supervisor: Cristina Maria Barrocas Dias Ph.D.

Co-Supervisor: Nicola Schiavon Ph.D.

Co-Supervisor: Ana Cristina Cabaça Manhita Ph.D.

University of Évora

University of Thessaloniki

University of La Sapienza

HERCULES Laboratory, University of Évora

Évora, Portugal, 2016

TO ALL MEN AND WOMEN FROM THE "OLD AND NEW WORLD" THAT OFFERED THEIR LIFE IN THE CONSTRUCTION OF THE PRESENT.

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Preamble

The Erasmus Mundus Master in Archaeological Material Science (ARCHMAT) is an academic program that offers through four academic semesters an interdisciplinary knowledge in the archaeometry field, that combined with the scientific background of each student, allows the development of specialized professional with the appropriate knowledge to answer with scientific rigor diverse analytical/archaeometric questions regarding the materials of cultural heritage artifacts.

Through a two years Master program the main objective is that in the end the different researchers will be able to be part in any kind of archaeometric/conservative project to increase the scientific knowledge of different kind of materials and the ability to obtain results that could be directly related with their respective historical/archaeological context globally.

The ARCHMAT students are trained under three semesters of theoretical and practical classes, combined with seminars, scientific meetings, summer schools and field works; to give them the necessary tools to develop research projects of excellence. The success of this training program is evaluated through a Thesis research project, developed in the fourth semester. When the aims of the project are accomplished successfully the degree is awarded with its respective Diploma, which accredit the individual as an international researcher able to execute a deep impact project in the creation of culture and knowledge.

According with the previously exposed, this Thesis research project was proposed intending that the new knowledge acquired will help in the creation, understanding and care of the World material cultural heritage.

Short Abstract

During the last two centuries the authenticity of Francisco Pizarro's Banner of Arms preserved by the National Museum of Colombia has been under discussion. The Banner collected in 1825 by General Sucre, has been catalogued as an unique object part of the history in the reunion of two societies, the Old and the New World. By first time a multi-analytical research is done to the Banner. Chromatographic, spectroscopic and microscopic techniques are combined with radiocarbon dating to characterize the different material components of the object and clarified it age and provenance. The analytic results with the historical documentation, allow to postulate that the Banner comes from an European manufacture, around the 16th century, arriving to America's lands possibly by Pizarro's expedition. Nevertheless, the Banner does not represent to Pizarro. In contrast, by the Banner manufacture, elements (weaved degummed silk, natural dyes (brazil wood, cochineal, indigotin and luteolin base) and silver gilded threads) and the coat of arms present on it, it is possible to postulate that the Banner represents the Royal Banner of the America's Conquest under the Crown of the King of Spain Charles V to symbolize his Realm in the New World.

Abstract

The study of textiles is an open area of scientific research, which for its variety of material components and physical chemical diversity of conditions, makes a field of interest for scientific studies in the cultural heritage field. Archaeological/historical textiles offer the possibility to carry out studies on organic materials such as fibers, adhesion elements, dyes, paper, etc., as well as on inorganic compounds for instance metals, alloys, precious stones and other added ornamentation. That variety of composition, allow to use a combination of analytical techniques to solve the questions coming from the object in an archaeometric research.

One kind of textile object that provides a valuable cultural information because of its linguistic representation employed by its carrier societies, are the flags/banners/emblems, objects made with a nonverbal communication purpose. As long as depending on the use and/or purpose of each object, varies both the materials/techniques used in its production and its iconography (style, color, emblem, shape), its study gives the possibility to extract information through their materials and manufacturing techniques about a temporal-spatial frame, a particular event or a specific character.

The flags/banners have been used since the eleventh century as representative objects of power, hierarchy, social or military organization, or as communicative media. The use of these objects has been spread throughout the world, possibly due to its easy interpretation and/or appropriation by different societies, making it part of their own culture. The flags as symbols of territorial control, using emblems that represent a family, order or army, were introduced to the New World (America) with the arrival of the European conquerors at the end of the fifteenth century. Flags/banners representing the Royal dominion over conquered territories, the Catholic Church and conquistadors' armies were the first to arrive.

One of those flags that have endured over time, that have an invaluable cultural meaning for both American and Iberian societies, is the so-called Francisco Pizarro's Banner of Arms. It is a textile object with metal threads decoration over a Royal emblem. According to historical sources, this object was used by Francisco Pizarro in 1532 on the conquest process of Peru, after received the permission by King Charles V to on behalf of him, to conquer the lands of the New World today known as Peru. After Pizarro's control of the Inca territory, it is believed that Pizarro left his banner on top of the Inca's Sun's Temple as symbol of his rule. Centuries later, in the America libertarian campaigns, General Sucre, military at charge of the independence army in Peru, reports have found what he considered the Pizarro's Banner, sending it to Bogotá as a symbol of victory, being kept since that time until today by the National Museum of Colombia.

Due to historical discrepancies in the different movements of the so-called Pizarro's Banner of Arms, its real meaning has been under discussion and because of the passage of time its physical condition has suffer deterioration. That is because its scientific study is now an interesting case study to respond to both historical and conservation questions of it.

Through a collaboration with the National Museum of Colombia, a set of 25 samples of so-called Pizarro's Banner of Arms were collected, covering the various components and areas from the object of study. These samples were subjected to analytical studies for physical and chemical characterization. Microscopic observation, VSEM-EDS analysis, Raman spectroscopy, chromatographic analysis (HPLC-MS, GCMS) and radiocarbon dating were done. Similarly, was sought through a direct *in situ* physical inspection to the object and through a research into historical sources, adequate information to solve the object's problems.

Results obtained allowed to identify as silk the textile used in the elaboration of the Banner's fabric, as well as the use of natural dyes for dyeing the fibers used on the emblem: use of cochineal and brazil wood as a source of red, luteolin plant-based for yellow color, indigotine plant-based for blue, and a mixture of yellow and blue dyes for green were identified. Similarly, the use of animal glue in the manufacturing process and the use of rag paper was evident. The metal threads study from the Banner give a confirmation to a silver core wire gilded with a thin gold sheet, being flattened and entwined with silk threads for their use. Finally, using the radiocarbon results, it was possible to postulate with huge accuracy that the Banner date manufacture was between the XV-XVI century and subject to restoration processes with addition of textiles in modern times. Together with, was evident that the state of degradation of the fabric is due to natural degradation in the silk fibers, having that its color has faded and its mechanical properties decreased, leading to loss of rigidity and disappearance of the physical

structure. Similarly, it was clear the original colors of the emblem and highlight problems of detachment of paper due to crystallization of the adhesive. In the same way, was found that the metal threads suffer corrosion by sulfur and detachment of its crystals.

Finally, combining the analytical results and the historical sources data found from the so-called Francisco Pizarro's Banner of Arms, allows to postulate that its manufacture process was done in Europe employing precious materials to obtain a long-life object with a deep message for its viewers. Also, the data obtained helps to support the possible idea that the object was employed by Francisco Pizarro in the Peru conquest process. However, by the symbols present in the object, its elaboration date and materials, this object its clearly unique in its kind, and the most important, by its linguistic message, does not represent to Francisco Pizarro or his army, meanwhile, represents the Spanish crown. Therefore, instead to be labeled as Francisco Pizarro's Banner of Arms, it should be called the Colonial Royal Banner of Charles V in the New World.

Resumen

El estudio de textiles es un área abierta de investigación científica, la cual por su variedad de componentes materiales y la diversidad de condiciones físico-químicas presentes en estos objetos, lo hace un campo de interés para estudios científicos en el patrimonio cultural. Los textiles arqueológicos/históricos brindan la posibilidad de realizar estudios en materiales orgánicos como fibras, elementos de adhesión, tinturas, papel, etc., e inorgánicos como metales, aleaciones, piedras preciosas y demás materiales decorativos añadidos. Por su variedad de composición, es posible emplear diversas técnicas analíticas para resolver aquellas preguntas propias del objeto en una investigación arqueométrica.

Uno de los objetos textiles que brinda gran información cultural debido a su representación lingüística empleada por las sociedades portadoras, son las banderas/estandartes/emblemas. Donde varía dependiendo de su uso y/o propósito, los materiales empleados en su elaboración, al igual que su iconografía (estilo, color, emblema, forma). El estudio de estos objetos construidos con un propósito de comunicación no verbal, da la posibilidad de extraer información a través de sus materiales y técnicas de elaboración sobre un rango temporal-espacial, un evento determinado en la historia o incluso a un personaje en específico.

Las banderas han sido empleadas desde el siglo XI como objetos representativos de poder, jerarquía, organización social o militar, o como medio de comunicación. El uso de estos objetos se ha extendido a lo largo del mundo posiblemente debido a su fácil interpretación y/o apropiación por distintas sociedades, haciéndolo parte de su cultura. Las banderas como símbolos de control territorial, empleando símbolos que representan a una familia, orden o armada fueron introducidas a el Nuevo Mundo (América) con la llegada de los conquistadores europeos al final del siglo XV. Las banderas/estandartes que representaban el dominio Real sobre territorios dominados, la iglesia católica y las banderas de ejércitos y/o conquistadores fueron las primeras en llegar al nuevo mundo.

Una de aquellas banderas que ha soportado el paso del tiempo, teniendo un gran valor cultural tanto para las sociedades americanas como para las ibéricas, es el denominado Estandarte de armas de Francisco Pizarro. Siendo un objeto textil con

decoración en hilos metálicos sobre un emblema Real. De acuerdo a fuentes históricas, este objeto fue usado por Francisco Pizarro en 1532 en el proceso de conquista del Perú, quien recibe por parte del Rey Carlos V el poder para que, en su nombre, Pizarro pueda conquistar las tierras del nuevo mundo hoy conocidas como Perú. Luego del dominio de Pizarro sobre el territorio Inca, se cree que Pizarro dejó su estandarte en la cima del templo Inca del sol como símbolo de su control. Siglos más tarde, en las campañas libertarias de América, el General Sucre, militar encargado de la armada independentista en Perú, reporta haber encontrado lo que él considera como el estandarte de Pizarro, enviándolo a Bogotá como muestra de victoria, siendo custodiada desde ese momento por el Museo Nacional de Colombia hasta la actualidad.

Debido a discrepancias históricas, el verdadero significado del llamado estandarte de Pizarro ha sido objeto de discusión y debido del pasar del tiempo su estado de conservación se ha deteriorado. Dejando de este modo, un caso de estudio interesante para que por medio de estudios científicos al objeto se pueda dar respuesta a preguntas tanto históricas como de conservación del mismo.

De este modo, por medio de una colaboración con el Museo Nacional de Colombia, se obtuvo un juego de 25 muestras del llamado Estandarte de armas de Francisco Pizarro, abarcando los diferentes componentes y áreas del objeto de estudio. Dichas muestras fueron sometidas a estudios analíticos para su caracterización físico-química. Análisis de observación al microscopio, análisis VSEM-EDS, espectroscopia Raman, análisis cromatográficos (HPLC-MS, GC-MS) y datación por radiocarbono catorce fueron realizados. Del mismo modo, por medio de una inspección física al objeto *in situ* y una profunda investigación en fuentes históricas del mismo, se buscó la información adecuada para resolver sus problemáticas.

Los resultados obtenidos permitieron identificar como seda el textil empleado en la elaboración del estandarte, así como el uso de colorantes naturales para teñir las fibras en el emblema: uso de cochinilla y palo de Brasil como fuente del color rojo, plantas a base de luteolin para el color amarillo, plantas a base de indigotina para el color azul y mezcla de colorantes amarillos y azules para el color verde fueron identificadas. Del mismo modo se evidencio el uso de adhesivos animales y el uso de papel de trapos en el proceso de manufactura. El estudio de los hilos metálicos, permitió evidenciar el uso de alambres con núcleos de plata con un fino recubrimiento de oro en su exterior, siendo

aplanados y entrelazados con hilos de seda para su uso. Finalmente usando la datación por radiocarbono, fue posible conocer con alta precisión que el estandarte fue elaborado entre los siglos XV-XVI y sufrió procesos de restauración con añadidura de textiles en tiempos modernos. Junto a lo anterior, es posible postular que el estado de degradación de la tela es debido a degradación natural en las fibras de seda, teniendo así que su color se ha desvanecido y sus propiedades mecánicas disminuidas, conllevando a perdida de rigidez y desaparición de la estructura. Del mismo modo se pudo conocer los colores originales del emblema y evidenciar problemas de desprendimiento del papel debido a cristalización del adhesivo. Asimismo, se comprobó que los hilos metálicos presentan corrosión por azufre y desprendimiento de sus cristales.

Finalmente, combinando los resultados analíticos y la información de fuentes históricas encontradas del llamado Estandarte de armas de Francisco Pizarro, se puede postular que su elaboración fue realizada en Europa, usando materiales preciosos para obtener un objeto de larga vida con un profundo mensaje para sus observadores. También, los datos obtenidos ayudan a dar soporte la posible idea de que este objeto fue usado por Francisco Pizarro en el proceso de conquista del Perú. Sin embargo, debido a los símbolos presentes en el objeto, fecha y materiales de elaboración, este objeto es claramente único en su tipo, y lo más importante, por su mensaje lingüístico, este no representa a Francisco Pizarro o su armada, al contrario, representa a la Corona de España. Por ende, en vez de denominarse como Estandarte de armas de Francisco Pizarro, este objeto debería nombrarse como el Estandarte Real de la Colonia de Carlos V en el Nuevo Mundo.

1. Introduction

1.1 Francisco Pizarro's Banner of Arms: Case study

This research deals study of a textile kept under the custody of the National Museum of Colombia (Dependence of the Ministry of Culture of the Republic of Colombia), denominated as "Francisco Pizarro's Banner of Arms" and identified with the register number 085129 in the museum data-base. The Banner is thought to be made from Silk fabric with embroideries made with metal threads.

Francisco Pizarro's Banner of Arms is stored in an individual metallic drawer, full-extended in an horizontal position at the textile reserve of the Museum (Figure 1). The whole object shows deterioration/degradation, with several lost parts. The main textile is discolored, and there are textile parts missing in the main body and in the coat of arms emblem. Bio-deterioration is likely to have played an important role in the current conservation status of the Banner. In general, the actual Banner (Figure 2) does not reflect its original visual appearance.

Figure 1 Drawer where the Francisco Pizarro's Banner is stored in the Textile Reserve of the National Museum of Colombia

Figure 2 Francisco Pizarro's Banner, photography given by the National Museum of Colombia ©Museo Nacional de Colombia Ca 1529, 166 x125.5 cm.

1.2. Francisco Pizarro's Banner of Arms Historical Description

The Banner thought to be the one used by the Conquistador Francisco Pizarro in his conquest of the area of the actual Peru in 1532, it is a textile artifact that has been in the collection of the National Museum of Colombia for almost two centuries.

To have an idea of the origin of this object, it is necessary to review all that is known about it, including the revision of the information contained in several documents available in historical sources.

Francisco Pizarro's Banner of Arms is a textile object with an actual approximate length of 166 cm x 125.5 cm due to the shrink of the material. Its shape can be related as a banner ended in two points (gonfalon, inverted V banner). Its manufacture is considered as: Silk and metal threads, sewing and embroidery by hand, and traditionally dated *c.a.*16 century. (Figure 2)

Until the decade of 60-70's of the previous century, the Pizarro's Banner was exhibited to the public in different rooms inside the National Museum, as well as in different locations where the Museum was located in the city of Bogotá (Figure 3A and 3B). Their exhibition always was in a vertical display covered by glass, without protection of the environmental conditions. In fact, the Banner was under direct light, relative humidity changes, atmospheric pollutants and temperature oscillations, among others conditions without control (L. Castelblanco, 2013).

Figure 3 A) flags room in the National Museum of Colombia previous 1970. Photo Recovered from the Documentation Center of the National Museum of Colombia. In red square the Banner location. B) Picture of the Pizarro's Banner taken from the National Library of Peru.

Consulting on the database of the National Museum of Colombia, it is possible to find the incoming date and provenance of the Pizarro’s Banner as museum’s object. That’s because a Presidential Donation it is documented at 1825 by Vice-President General Francisco de Paula Santander[1], just after being received the Pizarro’s Banner as a gift coming from General Antonio José de Sucre[2]. In the available document it is possible to learn, how is told that The General Sucre took the Pizarro’s Banner during the Liberty campaign in Peru, where, in the so called Temple of the Sun (Cathedral of Cuzco), Sucre had the opportunity to take down all the symbols from the Spanish Crown, including the different flags/banners used in the conquest and exhibit during the Colonial Period (L. Castelblanco,2013). See below for transcription and translation of the part of the text).

“Ejército auxiliar Libertador del Perú. Cuartel general de Potosí, a 19 de abril de 1825. El señor coronel graduado Antonio Elizalde, Ayudante general del Estado Mayor General y diputado del ejército para facilitar a S.E, el Vicepresidente, por el feliz término de la campaña de las tropas colombianas en el Perú, que ha finalizado la guerra de independencia, tendrá el honor de presentar a S.E el estandarte real de Castilla con que los españoles entraron a este rico país, trescientos años pasados. Este trofeo, que el ejército presenta a Su excelencia en testimonio de respeto y aprecio, recordará un día a los hijos de los libertadores que sus padres, penetrados de los deberes patrios y del sublime amor a la gloria, condujeron en triunfo las armas de Colombia a las frías y eminentes cimas del Potosí. También pondrá a los pies de Su Excelencia los cuatro pendones españoles de las provincias del alto Perú, que formaban la insignia del vasallaje y esclavitud de estos pueblos a los descendientes de Fernando VI, y que hoy han recobrado su libertad y sus derechos por valor, constancia y heroísmo de las legiones de la República"... Antonio José de Sucre. (Carta official del General Sucre al General Bolivar, 1825)

"Auxiliary Army Liberator of Peru. Potosi headquarters, 19 April 1825. Colonel graduate Antonio Elizalde, General Assistant of the General Staff and army’s deputy to provide to Your Excellency Vice President, by the successful conclusion of the Colombian troops campaign at Peru, which ended the independence war, will have the honor to present to Y.E. the Royal Banner of Castile with what the Spaniards entered this rich country, three hundred years ago. This trophy, which the army presented to His excellence in testimony of respect and appreciation, will remember one day to the liberators children, that their parents, imbued with patriotic duties and sublime love of glory, led in triumph the Colombian weapons through the cold and eminent peaks of Potosi. Also put at the feet of His Excellency the four Spanish banners of the provinces of Upper Peru, which were the insignia of serfdom and slavery of these people to the descendants of Ferdinand VI, and have now regained their freedom and their rights by courage, perseverance and heroism of the legions of the Republic “… Antonio Jose de Sucre. (Official letter from Gr. Sucre to Gr. Bolivar,1825)

[1] Francisco de Paula Santander (April 2, 1792 - May 6, 1840) was a military man and Colombian politician, famous for his role in American emancipation against the Spanish Empire.

[2] Antonio José de Sucre (February 3, 1795- June 4, 1830), was a politician, diplomat, statesman and military, founding father of American independence. It is considered one of the most complete military between the heroes of South American independence

1. Introduction

In the incoming of Pizarro’s Banner to the National Museum of Colombia (so called Museum of Bogota in those times), the object was described by the Museum Director as: “A fade Silk flag with patches of 2.60 m x 1.22 m in a “pennant shape” (Flag ended in two points). The Banner has the emblem of Castilla and Leon (with yellow, red and blue silks) in the center surrounded by the Chain of the Order of the Golden Fleece. In the upper part there is a hard linen structure where it was held to a pole. A green contour delimits the Banner. Metal threads (gold and silver) are visible in the emblem’s Banner and in the green stripe” (L. Castilblanco, 2013). In fact, the report states that the state of conservation of the Banner is bad, but no losses in its main body were appointed.

Until this point, the historical sources allow to think that the so-called Pizarro’s Banner could be in fact an object employed by Pizarro in his conquest of Peru, letting also open the option to be the Royal Banner used in that campaign. However, the different descriptions of the Banner arrived to Bogota, and the apparition of another two Banners also given by General Sucre (L.Castilblanco, 2013) and related to the same historical period further complicate the Banner attribution. Reason why the idea of three Francisco Pizarro’s Banners appears and the idea of a Royal Banner disappears from the descriptions.

About the other two textile banners related with the one in this study, it is well-known that one is in Caracas-Venezuela (without an exact location), which has an emblem in one side and the image of “Saint James” in the other (Figure 4). The second banner is related with the banner used in the burial of General San Martin, which is described on historical sources as a rectangle of fade silk with embroidery remains and patches around its body (today disappeared). Nowadays, historians agree that this last banner was likely to be the Lima city council flag, and not the Royal Banner or the Francisco Pizarro’s Banner (L. Castilblanco, 2013).

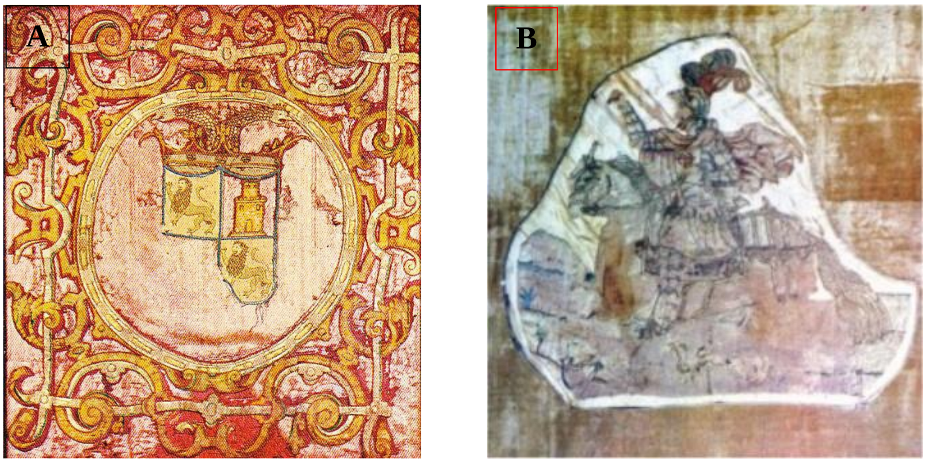

Figure 4 Banner related to Francisco Pizarro’s Banner of Arms located in Venezuela A) Emblem on front face B) Figure of “Saint James” on rare face

Before of the independence campaigns the historical information about the banner(s) is(are) unavailable. It is possible to find some written information referring different flags used by Francisco Pizarro, without any direct information about the object, most of which describing theories about the symbolism of those objects in the military missions and the representativeness of them in the social-political context of the 13^{th}-16^{th} centuries (H. Noejovich *et al.*, 2009; J. Ortiz-Griffin et al 2007).

1.3. Francisco Pizarro and the New World

In the late 15^{th} century the imaginary of the world from the European habitants were delimited by their known territories and the ideas from the governance of their monarchies that through a feudal system handled the World view in that historical age (J. Singman, 1999; J.D G.G. Lepage, 2002; C.R. Backman, 2003). Two of the most important kingdoms with a relevant importance were: the kingdom of Portugal and the kingdom of Castilla (actual within Spain), which were under a global competition for the control of products, land, ocean and commercial routes, among others (J. Ortiz-Griffin, 2007).

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Figure 5 Detail: Europe, North Africa, 1375, taken from Catalan Atlas (facsimile), Abraham Cresques, 1375

After the Reconquista of the Iberian Peninsula from the Islamic occupation, the Spaniards started their quest of a new way to arrive to India, and be able to compete against their neighbors: The Portuguese. This had as end the "discovery" by Christopher Columbus in 1492 of lands unknown for the Spaniards and the Europe population (Old World), what they call in a first step as "The New World" (J. Ortiz-Griffin, 2007).

Was not necessary so many time to spread through the different geopolitical powers the "discovery" of lands rich in resources with some populations of "low development". In consequence, and due to the economically-military power, were the Crowns from England, Spain (Castilla (Leon and future allies)) and Portugal, the most active and relevant in this strategic geopolitical play (R. K. Emerson, 2006; J.H Elliot, 2006; H. Thomas, 2010).

This new lands gave the opportunity for the inhabitants of the "Old World" to have new perspectives and ambitions; all offered by their Kings/Queens or Lords, with the sole compromise that they will help extend their lands and domains in the "New world" (R. K. Emerson, 2006; J.H Elliot, 2006; H. Thomas, 2010).

In this special period of time, one of the most famous and important characters nowadays remembered was Francisco Pizarro (Figure 6).

Figure 6 Portrait of Francisco Pizarro, copy of an original from XVII century by Jean Mosnier, © Musée national des Châteaux de Versailles et de Trianon, Versailles, France/Scala, Florence

Francisco Pizarro (1478-1541) native from Trujillo – Kingdom of Castilla, was an illegitimate son of the union of Gonzalo Pizarro, an infantry colonel of the Catholic Kings, and Francisca González, a woman of poor means. Pizarro also was direct cousin of Hernan Cortes[3] (Spanish Conquistador of the Aztec empire, founder of the Mexico Lands) (H. O. Noejovich *et al.*, 2009; B. Lavallé, 2013; M. Peronnet, 1934). Reason why possibly was immersed in military actions across his life being always a loyal servant from the Spanish Crown.

Pizarro young years were spent in the Iberian Peninsula, without care of an educational training, growing up as illiterate. In 1509, at the age of 31, Pizarro start his life as an explorer, joining the Alonso de Ojeda's expedition (Spanish navigator, governor and conquistador) to the Gulf of Uraba (Nowadays north of Colombia). There Pizarro had his first administrative position as First at charge of the new city of San Sebastian in the New World. In 1513 Pizarro join Vasco Nuñez de Balboa (Spanish explorer, navigator) in the expedition across the Isthmus of Panama reached the Sea of the East (Present Pacific Ocean). For his loyalty, Pizarro was rewarded with the positions of Mayor and Magistrate of the then recently founded Panama City from 1519 to 1523 (R. Arciniega, 1936; M.J. Quintana, 2013).

[3] Hernan Cortes (1485-1547) was a Spanish conquistador who led the expedition that caused the end of the Aztec Empire and the conquest of Mexico, also put the government of the Crown of Castile the territory of present Mexico in the early sixteenth century.

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In 1524, Pizarro formed a partnership with Hernando de Luque (Catholic priest) and Diego de Almagro (Spanish soldier) to explore and conquer the South region of the new coast recently discovered at the Sea of the East. Their agreement stablished to conquer and divide equally among themselves the opulent lands they hoped to discover (R. Arciniega, 1936; M.J. Quintana, 2013).

Unsuccessfully, due to the difficult encounters with the native populations, Pizarro and the others can only to arrive till the called "Punta Quemada" (Burnt Port), in what is now the north cost of the Pacific Ocean of Colombia (R. Arciniega, 1936; M.J. Quintana, 2013).

In 1526, with the permission of Pedrarias Dávila, Governor of Panama, Pizarro together another 160 men and several horses, depart from Panama as second attempt in his conquest of the new lands. This expedition was more successful than the previous one, gave him contact with a new population, obtaining from them a load of textiles, ceramic objects, and some much-desired pieces of gold, silver, and emeralds. In the same way, due to the new contact with the natives, Pizarro obtains also interpreters to communicate him with the new populations. This enterprise allowed the contact in the actual coast of Ecuador with the population of the Inca Empire, having as consequence for the Pizarro's army a big loose in men and resources, reason why Pizarro and his men are commanded to return to Panama. Pizarro stays and follow his campaign with no more than 13 more men in his quest (R. Arciniega, 1936; M.J. Quintana, 2013).

In 1528, Pizarro arrived to the Tumbes region of the lands called Viru, where he obtained the final motivation and evidence to show to the Castilla Crown the discovery of a new region, reported with incredible riches of the land, including the decorations of silver and gold around the chief's residence and the hospitable attentions with which they were received by everyone (R. Arciniega, 1936; M.J. Quintana, 2013).

In 1529, Pizarro obtained a Royal audience with the King Charles V (Holy Roman Emperor) at Toledo-Spain to present to the King his evidence of a potential new land full of resources and to ask his permission and help to continue the quest (R. Arciniega, 1936; M.J. Quintana, 2013). After their meeting, King Charles V accepted to help Pizarro giving him resources (men, horses, ships, and more) for a new expedition with the condition to extend the domains of the Castilla Crown (H. Thomas, 2010; J.H. Elliot, 2006; J. Ortiz-

Griffin, 2007). This was documented as the "Capitulaciones de Toledo" and given to Pizarro by the Queen Isabel of Portugal, wife of the King Charles V (Porras Barrenechea, Cedulario del Perú. I. pp. XIX-XX and 18-24). Pizarro stay in Europe until the end of 1530, making all the preparative for his third and final expedition (R. Arciniega, 1936; M.J. Quintana, 2013).

In 1531, Pizarro with his men arrives to the region of Esmeraldas (now north coast of Ecuador) starting his conquest of the new lands, establishing new cities, controlling the commerce and exploring them for the Castilla Crown (R. Arciniega, 1936; M.J. Quintana, 2013).

In 1532-3, Pizarro conquer the Inca Empire with his army entering the city of Cuzco, and declaring the expansion of the Castilla Crown in the New World with a new territory then called "New Castilla" (J. Ortiz-Griffin, 2007; H.O Noejovich, 2009; R. Arciniega, 1936; M.J. Quintana, 2013).

Figure 7 Spanish Explorations of South America, 1524-1542 Taken from Spain and Portugal: a reference guide from the Renaissance to the present / Julia Ortiz- Griffin and William D. Griffin.—1st ed Copyright © 2007

In 1541, after different quarrelling between the conquerors, Francisco Pizarro is death, killed in his Palace by followers of Diego de Almagro, being his body buried secretly (R. Arciniega, 1936; M.J. Quintana, 2013).

1.4. Francisco Pizarro and the representativeness of the Spanish Crown in the New World

Francisco Pizarro's time was an age of several changes around the world. Born during the reign of the Catholic Kings of Spain, he was surrounded by a military family loyal to the monarchy; had navigators and explorers as neighbors and local battles/wars that expanded an empire were the news at the time.

Pizarro's father defends the Royal Banner in the wars in Italy, Flanders and Navarre among others (Don Fernando Pizarro, 1639). The Crown of Castilla each year expand its domains. Facts that must to influence Pizarro's man imaginary in a society that was in transition due to the arrival of the Renaissance and a New World.

Figure 8 European Empire of Charles V Taken from Spain and Portugal: a reference guide from the Renaissance to the present / Julia Ortiz- Griffin and William D. Griffin.—1st ed. Copyright © 2007

The news of the “discovery” of the New World arrived to Pizarro in his early adulthood, and did not pass a long time before himself started to be part of that enterprise.

Pizarro as well as Almagro, Cortes, Quesada and all the Spanish conquistadors/explorers sailed to the New World leaving behind all their past, carrying the orders, law and image of the Crown. The grace of the King allows them to transform their regular lives to be men of honor, with labels of higher status, full of richness and lands, thanks to their compromise with the Crown (J. Ortiz-Griffin, 2007, H. Thomas, 2010). It is possible to confirm this assumption since the very first expedition unifying the two worlds, where in the Columbus’ diaries it is possible to read (Fray Bartolome de las Casas 16th century):

“A las dos horas después de medianoche pareció la tierra, de la cual estarían dos leguas. Amainaron todas las velas y quedaron con el treo, que es la vela grande, sin bonetas, y pusiéronse a la corda, temporizando hasta el día viernes, que llegaron a una isleta de los Lucayos, que se llamava en lengua de indios Guanahaní. Luego vieron gente desnuda y el almirante salió a tierra en la barca armada, y Martín Alonso Pinzón y Vicente Anes, su hermano, que era capitán de la Niña. ***Sacó el almirante la vandera real y los capitanes con dos vanderas de la Cruz Verde, que llevava el almirante en todos los navíos por seña, con una F y una Y, encima de cada letra su corona, una de un cabo de la cruz y otra de otro****. Puestos en tierra vieron árboles muy verdes y aguas muchas y frutas de diversas maneras. El almirante llamó a los dos capitanes y a los demás que saltaron en tierra, y a Rodrigo de Escobedo, escrivano de toda el armada, y a Rodrigo Sánchez de Segovia,* ***y dixo que le diesen por fe y testimonio cómo él por ante todos tomava, como de hecho tomó, posesión de la dicha isla por el rey y por la reina sus señores,*** *haziendo las protestaciones que se requirían, como más largo se contiene en los testimonios que allí se hizieron por escrito”.*

"At two hours after midnight the land appeared, which would be two leagues. Died down all sails and kept the treo, which is the largest sail without bonnets, and stood to the cord, clocking until Friday day, they reached a Lucayos cay, which was called in Indian language Guanahani. Then they saw naked people and the Admiral went on shore in the armed boat, and Martin Alonso Pinzon and Vicente Anes, his brother, who was captain of the La Niña. ***Took the admiral the Royal Banner and the captains taken the two Flags from the Green Cross, which carry the Admiral on all ships as signal, with an F and a Y above each letter his crown, one of the end of the cross and another other.*** *Toward the ground they saw very green trees and many water and fruits in different ways. Admiral called the two captains and others who jumped ashore, and Rodrigo de Escobedo, scrivener of all the armada, and Rodrigo Sanchez de Segovia****, and he said that they should give him by faith and witness, how him before all of them takes, as he actually it took, possession of that island for the king and queen their masters,*** *making the protestations required, as longer contained in the testimony that there were made in writing".*

1. Introduction

The ruling King at Pizarro's time was Charles I (1500-1558), also known as Charles V, Holy Roman Emperor. Son of Juana I (The Mad) of Castilla and Felipe I (The Beauty) and grandson by paternal route of Maximilian I and Mary of Burgundy and matrilineal of Catholic Kings, Isabel I of Castilla and Ferdinand II of Aragon who inherited Castilla, Navarre, the Indies, Naples, Sicily and Aragon (Figure 8) (J. Ortiz-Griffin, 2007; H. Thomas, 2010).

Charles V, together with his Queen reagent; Isabella of Portugal, they had a direct ruler with the ordainment and dispositions of the overseas territories, reign the territories of the New World (Figure 9). Reason why Charles V was called by Hernan Cortes as "his Majesty the Lord of the World" (J. Ortiz-Griffin, 2007; H. Thomas, 2010).

It is important to underline the historic relationship of the King Charles V with the House of Castilla. Principal House of the new kingdom of Spain that expanded their dominions in the "Old World" joining with the House of Leon, Granada, Navarre, among others (J. Ortiz-Griffin, 2007; H. Thomas, 2010).

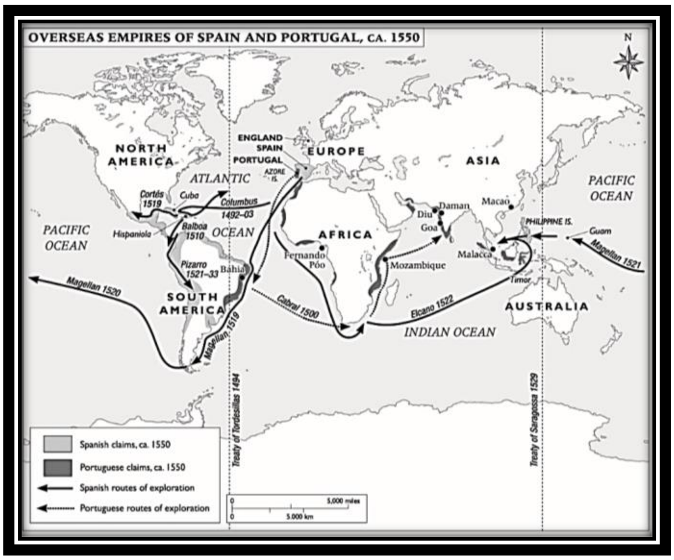


Figure 9 Overseas Empires of Spain and Portugal ca. 1550 Taken from Spain and Portugal: a reference guide from the Renaissance to the present / Julia Ortiz- Griffin and William D. Griffin.—1st ed Copyright © 2007

Pizarro, following the tradition of taking permission from the Ruler that granted support and avoiding illegal movements, is forced to return to Europe and talk directly with the King Charles V, due to the obstacles obtained from the governor at Panama City, who stops Pizarro and his men to continue their expeditions in the new lands. Pizarro taking advantage of being a Hernan Cortes relative (which had an important character for the Crown for his role in the conquest of the Aztec Empire at that time), got the opportunity to have an audience with the King Charles V, where Pizarro could explain thoroughly what were his intensions in the New World (Figure 10) (J. Ortiz-Griffin, 2007; H. Thomas, 2010; H. O. Noejovich, 2009).

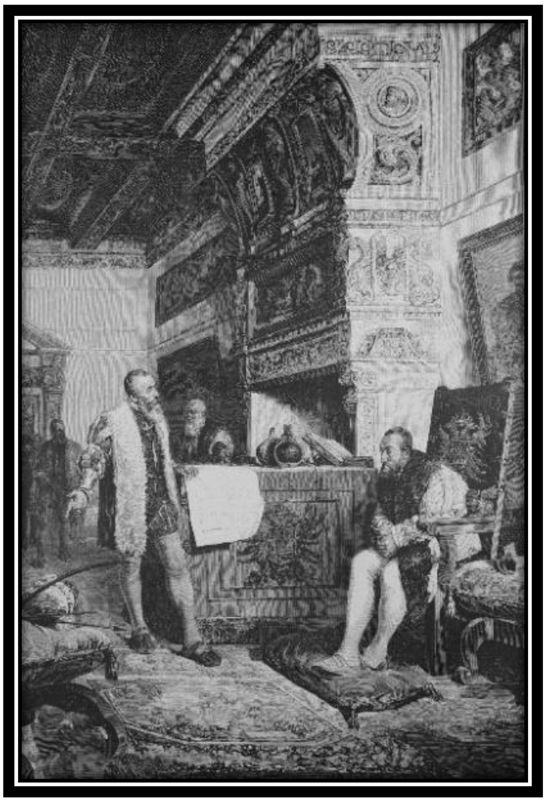


Figure 10 Engraving representing the Spanish conquistador Francisco Pizarro exposing to King Carlos I of Spain testing fabulous discovery of the Inca Empire. 1885 - Die Gartenlaube

Due to the coronation process of the King Charles V in Italy to become as Emperor of the Roman Empire, Pizarro ends under the supervision of the Queen Isabella of Portugal and the Audience of Indies (J. Ortiz-Griffin, 2007; H. Thomas, 2010). In 1529, in the Royal city of Toledo, the Queen Isabella confers the permit and the military-economic and religious support for the third Pizarro's expedition. Today it is possible to read the agreement in the "Real Cedula" of July 26th of 1529 as follow:

"Preámbulo:

***La Reina. Por quanto vos el capitán Francisco Piçarro, vezino de Castilla del Oro**, por vos y en nombre del venerable padre don Hernando de Luque, maestrescuela e provisor de la Iglesia del Darién sede vacante, que es en la dicha Castilla del Oro, e del capitán Diego de Almagro, vezino de la cibdad de Panamá, **nos hizistes relación, que vos e los dichos vuestros compañeros, <u>con desseo de nos servir e del bien e acrescentamiento de nuestra Corona real</u>,** puede aver cinco años, poco mas o menos, que con licencia e paresçer de Pedrarias Dávila, nuestro governador e capitán general que fué de la dicha Tierra Firme, **tomastes cargo de ir a conquistar, descobrir e paçificar e poblar por la costa de la mar del Sur de la dicha Tierra**…*

*…1. Primeramente, **doy licencia e facultad a vos, el dicho capitán Francisco Piçarro, <u>para que por Nos, en nuestro nombre e de la Corona Real de Castilla,</u> podais continuar el dicho descobrimiento, conquista e población de la dicha provincia del Perú**, fasta dozientas leguas de tierra por la misma costa. Las quales dichas dozientas leguas comiençan desde el pueblo que en lengua de indios se dize Teninpulla y después le llamastes Santiago, fasta llegar al pueblo de Chincha, que puede aver las dichas dozientas leguas de costa poco más o menos…"*

"Preamble:

The Queen. Because you Captain Francisco Pizarro, a resident of Castilla del Oro**, for you and on behalf of the venerable father Don Hernando de Luque, schoolmaster and vicar of the Church of Darien vacant seat, which is in the said Castilla del Oro, and the captain Diego de Almagro, a resident of the city of Panama, **you did us relationship, that you and your said peers, <u>willingness to serve us and for the good of the expansion of our Royal Crown</u>**, may to have five years, more or less, than with license and agree of Pedrarias Davila, our governor and commander in chief at mainland, **you took charge to goes to conquer, discover and pacify and populate the sea coast the South Sea of such Earth ...

*... 1. First, I license and authority to you, the said Captain Francisco Pizarro, **<u>that by us, on our behalf and the Royal Crown of Castile,</u> continue on this discovery, conquest and colonize of that province of Peru,** till two hundred leagues of land for the same coast. These two hundred leagues which start from the people that in indian language is called Teninpulla and then you called Santiago, to the village of Chincha, which may have the said two hundred leagues of coast more or less… "*

In the previous lines it is possible to deduct the intentions of both: Pizarro and the Spanish Crown. The ambition of a man to continue his vision of conquistador and master in foreign lands. As well as the needs of a Crown, which needs to obtain the resources and the power to control and rule the World. This also can be confirmed with the document of the general archive of Indies justice 406 no. 6, where the Nobile Titles granted to Pizarro appear, letting behind the man of illegitimate ascendency, showing at the same time the richness sent to the Crown from the New World.

"…The Marques Don Francisco Pizarro, advanced and Captain General and governor by your majesty in this realm of New Castilla called Peru and from his council,

Considering that you, the Captain Hernando Pizarro have been a serve to your Majesty in the pacification of this kingdoms, as well in the capture of Tabalipa, Sir of these lands, that was the principal reason why these kingdoms were taken and why your Majesty was served in the Earth, as have been with the richness that have been taken from the lands in question…"

In order that, it is possible to see a deep relationship between Pizarro and the King Charles V representativeness in the new world, letting open the idea that between the objects used by Pizarro in his quest, must to exist a precious object that reflect the King's control, transmitting to the new population the message of dependence and/or relation with the Kingdom at the Iberian Peninsula, being possible a Royal Banner.

1.5. Flags: Meaning and power

During Medieval times, the relationship between the domination of a social structure and the ruler was changing due to the appearing role of the social classes in the Feudal system (C.R. Backman, 2003; R. K.Emmerson2006). The different status, labels and hierarchies start to need to be distinguished among them. The heraldic helps easily to define each family, clan or army in times where symbolism represent more than words (T. Hylland *et al.*, 2007). According to the vexilloids, each part of the emblem transmits a special meaning, where each character, symbol, color and tone (Figure 11), among others, create a difference on the final message (C. Wills, 2008), it could have no sense for the inexpert eye, but indeed, for an improved spectator where even a subtle change could change completely the meaning seek.

1. Introduction

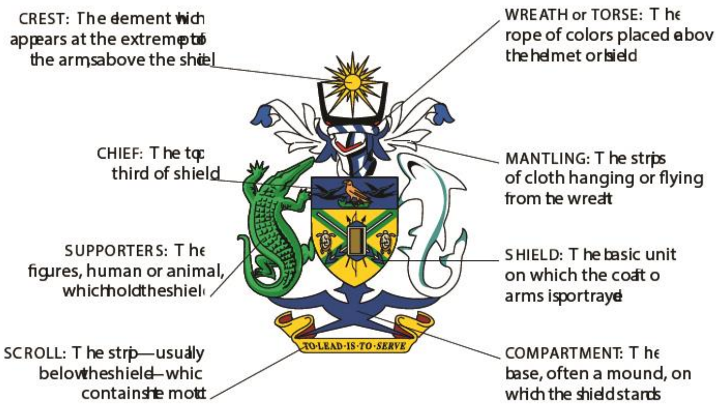


Figure 11 Heraldic terms on an emblem or coat of arms taken from Complete flags of the world, DK Publishing, 5th ed. 2008

The first coat-of-arms are dated in the 11th century, being followed for the appearance in flags or banners. In Middle Ages it is possible to distinguish several kinds of banners and flags (T. Hylland *et al.*, 2007), being of interest in particular two for this study: The banners that have military significance, as distinction. And the banner of the King, representing the symbol and embodiment of the kingdom in the Real Persona, placing the symbols of the King ruler or his House on the flag.

"Dicho día se celebraba por la mañana ayuntamiento extraordinario en el que todos asistían de gala con vestidos blancos festoneados de colores. Los comisarios que estaban nombrados al efecto traían el pendón y entraban ambos (portando el pendón el más antiguo de ellos) acompañados como siempre por los sofieles. Se lo entregaban en sus propias manos al corregidor el cual lo recibía y lo pasaba al alférez mayor. Este, mientras toda la ciudad estaba en pie y descubierta, partía hacia el corredor exterior siguiéndole detrás toda la ciudad conservando en su orden de sala. Salía el alférez al balcón del ayuntamiento y lo enarbolaba, descubierta su cabeza y en voz alta decía: «Oid, oid, oid, Este pendón levanta Toledo en nombre de estos reinos por el Rey don Fulano tal, que Dios guarde muchos y felices años. Amen, amen, amen» El pueblo que abarrotaba la plaza, respondía clamorosamente con los mismos tres amenes. El pendón se colocaba sobre este balcón y se le ponían guardas hasta la tarde de ese mismo día…" Poder y poderes en la ciudad de Toledo: gobierno, sociedad y oligarquías. Por Francisco José Aranda Pérez

"This day was celebrated in the morning an extraordinary council in which all attended it with gala dresses, festooned with white color. The commissioners who were appointed to effect brought the banner and entered both (carrying the banner the oldest of them) accompanied as always by the sofieles. They delivered it in their own hands to the Corregidor which received it and passed it to major- lieutenant. This, while the whole city was up and exposed, started to the outside corridor, being followed behind for all the citizens retaining the order in room. The lieutenant went to the town hall balcony and ensign brandished, exposing his head and said aloud: «Hear ye, hear ye, hear ye, this banner raises Toledo on behalf of these realms by King Don Fulano, God save the king and give him many happy years. Amen, amen, amen» The people who filled the plaza, responded resoundingly with the same three amen. The banner was placed on the balcony and they put guards until the afternoon of the same day ... "Power and powers in the city of Toledo: government, society and oligarchies. By Francisco José Aranda Pérez

The Spanish Crown as other kingdoms in the Medieval Age, use this symbolism to express their presence around the world: The Old and the New. There is historical documentation about the use of this items since the 13th century, where the King Ferdinand III unifyed the symbols of the house of Castilla and Leon in a system of four quarters to create the flag combined of both realms (Figure 12). This system was quickly accepted in the Iberian Peninsula, and copied in other realms (J. Ortiz-Griffin, 2007; H. Thomas, 2010; C. R. Backman, 2003).

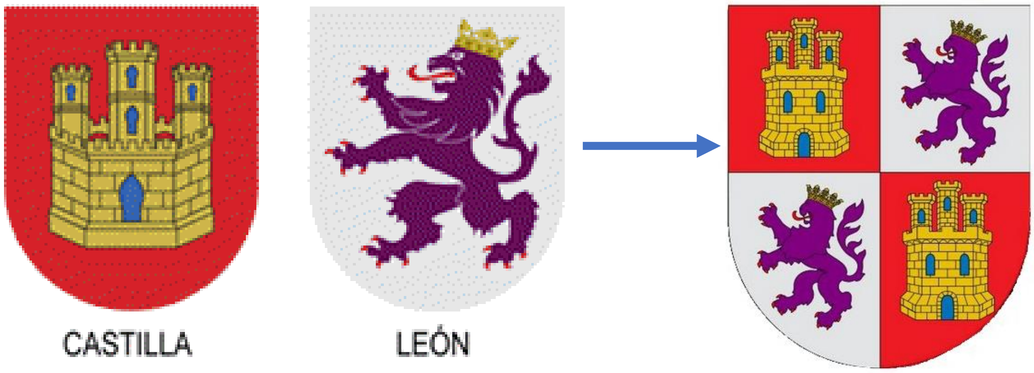


Figure 12 Coat-of-arms of Castilla and Leon from the joint of the Emblems of the kingdom of Castilla and the Kingdom of Leon

The flag is not only an inert object, is an item that wraps up several ideas, give identity to a nation, being used as a totem while have a sociologically and linguistic character that gives an essential function to join a group (R. Shanafelt, 2008). The Flag has become a sacred object, being the smaller part as relevant as the whole. This symbolic item has a direct link with the power of one person, one group or one idea (R. Shanafelt, 2008).

"… flag displays trigger an evolved sensitivity to cues about social dominance. Not only are they linked with totems, magic, mythology, ritual, and death, as the Durkheimian view suggests, they are also linked with primate dominance displays. They are thus not just symbols with arbitrarily constructed meanings; they are political signifiers that evoke predispositions related to dominance and subordination.

In-group flag raising evokes social solidarity among those who consent to the flag's authority. A solidarity (or communal sharing) orientation is thus akin to the group's submission to an authoritative leader. However, even within a group, submission and solidarity are not guaranteed. This is because a flag symbol can be interpreted as a *challenge to the authority position of any individual. Thus, an individual's resistance to a call for flag solidarity is akin to an individual's resistance to a dominant other. Between groups, the hierarchical challenge posed by flag display is even more evident. If two sides meet under conditions of rivalry and relatively equal power, then one flag display will evoke a reciprocal act, a rival display in which the height of the emblem, the size of the emblem, and public gestures of support will be equaled or bested."* (R. Shanafelt, 2008)

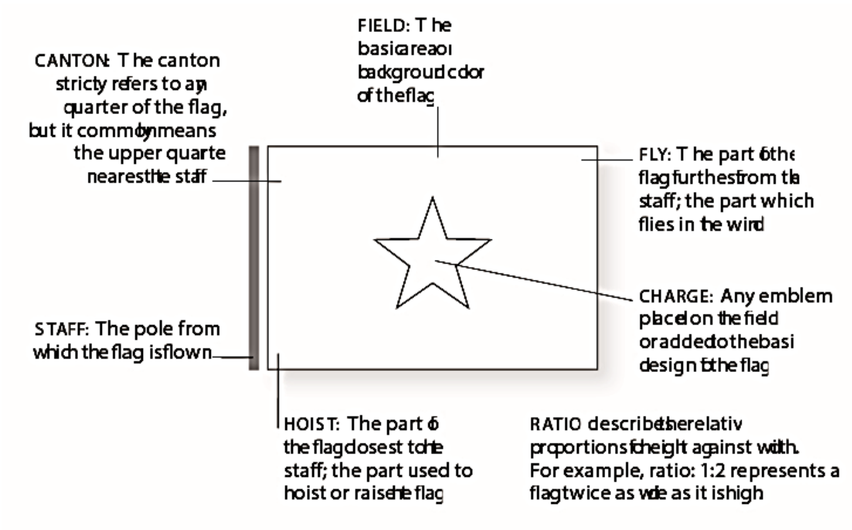


Figure 13 Basic Parts of a flag taken from Complete flags of the world, DK Publishing, 5th ed. 2008

The flags and banners are a special item which played a crucial role in the Medieval Ages, transforming the architecture, the fashion and even the arms used. Giving a representativeness to the people whom deposited their faith and lives to protect it and guaranty the continuity of their linages.

Meanwhile, Francisco Pizarro was not stranger to this rule of symbols and power as the rest of conquistadors. Being Pizarro under the flag of King Charles V in his third expedition to Peru, he received from the same King the possibility to obtain his own coat-of-arms (Figure 14) after his conquest of new lands for him and his descendants.

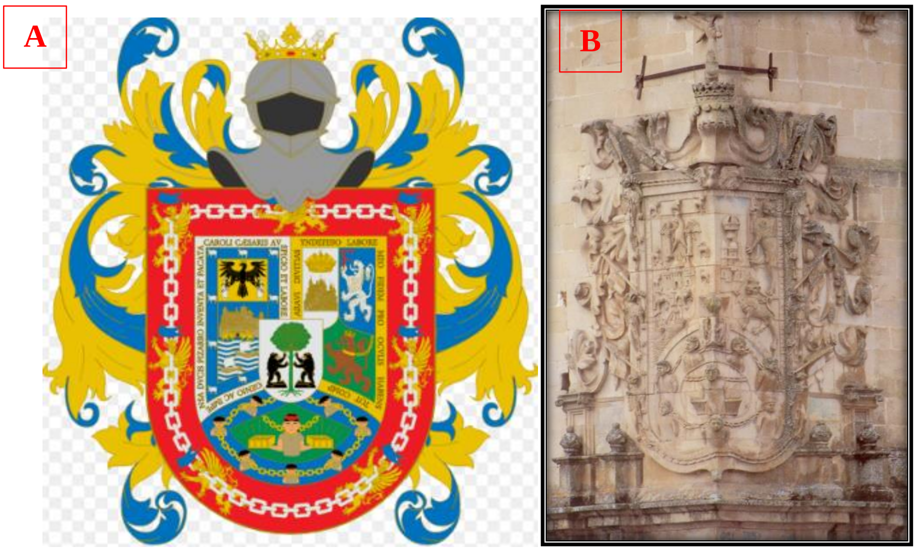


Figure 14 A) Design of Francisco Pizarro's coat of arms given by King Charles V. B) Picture of the Coat of arms on the Conquer Palace façade. Trujillo-Spain

Different kind of rituals for banners, flags or coat of arms are documented in several historical and text books, i.e. the one that declares the regulation of these acts. In the 19th century, the Crown of Spain trying to declare by law the equality of the lands in the New as in the Old Worlds due to the protestation of the American Spaniards (Criollos), the Crown sent to Lima the Royal decree after the treaty of Cadiz:

"…Considering the positive acts of peculiar inferiority to the people overseas, monument of the old system of conquest and colonial inferiority should disappear behind the majestic idea of equality: ***-Keep abolished the Royal Standard ride that used to be in the cities of America, as a testimony of loyalty and a monument of the conquest of those countries****. This great solemnity for the Royal Standard will be reserved, as in the peninsula, only for those days when a new monarch is proclaimed…"*

Nowadays, it is possible to find how the tradition and solemnity to this kind of objects continue, being part of the nationalism of each country, as part of the culture and relationship of identity between the people and their nations and ideas.

1.6. Materials used in the making of a Medieval Age flag/banners

The setting up of the representation of power in a symbol has in the beginning the idea of what it is to be represented. The emblem, the colors, the disposition of the symbols, even the audience to whom it is to be shown is thought-out in a first step.

The flags/banners are usually made of a coat-of-arms over a textile of different dimensions (from less than 20 cm^2 to dimensions larger than 2 m^2) and shapes (square, triangular, two-points, etc.). flags/banners are elaborated through the union of different kind of materials in a specific order, with each material having a representativeness regarding the hierarchy, wellness and power of the owner.

1.6.1. Textiles

The textile or fabric is a special item being the fundamental axis of the construction of the Flags (banners, standards, etc.). Over this material the flag is build up in extension the flag (main body of the object), and can be a single layer or a basis to join different layers in different areas of the flag. The different textiles used can be an indicator of the relevance of the object in its use and in its purpose (C. King, 1952).

Weaving fabrics in the Medieval Ages was a manual but technified industry (C. King, 1952), and the knowledge and technique for their production varies from one region to other around the world. The kind of raw material used, depended on the economical options of the community and the flora-fauna availability of the area, making some communities more specialized in the production of one kind of fabric or in the handling of a specific fiber than other (L. Weigert, 2015).

The textile industry begins with the selection of the fibers. In Medieval times those were natural and could be from a vegetable origin as well as animal origin (Figure 15) (R. Mastura,1996).

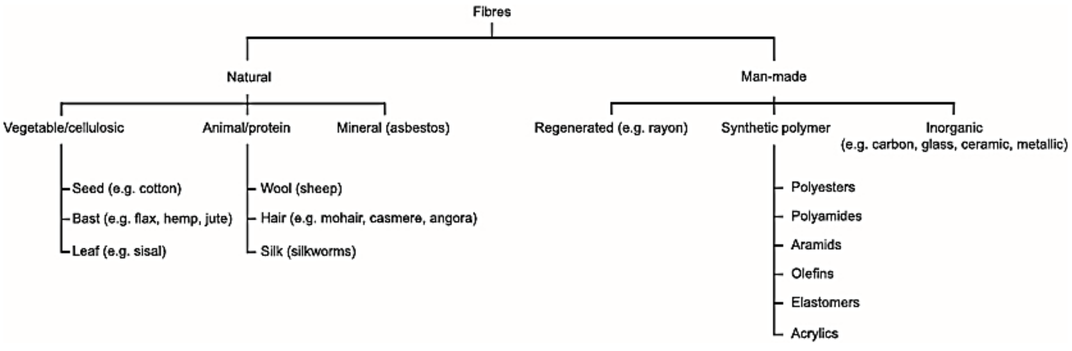


Figure 15 Fiber classification according their nature. Figure Taken from Handbook of Natural Fibers, Woodhead Publishing, 2012

The textile fibers employed in the woven of fabrics can be also classified as: staple, or filament. Most natural fibers are classified as staple of relatively short length, from a few millimeters to around a meter. While a filament is a fiber of indefinite length and the various silks are the only natural filament fibers (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

Due to the small length of the staples fibers, or the need to increase the length of the filament fibers it is necessary to do a process of drawing, spinning or twisting that allows the union of the different fibers to obtain a yarn. Yarns can be: monofilament, multifilament or staple. Being the most common the multifilament due to the tensile properties obtained (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

Natural fibers can be easily distinguished by different physical chemical properties that differ from each one to another or by the fiber's morphology/shape, either the cross section or lengthways (Figure 17). Typical textile fibers have a diameter of between 10 and 20 µm, though some can reach 50 µm. Natural fibers range in diameter from silk (10–13 µm) to wool (up to 40 µm) (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

The most common vegetable fibers are: cotton, jute, flex, and hemp. The main component of the vegetable fibers is cellulose (Figure 16), so that all the natural vegetable fibers have similar characteristics of high water absorbency, low resilience, a tendency to wrinkle easily, resistance to alkalis and organic solvents, and are highly combustible (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

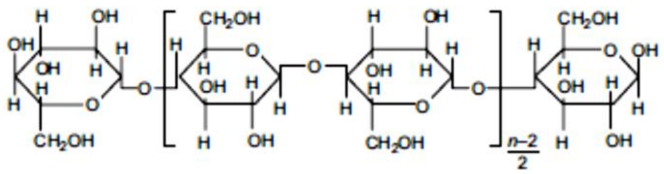


Figure 16 Chemical structure of Cellulose.

Between the most common animal fibers are: wool, other animal hairs, and Silk. These fibers are composed of a protein base varying from the genetics of each animal.

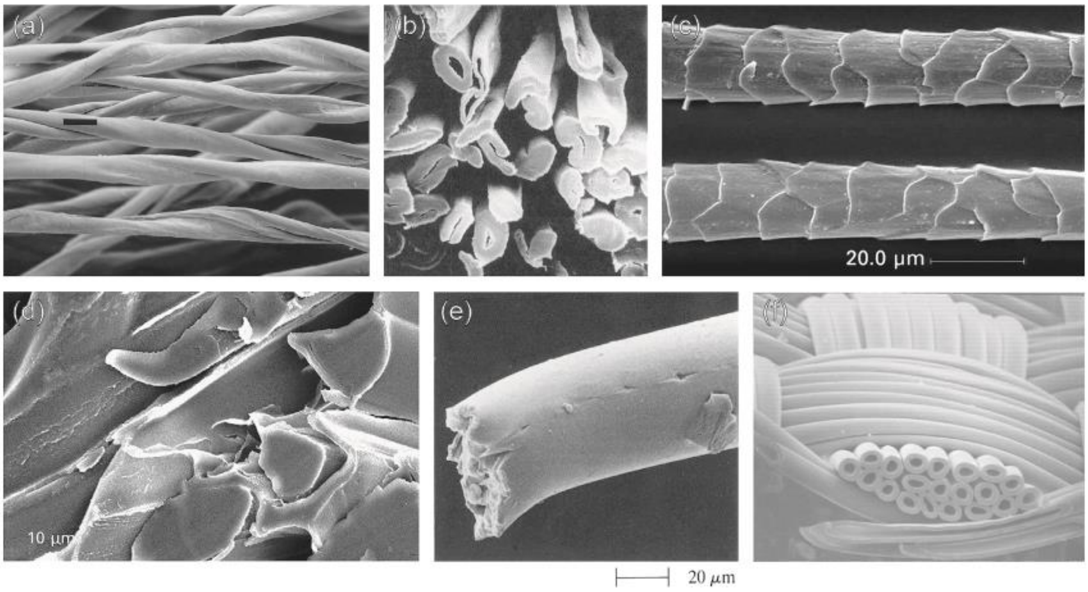


Figure 17 Images of a range of fibers a) longitudinal view of cotton, b) view of cross section of cotton, c) longitudinal view of wool fibers d) silk fibers, e) nylon fiber with round cross section Figure Taken from Handbook of Natural Fibers, Woodhead Publishing, 2012

From the long list of possible materials used for textiles manufacture, one stands for its softness, color and beauty: Silk. This special textile material was selected for their properties by the nobility as a symbol for status, acquiring an high value.

The different methods to which are processed the fibers/yarns, have an effect in the properties of the final fabric. The most relevant mechanical properties to measure are: the tensile strength, extension (elongation), flexibility (stiffness), elasticity, resiliency and abrasion resistance. Another important property that affects not only in the use of the fabric but its durability is its capacity for moisture absorbency (the hygroscopic capacity of the fiber to absorb and retain water from the media), factor that can impact the body structure of the fiber which could produce fatigue in the material (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

There are several processes to obtain the yarns, being the spinning one of the most used since ancient times, existing several processes of doing it, namely, the ring-spun, motor-spun, twist-less, wrap-spun and core-spun. The twisting is a special process, due to the possibility to give a new texture to the yarn, and exists two kinds of twisting namely the real twist and false twist. In the real twist, after the mechanical process is obtained a yarn with an inclination of helix in accordance with the direction of rotation, which could be “Z” if the yarn is obtained in a clockwise spiral or “S” in a counter-clockwise spiral (Figure 18) (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

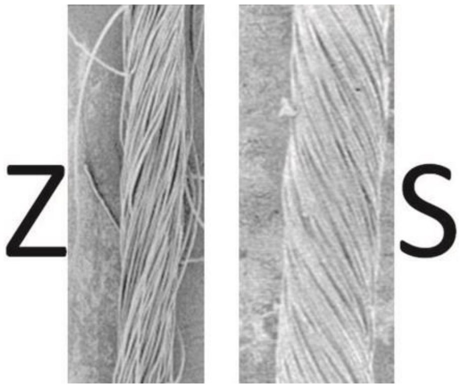


Figure 18 Z- and S-twisted yarns. Figure Taken from Handbook of Natural Fibers, Woodhead Publishing, 2012

To obtain cloths, fabrics, or any kind of textile it is necessary the union of the different yarns/fibers in a special pattern, according with the style, shape or decoration sought. Since ancient times this process is done using looms, where two sets of threads are put together making the weaving process. The set of threads that runs vertically through the length of the fabric is called “The Warp”, while the one that goes horizontally is called “The Weft” (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

The use of looms is found since prehistory, existing different types of it. The function of this artifact, regardless the complexity of it, is to hold the warp yarns under tension, whilst weft yarns are inserted and beaten into, to build up the fabric in a sequence of sheds (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

This structure of weaving, can have several variations, depending of the material used, as well the final use for the fabric. The order in which warp and weft are interlaced creates a weave structure. The simplest structure is the plain weave, where there is an interlacing of one thread of the warp over one thread of the weft. Those structures can be affected by the proportion from Warp to Weft. The weave structure where the proportion between Warp to Weft is 1:1 is called a balanced weave, while the others are unbalanced weaves (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

It is important to underline in this point that each fabric can be subject of previous or posterior treatments to change their characteristics, as color, weight, and softness, among others. All this depend of several factors, including socioeconomically factors or the foreseeable use for the fabric (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

The natural fibers due to be a protein base structure or cellulose based, are subject to a natural degradation. This process could be increased or accelerated by the use of different chemical agents applied during their treatments, or in their daily use. Acidic conditions affect cellulosic fibers, whilst protein fibers are more to resistant this pH condition. Basic conditions affect protein fibers, like silk and wool, while cellulosic fibers are most resistant to this pH conditions. Oxidation combined with sunlight exposure can produce polymer degradation, as result of ionizing radiation, free radicals, oxidizers and chlorine. Temperature, relative humidity, light, and pollution, have a direct effect on the rate at which a textile ages. In particular, another important agent that create damage in textiles are the biotic agents: micro-organisms as bacteria and fungi, or even insects or plagues (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

As an object of common use, the textiles also have a daily deterioration by their respective use, however, also can suffer damage by their storage. Fluctuations of relative humidity and temperature cause on the textiles to take up or lose moisture. These fluctuations cause dimensional change and mechanical stress that can lead to breakage and to have structural damage of weak yarns. Natural and artificial lighting cause fading over the textile dyes and even over the no dyed fibers. UV radiation causes fading to happen quickly and fibers to become brittle. Pollution, including dirt, settles in the structure of a textile, causing its character to change completely. Pollutants also affect dyes, finishes, and many embellishments (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

1.6.1.1. Silk

Silk is considered as one of the most precious textiles due to their high (tensile) strength, luster, and ability to bind chemical dyes. Due to their high capacity to absorb water makes it comfortable to wear in warm weather, and due to its low conductivity it is appreciated in cold weathers. Being one of the oldest textiles (known to be used for more than 4000 years), it is often used for clothing, but its elegant soft luster and beautiful drape also make it perfect for many furnishing applications (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

Silk is obtained from certain insects that secrete this substance as natural filament to build their cocoons or webs (Figure 19). The most commercial silk is the obtained from the larvae of the caterpillar from the cultivated *Bombyx mori*. The obtaining process of silk starts with the sericulture and cocoon production, followed with the silk reeling, to finish with the silk manufacture, leaving the yarn/thread ready to weaving (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

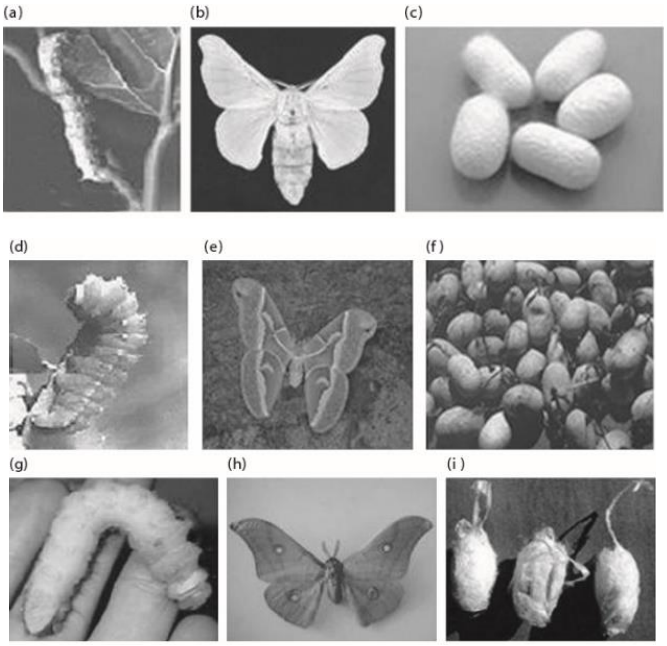


Figure 19 Some Types of Silk. Mulberry silk: (a) worm, (b) moth and (c) cocoons. Tasar silk: (d) worm, (e) moth and (f) cocoons. Oak tasar silk: (g) worm, (h) moth and (i) cocoons Figure Taken from Handbook of Natural Fibers, Woodhead Publishing, 2012

Silk fibers structure from the silkworm cocoons, are divided in two parts: two (usually) central inner fibers of fibroin (75-83% w/w) and an outlet layer of sericin (17-25% w/w) (Figure 20). The fibroin filaments have a usual diameter of 10-14 µm and this give the fiber an higher tensile strength than glass fiber or synthetic organic fibers, good elasticity, and excellent resilience. Silk fibers are protein based, highly crystalline with a well-aligned structure (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

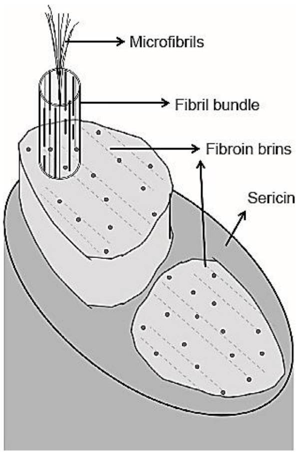


Figure 20 Structure of raw silk filament Figure online available

The proteins on silk amass for more than 95% of its content; other impurities, such as waxes, mineral salts, and ash, constitute about 4–5%. The amino acid composition varies according to the variety of silk, being serine, glycine, and alanine the three major amino acids found (Figure 21). The amino acids content of Silk are usually related to the degummed fibers (only fibroin) where the sericin is extracted (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

Amino acid composition (mol%)				
Amino acid	Bombyx mori (Mulberry)	Antheraea mylitta (Tasar)	Antheraea assama (Muga)	Phylisomia ricini (Eri)
Aspartic acid	1.64	6.12	4.97	3.89
Glutamic acid	1.77	1.27	1.36	1.31
Serine	10.38	9.87	6.11	8.89
Glycine	43.45	27.65	28.41	29.35
Hystidine	0.13	0.78	0.72	0.75
Arginine	1.13	4.99	4.72	4.12
Threonine	0.92	0.26	0.21	0.18
Alanine	27.56	34.12	34.72	36.33
Proline	0.79	2.21	2.18	2.07
Tyrosine	5.58	6.82	5.12	5.84
Valine	2.37	1.72	1.5	1.32
Metheonine	0.19	0.28	0.32	0.34
Cystine	0.13	0.15	0.12	0.11
Isoleusine	0.75	0.61	0.51	0.45
Leusine	0.73	0.78	0.71	0.69
Phenylalanine	0.14	0.34	0.28	0.23
Tryptophan	0.73	1.26	2.18	1.68
Lysine	0.23	0.17	0.24	0.23

Figure 21 Amino acid composition of degummed common silk fibers cocoons Figure Taken from Handbook of Natural Fibers, Woodhead Publishing, 2012

Due to the presence of both acidic and basic groups in the Silk structure, these amino acids exhibit an amphoteric nature in solution. Silk has good resistance to acids, but hot concentrated acids break the peptide bonds of the amino acid molecular chains. Silk fibers have low resistance to alkali and are easily damaged by exposure to weak alkali at elevated temperatures. Alkaline conditions hydrolyze the polypeptide bonds of fibroin from its molecular chain ends, thus degrading the silk fiber rapidly. On the other hand, silk fibers exhibit good tolerance to reducing agents commonly used for textile materials. Prolonged exposure of silk to steam or boiling water results in hydrolyses of peptide bonds, thereby damaging the silk fiber (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

Since silk fiber contains amino acids with neutral, acidic, and basic side chains, any class of dyes can be used for dyeing silk fibers. Acid dyes are preferred for silk when maintaining a high luster is a priority; reactive dyes provide exceptional fastness properties to the dyed silk (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

Silk is a very hygroscopic textile fiber. Silk fibers swell about 30% of their volume under wet conditions: because of this, silk textile materials have a lower dimensional stability compared to other natural fibers. Due to the swelling action, silk fibers display partial loss of strength under wet condition (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

Silk as a natural fiber is susceptible to suffer transformation in its structure due to exposure conditions as sunlight, moth, mildew, bacteria, fungi, and beetles. Prolonged exposure to sunlight or UV radiation causes yellowing and irreversible photochemical degradation of the silk fibroin, which damages the silk fibers. During the photochemical degradation of silk fibroin, is appreciable the changes in the amino acid content by hydrolysis of serine, tyrosine, and arginine, loses of glutamic acid and aspartic acid, with an increase in the amount of ammonia gas released (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

The longitudinal view of Silk under a scanning electron microscope, allows detection of the fiber degumming, and also the identification of the fiber characteristic tubular shape and smooth surface, having or not some striations characteristic from the species of animal that produce it (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

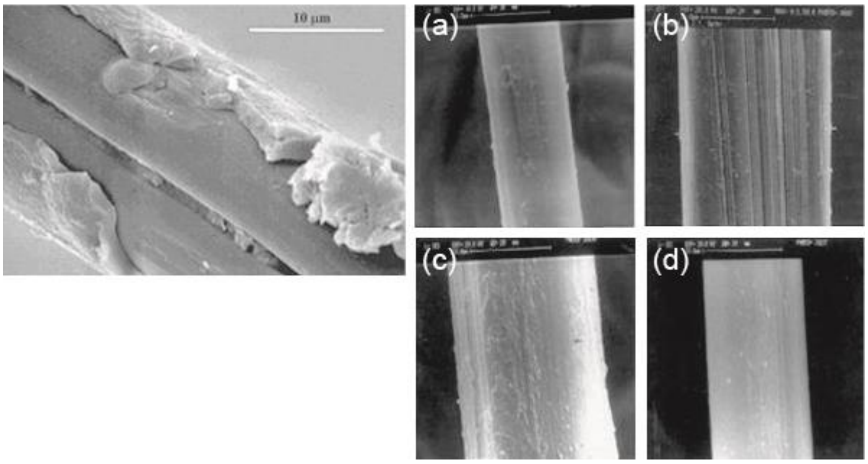


Figure 22 On the left, a longitudinal view of silk fibers (non-degummed). On the right, longitudinal views of silk fibers (degummed): (a) mulberry; (b) tasar; (c) muga; (d) eri. Figure Taken from Handbook of Natural Fibers, Woodhead Publishing, 2012

The cross section view of Silk under a scanning electron microscope allows the visualization of the fibroin filaments if the fiber is degummed (Figure 23), and how the sericin envelop the fibers in the case that the fiber is not degummed (Figure22). Several variations could be seen depending upon the variety of silkworms and also among individual cocoons (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012).

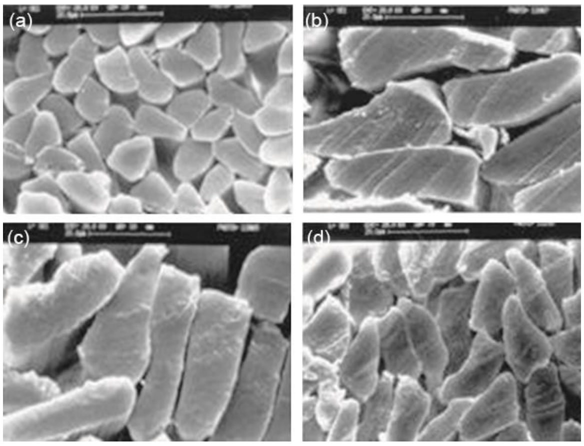


Figure 23 The cross-sectional view of silk fibers (degummed): (a) mulberry; (b) tasar; (c) muga; (d) eri. Figure Taken from Handbook of Natural Fibers, Woodhead Publishing, 2012

1.6.2. Dyes

The dyes on flags are one item of huge relevance due to the possibility to show and/or change the colors to display to an audience, giving or changing the message in it.

The history of dyed textiles is related to their archaeological findings. The early known fiber dyed found is from 1500 BC and the use of natural dyes from roots of a plant, a parasitic insect and the secretions of a sea snail were identified (M.E. King, 1978).

The dye process is a physical-chemical reaction of a chemical reagent also called chromophore or chromogen with a fiber to change its color permanent or partially. The dye, that is generally an organic compound soluble in a solvent (different to a pigment that is inorganic and insoluble) is fixed to the surface or trapped to the fiber by a chemical bond that even could be helped through a metallic ion aid known as mordant. The dyestuff could be from a natural base (as before the 19th century) or synthetic. Mordant as aluminium (from alum), is found in historical textiles as well iron, copper and tin ions (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012, T. Bechtold, 2009).

The final color obtained in the fiber is due to an optical effect of the interaction between the chromophore and the metal (if it is present) with the light and the textile fiber, letting as result the emission of different wavelengths that could be perceived for the eye of the spectator (Figure 24) (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012, T. Bechtold, 2009).

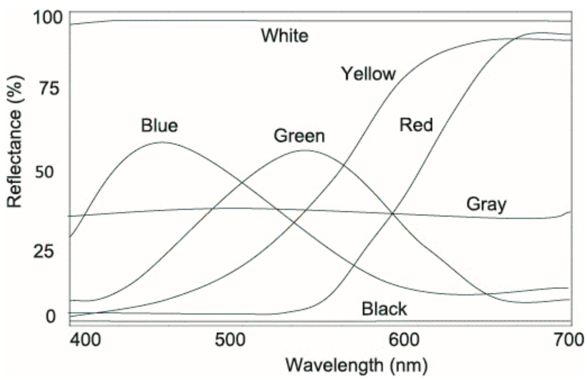


Figure 24 Examples of spectrophotometric curves of colors figure free online available

Dye process is usually done in a wet media, where the dying agent is dispersed before being fixed to the fiber. Dyes are classified according to their principal chemical group. The principal types of dyes are (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012, T. Bechtold, 2009):

***Acid dyes** have ionized acidic groups; they are usually applied under acidic conditions to wool, silk, polyamide fibers, and leather.*

Basic dyes *have cationic groups; they are applied to acrylic and other fibers containing structural anionic groups.*

Direct dyes *stain cellulosic fibers and do not require a mordant to fix the dye on the fiber. They are applied from salt-containing baths.*

Disperse dyes *are sparingly soluble in water and are applied as dispersions.*

Insoluble azo dyes *are produced in situ by depositing a temporarily solubilized phenolic compound (naphthol) in the fiber and subsequently coupling the phenol with a diazonium salt.*

Natural dyes *are the group of compounds coming from the extraction of chromophores in animals or plant e.g. alizarin, indigo, catechu, logwood, cochineal, and kermes.*

Fiber-reactive dyes *are anionic dyes containing a reactive group capable of forming a covalent bond with a compatible fiber group, eg, typically the hydroxyl group of cellulose. It is the only class of dyes resulting in such a bond.*

Sulfur dyes *have affinity for cellulosic fibers in an alkaline reducing bath. Some of their structures have not been established.*

Vat dyes *are applied in a similar manner as sulfur dyes. Insoluble in water, they are applied as dispersions and reduced in an alkaline bath, where they form the water-soluble leuco compound with an affinity for cellulosic fibers. They are insolubilized by oxidation and fixed to the substrate by entrapment.*

Mordant dyes *are a special group of acid dyes that undergo a chemical reaction with a metal atom, usually chromium. The mordant can be applied before the dye, together with the dye, or after the dye. In the first case, the fiber is impregnated with a solution of a salt of the mordanting metal. In the second case, dye and metal salt are applied together, and in the third case, the dye is first applied like any acid dye and then treated with the metal salt. Reaction with the metal changes the color of the dye and substantially improves fastness properties.*

Solvent dyes *are water-insoluble dyes that are soluble in organic solvents.*

The different dyes also can be divided by color, as red, yellow, blue, brown, black, etc. and in turn classified by their chemical family (T. Bechtold, *et al.*, 2009). Being in the past only extracted the primary colors (Blue, red, yellow) and created by combination the complementary ones (M.J. Melo,2009).

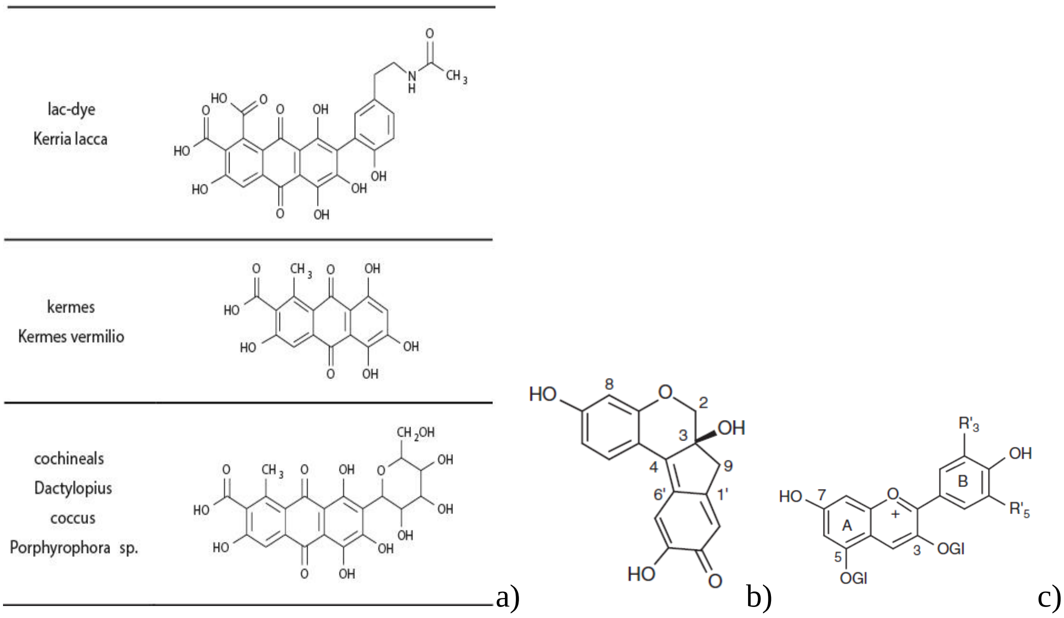


Figure 25 a) Chemical structure of Anthraquinone based Reds b) Chemical structure of Brazilin c) Chemical structure of anthocyanin

The brazilin reds tend to fade, while the anthraquinone ones are more stables. After 16th century, the American cochineal starts to have a great importance due to the commercialization of the previous domesticated insect from the pre-Hispanic cultures in the new World, replacing almost all the reds dyes used in Europe at that time.

The ancient blue most used were those based from indigo chromophore (Figure 26) from Indigofera plants as *Isatis tintoria* (grown in Europe) and *Indigofera tinctoria* (grown in Asia) this last commercialized in Europe through Persian/Islamic routes since Spain (T. Bechtold, *et al.*, 2009).

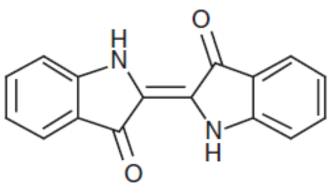


Figure 26 Chemical structure of Indigo

Thanks to the different kind of plants that have yellow chromophores (Figure 27) and their easy extraction and use, the number of sources of this dye is large and diverse. Between the most common classifications are the flavonoids yellows, the carotenoid yellows and chalcone and aurone yellows (T. Bechtold *et al.*, 2009).

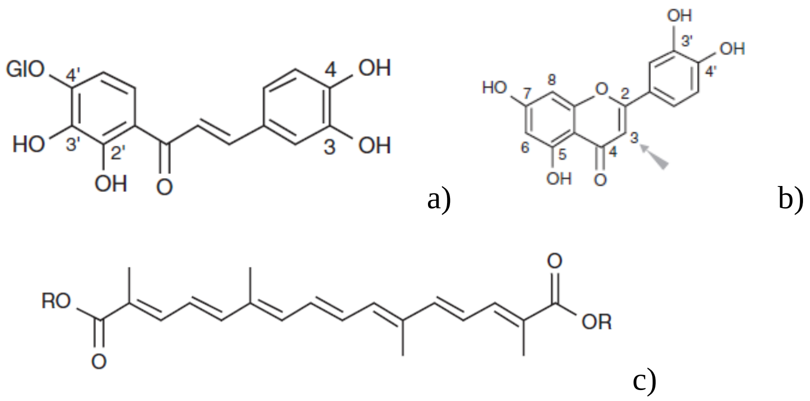


Figure 27 Basic Chemical structure of a) chalcone b) carotenoid c) flavone

Flavone yellows (Figure 27C) can be divided in those with and those without a hydroxyl group in the 3 position. The first group chromophores such as apigenin and luteolin are present inplants such as weld, one of the most used yellows sources. The second group (flavonols) with chromophores as quercetin, kaempherol and rhamnetin, and also morin, myrecetin and fisetin (T. Bechtold *et al.*, 2009).

The dye process in proteinaceous fibers is followed usually through the use of acid dyes. For Silk dyeing is carried out at pH 5.0–5.5; the bath contains 0.5% of an ethoxylated fatty acid derivative. Best exhaustion of acid dyes on silk is achieved at c.a. 85°C (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012, T. Bechtold, 2009). The proteinaceous textiles are usually immersed in a bath of water, following a specific process for the dyeing as follows:

With agitation and heat, the dyestuff diffuses through the solution, is sorbed at the fiber surface, and then diffuses into the fiber. If the dye is aggregated or dispersed, the sequence is preceded by a dissolution of dye or breakdown of aggregates.

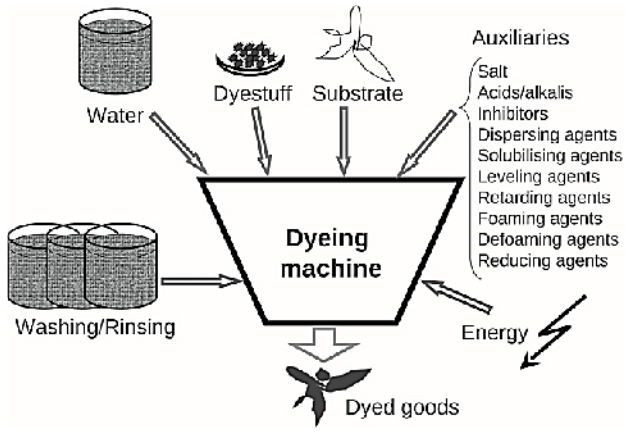


Figure 28 Dyeing process: requirements for a general dyeing process Figure taken from Handbook of Natural Fibers, Woodhead Publishing, 2012

Silk dyeing has a process similar to the wool (both are animal proteinaceous fibers), differing with the pre-treatment of the silk to take out the sericin (degumming) in order to develop the silk luster and dye ability. The degumming is obtained with an alkali soap cleaning (25-30% owf) on the raw fiber (R. Sinclair *et al.*, 2015; R. Kozlowski *et al.*, 2012, T. Bechtold, 2009).

1.6.3. Metal Threads

The different fabrics used in the assemblage of the flags were not only decorated with dyes to obtain striking colors, also precious or luxury metals/alloys were used in metal threads. The metal threads are a solid metal wire (usually flattened) or a strip, can be twisted around an animal or vegetable thread being used in the final decoration of the fabrics, technique used also in cloths or tapestry since several hundreds of years (M. Jaro, 2003; 1990).

The metal used can vary, being used: silver, gold, copper or alloys. While the core of the thread could be: cotton, silk, wool or linen among others (M. Jaro, 2003; 1990). The union between these two different materials, can be an indicative of the provenance and age of the object.

The process to obtain the metal thread is based in to wrap a fiber with the metal layer in a clockwise or counter-clockwise direction as in the elaboration of yarns. The metal used could be a metal gilded in one side, both sides or surrounded completely. This process of metal threading is documented since very old times, with the introduction in

Europe since the 11th century, and beautifully dominated in countries as Spain and Italy (M. Jaro, 2003; 1990).

1.6.4. Paper

The paper is a hidden item in the manufacture of the flags, as this component is usually used to give volume to the heraldic emblem in the flag, and was typically covered by another layer of textile or other decoration, being invisible for the viewer.

The manufacture of paper in medieval times differ from the modern technologies and techniques, being called rag paper (R.I. Burns 1981; M. Gutierrez-Poch, 2012). The rag paper was elaborated from the mix of different kind of fibers (recycle textiles, raw fibers, parts of wood, among others) in an alkali solution to obtain a moldable paste to create the different sheds (Figure 32). The technology to produce this paper was coming from China to Persia and was introduced in Europe by the Islamic culture (R.I. Burns 1981; M. Gutierrez-Poch, 2012).

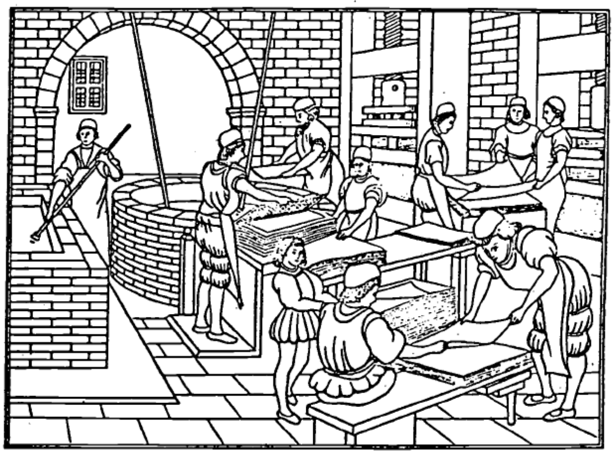


Figure 29 Production of paper-mill in the middle of the 15th century.

The rag paper is dated in Spain since the 12th century, being a well-known producer the region of Valencia, Catalonia (region conquered by the Crown of Castilla in the 13th century) and Toledo (R.I. Burns 1981; M. Gutierrez-Poch, 2012). Same region where the use of mills was introduced and modification of the hydraulic system in the production of the craft paper.

The rag paper in the 11th century from the Islamic production was based on flax, while the Spanish production after the 13th century starts to add cotton as raw material due to the increase in the production of linen fabrics and concomitant discard of cotton textiles (R.I. Burns 1981; M. Gutierrez-Poch, 2012).

1.6.5. Adhesives

The use of adhesives was a need in the elaboration of flags to joint some components to create layer over the main textile. The different adhesives used were generally of two kinds: animal glues or vegetable sources (resins and waxes).

The animal glues were usually obtained through the hot digestion of animal bones, skin, or residual parts, letting out the collagen and fats that allow the adhesive function, while the vegetable resins were used almost directly from their origin with almost no processing.

2. Research Proposal

By means of the collaboration between the National Museum of Colombia (Bogotá D.C.-Colombia), HERCULES Laboratory (Évora, Portugal) and the University of Évora (Évora, Portugal), it was proposed as thesis' project the study of the Banner ascribed to Francisco Pizarro.

Different areas of the Pizarro's Banner (textile, paper and metal) will be sampled under the supervision of the Conservators of the National Museum of Colombia. Samples will be taken in adequate number and proportion to carry on the research.

The Banner will be subject to visual inspection and several analytical techniques will be applied for sample analysis, namely: Liquid Chromatography coupled to Mass Spectrometry, Pyrolysis-Gas Chromatography coupled to Mass Spectrometry, optical microscopy (stereomicroscopy, dark/bright field microscopy), Raman Micro-Spectroscopy, Scanning Electron microscopy coupled to Energy Dispersive X-Ray Spectroscopy and Radiocarbon dating ^{14}C. The application of the above techniques will help to identify and characterize the different components of the object and answer to the following questions:

Historical Questions

1. Radiocarbon dating result match with the entrance period of Pizarro in the Peru lands?
2. Was this Banner possible used by Pizarro in the conquest of Peru?
3. It is this Banner from the Spanish army?

Analytical Questions

1. In which date was the object produced?
2. What is the composition of the organic and inorganic materials of the Banner?
3. Is it possible to obtain information regarding the degradation process suffered by the object?
4. How was the manufacture process of the Banner?

2.1. Research Relevance

During almost two hundred years this object has been subjected to a great debate about its representativeness as Pizarro's Banner, as well as if it is authentic.

Due to the important period in which was possible to insert the Banner, the different socio-cultural facts in which it was possibly involved and the different technologies and materials used in its manufacture, there are different studies that aim to help in topics such as conservation, style, history and possible restoration. Nevertheless, no scientific studies have been done in the object. The analytical study of the Francisco Pizarro's Banner of Arms, makes a unique opportunity to gain new chemical data of an interesting period, as it also helps to elucidate a possible participation in the history of the New and the Old World.

3. Aims

3.1. General Aims

By means of the use of different analytical techniques in samples extracted from the textile labelled as Francisco Pizarro's Banner of Arms, it is expected to obtain new scientific information from the object. These data, combined with the historical context, allow to characterize the object, help to elucidate its origin-provenance. At the same time, the whole process will provide tools for its future conservation-restauration exhibition and storage.

3.2. Specific Aims

This research has the following points as goals:

- Use analytical techniques to obtain information on the organic/inorganic component of the object
- Identify materials from the different parts that compose the Banner
- Identify and characterize the textile fibers from the Banner
- Identify the dyes used in the elaboration of the Banner
- Identify and characterize the metallic thread used as decorative part in the Banner
- Characterize the manufacture of the Banner
- Assign a production date to the Banner
- Postulate the origin-provenance and use of the Banner
- Give an analytical answer to the historical question of authenticity of the Banner
- Promote the interest in the study and research of South-American objects
- Use the knowledge (theoretical and practical) obtained through the EMM ARCHMAT to give a scientific answer to solve the questions of the object within an historical context
- Combine interdisciplinary ideas, sources and data to offer a valid answer to the problem under study
- Offer an open result to the scientific/historical community, for future discussion

4. State of art – Analytical methods

The study of historical/archaeological textiles is of great significance in cultural heritage studies due to their limited existence. These objects, generally of organic composition, are easily susceptible to degradation, that diminishes their area/volume, without requiring big energies to be transformed.

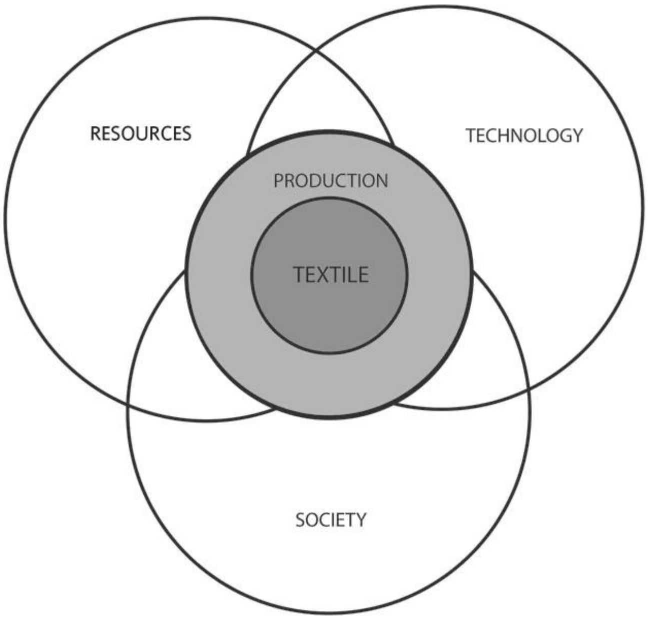


Figure 30 A model of textile and textile production as interaction between resources, technology, and society. Graphic work by Marianne Bloch Hansen.

Therefore, sampling using destructive techniques is nowadays in disuse, preferring *in situ* methodologies and non-intrusive techniques (E. Varella *et al.* 2012).

However, for some analysis it is mandatory to perform sampling by cutting, being necessary (or recommended) the use of micro-sampling, and only from areas showing damage, but still with enough representative analytical information to be extracted from the whole object. This process of sampling must have a statistical representativeness in the whole body, avoiding the increase of errors in the measurements to make (E. Varella *et al.*, 2012).

The study of archaeological/historical textiles from an analytical point of view is conducted as a forensic case study, where all the fibers, threads and related components have a dialogue that helps to reconstruct the original story of the object (J. Was-Gubala. 2013). Each fiber is denominated as a unit, where all the units under analysis must be similar to the units inside the object, ensuring random sampling of those units in order to create an accurate context to solve the problem under study.

Textile studies are centered predominantly in the type of material used in the fabric, due to the variety of animal and vegetable sources. It is necessary to follow a rigorous procedure to distinguish the fibers and characterize them with precision, to avoid confusion between similar fibers, or to understand if the fibers are of wild origin or domesticated (M.M. Houck,*et al.*, 2009). To achieve this goal, it is possible to use simple optical techniques (microscopy) or more complexes techniques like electron microscopy, where by examination of the fibers it is possible to identify the fiber type.

The next step after fiber identification is to know if the fiber was modified, where it is necessary to know if the fiber suffered some kind of treatment after spinning (dyeing, twisting, mordanting, etc.) (M.M. Houck,*et al.*, 2009). These processes are usually done by means of chromatographic and spectroscopic techniques, providing accurate results that help to understand the process and raw materials involved in the fabric manufacture.

Francisco Pizarro's Banner of Arms has not been studied using any modern scientific analysis, and has only been characterized by conservators through visual inspections, discussing its components in order to formulate plans of conservation, exhibition and storage. It is not easy to find documented references concerning objects related to the Banner (in composition and time), therefore the following lines will give a better idea to the reader of the state of the art of textile analysis in the actual scientific media, in order to make a starting point for the analysis proposed for the historical object. Some tests such as burning, density, refractive index, moisture regain, strength, elongation, micronaire or solubility, among others, will not be discussed due to the subjective data collected in some tests and/or the high amount of sample required for some of them.

4.1. Optical Microscopy

Optical microscopy is the first technique to be used in any kind of textile research, being used in all the documented researches of this type of material.

Optical microscopy uses of a set of lenses to obtain magnified view of the fibers’ details in different modes (longitudinal/transversal/cross section view), allowing a direct measurement of the samples and helping in the process of yarn or fiber identification (M.M. Houck,*et al.*, 2009).

A fiber sample analyzed under the optical microscopy can provide different information depending on the illumination system used. If the sample is illuminated from the top (reflected light) it is possible to detect the details of the surface of the fibers, helping to discriminate between animal or vegetable fiber. Morphological characteristics include convolutions, lumen and reversal zones (cotton), fiber bundles with or without cross-markings (bast and leaf fibers), presence or absence of scales and scale margins (animal fibers), and smooth profiles without scales or convolutions (silk). In samples illuminated from the bottom (transmitted light), and taking advantage of the optically transparent or translucent composition of the fibers, it is possible to detect internal conducts, longitudinal shape and regularity of diameter, among others (M.M. Houck,*et al.*, 2009; R. Kozlowski, *et al.*, 2012). Neither reflected nor transmitted microscopy give any chemical information of the samples under study.

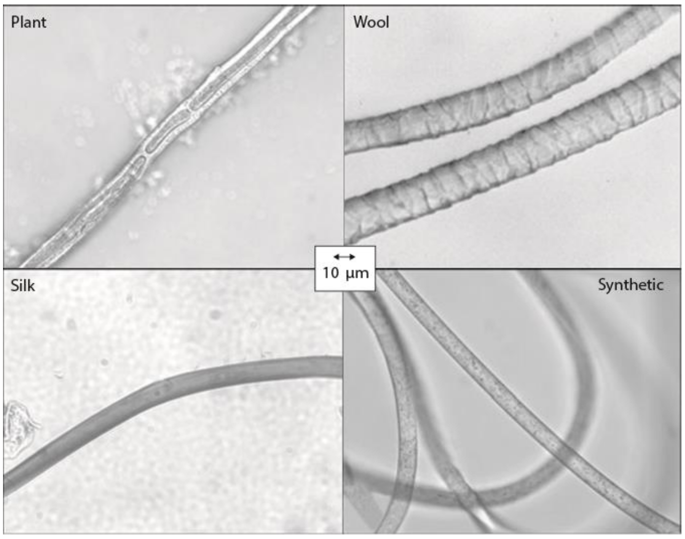


Figure 31 Typical plant (jute), wool, silk and synthetic fibers, as observed with transmitted light microscopy. Figure Taken from Handbook of Natural Fibers, Woodhead Publishing, 2012

Microscopic analysis of longitudinal view of fibers helps in identifying the type of fiber: cellulosic, animal or man-made. When a longitudinal analysis is not enough for the identification, a cross section study can help distinguishing them. It is, even possible to distinguish between species (i.e. from 10–13 μm (cultivated silk) up to 40 μm (US wool)).

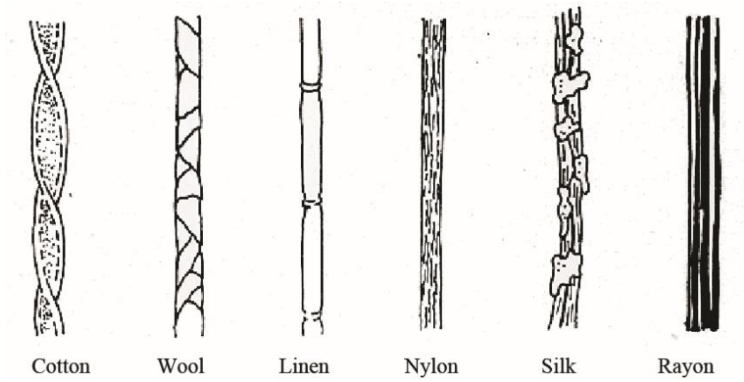


Figure 32 Surface shape of some typical fibers Figure free online available

Optical microscopy can also give information about the possible twisting in the fibers to form the thread or the yarn, the weaving used to make the fabric and the use of the threads in the textile, and also elucidate on the possible use of dyes or some kind of biotic attack (M.M. Houck,*et al.*, 2009; R. Kozlowski, *et al.*, 2012).

4.2. Scanning Electron Microscopy coupled to Energy Dispersive X-Ray spectroscopy

The interaction of the electrons under a high voltage field with the surface of the materials allows to obtain as an image that reflects in a monochromatic tone, the surface analyzed, existing two principal techniques (G. Artioli, 2010).: Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). Both techniques give information on the internal structures and/or the surface with large zoom and much better resolution than optical microscopy. TEM technique needs ultra-thin sections from the samples to obtain results, in contrast, SEM needs no sample preparation and in some equipment it is even possible the analysis of samples of big dimensions.

Modern electron microscopy is usually coupled to energy dispersive X-Ray spectroscopy (EDS), taking advantage of the secondary electrons produced in the interaction electron-matter or the backscattered electrons. Through EDS it is possible to achieve chemical (elemental) information of the materials under analysis with great accuracy in point, multipoint and area/mapping analysis (G. Artioli, 2010).

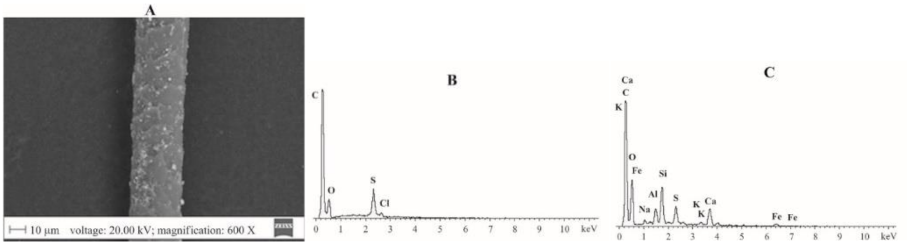


Figure 33 A) SEM picture of fiber. SEM-EDS spectra B) point analysis, C) area analysis Figure taken from Zeiss co

The analysis of textiles under the SEM-EDS can produce an irreversible damage in the fibers due to the high energy applied to the organic materials that alters the fiber surface (changes in shape, composition and loss of physicochemical information). It is possible to avoid this effect through the use of a coating (carbon or gold) or using a lower vacuum (higher pressure) with the new environmental SEM (VSEM) systems.

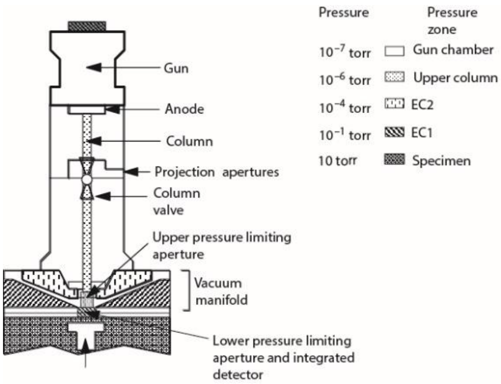


Figure 34 Schematic drawing of the VSEM column, showing the different pressure zones. 1 torr ~133 Pa Figure taken from Hitachi co

The use of an VSEM-EDS equipment in the analysis of fibers also helps in their elemental chemical analysis and allows to identify the organic structure of the fibers and their respective changes. The SEM-EDS and VSEM-EDS have been used to clarify typology of the fibers, bio-deterioration and the use of mordants. Also, the analyses of metallic threads gives enough information to characterize them in shape, deterioration and composition.

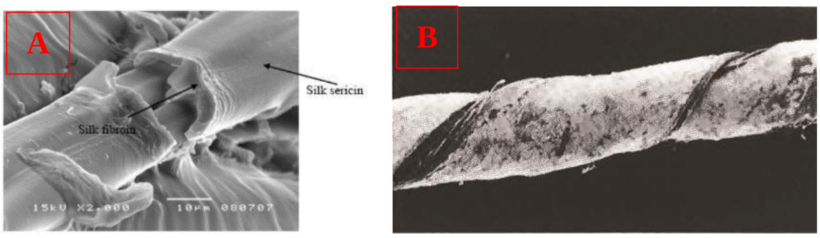


Figure 35 SEM image of A) Silk Fiber no degummed Figure taken from A. Pornanong, 2015 B) Metallic thread Figure taken from M. Jaro 1990

Literature of SEM-EDS analyses on textiles can be easily found as the reported by Akyuz *et al*. 2014, Manhita *et al*. 2014, Margariti *et al*. 2013, among others.

4.3. Chromatographic techniques

Textile analysis as was discussed previously has a multicomponent configuration, where the fibers can be modified to change their physiochemical properties. One of the most advantageous techniques to separate and elucidate the different components present in textiles are the chromatographic techniques. The major part of research developed with these techniques comprises the identification of dyes, mordants and degradation products, as well as the identification of organic binders, waxes, gums and papers.

Chromatographic techniques are divided according to the mobile phase and stationary phase used in the separation processes (C.F. Poole, 2003). The two most used techniques are: High Performance Liquid Chromatography (HPLC) and Gas Chromatography (GC).

HPLC uses a liquid mobile phase which helps a solid stationary phase inside a column to generate a retention gradient among the different components, resulting in elution of the components separated from the injected matrix at different times (C.F. Poole, 2003).

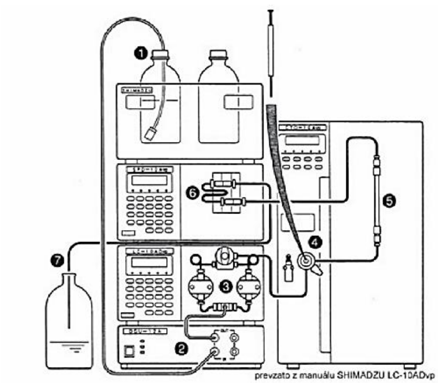


Figure 36 HPLC Basic scheme 1) Mobile phase reservoir 2) Degasser 3) Pump 4) Injector 5) Column 6) Detector 7) Waste Figure adapted from The Essence of Chromatography, C.F. Poole 2003

The GC system uses a gaseous mobile phase to separate the different components of the matrix through a capillary column that is under continuous heating. Separation is based in the different volatilities and/or interactions of the gaseous compounds with the column (C.F. Poole, 2003).

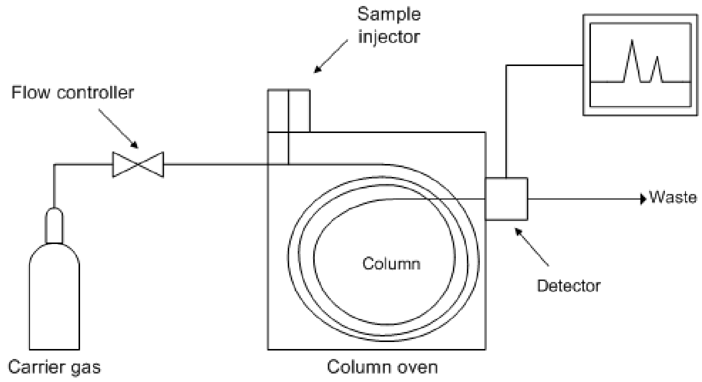
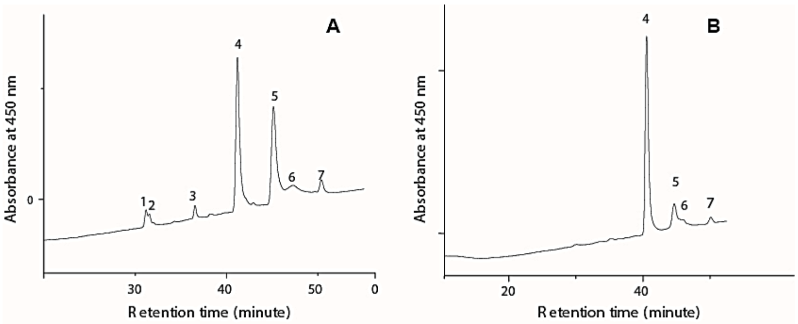


Figure 37 GC Basic Scheme Figure adapted from The Essence of Chromatography, C.F. Poole 2003

As a result of the separation processes it is possible to detect the different components of a sample at different retention times, and this is done using different detectors (one or more coupled) to report the result in the form of a chromatogram (retention time vs intensity of the signal in the detector). The Diode Array Detector (DAD) and the Mass Spectrometer (MS), are the most useful and used detectors in fiber analyses and allow to detect components in low concentration and even compounds that have been under degradation processes (C.F. Poole, 2003).



Peak	Retention Time (min)	UV max (nm)	Mass (Da)	Possible compound
1	31.2	406	564	Lucidin primeveroside
2	31.5	414	534	Ruberythric acid
3	36.5	410	548	?
4	41.2	428	240	Alizarin
5	45.1	480	240,256	Xanthopurpurin(?) + Purpurin
6	47.3	478	284,240,256	Munjistin +? + ?
7	50.4	416	254	Rubiadin(?)

Figure 38 Example of HPLC profiles and mass spectrum data of red textile extracts. (A) Formic acid extract showing the presence primarily of alizarin (4) and purpurin (5), as well as small amounts of the glycosides, lucidin primeveroside (1) and ruberthric acid (2). (B) Formic acid extract showing alizarin (4) and smaller amounts of other anthraquinones

Regarding gas chromatography, it is also possible to couple another device to the chromatographer to improve response in different types of matrixes like paper, gums, waxes, etc. One of the most relevant accessories in textile analyses is the pyrolysis (Py) furnace. The pyrolysis furnace is a device that increases the temperature of the sample in a controlled chamber, obtaining as result new volatile products that can be separated by the chromatographic system. To improve the results in the pyrolysis chamber it is possible add a chemical derivatization agent to the matrix sample, obtaining molecules that are easily detectable similarly to other types of gas chromatography.

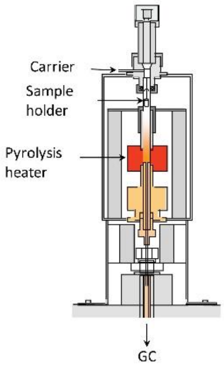


Figure 39 Pyrolysis furnace basic scheme Figure free online available

Results concerning accurate separation and identification of different compounds in textile analysis by HPLC and GC have been reported by researchers such as Colombini *et al*. 2007, 2009, 2013, Degano *et al*. 2015, Lech *et al*. 2011, Liu *et al*. 2011, Manhita *et al*. 2014, among others.

4.4. Colorimetry

Due to the fact that the color perceived by the human eye is a subjective measure, an analytical methodology to achieve a description of the color in terms of coordinates was developed, allowing to represent each color in a referential scheme of colors coordinates that represents the measure taken (R. Johnston-Feller, 2001). This process, called colorimetry, has been used in the recent years as a support tool to characterize textiles, helping to analyze the color present in textiles and relating it with dye sources without making intrusive sampling, as reported by Manhita *et al.* 2014.

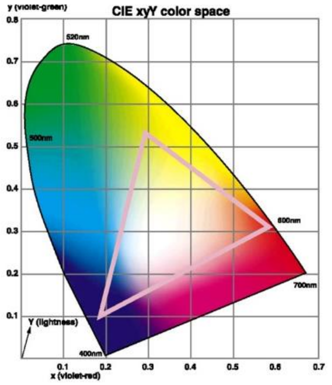


Figure 40 CIE coordinates to characterize colors

A full plot of all visible colors is a three-dimensional figure. However, the concept of color can be divided into two parts: brightness and chromaticity. The CIE system characterizes colors by a luminance parameter Y and two color coordinates x and y which specify the point on the chromaticity diagram color space, defined by the International Commission on Illumination (CIE, the initials of its French name) (W.D. Wright, 2007).

4.5. Raman spectroscopy

Raman Spectroscopy is an analytical technique that uses the scattering process from the interaction of light at a specific wavelength with the matter to obtain characteristic profiles that elucidate the chemical composition of the sample under analyses (E. Howell G.M.*et al*., 2005).

Due to the Raman spectroscopy precision, the possibility to be used *in situ*, the ability to analyze organic and inorganic compounds and the low degree of sample preparation, it has been used more and more in different cultural heritage case studies, as reported by Bernardino *et al.* 2015 and Woodhead *et al* 2016, among others. In textile studies, Raman spectroscopy has been used in the identification of fibers, dyes and pigments.

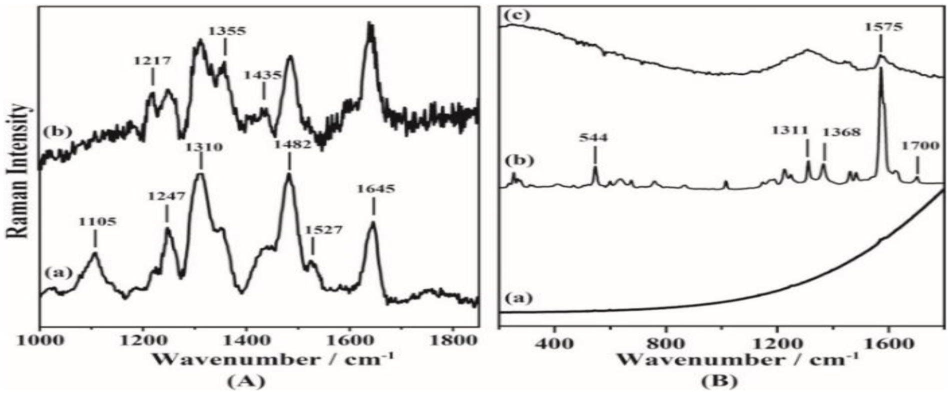


Figure 41 Example of Raman analysis (A) Raman spectra of (a) carmine dye and (b) red archaeological fiber (baseline correction applied) using λ0 = 488 nm. (B) Raman spectra of the indigo dye using (a) λ0 = 632.8 nm, (b) λ0 = 1064 nm and (c) blue archaeological fibers using λ0=1064 nm.

4.6. Radiocarbon dating (^{14}C)

Textiles, due to their organic nature, are easily degraded. For this reason, some of the most used ways to date them is by stylistic comparison. Nevertheless, for this to happen, there must exist another similar object with an archaeological context that allows to stablish an approximate date. Reports of radiocarbon dating can be found as Fedi *et al.* 2008, Hajdas 2014. Jull *et al.*. 1996 or Richardin *et al.*, 2010, among others.

Textiles that are well preserved and have enough material to be sampled can be analyzed by the radiocarbon dating technique. Natural fibers can be managed as any other organic material, where due to their high amount of natural carbon (of biosynthetic origin), can provide enough ^{14}C isotope to obtain an absolute date.

Radiocarbon dating of textiles is nowadays more used thanks to the development of new instruments (like the Accelerator Mass Spectrometer, AMS) that require minor amount of sample for the analysis (less than 10 micrograms), making the analyses less expensive. However, the date obtained has a statistical imprecision dependent from the sample and its conservational state. It is possible to achieve a more precise date if the object is related with its context and the results from other analytical studies.

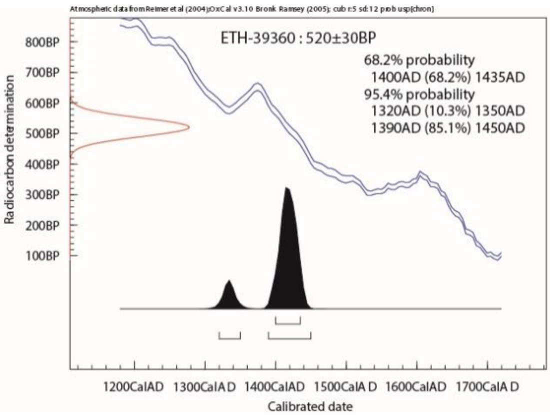
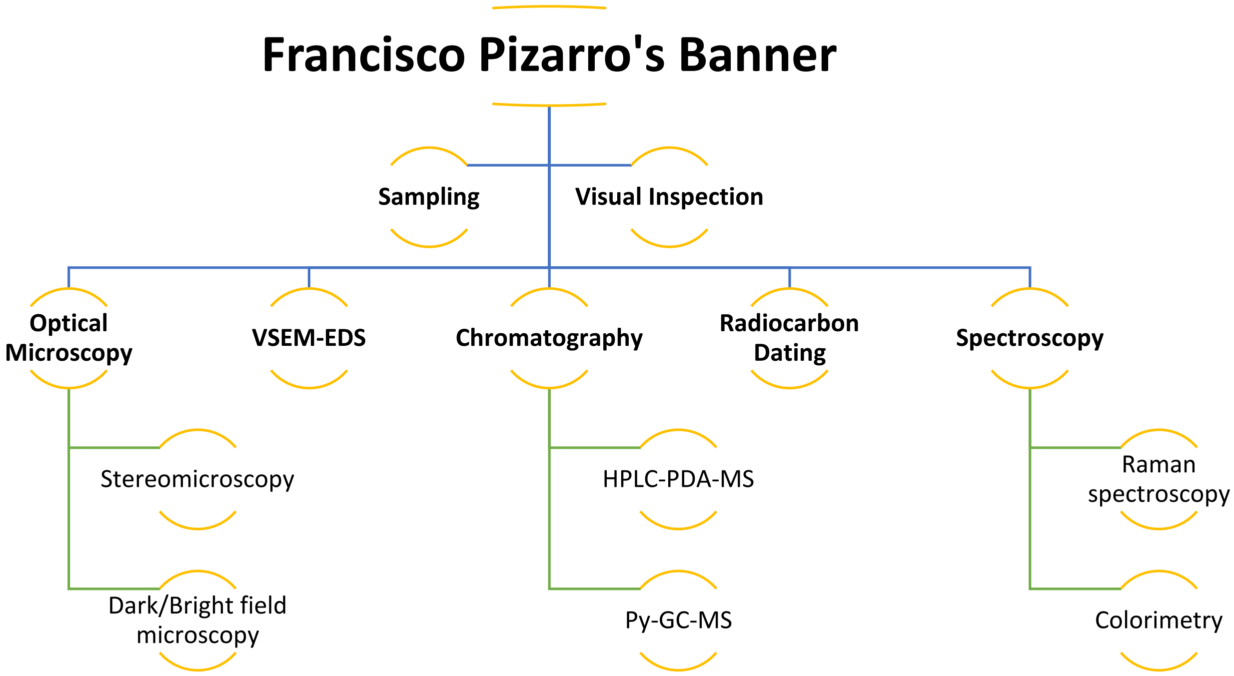


Figure 42 Fig. 3. Example of calibration of the ^{14}C age determined for 14C dating results of a cotton sample, dated to AD 1390–1450

5. Materials and Methods

The following diagram shows the analytical studies done on the research of the Francisco Pizarro's Banner of Arms.



5.1. Sampling

The sampling process was done by the Conservation Department of the National Museum of Colombia funder supervision of Maria Catalina Plazas, Head Restorer. The process took place at the National Museum, and samples were removed by cut in areas already presenting damage. Sampling was random, and in representative points that allow to obtain information of the whole object. Each sample was collected, packed and labeled individually in polymeric envelopes to avoiding external contamination.

A total of 25 samples were collected and sent from Colombia to Portugal for analysis. Sample size ranged from approximately 1-6 cm^2. The figure 43 shows the exact position of each sample taken from the Banner.

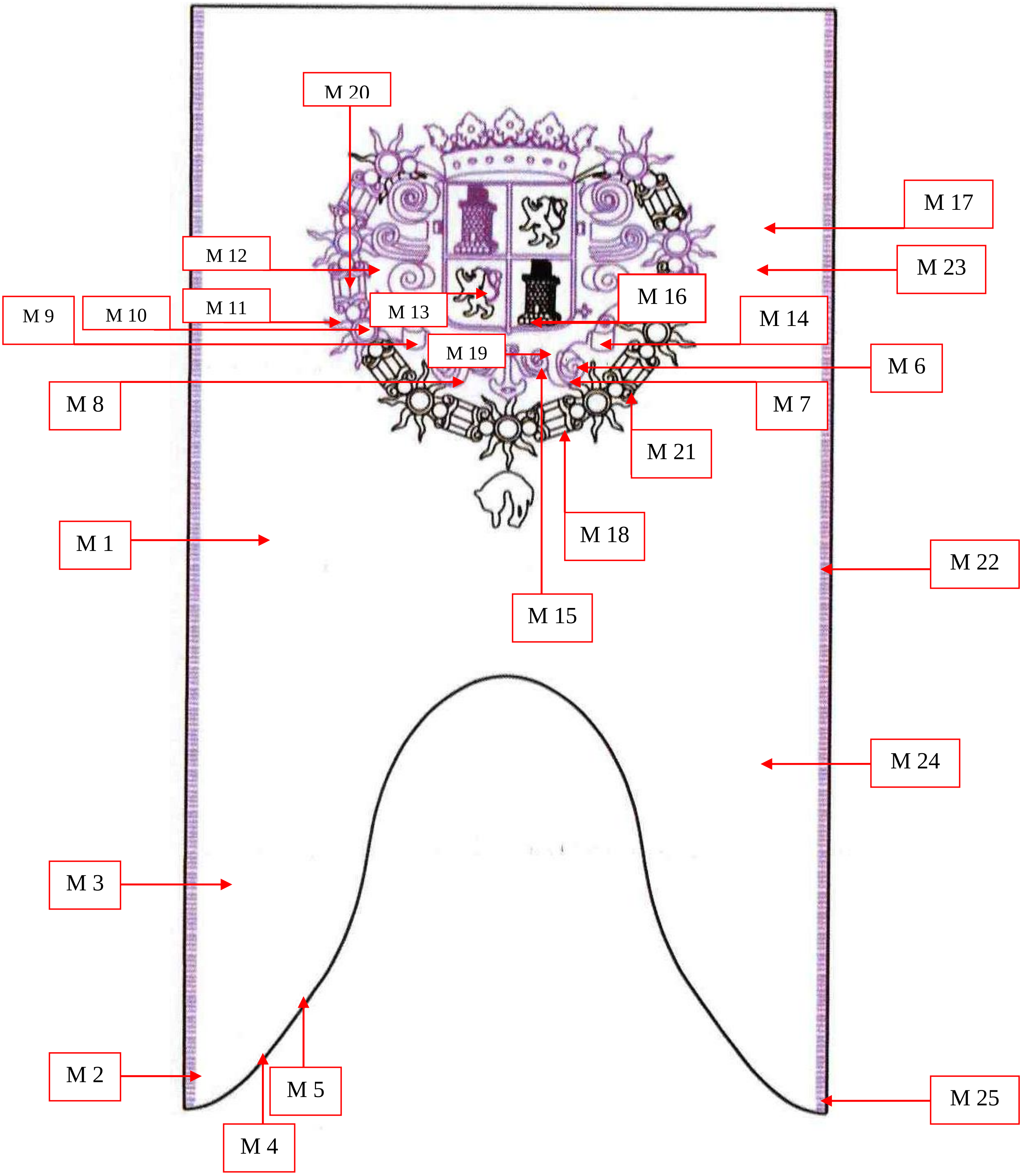


Figure 43 Detail of exact position of each sample taken from Francisco Pizarro's Banner of Arms

Table 1 Description of the samples taken from the Francisco Pizarro's Banner by the conservators of the National Museum of Colombia

SAMPLE NUMBER	SAMPLE DESCRIPTION
1	Beige background or back fabric from the Banner
2	Braid, Silvered metal thread
3	Beige thread corresponding to the front of the Banner
4	Fringes threads
5	Union sewing threads
6	Metallic thread flanged sewing.
7	Red fabric
8	Green threads
9	fabric over is sewing the green threads
10	Material with trace of blue pigmentation
11	Material with trace of red and yellow pigmentation
12	Loose material
13	Blue material from the central area of the lion in the emblem
14	Material with evidence of blue pigmentation
15	Inferior zone of the emblem
16	Central area of the emblem
17	Beige textile from the front area
18	Green thread
19	Paper (or parchment) support add in the rear area of textile
20	Paper (or parchment) add to the fabric
21	Material with evidence of yellow pigmentation
22	Beige background of the rear fabric
23	Beige Front fabric
24	Beige front fabric
25	Green fabric from the edge of the Banner

5.2. Visual Inspection

A personal visit to the National Museum of Colombia and its Textile Reserve Room in Bogotá-Colombia, in company of delegates of the Museum, was done some time after the sampling process. The Banner was inspected *in situ* in its full dimension: exposed surface (front) and partially in the back face. Several pictures without flash were taken to document the actual states of the object. A Nikon COOLPIX S9600 Photo-Camera with a resolution of 300 ppp, f point of f/4.5, exposition time of 1/13 s, focal distance of 9 mm and a maximum aperture of 3.3 was used. The white mercury bulbs installed inside the reserve room in the roof were used as illumination system.

During inspection, the Banner's conditions were detailed and the historical conditions of temperature (T) and relative humidity (RH) measurements of the last year inside the room were collected.

5.3. Optical Microscopy

Each one of the samples was observed under a LEICA M205C stereomicroscope coupled to an eyepiece (10x), camera adapter (5x), Tube (1x) and a set of LED lamps, with magnification lenses ranging from 1-20 X. Using the software LEICA Application Suite Version 4.4.0 (LAS) (LEICA Microsystems Limited (Switzerland), LEICA Microsystems CMS GmbH) the details of each sample were documented digitally by photography. Initial measurements of length were done.

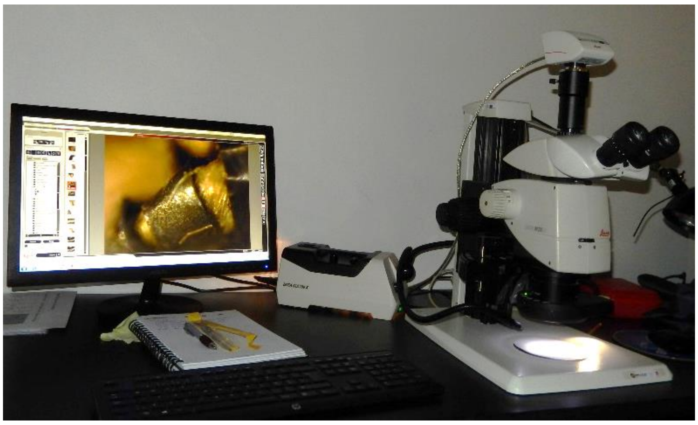


Figure 44 LEICA M205C microscope used in the study of the Francisco Pizarro's Banner

After reflective observation, each textile sample was divided into warp and weft, and the metal threads were split into metal and textile core. Each resultant sample was labeled and stored in an individual eppendorf.

From each of the resultant samples, single fibers were selected, which were observed under a dark/bright field LEICA DM2500 M microscope, with magnification FLUOTAR lenses of 10, 20, and 50 X, coupled to an external Camera LEICA MC170

HD. Using the software LEICA Application Suite Version 4.4.0 (LAS) (LEICA Microsystems (Switzerland) Limited, LEICA Microsystems CMS GmbH) thedetails of each sample were documented digitally by photography. Initial measurements of length were done.

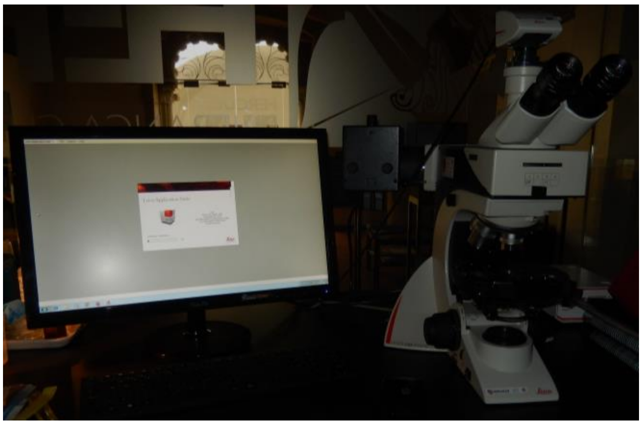


Figure 45 LEICA DM2500 M microscope used in the study of the Francisco Pizarro's Banner

5.4. Colorimetry

A portable spectrophotometeter Datacolor Check II Plus (Applied Color Systems, Inc, Suzhou, China), equipped with a Xenon lamp and a photo-diode sensitive to the 360–750 nm spectral range with an effective bandwidth of 10nm and a wavelength bandwidth of 2nm, coupled to a Palm (Hewlett Packard) was used for colorimetric studies. The system was calibrated with black and white standards. The color of the different samples was measured in a CIELab scale (L*,a* and b* CIELab space defined by Commission Internationale del'Eclairage in 1976) at three different points of each sample, the average value was used for data interpretation.

Figure 46 Colorimetry instrument used in the study of the Francisco Pizarro's Banner

5.5. Variable pressure Scanning Electron Microscopy-Energy Dispersive Spectroscopy

The different samples obtained (metallic and organic) were previously analyzed without coating under the environmental scanning electron microscope coupled to energy dispersive X-Ray spectroscopy, to characterize their topography and to obtain elemental information from each one.

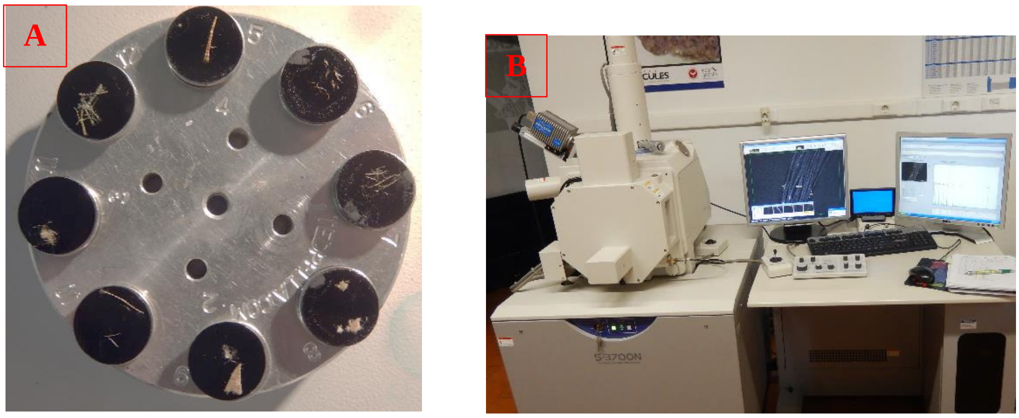


Figure 47 a) Samples mounted in carbon coat for VSEM-EDS analyses b) VSEM-EDS instrument used in the study of the Francisco Pizarro’s Banner

For this part of the analyses, an VSEM-EDS Hitachi S-3700 Variable Pressure equipped with a tungsten filament microscope, and an EDS Xflash 5010 detector Bruker with a resolution of 129 $e^{-}V$ (Hitachi-Technologies Corporation) was used. The analyses voltage was set at 10 kV and the vacuum at 40 Pa.

5.6. Chromatographic techniques

5.6.1 High pressure Liquid Chromatography coupled with Photodiode Array and-Mass Spectrometry

To identify the possible dyes/dye sources of The Francisco Pizarro’s Banner of Arms, HPLC-DAD-MS technique was used after a dye extraction protocol was applied to each fiber.

Table 2 List of samples extracted to analyze under HPLC-DAD-MS

Apparent color	Sample id	Sample mass/mg	Apparent color	Sample id	Sample mass/mg
Beige	1E	2	**Red-Yellow**	11E2	1
Red	2E	5	**Blue**	14E	1
Beige	5E	2	**Red-Yellow**	16E	1
Red	7E	2	**Beige**	17E	2
Blue	8E	1	**Yellow**	20E	3
Green	9E1	1	**Red-Yellow**	21E	2
Green	9E2	1	**Beige**	22E	1
Beige	9E3	1	**Beige**	23E	1
Red	9E4	1	**Beige**	24E	1
Beige	10E	1	**Beige**	25E	1
Beige	11E1	1	**Green**	25E	3
			Red	25E	1

All the fibers with evidence of pigmentation were isolated from their matrix until a weight of 1-2 mg was obtained. Similarly, some samples without evident pigmentation were collected. Each sample was placed in individual labeled eppendorf vials. 1.0 mL of 0,1 % EDTA (etilendiamintetracetic acid, ACS reagent Sigma Aldrich) in H_2O/DMF (1:1; v/v) (Water Milli-Q Millipore Simplicity UV 18.2 mΩ 25°C/(N-N Dimethylformamide ACS reagent Fluka) was added to each sample. The eppendorf vials were capped and placed in a hot bath (100°C) for half hour with magnetic stirring.

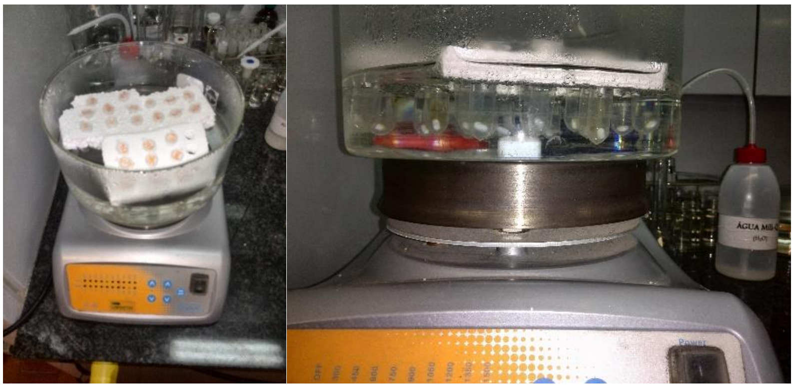


Figure 48 System of hot bath used to extract the natural dyes from the fibers of Francisco Pizarro's Banner

The vials were removed from the bath, cooled down to room temperature and placed in a lyophilizer (Telstar HT40 Lyo Quest) over night to evaporate the solvents. Dried samples were redissolved in 250 µL MeOH/H_2O (1:1 v/v) (Methanol Hypersolv Chromanorm vWR Prolab), stirred and sonicated for 1 min (Ultrasonic cleaner VWR). Blue and green samples were redissolved in 250 µL MeOH/DMF (1:1 v/v). All the samples were filtered through a 0.45 µm syringe filter and placed in vials for injection in the HPLC system.

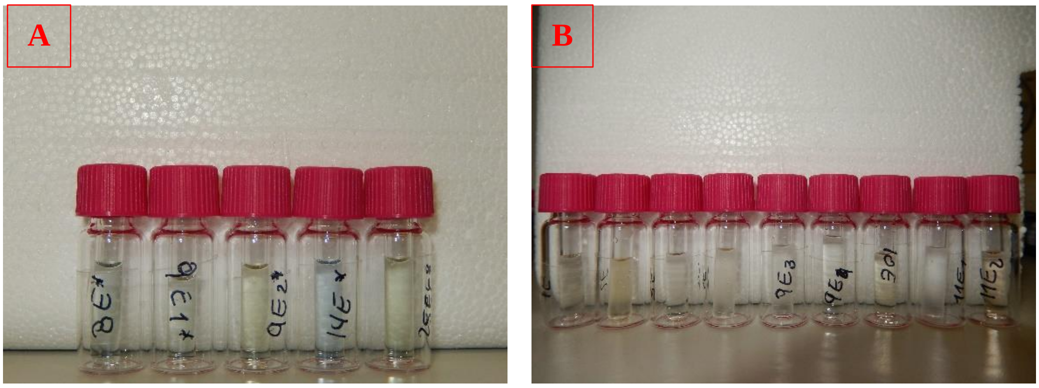


Figure 49 Vials with the extract of natural dyes obtained from the fibers of the Francisco Pizarro's Banner a) blue and green samples b) non-blue/green samples

The HPLC-DAD-MS analyses of the extracts was done using an LCQ Fleet Thermo Finnigan coupled to an auto sampler, degasser and a mass spectrometer instrument equipped with an electro-spray ionization (ESI) source and. an ion trap mass analyzer. A photodiode array (PDA) detector was also used (San Jose, CA, USA). To control, acquire and analyze the data software Xcalibur 2.0.7 (Thermo Fischer Scientific Inc.) was used.

Figure 50 HPLC-DAD-MS instrument used in the study of the Francisco Pizarro's Banner

For the experimental conditions of separation, a volume of 10 µL was injected in each analysis through a column Zorbax Eclipse XDB-C18 (Agillent) (narrow bone of 2.1 x 150 mm, and 3.5 µm of particle size). A flow of 0.2 mL/min of a set of two solvents was employed, solvent A: H_2O + 0.1 % FA (Formic Acid Hypersolve Chromanorm VWR Prolab); Solvent B: ACN (Acetonitrile Hypersolve Chromanorm VWR Prolab); in a gradient of 100 % A until 14 min, 37 % A until 25 min and 10 % A until 30 min. Column temperature was set at 30 °C. The PDA detector was set in a range of 190-800 nm and the mass analyzer set in full mode in a range of 100-800 *m/z*.

Each extract was injected four times to have a more complete analytical information from the samples as follow: positive mode with source of fragmentation 30V, positive mode without fragmentation; negative mode with source of fragmentation (0-12 min 10 V CID, 12-30 min 30 V CID) and negative mode without fragmentation.

The tuning process to calibrate the ion trap mass detector was done by direct injection of a standard solution of gallic acid (169 *m/z*) in negative mode and a standard solution of alizarin (241 *m/z*) in positive mode.

5.6.2 Gas Chromatography coupled with Mass Spectrometry

To identify possible gums in the samples and try to identify the kind of paper that was used as the support present in the samples Py-GC-MS technique was used. Samples number 12 and 16 were cut under the microscope, isolating the inner paper in the sample and the possible gum. 0.1mg of each sample were used in the Py-GC-MS analyzes. Analyses were divided in two: pyrolysis with and without derivatization.

The derivatization process was done by direct addition of 3.0 µL of TMAH 25 % wt in MeOH (Tetramethylammonium hydroxide Sigma Aldrich) to each sample, letting them in reaction for 10 min.

The pyrolyzer (Pyrolyzer Frontier Lab. EGA/PY-3030D multi shot) cell was set through the software EGA/PY-3030D control ver 1.60 to a 12 seconds pyrolysis at 500°C with an interface temperature of 280°C in single shot analyses. The GC-MS instrument used was a GC-2010 (Shimadzu Corporation) coupled to a GCMS-QP2010 Plus MS detector (Shimadzu Corporation), equipped with a column ZB-5HT Inferno (30.0 m of length, 0.50 µm of thickness and 0.25 mm of diameter). GC-MS equipment was controlled with the software Lab Solutions GCMS solutions Ver. 4.20 (Shimadzu Corporation).

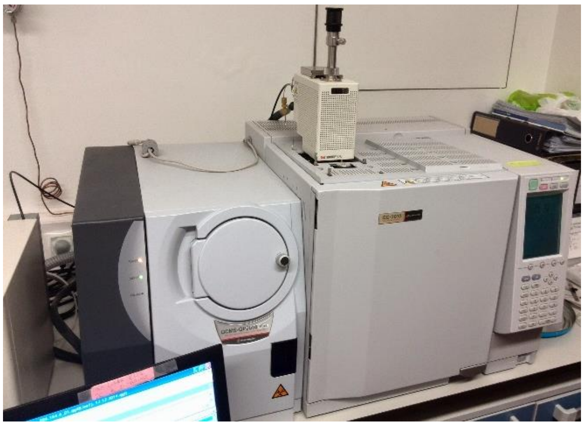


Figure 51 Py-GC-MS instrument used in the study of the Francisco Pizarro’s Banner

Experimental conditions of this method were: column oven temperature of 50°C, injection temperature of 250 °C, split injection ratio of 100, helium was used as carrier gas with a column flow of 1.48 mL/min. The batch was done using a temperature gradient of an initial temperature of 50 °C for 2 min, after a lineal gradient with a rate of 20 degrees per minute until 300°C to end with a hold temperature of 300°C for 5 minutes. The conditions in the detector were: ion source temperature of 240 °C, solvent cut time of 2.5 min, and full scan in a mass range of 40-850 *m/z*.

The collected data was analyzed using the software Automated Mass Spectral Deconvolution & Identification System (AMDIS ver. 2.70) and using the National Institute of Standards and Technology mass spectra library database (NIST Standard Reference Database 1A NIST/EPA/NIH mass spectral library).

5.7. Raman Spectroscopy

Raman Spectroscopy was used to identify a black pigment present in some samples. The instrument employed was a Raman XploRa (Horiba Sc) with a set of two emission lasers (785 nm and 635 nm) and three objective lenses (10, 50 and 100 X). The spectra were collected with the software Labspec 5 and compared with spectral databases.

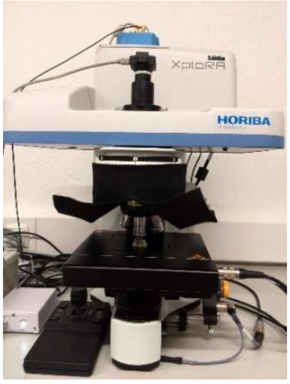


Figure 52 Raman spectrometer used in the study of the Francisco Pizarro's Banner

5.8. Radiocarbon dating (^{14}C)

Seven samples from different areas of the Banner were collected, weighted and delivered to the Center of diagnostic dating laboratory (CEDAD) dependence of the University of Salento, where it was subject of analyses under the AMS ^{14}C dating.

Table 3List of samples sent to AMS 14C analyses

Sample number	Sample mass/mg	Sample description	Material
FP1	27.20	Background Banner	Textile
FP22	12.39	Back fabric Banner	Textile
FP15C	23.97	Coarse textile in emblem	Textile
FP15M	6.70	Medium textile in emblem	Textile
FP15F	8.39	Fine textile in emblem	Textile
FP16	81.69	Paper from the emblem	Paper+Textile+Gum
FP17	36.10	Front of the Banner	Textile

6. Results and discussion

6.1. Visual Inspection

After a visit to the National Museum of Colombia (Cra 7 No 28 Bogotá D.C. Colombia) a visual inspection of the actual conservation status of the Francisco Pizarro’s Banner and its respective storage conditions was possible.

The Banner is located in the textile reserve of the museum (Second floor inside of the permanent exposition), together with other priceless objects of the Latin American history. The textile reserve room has no public entrance (not visible neither accessible for visitors). The room has with a window that allow the incoming sun-light (leads to the central yard of the museum) covered with a protector film to diminish the incoming UV light (Figure 53). The room has no environmental control, being susceptible to the same conditions as the rest of the building.

Figure 53 Detail of the window and shelf of the Textile reserve of the National Museum of Colombia

The Museum is located in front of one of the areas of Bogotá D.C city- Colombia with most traffic, near to the Easter mountains (Central mountain range of the Andes), in a building from the 19^{th} century.

The Banner is stored in horizontal position over a textile support and these in turn over a polymeric net (Figure 54). The Banner is inside a metallic shelf in an individual drawer without any kind of cover. The drawer is labeled in the front with the name of the object. The polymeric net has no visible damage, but the textile support shows visible damage (holes in different dimensions) around its structure.

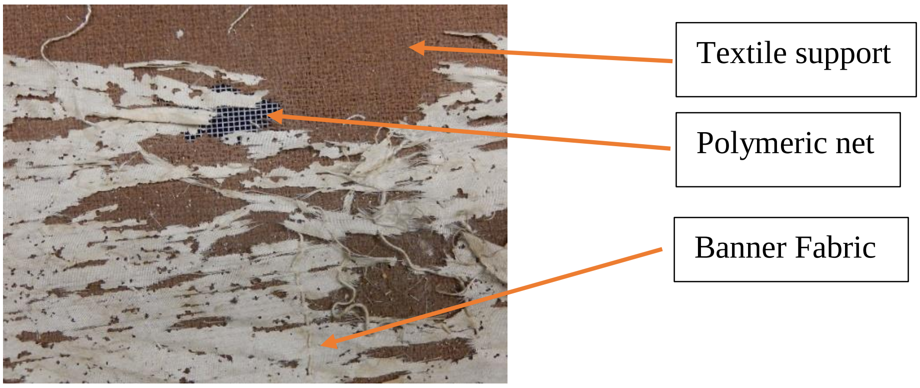
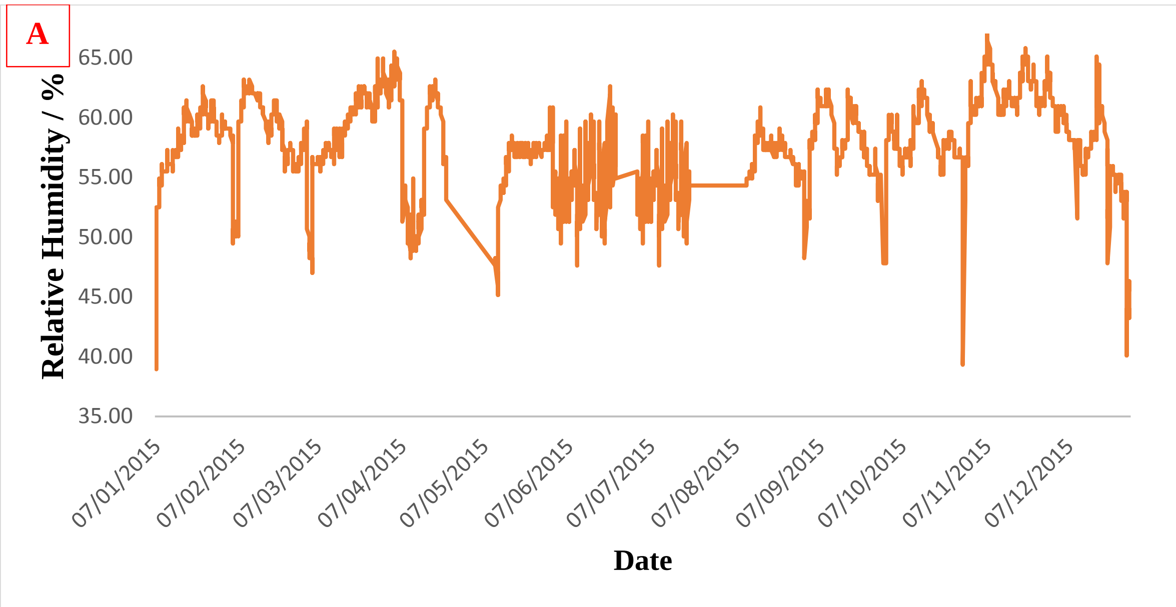


Figure 54 Detail of the Francisco Pizarro's Banner over its respective support in the storage inside of the Textile reserve of the National Museum of Colombia

Over the textile support insects and particles of foreign material were visible (Figure 55), being and indicator of pollutants and bio-contamination present in the room. Condition that could produce an immediate damage in the materials stored in the room. Insects use as food the textiles leading to the degradation of the material Pollutants and other foreign materials can introduce new chemical compounds that help in the degradation processes or in apparent visual change of the textiles (soil dust cover, fading, color spots, etc.). Also, the presence of foreign elements in the Banner support textile provides us with an indirect information of the atmosphere conditions of the room, showing that not only the macroscopic agents from the exterior are present, also, the incoming of gas pollutants are likely to be present inside the room (SOx, NOx, COx, similar to the exterior of the building).

Figure 55 Detail of foreign material over the textile support in the Francisco Pizarro's Banner storage a) Insect b) Plastic

The information of the environmental conditions measurements of the textile reserve in the last year was provided by the Museum (Figure 56). However, the instrument used to record it was not present in the room at the day of the visit. The data provided by the museum shows an acquisition of Temperature and Relative humidity each two hours each day. The data shows lack of measurement in some complete periods of time (April 24-May 11; June 24-July 2; July 22- August 11), as in some periods during the day, i.e., September 30 where the morning conditions were not measured.



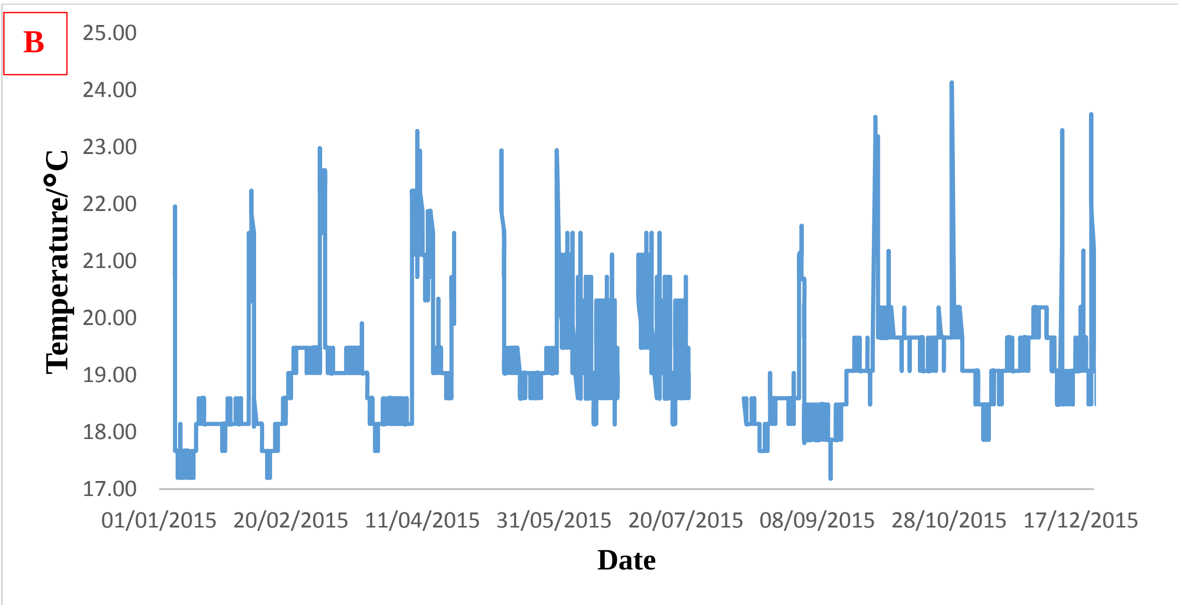


Figure 56 Plot of the 2015 environmental conditions in the Textile Reserve of the National Museum of Colombia A) Relative humidity % B) Temperature

If it is true that the conditions obtained in the room do not reflect an extreme environment, the high oscillation in the storage conditions of RH% and T are not the optimal for a museum collection. This conditions are not favorable for historical materials, due to the material stress created in the fibers of the fabrics that produces an irreversible enfeeble of them, and carry on the disintegration of the object in long term.

Changes in humidity, helps in the transmission of micro-chemical pollutants to the whole body of the objects due to their capillarity properties, as well increase the possible change of pH of them, and helps in the biotic grown (National Park Service, 2002).

Figure 57 Detail of the deterioration present in the surface of the Francisco Pizarro's Banner

The object shows a textile with a mixture of components, that could be described as a rectangular banner with a two-point ending shape. It is possible divided the object in two: a fabric and a central coat of arms/emblem. The full object's body shows a big visible degradation, holes of biotic attack are present in the whole object, lack of full areas are evident, and fade in the fabric is predominant (Figure 57 and 58). Also is remarkable the loss of rigidity in the object and the distortion in the shape, likely due to the change in the fiber properties and the presence of color-spots due to humidity or contact with liquids.

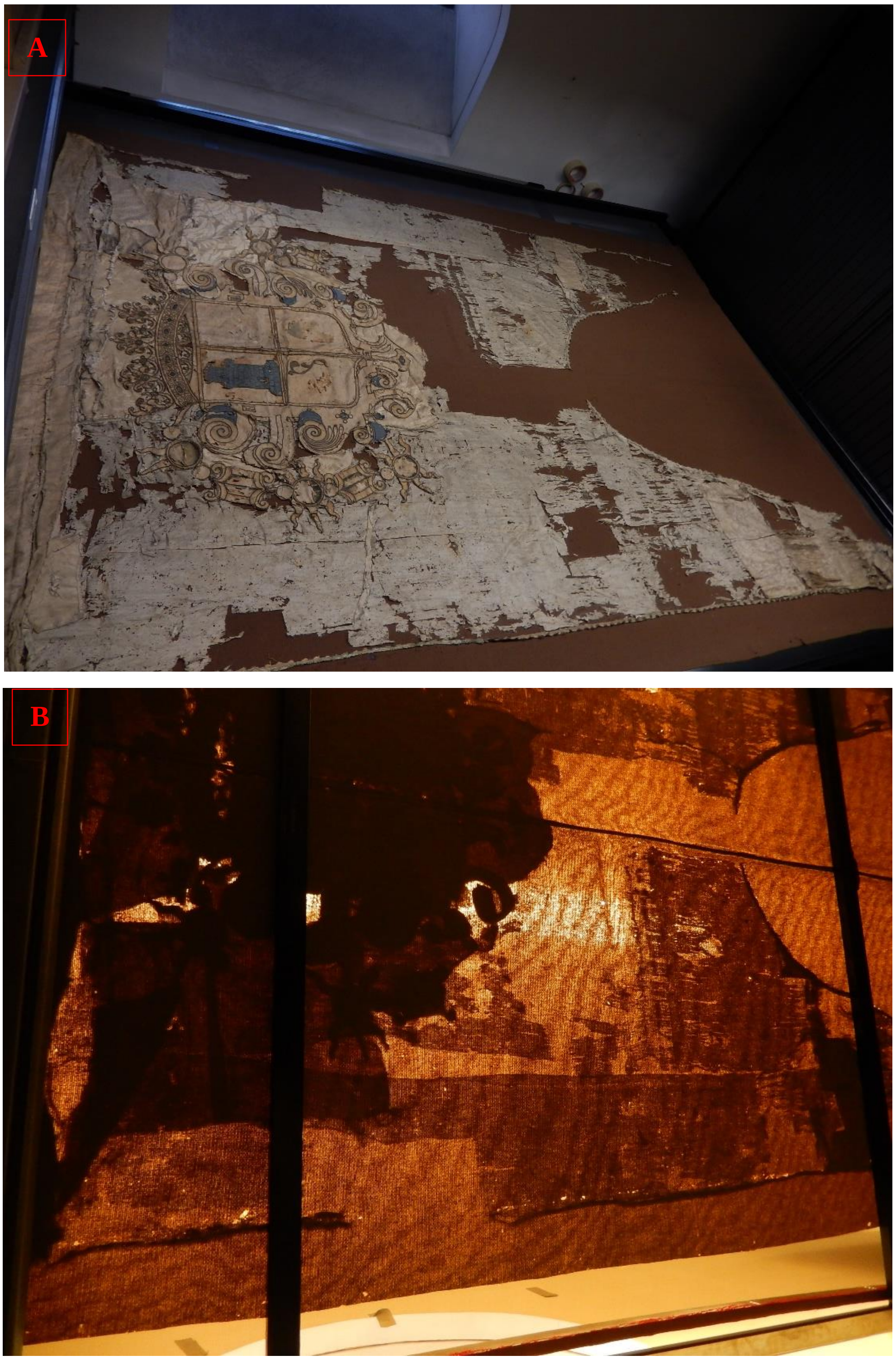


Figure 58 Photography of the Francisco Pizarro's Banner a) View from top b) View from bottom

6.1.1. Fabric

To discuss the composition of the Banner, it is important to divide it in its different visible areas:

- Green color edges (braid): The braid shows two fabrics joint: a green weaving in the front face and a brown with metal threads in a regular pattern in the back. This braid surrounds the left, right and bottom edges of the Banner (Figure 59).

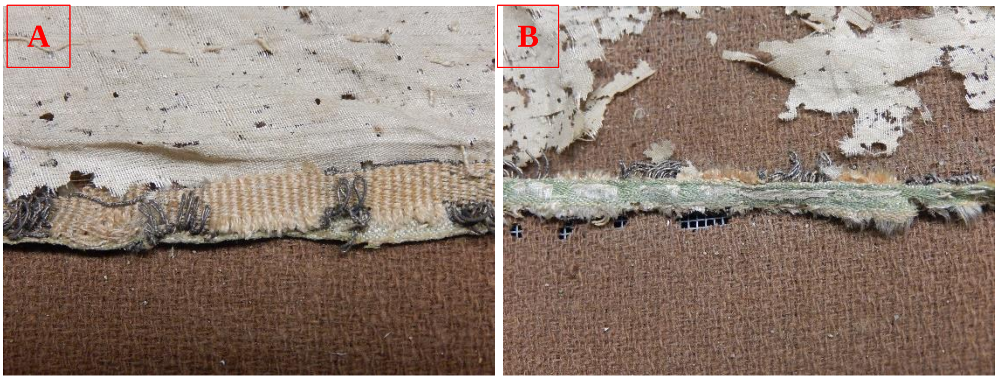


Figure 59 Braid detail a) rear face b) front face

- Pole holding area: A brown-beige color fabric is visible in the area where the Banner could be held to a pole (Figure 60). The texture of this material looks rough as well as the weaving, being different from the rest of the object. It is also visible the sewing stiches, used to attach this material to the field of the Banner.

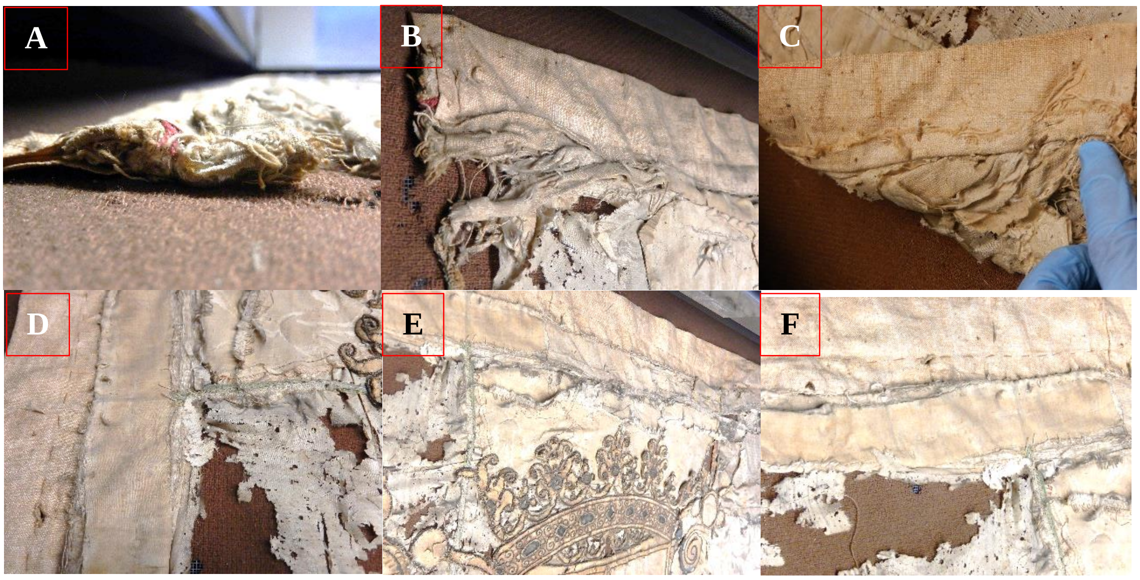


Figure 60 Francisco Pizarro's Banner detail of the pole holding area A) Lateral view B, D, E, F) Superior view C) Back face

- Horizontal view: Three textile areas joined by sewing stiches are visible, two lateral (larger) and one central (shorter) (Figure 61). The whole structure builds the background body of the Banner. The two lateral textiles start in the top straight, ending in the bottom in point. The structure of the lower right lateral area disappeared, while the left shows the presence of a fringed textile (Figure 62).

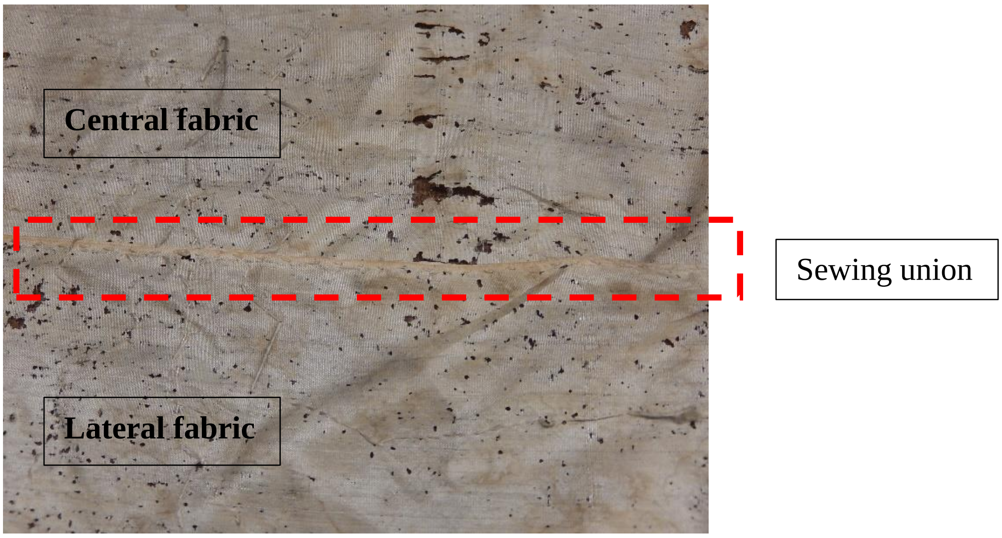


Figure 61 Detail of the central area joined to the lateral area in the Francisco Pizarro's Banner

Figure 62 Detail of the three different ending areas of the Francisco Pizarro's Banner A) Right B) Center C) Left

- Central support cords: Symmetrical cords of a green stripe were detected on the top of the field's Banner (Figure 63). Those stripes run from the pole host to the bottom braid on the Banner length, creating and square area to held the coat of arms. Those stripes are similar to the green fabric used on the braid. The position of this part of the Banner suggests that it was possible added to the main fabric before the coat of arms was assembled on top of it. It has likely an utilitarian function more than stylistic, possibly used to give enough strength to the main fabric to hold the metallic emblem.

Figure 63Detail of the support line in the Francisco Pizarro's Banner A) Left line B) Right line C) Bottom view

- Textile strata (Vertical): The Banner fabric is composed by three textile layers. The fabric shows a central (inner) fabric with a simple weaving in all the Banner (Figure 64). The back face presents a textile with different weave (not seen in detail because the fragility of the object prohibits its handling). The front face shows the use of different types of textiles with different weavings (motives as flowers, diamonds among others are visible), being perceptible the possible original one by its distribution on different sectors of the Banner (flowers motive), included under the coat of arms, and the left-down corner of the Banner. The three textile layers possibly were joined in the edges of the Banner by the braid and possibly by extra sewing.

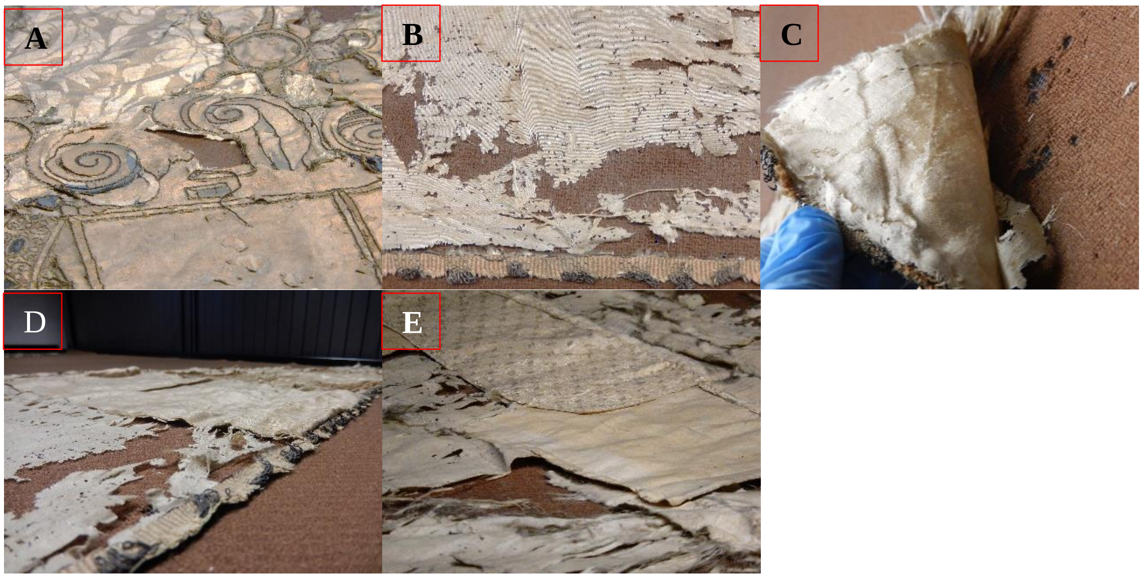


Figure 64 Detail of the textile strata of the Francisco Pizarro’s Banner A) Front layer B) central layer C) Back layer D) Strata joined by the braid E) Extra patches.

6.1.2. Coat of arms

The emblem in the Banner is its most noticeable part due to the central position, colors and shape (Figure 65). The actual emblem shows a big loss in its integrity, being only appreciable an open crown as crest, with a shield divided in four quarters surrounded by what most to be the Chain of the Order of the Golden Fleece. Three quarters of the shield are lost, while only the first quarter is almost intact showing a blue tower/castle.

The coat of arms shows a multilayer construction attached to the main fabric, starting with a base of a coarse textile followed of rag paper with evidence on top of different dyed fibers (yellow, green, blue, red), terminated with a metal thread decoration.

The rag paper is breaking out from the object, losing each time more details in the design, making more difficult its understanding.

The emblem is fully decorated with metal thread with a black appearance that surrounds in contour the edges of all the motives (sun, crown, castle, shield, etc.). The metal thread is braided and not embroidered through the textile, instead is sewed with a beige thread that join it to the base fabric for the emblem. In points where the union thread is loss, the shape of the motive is also defaced.

The Chain of the Order of the Golden Fleece is the part of the emblem with the biggest loss, with the almost complete disappearance of the inferior portion of it, including the golden calf, which in some moment should have adorn the Banner. This golden calf, should have had a big weight due to the amount of metal embroidery in it (as in other Chain of the Order of the Golden Fleece of Spanish banners), reason why the emblem structure in the Banner must have needed the extra central support, providing a better rigidity and a longer life to the object. Without the presence of the previous mentioned cords, the fabric would likely rip up due to the weight-movement.

Figure 65 Details of the coat of arms in the Francisco Pizarro's Banner A) Coat of arms B) Crest: Crown C) Tower in first quarter D) tail of possible Lion in the third quarter E) Supporter F-G) Chain of the Order of the Golden Fleece H) Metal thread contour

According to the visual inspection, the area where the golden calf should have been, there is a linear straight cut in the textile and in the metal thread from the central braid (Figure 66). This is likely evidence that the loss of the golden calf was not a natural process of degradation of the object, but was, on purpose damage, presumably by a thief, who, with help of an instrument (knife or scissor), cut the Banner to subtract the brightest part of the object. Due to the lack of detailed information of the Banner in the historical documentation it is impossible to determine the exact time when this damage was inflicted on the Banner.

Figure 66 Detail of the damage in the central are of the Francisco Pizarro's Banner A) Detail of area missed from a top view B) close up of the straight cut C) Detail of area missed from a bottom view

The shield shown in the coat of arms of the Francisco Pizarro's Banner correspond to the one used by the Castilla and Leon Kingdom according with the different stylistic studies done to the Banner (there is not a Pizarro emblem or from his army) (L. Castiblanco, 2013). However, all the documents that make a reference to the coat of arms of Castilla and Leon talks about the use of a golden/yellow castle with three battlements in the emblem in the first and fourth quarters (L. Castiblanco, 2013). The emblem present in the object of study shows a blue tower with one battlement. This could be a discrepancy in a vexillology way, due to the change in shape or color of the parts in the emblem, being possible to represent a different family or give a different territorial area.

A bibliography/historical review about the colors used in the representation of the castle of the Castilla and Leon emblem revealed out that the blue castle, indeed was used to represent the Castilla Family, as in the Royal Emblem of the Catholics Kings located in Toledo-Spain (Figure 67E), as well in the first illuminations of world maps that shows the kingdoms around the world (World map Spain and Portugal borders and kingdoms, 1580) (Figure 67 A and B). This likely indicates that the color used in the Francisco Pizarro's Banner was not an aleatory option, on contrary, was following the rules of an old tradition.

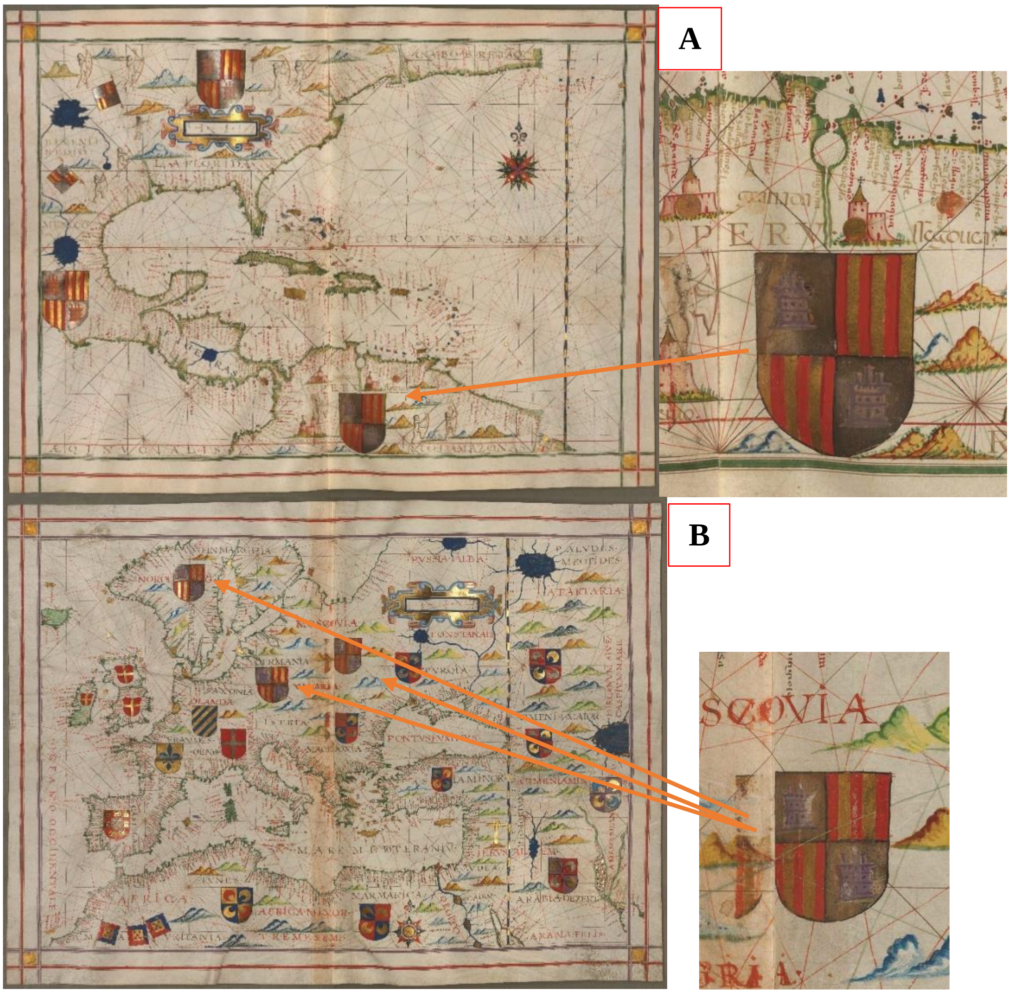
The historical evidence, allows to postulate the possible use of the emblem of the Castilla kingdom representing this noble house as it should have been represented before the 17th century, after which Spanish kingdom established the golden castle with an enclosed crown as one of his symbols (F. Menendez, 2004). Furthermore, it can be used to give an idea about the Banner dating, allowing the object to be temporally located in the Pizarro's time with King Charles V as ruler.

There is also similitude between the Castle shape in the Francisco Pizarro's Banner and the coat of arms of the city of Lima (originally the city of the kings, converted in the capital of Peru) (Figure 67 C) (J. Gunther, 1983). In the same way, the Flag of the "Trujillo's volunteer cavalry" (Figure 67D) used in the Peruvian independence wars shows a similar structure to the Pizarro's Banner (two points shape with the emblem of Castilla and Leon crown in the center) (L. Suarez, 1992). Those similar objects can give a clue of an imaginary created for the representativeness of similar ideas, as it is impossible that were done by the same person (they come from a different times and places of manufacture). The analysis of these objects, suggests that the different producers used those symbols and/or shape due to the influence of its alive interactions with another object of the same or more relevance. In this way it is possible to postulate that the Francisco Pizarro's Banner of Arms had influence in its manufacture in the Old World and influenced another manufacturer in the New World.

At this point it is important to try to understand the meaning of the Francisco Pizarro's Banner. This flag named as if it represents to Pizarro, or even his army, has not emblem that makes a direct reference or link to Pizarro. In contrast, it shows the Royal emblem of the King of Spain. This could be nothing, if we don't take into account the representativeness of this objects at that time. The flags or banners have not a decorative purpose, instead they provide to the viewers an indirect speech, with information not in words, but in colors, shapes and textures.

At this level we don't have enough data to precise dating of the Banner, but we can start to suggest that it has no the intention to talk to us about Francisco Pizarro, but instead to send a message about Castilla and Leon Crown, in other words, it is not a Banner which a group of persons participate in a quest to follow a man (Pizarro), is an object that represent the power and domain of one Realm that is conquering new lands.

If the following analytical study lead to prove the originality of the object in time and materials, we should start to think that the object under study is not the Francisco Pizarro's Banner, being instead the Conquest Royal Banner.



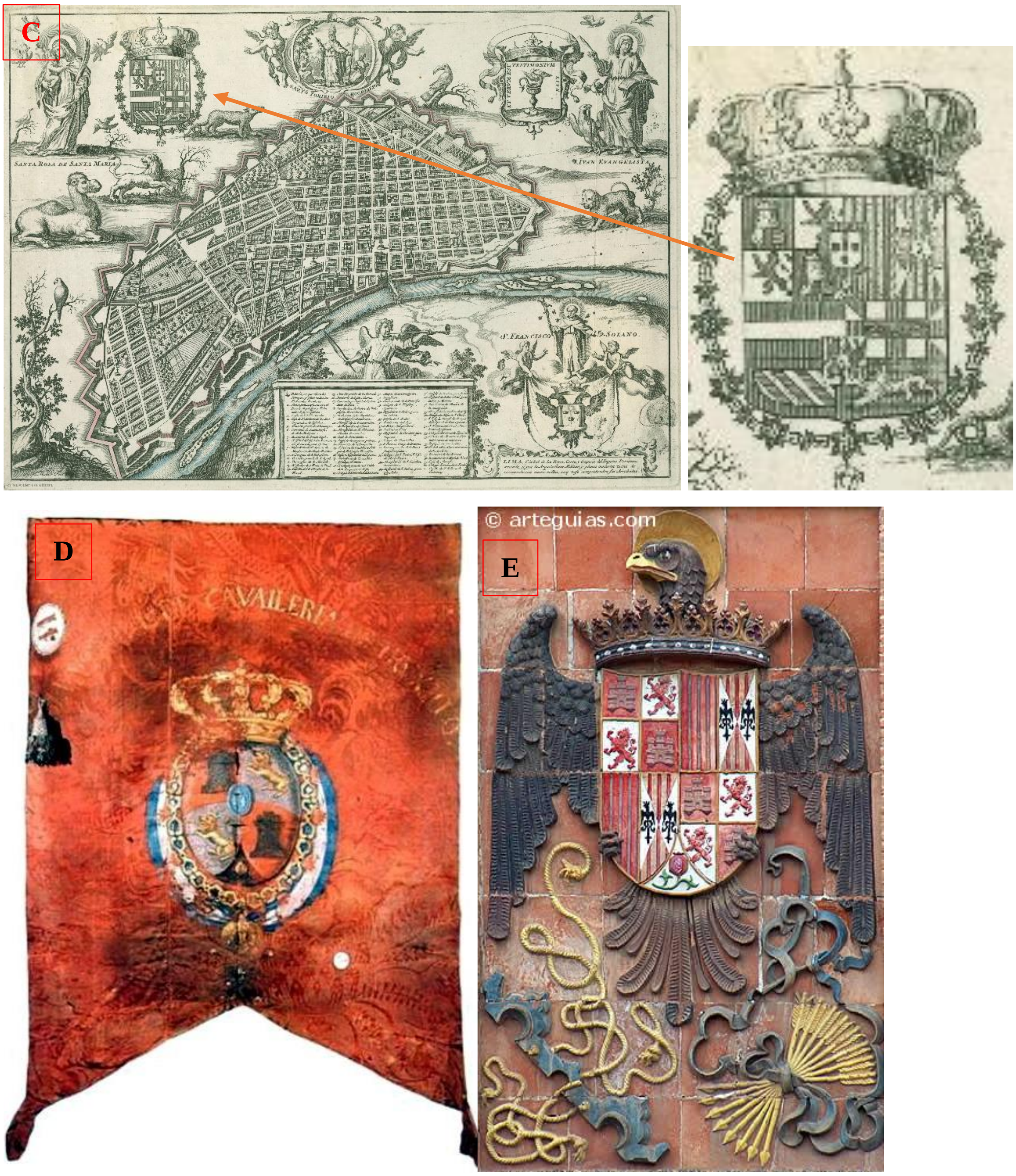


Figure 67 A) Detail of 1580 Portuguese sailor's world map with blue coat of arms of Castilla in the New World B) In the Old World C) Map of the city of Lima from17th century with castles in similar shape as the Pizarro's Banner emblem D) Flag of independence wars of Trujillo-Peru 19th century with similar shape to the Francisco Pizarro's Banner E) Coat of arms of the Catholic Kings of Spain on Toledo's facade, Spain

6.2. Optical Microscopy

Through the microscopically inspection of each sample taken from the Francisco Pizarro's Banner, were visualized and classified the different materials present in the structure of the Banner, giving a first idea about the making up process of the object (Figure 68) (See Appendix A).

The samples taken (See Figure 68) can be divided in the following groups:

- Textile: Samples 1, 2, 5, 9, 10, 15, 17, 22, 23, 24, 25, are pieces of weaved textile (wefts and warps). Samples 3, 4, 18, are threads.
- Rag paper: Samples 7, 8, 11, 12, 13, 14, 16, 19, 20, 21, have pieces of weaved textiles together with rag paper.
- Metal threads: Samples 2, 6 and 15.

The sample 1, shows a simple plane weaving (3wefts x 3warps/mm) of a beige color textile with the presence of black particles on its surface. The weaving shows the use of yarns of 200 µm of diameter in average, in similar dimension to the wefts (1A) and the wraps (1B). The different yarns used show no apparent twisting. Degradation in the fibers is evident, no fiber elasticity and easily breakage when handled. Holes of different sizes are visible in the sample. The holes marks are likely due to use of needles when sewing and result from the break of the fiber by penetration of the needle through it. The fibers used in the weft and the warp, were likely silk.

The sample 2, shows the presence of two fabrics joined by a thread (2H), weaved to metallic threads. The first fabric shows a complex weaved of beige yarns in S twist, some yarns are visible red, and others beige, being likely Silk (2A (weft), 2B (warp), 2BR (red warp)). The second fabric shown the same structure as Sample 1. The metal thread, is composed by a beige fiber core in S twist (2MF) of a fiber likely silk, surrounded by a S twisted metal stripe with evidence of silver-golden color in the surface (but almost complete black) of 0.4-0.5mm of wide 0.03 mm of depth, and a space between each loop of 0.23 mm. Some of the metal threads shown a double layer of the metal stripe.

Sample 3, shows an open twisted beige textile characterized likely silk. Hatched insect eggs were found in the textile.

Sample 4, shows multiple yarns joined to form a thread. The fibers have a beige color with a Z twist, being characterized likely silk.

Sample 5 shows a beige fabric with equal characteristics as Sample 1. A beige thread in S twist sewed (5H) to the main fabric was present. The fabric was characterized likely silk, while the thread was identified likely cotton.

6. Results and discussion

Sample 6 shows a metal thread twisted with a similar composition than the observed in sample 2. A beige-yellow inner fiber identified likely silk (6MF), surrounded by a metal strip with the same dimensions as in Sample 2 was observed. This metal strip shows a darker color in the surface, being almost imperceptible the golden-silvered areas.

Sample 7, shows rag paper with two faces, the front with red colored fibers attached, and the back with some kind of adhesive added. The fibers attached (7F) were identified likely silk, present red areas of major intensity with others more beige/yellow color, those fibers shown also the use of a gum to be added to the rag paper, no traces of sewed were found. The rag paper (7PF) show the presence of different fibers joined by a mass, being evident some fibers likely silk, as vegetable fibers. The rag paper sample shows a 0.5 mm diameter hole, being an evidence of the us e of a needle to sew the paper to the fabric.

Sample 8 shows rag paper with a blue-yellow color textile added in the front face and a gummed back face. The blue-yellow textile shows a plane weaving of dyed fibers characterized likely silk (8F). The back face shows a black line of pigment over some of the gummed area. The rag paper shows a matrix of different fibers (cotton, silk, linen).

Sample 9 shown a complex weaving of different color yarns (white weft, green dark and green light as warp) without apparent twist particles of different colors and sizes are evident over the surface. An inner central red yarn was observed in the edge of the fabric sample. All the fibers dyed or not were identified likely silk.

Sample 10 is made of a fabric similar to Sample 1. A big number of particles over the surface are evident. A grey/brown thread over the textile was detected. The fibers in weft (10A), warp (10B) and thread (10H) were identified likely silk.

Sample 11 shows a fabric with two colors: red and yellow in a similar weaving structure as Sample 1. The fibers in weft (11A) and warp (11B) were identified likely silk.

Sample 12 is a composed sample with a yellow textile over a rag paper sample. The textile fibers (12F) were identified likely silk added to the paper by the use of a gum/glue. The rag paper fibers (12 PF) were identified likely silk, cotton, and linen in a big matrix with gum/glue.

Sample 13 shows the structure of rag paper with evidence of a gum/glue over its two faces. A hole through its body is evident, where fibers of a thread were detected (13H), being identified likely silk, and the whole shows the structure of needle sewing.

Sample 14 shows rag paper sample with a blue textile added in one face. The rag paper (14PF) shows presence of different fibers equal to the rag papers already observed. The blue textile was identified likely silk, being added to the paper by the use of a gum/glue.

Sample 15 was the sample more complex from all the set of samples taken from the Banner. It is composed by four layers of fabric joined by a thread that join them together with a little piece of rag paper. Also a metal thread is present in the sample. The first textile layer was identified as a beige coarse plane weaving fabric presumably silk (15CF); the second and fourth layer is a beige textile with a complex weaving (15MF), identified likely silk; the third textile layer (15SF) as a structure similar to Sample 1. The thread used to sew all the layers (15H) has a beige color and has an S twist, being the fiber of the yarn identified likely Silk. The rag paper in the sample shows the same characteristics as the other paper samples, with traces of gum/glue on both surfaces. The metal thread at the same time, shows the same characteristics as the metal threads of Sample 2 and 6.

Sample 16 is made of rag paper with a brownish textile added to the front face and a gum/glue in the back. The dyed fibers (16F) were identified likely silk, while the fibers in the paper (16PF) shown the same characteristics as the rest of paper samples.

Sample 17 is a beige textile with the same structure as Sample 1, and its fibers were identified likely Silk.

Sample 18 shows a beige thread in an S twist of 0.5 mm of diameter approximately, being identified likely Silk.

Sample 19 is a rag paper sample with a bluish-yellow textile added in the front face and a back face with a straight black pigment line. Several circular holes in a patron series is evident in the edge of the sample, where traces of yellow fibers were found. The bluish fibers (19F) were identified likely silk, as the yellow ones (19YT). The rag paper presented the same matrix of fibers than the other samples.

6. Results and discussion

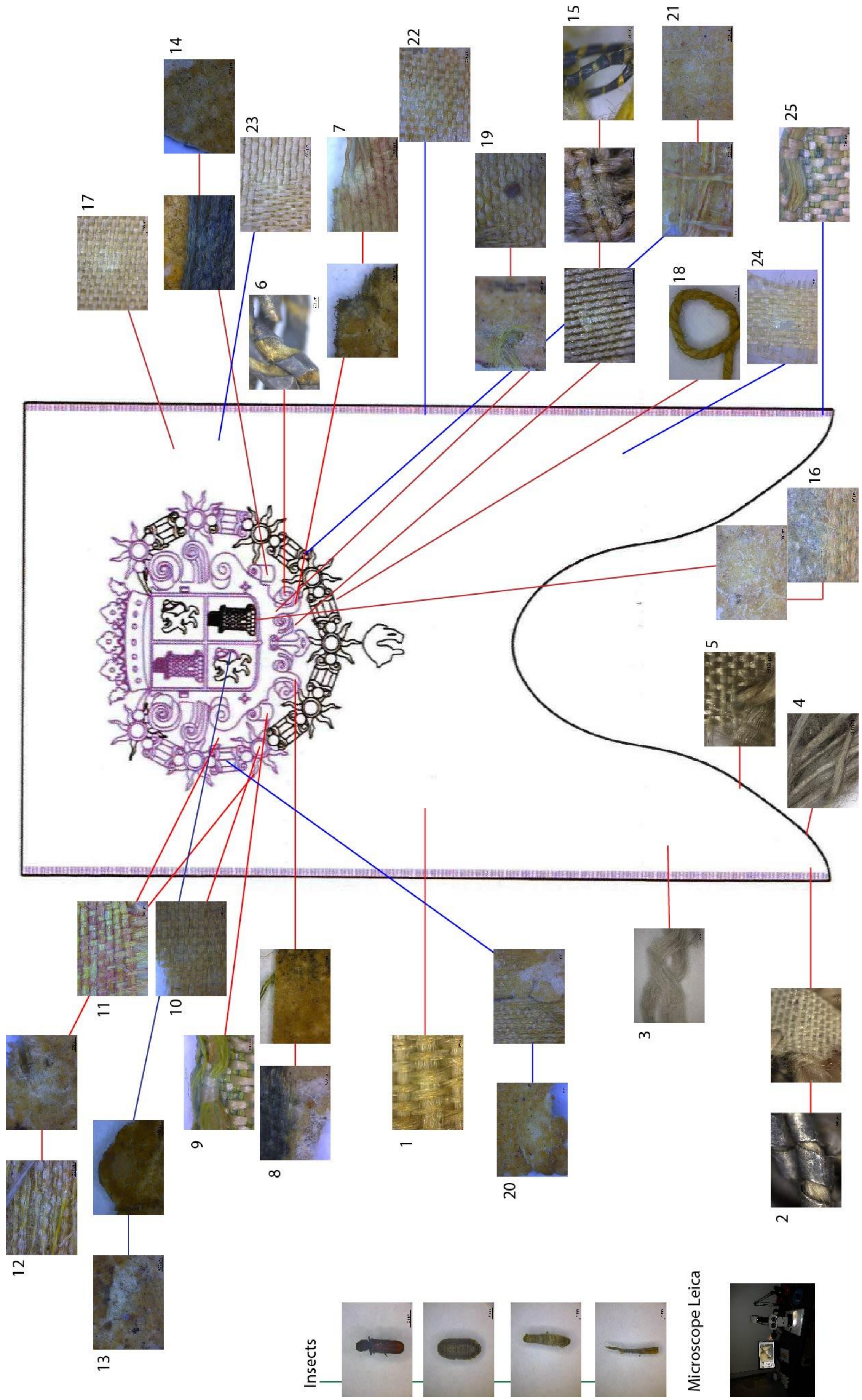


Figure 68 Detail and location of the samples taken from the Francisco Pizarro's Banner

Sample 20 and 21 present a structure similar that of the other rag paper samples, with a dyed textile added in the front and a gum/glue back face. The dyed fibers were identified likely silk.

Sample 22 shows a structure similar to Sample 1, being identified likely silk the fibers in the sample.

Sample 23 shows a structure similar to those of layers 2 and 3 of Sample 15, being the textile fibers identified likely silk.

Sample 24 shows the same structure as Sample 1, being identified likely silk. The grey-brown thread on the surface was identified likely silk.

Sample 25 shows the same structure as Sample 9, being identified likely silk.

6.3. Raman Spectroscopy

The black pigment drawn in some rag paper layers in some of the samples (Sample 8, 19, 20) was analyzed to identify the composition of this element in the Banner. The Raman spectrum enabled the identification of carbon black as medium to draw the paper (Figure 69) (I. M Bell *et al.*, 1997; L. Burgio *et al.*, 2001).

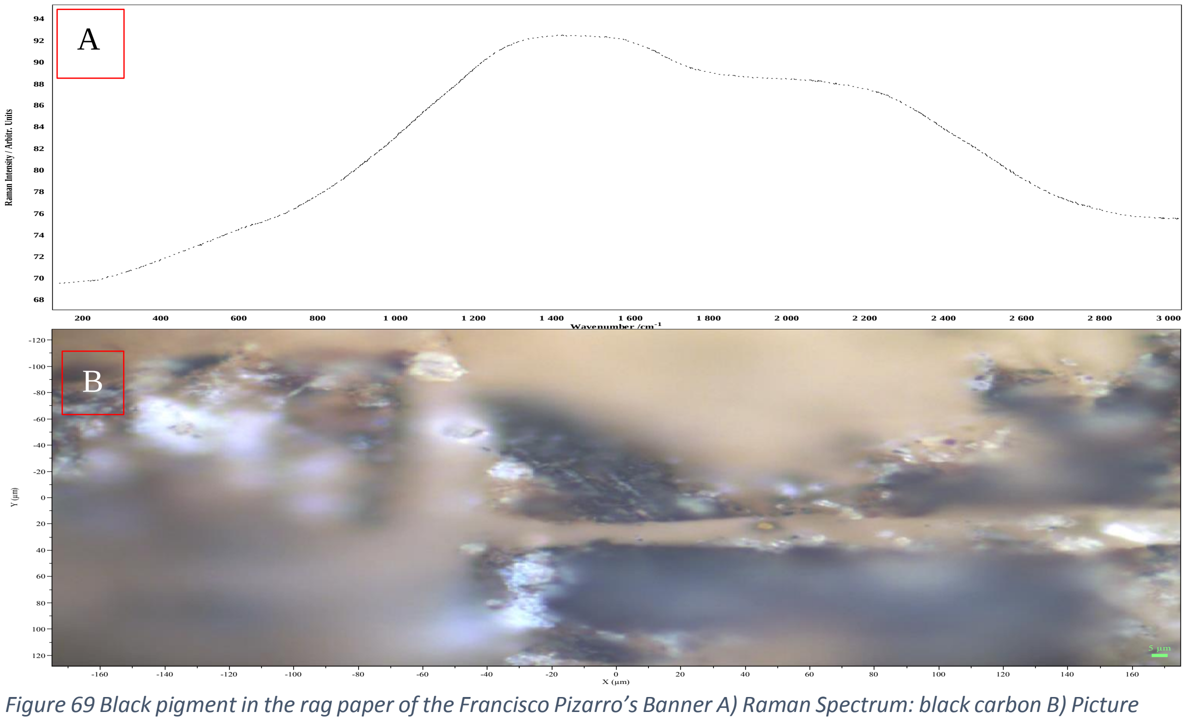


Figure 69 Black pigment in the rag paper of the Francisco Pizarro’s Banner A) Raman Spectrum: black carbon B) Picture of the pigment.

6.4. Variable pressure Scanning Electron Microscopy Energy Dispersive Spectroscopy (VP-SEM-EDS)

The use of the VP-SEM allows the acquisition of images from the different fibers surfaces without coating. Damaged textile fibers suffered some minor burnt at their surface at the focus process, being necessary move the place of measure to guaranty a representative measurement of their topography (See Appendix 2).

The use of the EDS, allowed the chemical characterization of the uncoated fibers as a proteinaceous organic material, even if it is not the more adequate technique, where after the mapping over the fibers can be detected their content on carbon, nitrogen and oxygen (Figure 70) (See Appendix 3).

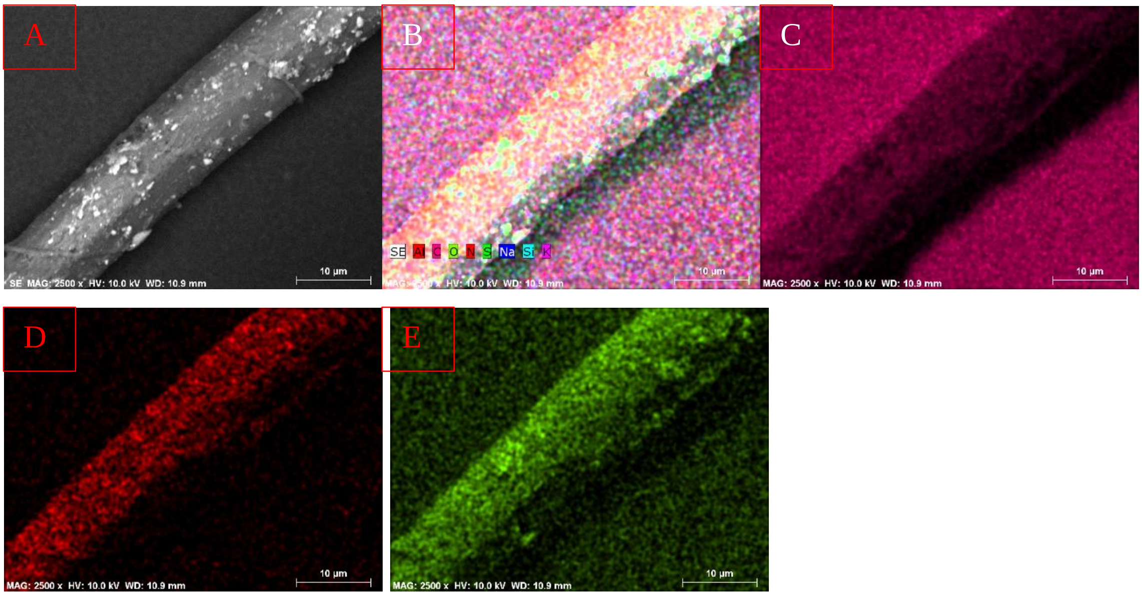


Figure 70 EDS Mapping of a silk fiber from the Francisco Pizarro's Banner A) image B) composed mapping C) Carbon D) Nitrogen E) Oxygen

All the fibers coming from the different textile samples from the Francisco Pizarro's Banner were subject of a surface analyses under the electron microscope due to the necessity to confirm the kind of fiber employed in the Banner's manufacture. All the textile samples were confirmed as silk (Figure 71 A and B), except the thread of the sample 5H, being confirmed as cotton (Figure 71 C and D) according to the morphology showed on their fibers (longitudinal and cross section).

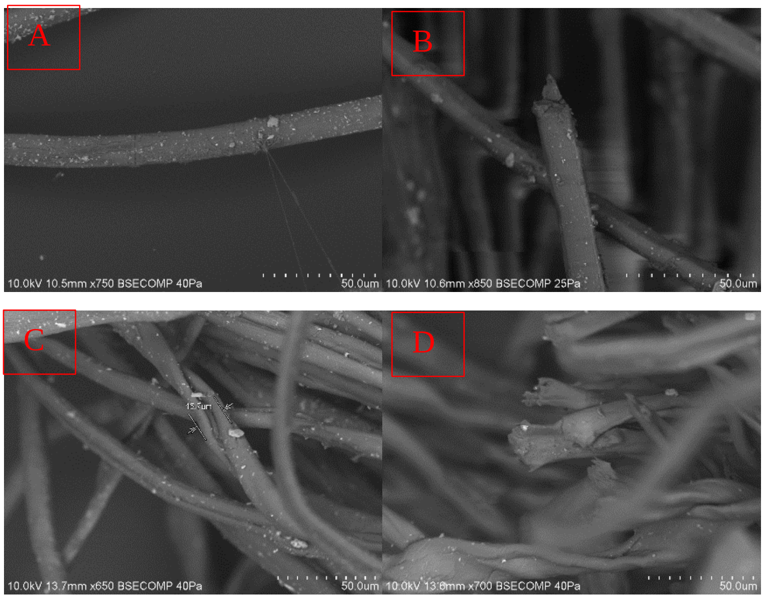


Figure 71 VP-SEM images from: silk sample 1 A) length view B) Cross section; Cotton Sample 5H C) length view D) Cross section

Silk fibers on the Banner had a diameter of 14 µm as single fiber, while the different silk threads presented diameters around 180-250 µm (Figure 72).

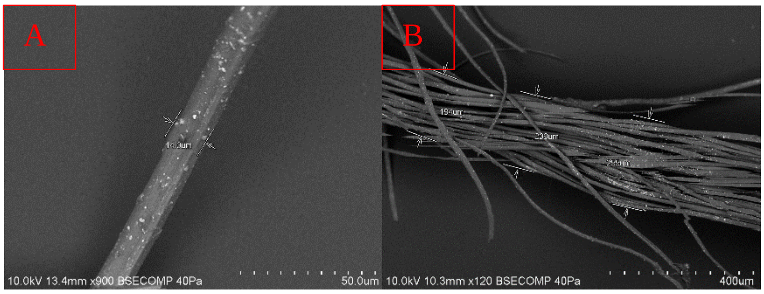


Figure 72 Fibers of silk A) single B) yarn

The silk fibers shown in their surface different types of pollutants (Figure 73): soil dust, particles from the metal threads and insect eggs. The fibers also present different kind of degradation: deformation in their length, residues of sericin and/or folds (even until their break). Some fibers shown axial cuts forming ending points.

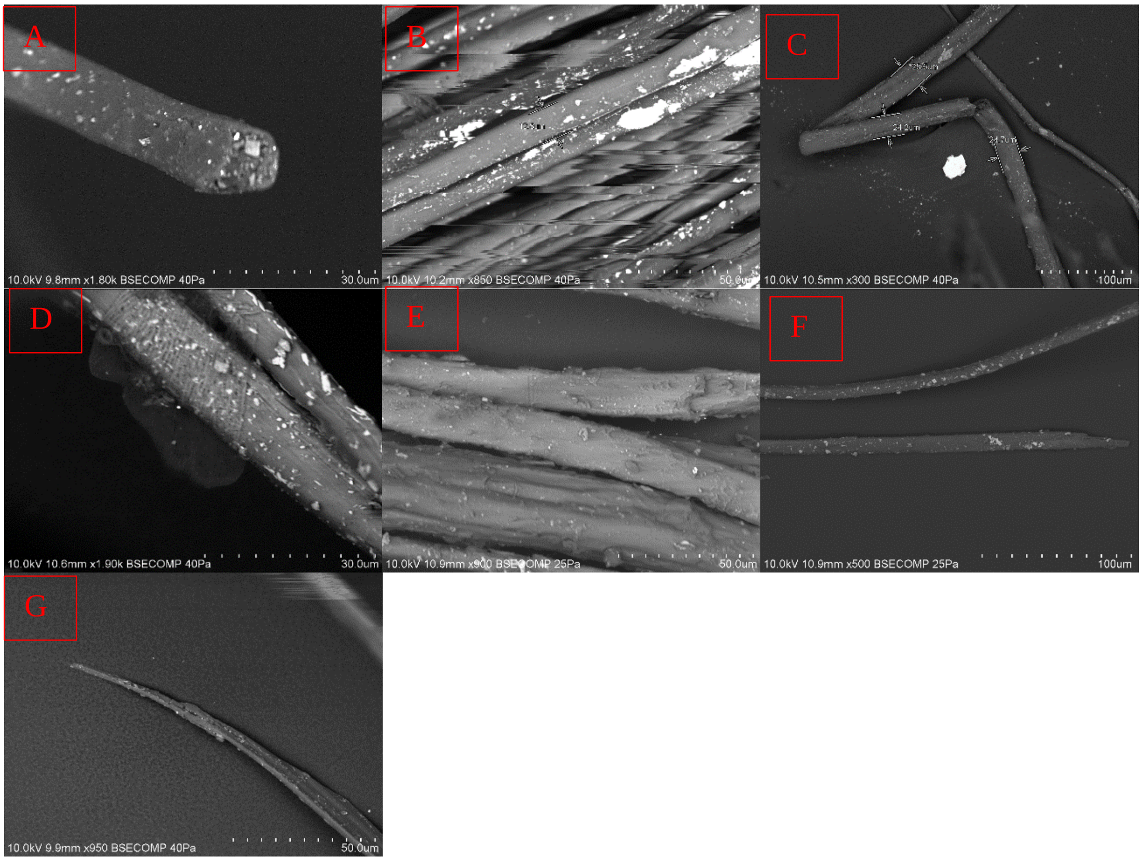


Figure 73 Pollutants and degradation in silk samples from the Francisco Pizarro's Banner. A) Soil dust B) metal thread particles C) folding D) insect egg E) loss of body shape F-G) ending cut

The EDS analysis over the points with high backscattering on the fibers lets to confirm the presence of silver and sulfide elements due to the difference in elemental composition with the regular areas on the fibers (Figure 74). This result suggests the presence of silver sulfide coming probably from crystals detached from the metal thread falling over the textile fibers. Result that is congruent with the black color present on the metal threads and the black spots over the fibers seen under the Optical Microscopy. This loss of mass from the metal corrosion indicates a possible future disappearance of the metal threads if it is not stopped.

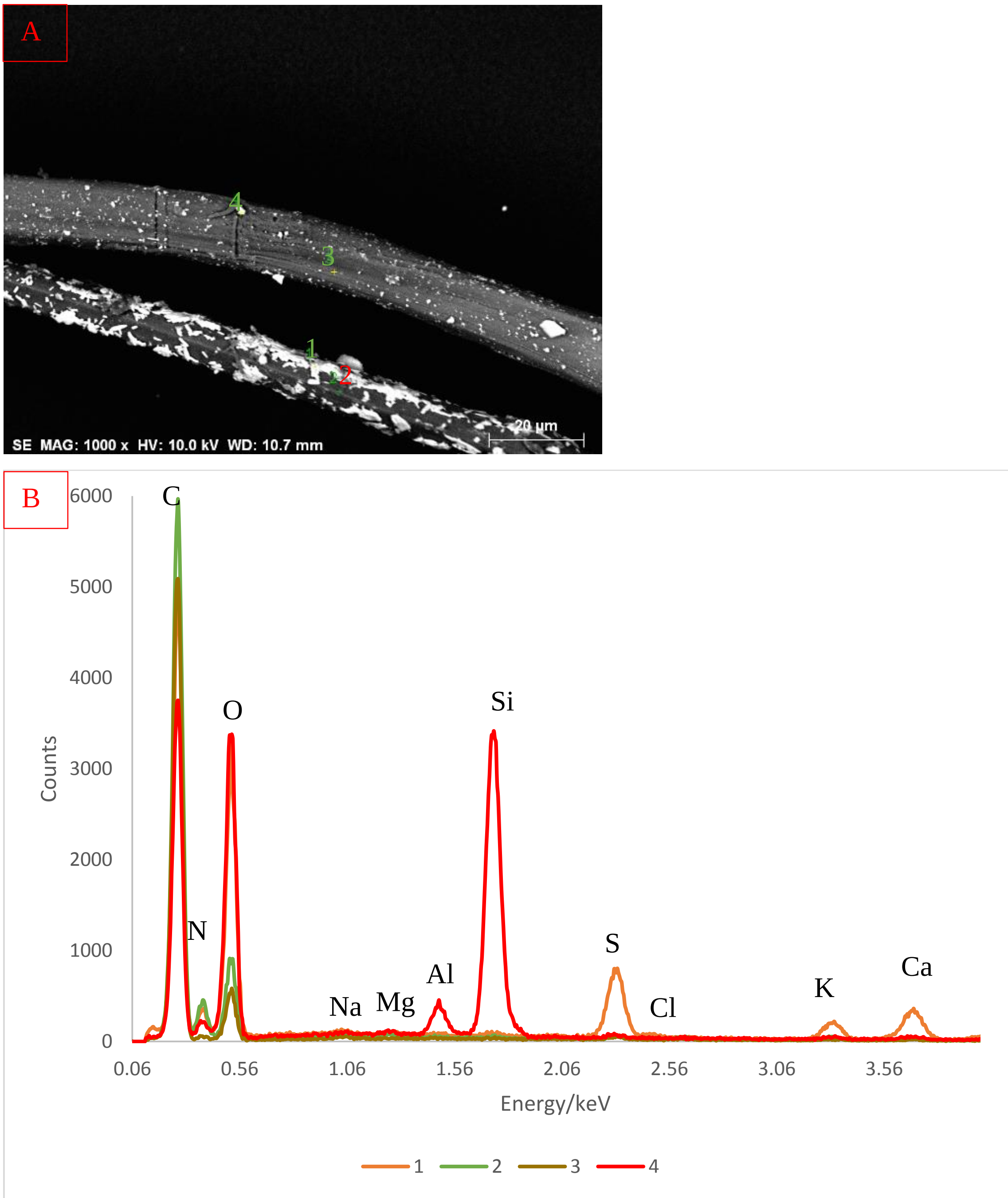


Figure 74 A) image of a silk Sample with pollutants in the surface B) EDS result over points analysis on fibers

The degumming process which were subject the fibers is evident in the samples corresponding to the background of the Banner, free fibroin fibers are visible (Figure 75 A and B). Fibers taken from the emblem shows a lower degree of degumming. Only the sample corresponding to the first textile layer of the emblem (15C) shows fibers without degumming (Figure 75 C and D).

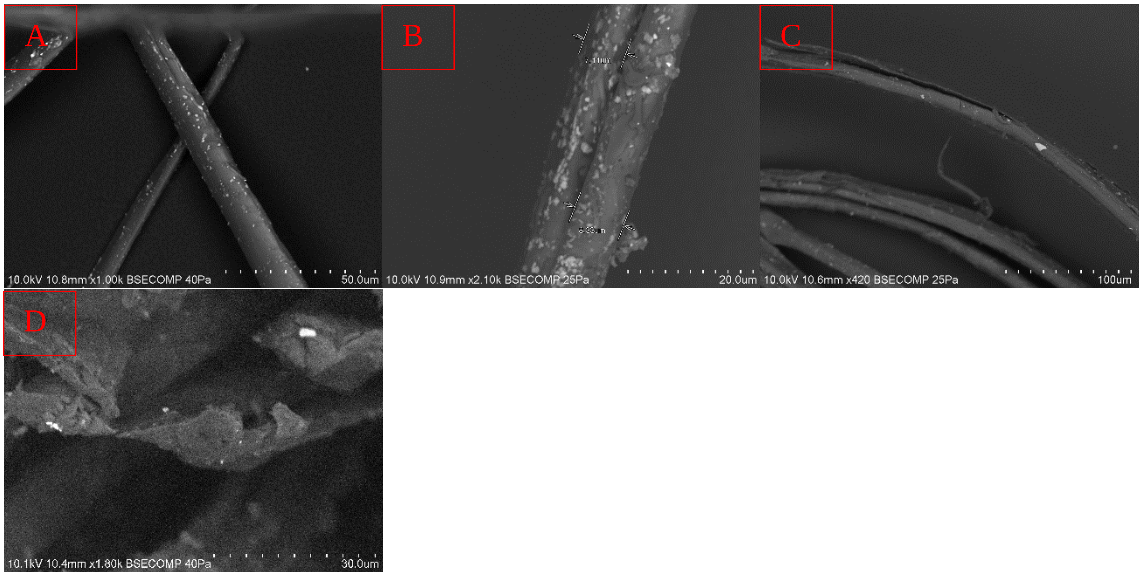


Figure 75 Gummed and degummed silk in the Francisco Pizarro's Banner A) Degummed B) partially degummed C-D) not degummed length and cross section view respectively.

The EDS analysis of the samples allow the identification of alum as mordent in some of the dyed fibers (reds and yellows) (Figure 76), while the green, blue and beige textiles showed no evidence of mordent use.

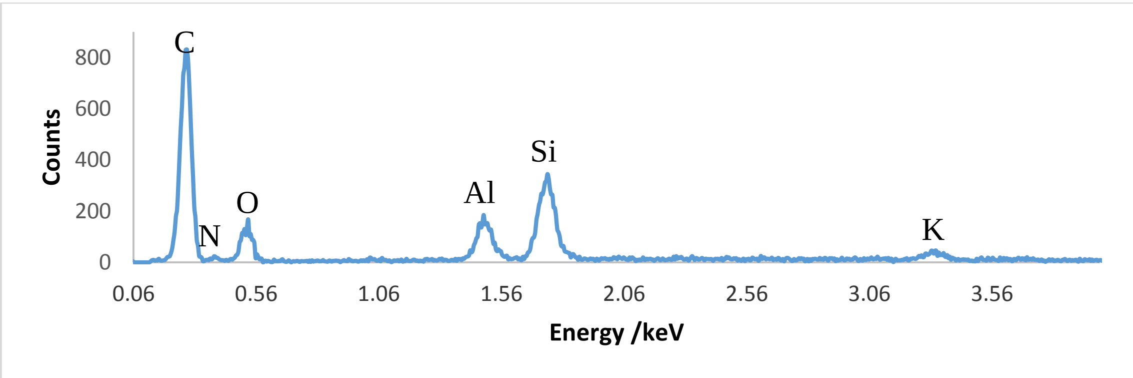


Figure 76 EDS spectrum of a punctual analyses of a dyed silk fiber from the Francisco Pizarro's Banner

The analyses of the rag paper coming from the Francisco Pizarro's Banner (Samples 7, 11, 12, 13, 16 and 19) allowed to see how this material is a complex matrix of fibers (silk (gummed and degummed), cotton, and other vegetable fibers) mixed in different sizes in a hard paste that cover them (Figure 77A). Over the surface there is a layer of a cracked material that correspond to the adhesive (Figure 77 B and C), showing that by different conditions have lost their homogeneity, being crystalized in some areas creating edges in the material, this could create loose of adhesive strength, showing why the Banner have lost some areas where the paper should have been present.

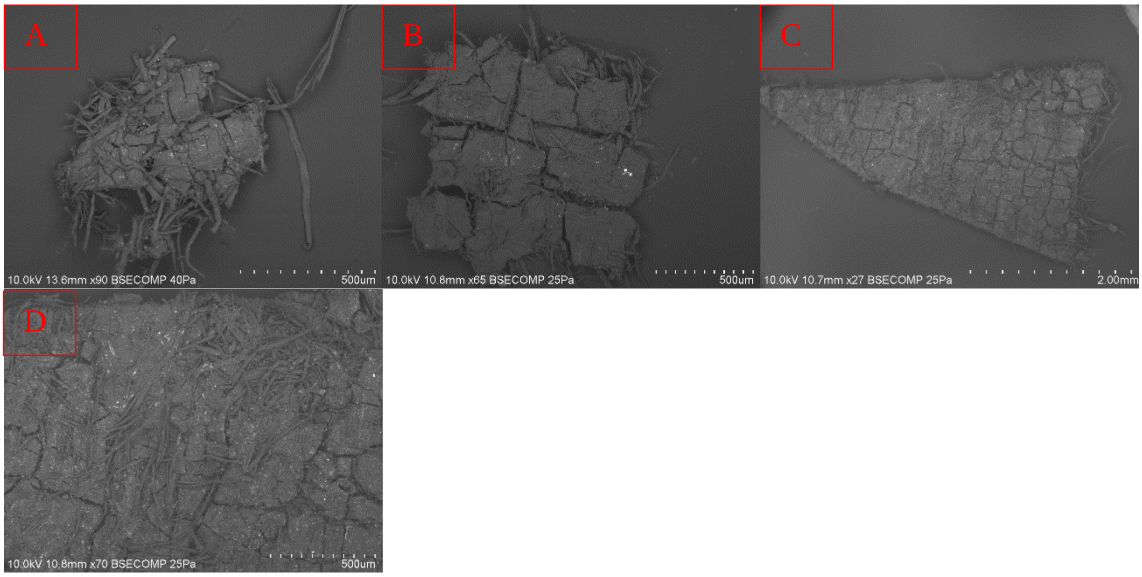


Figure 77 VP-SEM rag paper images A) fibers in matrix, B-C) surface of paper with cracked adhesive D) surface with evidence of fibers attached

The EDS result of the paper shows a complex of elements, where the most relevant are the traces of Ag_2S and the presence of calcium and phosphorus (Figure 78). The Ag_2S shows a contamination from a metallic origin, while the calcium and phosphorus are probable due to the paper manufacture process. After the EDS analysis over the paper and the low presence of elements that suggest a large use of fillings in their manufacture, it gives a clue about a rag paper avoiding the idea of a modern paper.

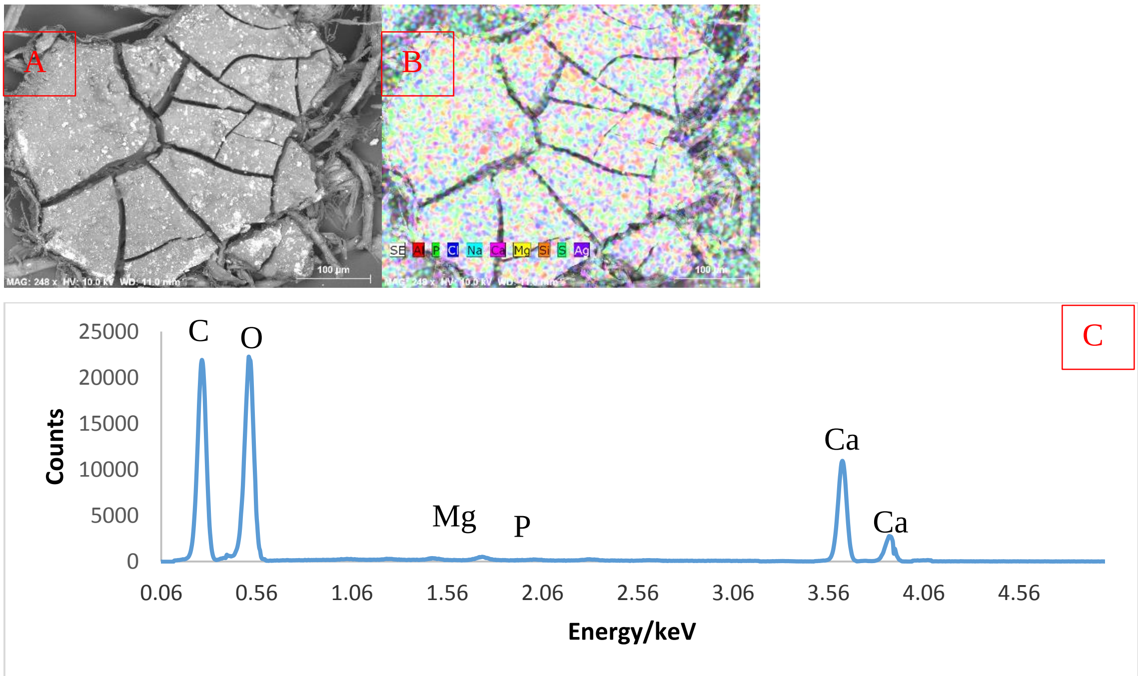


Figure 78 A) VSEM image of the Surface of rag paper simple from the Francisco Pizarro's Banner B) EDS mapping C) punctual analyses

Finally, all the metal threads samples coming from the Francisco Pizarro's Banner were analyzed, having similar results among them. The stripes contain two faces: one visible, and another in the inner surface and in contact with the silk fiber core. The strip used in the metal threads have a diameter around the 448 µm and a thickness around 25.3 µm.

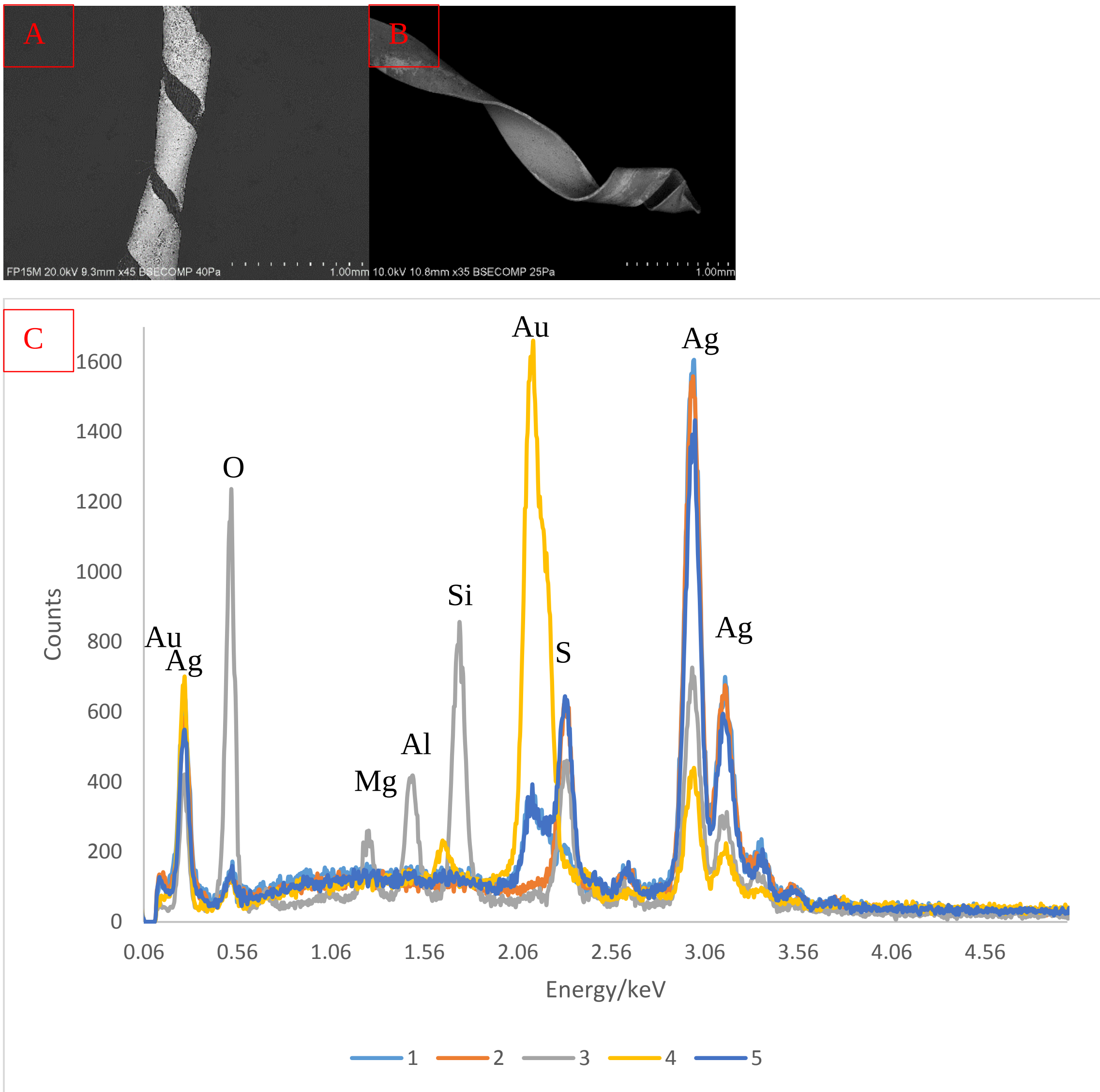
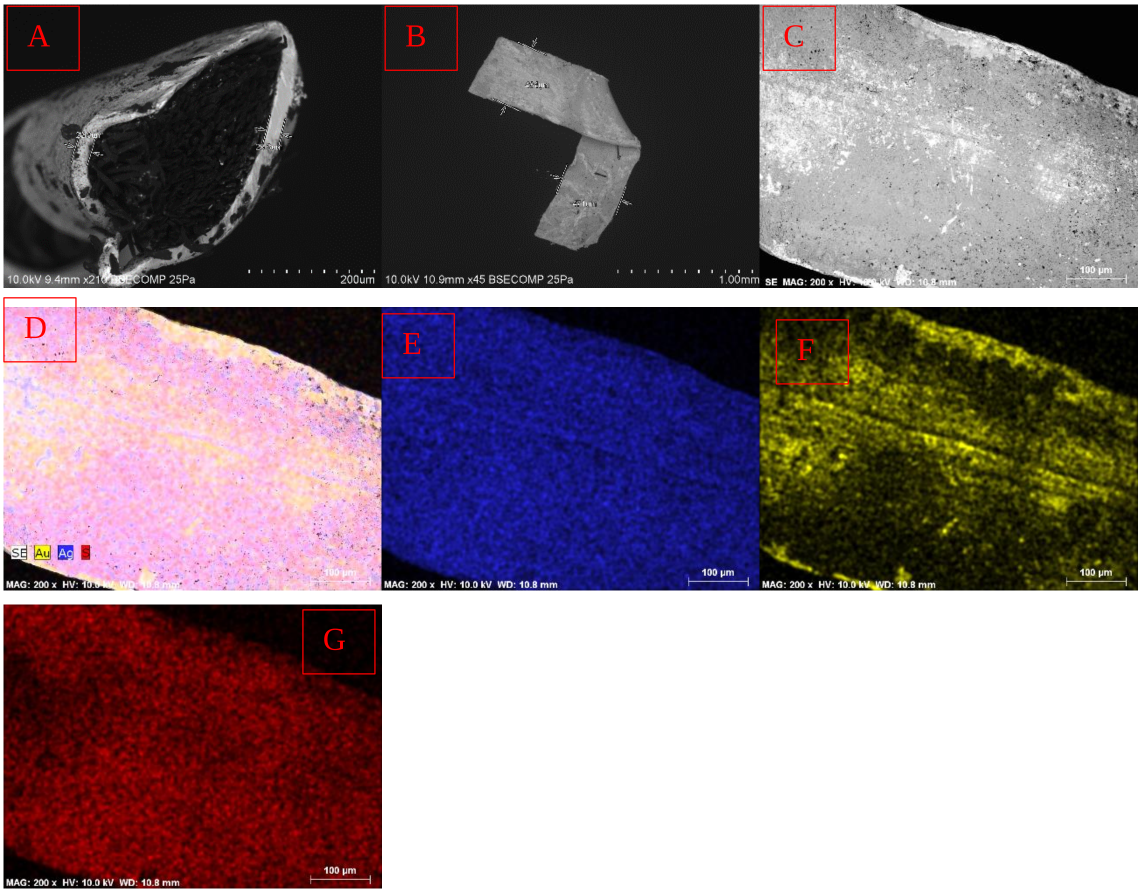


Figure 79 Metal thread from the Francisco Pizarro's Banner A) VP-SEM image before cleaning B) VP-SEM image after cleaning C) EDS spectrum over a multi- point analysis on a metal stripe of a metal thread from the Francisco Pizarro's Banner

The VP-SEM-EDS images revealed an upper layer of Ag_2S in both faces of the stripes as in the borders (Figure 79). After the soft acidic bath, the surfaces of the stripe were exposed in some areas, removing the Ag_2S layer. EDS measurement over the cleaned/exposed surface and borders lets to identify the presence of silver and gold, a composition of Ag 71-76%, Au 18-23% and some traces of Al and S were identified (Figure 80). However, at this point it is impossible to clarify if this measurement corresponds to an alloy or a gilded metal.

A lineal measurement through the cleaned border surface of the stripe was done, confirming an equal variation in the Au/Ag composition cross the edges. Both elements Au and Ag had the same behavior. This result indicates that the gold is mixed around the whole stripe with the silver removing the idea of the use of a double gilded metal in the manufacture of the metal thread.

To corroborate if the metal thread is an alloy or not, lineal and point EDS measurements are done over a cross section of the stripe. As result a core of silver (Ag 97.81 %, Al 0.48 %) of approximately 16 µm of diameter, surrounded by gold layer of approximately 4 µm on top and bottom were identified. The exact composition of the gold was not possible to measure, but due to have not detected other elements in the previous analyses it is possible to postulate the use of a pure or almost pure gold in the manufacture of the metal thread.



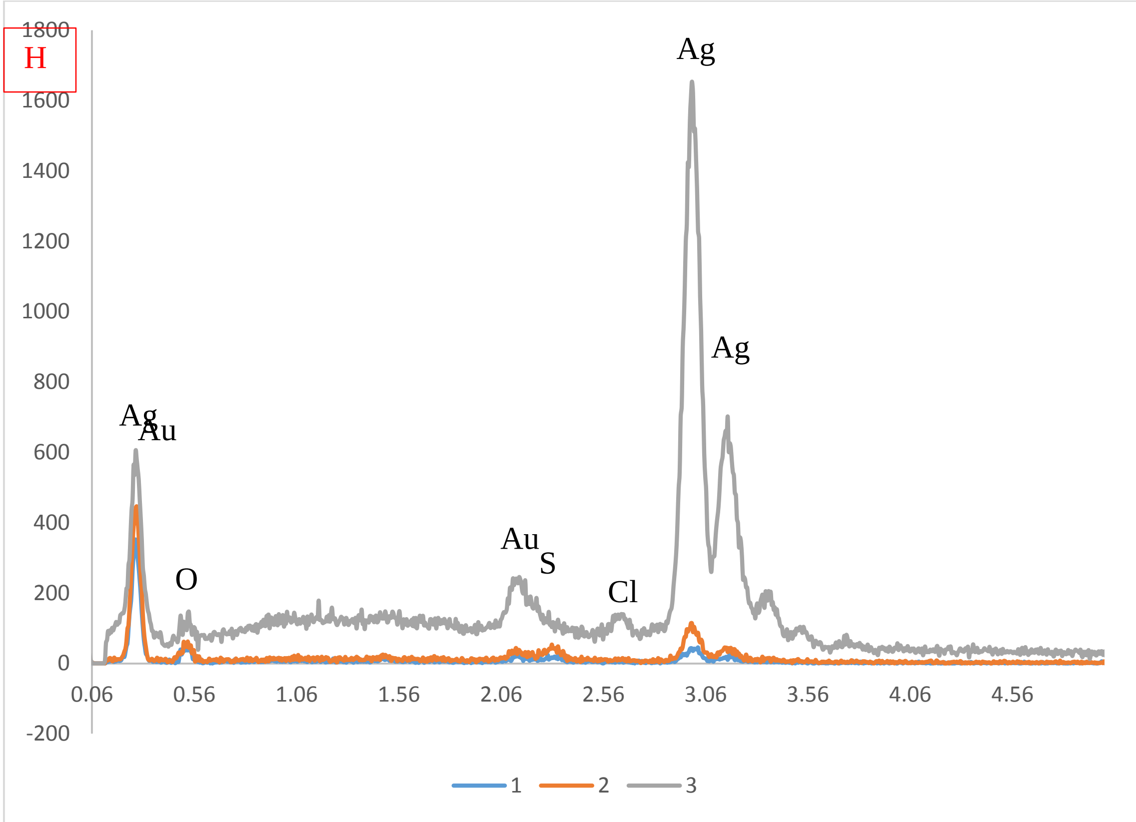


Figure 80 Metal thread VP-SEM-EDS analyses from the Francisco Pizarro's Banner A) Cross section B) Stripe fold to see the two faces C) Frontal face stripe D) EDS Mapping E) Silver mapping F) Gold mapping G) sulfur mapping H) Punctual EDS analyses.

The previous results indicate the use of a silver wire that was gilded and finally flattened before it was wrapped around the silk fiber core to produce the metal threads. Possibly due to the stress subject by the metal thread during its manufacture or by the Banner use throughout the time and the slight thickness of the gold layer, some cracks around the stripe could appear, exposing the silver core in some areas, allowing its corrosion either by sulfur belongs to the silk or from the environment. Over the time the crystals of Ag_2S have being grown until cover almost completely both stripe's surfaces, impressing the new black color over the metal thread.

6.5. Chromatography

6.5.1. Colorimetry

The different textile samples were measured to obtain their respective visible colors in the Banner being represented the samples in the Table 4. From these result is possible detect that all the samples without visible dyed present a similar beige tone.

Colors as blue, green and red were detected suggesting the use of a dyed textile process. Colors as black, or white were not detected. It is possible suggest that the colors measured have a direct relation with the conservation state of the textile, where their color can be the sum of it dyed with the fading in the textile. These result was used to classify the different samples extracts by possible colors.

Table 4 Cielab color measured in the samples form the Francisco Pizarro’s Banner

Sample	CIE L	CIE A	CIE B	CIE C	CIE H	Color
1	73.51	2.36	18.66	18.8	82.8	Beige
2	62.39	7.71	21.21	22.57	70.02	Beige
3	71.01	1.76	14.31	14.42	82.98	Beige
4	58.02	2.57	12.04	12.31	77.97	Beige
5	69.77	2.52	16.63	16.82	81.37	Beige
7 paper	66.29	6.41	24.44	25.27	75.29	Yellowish
7 textile on paper	62.77	8.7	18.69	20.61	65.03	Reddish
8 paper	63.66	6.45	20.69	21.68	72.69	Yellowish
8 textile on paper	51.69	-1.45	16	16.07	95.18	Bluish
9	56.01	-5.27	17.56	18.33	106.7	Green
10	56.3	6.07	22.3	23.11	74.76	Yellowish
11	75.23	4.48	20.35	20.84	77.59	Reddish
12 paper	70.03	5.33	11.27	12.47	64.71	Yellowish
12 textile on paper	65.4	4.64	27.24	27.63	80.32	yellowish
13	73.03	5.46	10.88	12.17	63.37	yellowish
14 paper	67.08	5.99	24.51	25.23	76.28	Yellowish
14 textile on paper	57.6	-1.4	6.03	6.19	103.09	Blue
15	69.2	4.54	18.2	18.76	76	Beige
15 fine textile	72.06	2.54	17.7	17.88	81.85	Beige
16 textile on paper	57.37	9.33	23.47	25.25	68.32	Yellowish
16 paper	62.49	9.27	32	33.32	73.84	Yellowish
17	68.55	1.76	16.78	16.87	84.03	Beige
19 paper	63.7	6.5	25.12	25.94	75.49	Yellowish
19 textile on paper	62.18	3.13	23.47	23.68	82.39	Yellowish
20 textile on paper	68.31	4.54	13.47	14.22	71.36	Yellowish
20 paper	64.33	9.35	29.95	31.38	72.67	Yellowish
21 textile on paper	60.68	8.67	25.91	27.32	71.5	Reddish
21 paper	70.3	8.45	31.66	32.77	75.05	Yellowish
22	75.83	1.52	17.61	17.67	85.08	Beige
23	66.39	2.69	17.55	17.75	81.27	Reddish
24	67.45	2.23	18.03	18.16	82.96	Beige
25	55.16	-5.24	17.2	17.98	106.95	Green

6.5.2. High Pressure Liquid Chromatography coupled with Photodiode array and Mass Spectrometry (HPLC-PDA-MS)

After the extraction process of the different fiber samples (See Experimental part for details), a set of solutions some with apparent color (red, yellow, blue and green) and others without were obtained.

To control the extraction procedure a blank experiment was run where the extraction procedure was carried out in an empty Eppendorf and the resulting extract was run using the solvent program to be used for the samples. Some peaks (r.t=2.20 min, 10.49 min and 23.19 min) arising from the solvents or other causes could be identified and disregarded in the chromatograms of the rate of the mobile phase elution.

In Figure 81 the chromatogram obtained for Sample 1, a beige fiber likely undyed, is presented.

The PDA chromatogram shows four peaks of different intensities in the range of 10.0-18.0 min with a maximum UV absorption between the 240-280 nm. The mass spectrum of each peak presented a mixture of signals that indicate a diversity of compounds of different masses with more abundance of some compounds. The mass spectra detected are characteristic of oligopeptide sequences, and are likely derive from the degradation products of the silk proteins, which with the ageing of the fibers.

Samples 5, 9EW, 10E, 17E, 22E, 23E, 24E, 25EW, all of them shows the same analytical behavior as Sample 1, changing only in the relative intensities of the peaks, maybe due to some fibers have a bigger degradation than others. This result indicates that all those fibers were likely not subject to a dye process, being originally white-silk colored.

Thanks of the previous data, the chromatogram of the dyed samples are less complex to study, as the peaks arising from the silk or the blank are now easily assigned and the remaining peaks are highly arising from the different dye sources.

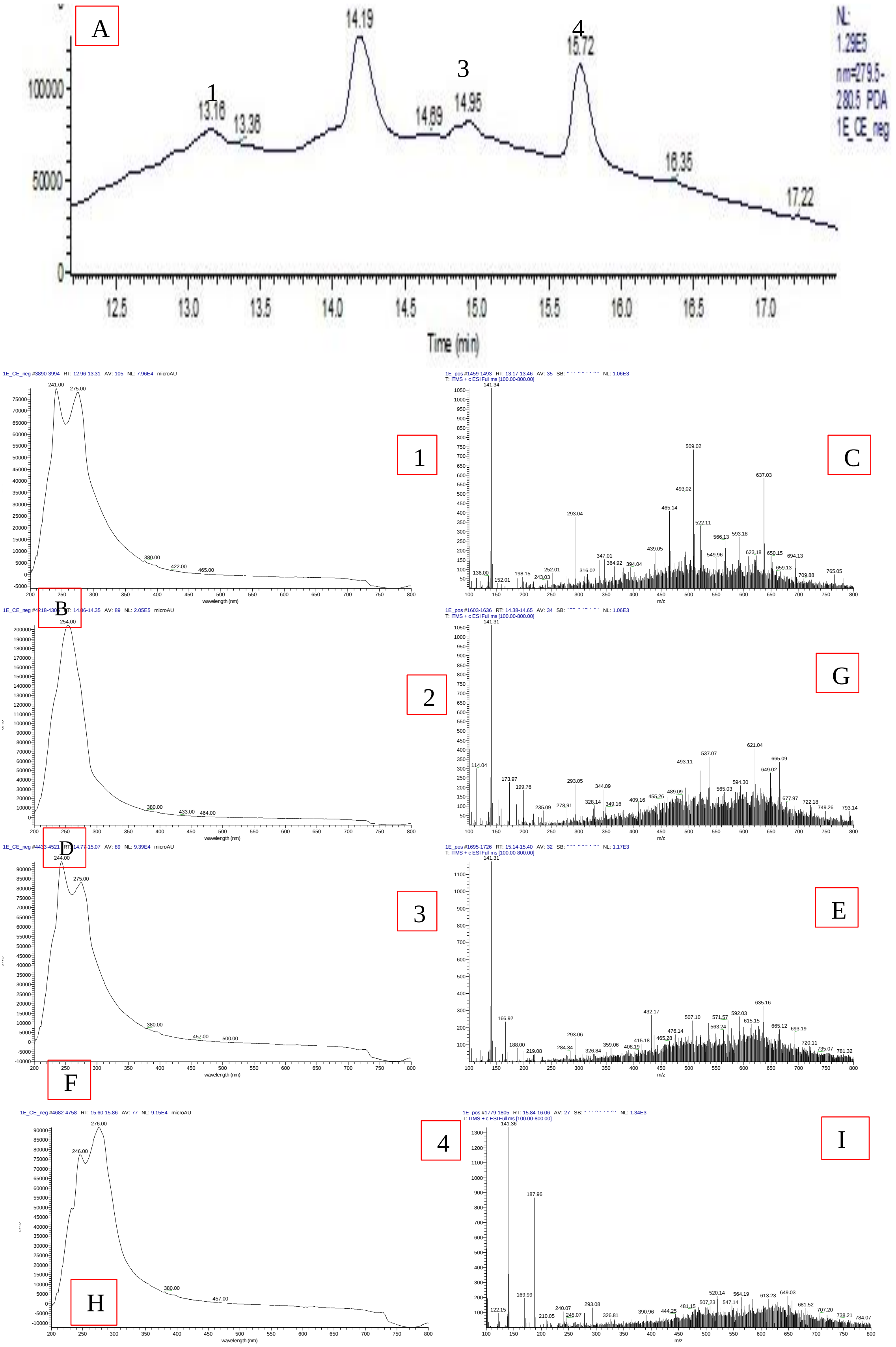


Figure 81 A) PDA chromatogram of sample 1E with blank subtracted. B, D, F, H) UV/Vis Spectra of peaks r.t.= 13.14 min (1), 14.17 min (2), 14.93 min (3), 15.71 min (4) C, E, G, I) mass spectra of selected peaks showing the mixture of compounds present due to the oligopeptides extracted from the natural degradation of silk

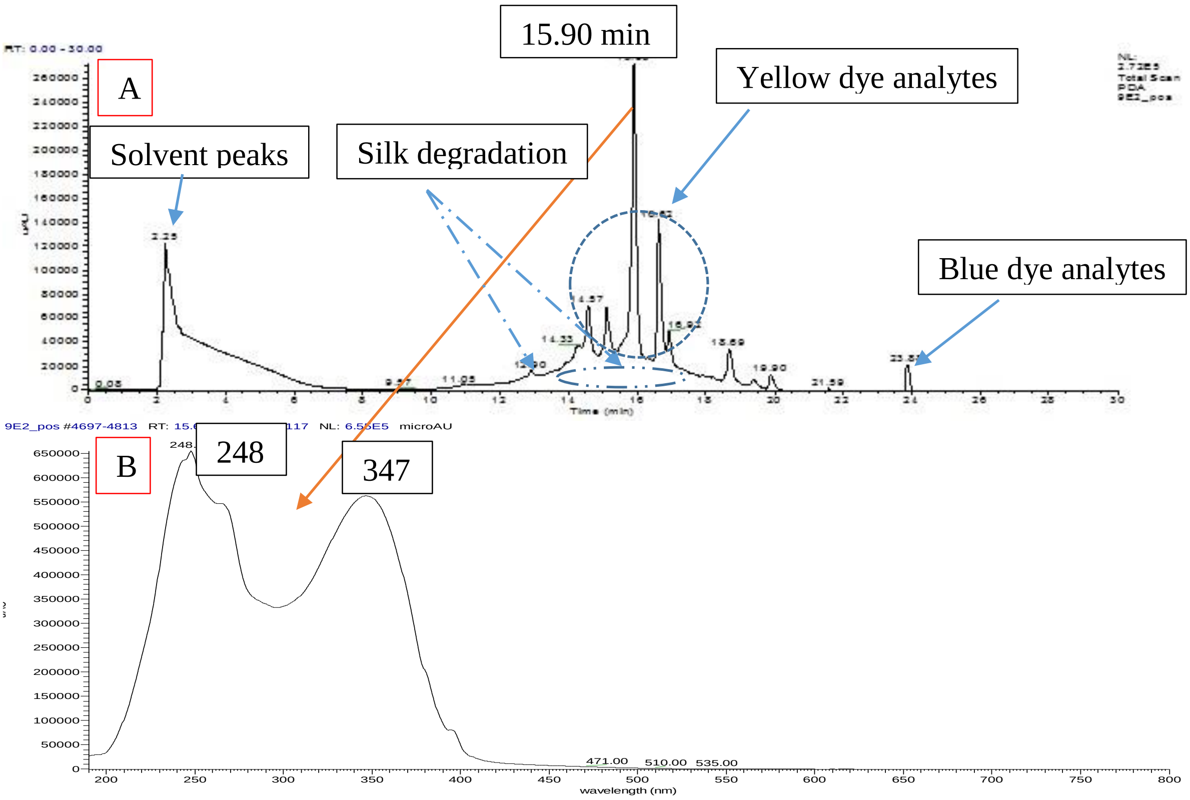
Table 5 List of principal dyes sources identified through HPLC-PDA-MS from the Francisco Pizarro's Banner textile samples

Color	Sample	r.t. /min	UV/Vis	m/z		Identification	Possible dye source
				+	-		
Silk	1E	13.14	241, 275	509, 566, 593, 637, 694, 765, 781	507, 591, 635, 692, 763, 779	Silk peptide degradation	no dye
		14.17	254	537, 665	535, 663		
		14.9	243, 275	635, 693	165, 633, 691		
		15.71	239, 246, 276	186, 247			
Yellow	20E	14.1	254	537, 665	535, 663	Silk degradation	Weld
		14.88	248, 394	585, 565	563		
		15.45	255, 353	465, 611	609	Luteolin di-O-glucoside	
		15.62	268, 341	611, 655, 465	609, 653, 463	Luteolin 3,7'-di-O-glucoside	
		15.82	268, 341	465	463		
		16.05	255, 353	625, 595	623, 593		
Red	16E	14.07	245	299	315		Brazil-Wood
		14.64	245,278	287, 432	178, 285, 303		
		14.77	248, 278	476, 428, 344, 285	426, 344, 283		
		15.19	245, 276	285	344, 283, 153		
		15.74	246, 280	305, 285,	303, 283		
		16.41	245, 276, 444	285	283	Brazelein	
		16.91	285, 305	245	243	Type C Compound	
Red	7E	14.11	233, 253		345, 191		Cochineal
		14.65	231, 247, 271	493, 149	491, 344		
		14.92	245, 275, 493	493	491	Carminic Acid	
Blue	14E	14.25	253		239		Woad
		15.77	242, 293	241	239		
		18.6	247, 299		333, 311, 239, 162		
		18.92	246		322, 239		
		23.89	249, 285, 608	374, 330			
		24.52	290, 542	330, 356		Indigotin	

After obtain the PDA chromatogram of each sample under study, are identified and subtracted the peaks coming from the blank and the silk degradation. Next each remaining peak in the chromatogram is characterized by its UV spectra. Similarly, on the Total Ion Chromatogram is located the area corresponding to the elution of the peak detected on the PDA and the Mass Spectra of the peak is measured. Obtaining in this way the two parameters needed to make a comparison and obtain a clear identification of each compound eluted after the chromatographic process (or the mixture in the case of compounds with similar chemical-physical properties).

As an example in Figure 82 is given the identification of the peak at r.t.= 15.90 min of the Sample 9Green, which was identified as Luteolin-7-O-glucoside (448.97 *m/z* positive mode).

After the chromatographic analyzes of the colored extracts and taking advantage of the natural origin of them, the different analytes or degradation products extracted from the fibers can be identified to finally relate them to a probable color and source (See Appendix 4) based on the UV maximum and mass spectra of each resultant peak (A. Manhita, *et al.*, 2014; I. Petroviciu, *et al.*, 2010; K. Lech, *et al.*, 2011; M. Puchalska *et al.*, 2004; B. Szostek, etall, 2003; I. Degano *et al.*, 2011; K. Pawlak *et al.*, 2006).



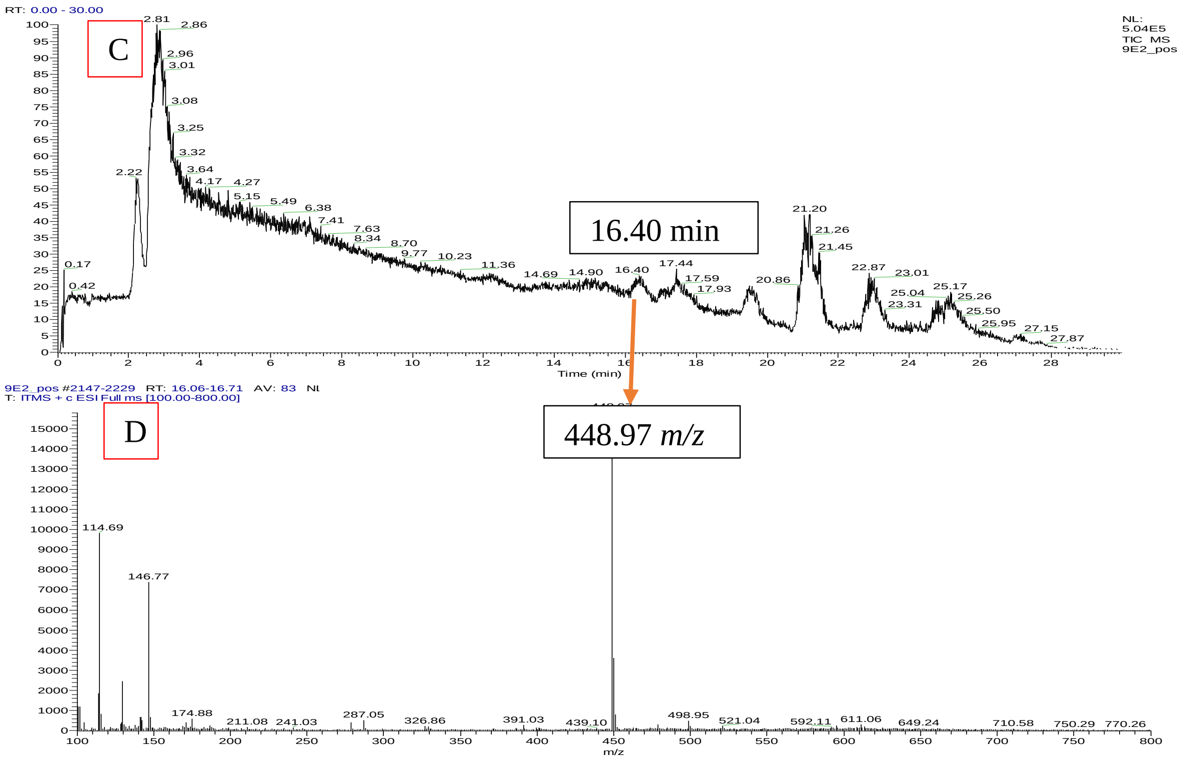


Figure 82 Example of chromatographic results of the Sample 9 green in Positive mode without fragmentation A) PDA result B) UV/VIS spectrum of the peak at r.t. 15.90 min C) TIC spectrum D) Mass Spectrum of peak at 16.40 min identified as Luteolin-O-glucoside

Yellow fibers extracts in Samples 11E2, 20E and 21E present a large amount of analytes of high relative intensity in comparison with blue and red samples. In any case, the presence of luteolin, luteolin di-O-glucoside and Luteolin 3,7´-di-O-glucoside suggest the use of luteolin based plants such weld as source for the yellow color. Being weld a good match if the Banner has as date an origin the 16th century Spain (J. Quer et al., 1784).

Analysis of Samples 2, 7, 9R, 11, 21, 16, and 25R allowed the identification of brazilein, type C compound and Carminic acid analytes, compounds characteristic for brazil wood and cochineal dyes. These red dyes where identified as used alone in samples 2, 7, 9 and 16. Or in a mixture together to yellow dyes (luteolin based dye) in samples 11, 21 and 25R which suggest the presence of oranges hues on the Banner. The brazil wood samples shown an high color degradation, showing nowadays a beige/brown hue in the textile fibers, while the cochineal red is more light stable and fibers still present a red hue. Two dyestuff that not go against the possibility of a Spanish manufacture of the Pizarro's Banner, due to the control from the Spanish Crown of the 16th century over those products (T. Bechtold *et al.*, 2009).

The blue color was identified as an indigotin base dye, probably *Isatis tinctoria* based indigo, if the making time of the Banner and location correspond to the Iberian Peninsula in the 14th-16th century. As it was expected due to the light stability of the indigotin chemical structure, the blue color has is the most alive color in the whole object.

The different shades of green color obtained in the fabrics (Samples 9G1, 9G2 and 25G) shown the use of the combination of blue dye (indigotin) with a yellow dye (luteolin based), likely varying the amount of yellow dye to change the hue. Some samples present a bluish tone, probably due to the degradation of the yellow dye, letting out only the blue color.

No other analyte was identified from the chromatographic analyses of the textile fibers from the Francisco Pizarro’s Banner of arms, either, because the sensitivity of the technique employed in this research which do not allow to detect them or because no more dye sources were employed in its manufacture.

6.5.3. Pyrolysis Gas Chromatography coupled to Mass Spectrometry (Py-GC-MS)

The analysis of the adhesive and the rag paper used in the manufacture of the emblem of the Francisco Pizarro’s Banner was done with Py-GC-MS with a derivatization agent.

The analysis of the adhesive pyrogram, shows the separation of different carbohydrates, amino acids and lipids in their methyl-ester forms due to the derivatization (Figure 83) (See Appendix 5). The different compounds reflect a composition of an animal glue. While the specific animal(s) used cannot be identified by the use of this analytical technique, it is question for possible proteomics studies. It is possible put up the hypothesis that rabbit glue was used, if the time and location of the Banner manufacture corresponds to the Pizarro’s time, due to the common use of rabbit glue by the medieval artists (F. Pacheco, 1990).

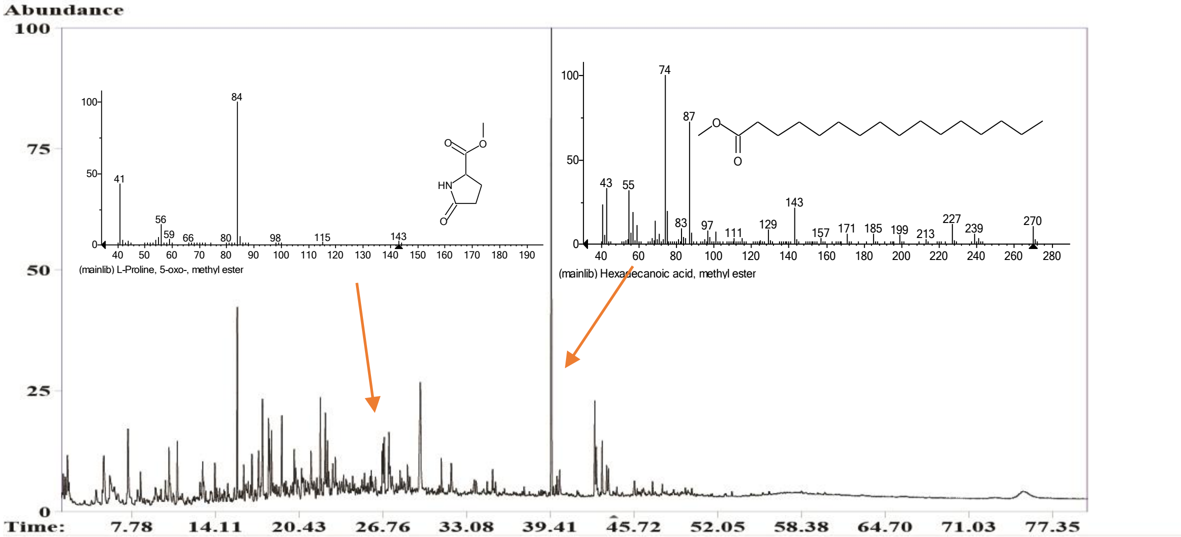


Figure 83 Pyrogram of the Py-GC-MS analysis of the adhesive present in the external faces of the sample 12

The analysis of the rag paper showed the presence of several carbohydrates derivatives, accompanied by some proteins and lipids (Figure84) (see Appendix 5). These results suggest that the rag paper was made from cellulose based fibers with possible a minor amount of animal fibers. It coincides with which was observed under the microscopy and VP-SEM analyses, confirming a rag paper with the composition expected for Pizarro's time in a Spanish manufacture (K.D. Vickerman, 1995; R. I Burns, 2014).

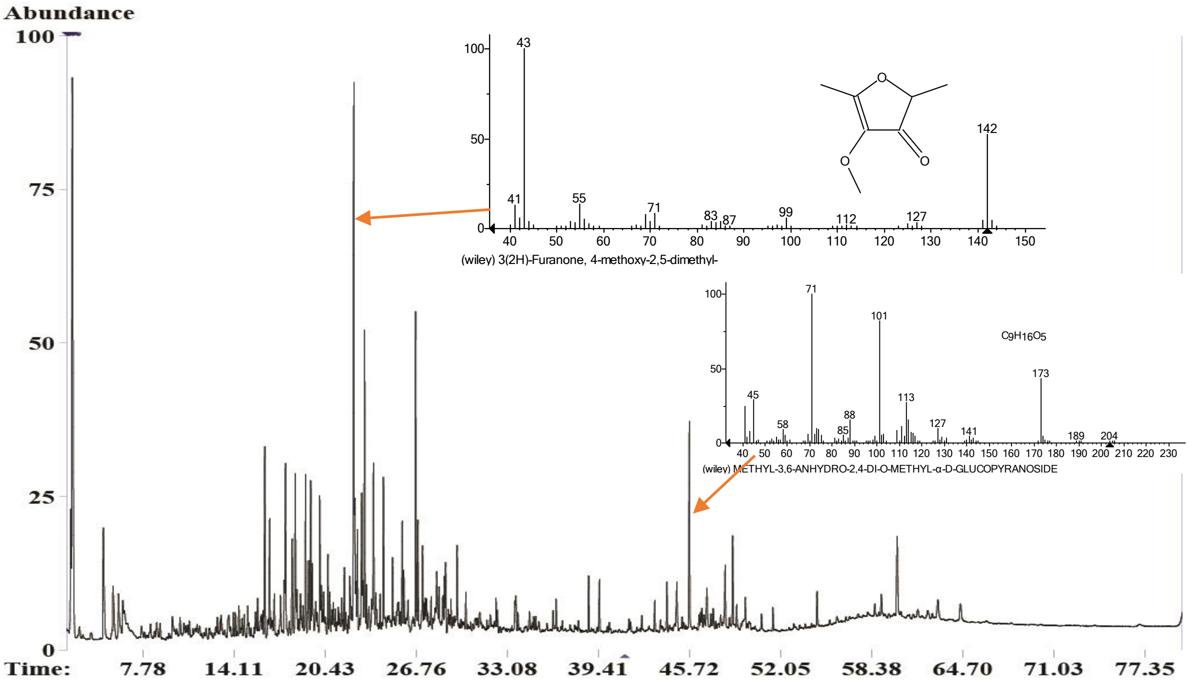


Figure 84 Pyrogram of the Py-GC-MS analysis of the rag paper present in the sample 12

6.8. Radiocarbon dating (^{14}C)

The results obtained from the seven textile samples sent for their ^{14}C Radiocarbon dating by AMS to the CEDAD are given on the Table 5. The calibration curves for the different samples shown an unfavorable form, due to the recent age of the samples, being their results broad in calibrated time ranges, but enough clear to extract the information needed to elucidate the time and originality of the object under study.

From the table 6 it is possible to see with high degree of confidence that the results obtained for the samples FP1, FP15C, FP15M and FP16 show a frame time corresponding to Francisco Pizarro and his expedition to the New World. While the sample FP15F, FP17 and FP22 have another temporal frame, more recent.

The sample FP1 as the sample FP15M, correspond to the Banner itself, indicating that possibly the whole textile as flag was elaborated in a same period of time, and in a same place.

Table 6 Radiocarbon dating results from the AMS analysis of the set of samples from the Francisco Pizarro's Banner

Sample	Radiocarbon age *(bp)*	$\delta^{13}c$ *(‰)*	Calibrated dating (confidence level 2σ)	CEDAD sample ID
FP1	384 ± 40	-21.5 ± 0.5	1430AD (57.3%) 1530AD 1540AD (38.1%) 1640AD	LTL16550A
FP15C	394 ± 45	-25.3 ± 0.5	1430AD (59.6%) 1530AD 1540AD (35.8%) 1640AD	LTL16551A
FP15F	80 ± 35	-23.1 ± 0.4	1680AD (26.2%) 1740AD 1800AD (69.2%) 1930AD	LTL16552A
FP15M	290 ± 40	-27.9 ± 0.3	1480AD (93.4%) 1670AD 1780AD (2.0%) 1800AD	LTL16553A
FP16	325 ± 40	-26.8 ± 0.3	1460AD (95.4%) 1650AD	LTL16554A
FP17	85 ± 35	-23.1 ± 0.3	1680AD (26.4%) 1740AD 1800AD (69.0%) 1940AD	LTL16555A
FP22	203 ± 45	-26.0 ± 0.3	1630AD (74.6%) 1890AD 1910AD (20.8%) 1950AD	LTL16556A

The sample FP15C, that correspond to the coarse silk textile used as base for the manufacture of the emblem shows a radiocarbon dating non-calibrated older than the rest of samples, while their calibrated dating coincides with the time of the textile. This suggest that the emblem and the textile were manufacture simultaneously. In other words, the emblem and the flag were one object since its conception. This avoid the idea of an older emblem restored in a newer textile, habit in the medieval times not employed in this object of study.

The sample FP16, being the most complex sample by its composition (rag paper, animal glue, textiles and dyed silk), was expected to give an unusual value for its dating. Nevertheless, its dating fall in the expected time for an object carried by Francisco Pizarro, without to arrive to recent times. If it is true that its calibrated dating gives a broad time, it could be due to the nature of the sample, which due to be located in the emblem, could be subject to cleaning and/or restoring processes to try to reestablish its original aspect. This result of dating, match with the textile of the emblem and the flag textile, suggesting in this way, that the full object was finished in all its components before its respective use in the possible displacement to the New World.

These samples results, together with the previous analytical studies, give an originality idea to the Banner in time and space. The materials found in the study of the Banner fall in the time of the Spanish conquest of America, showing a unique object that represents the XV-XVI century Spanish manufacture. Due to its time of elaboration and composition it is impossible its manufacture in American lands, being only possible its manufacture in the Old World. The materials employed as well techniques, were accessible for the craftsmen in the Iberian Peninsula in Pizarro's times, were with selected materials of precious value, used all masterfully, was possible obtain a unique object to endure in time, bigger enough to transmit its message from the distance for a new population in the New World.

The samples FP15F, FP17 and FP22 show recent dates. Dates that by principle are over the life time of Francisco Pizarro. This could be interpreted as not genuine materials employed in the construction of the Banner. As was possible to evidence in the visual inspection, the Banner has several newer textiles in different areas, including the emblem's bottom area (FP15F), the upper right area (FP17) and the right back down area (FP22). Those patches added to the Banner, could be explained as restoration processes done to the object by its precious value for its custody people. These not matched textiles, talk about an object that trough the time had a special meaning and value for a society who take care from it, trying with local resources and techniques to preserve it for future generations, trying to keep its symbolism useful.

Now, with an object coming from the Old World probably by hand of Francisco Pizarro and his army, with the emblem of Castilla and Leon Kingdom, and preserved during centuries by its holders, suggest two probable hypotheses from the object: 1) The Banner’s holder really appreciate to Francisco Pizarro and its conquest or 2) The Banner had a deeper meaning to its holders and viewers, being possibly the symbol that represents the Spanish Kingdom in the New World.

The first hypothesis can be controverted by the following facts: A) the object was taken from a location ruled by the Spanish Crown and not by Francisco Pizarro’s followers. B) Francisco Pizarro dies due to internal conflicts between different lines of thinking in the way to rule the New World, reason why the possible objects that represented his ideas could be suffer damage or disappeared (i.e. Pizarro’s body was buried in an unknown location). C) After Pizarro’s death, the King of Spain taken and determined a stricter control over overseas lands to avoid future/near conflicts. D) If the Banner represents to Francisco Pizarro or his army, possibly could be not subject to restoration but to be hide (by his dimensions) and possible to have bigger degradation processes in it.

Due to the previous arguments, the second hypothesis could be stronger, and partially logic. Some literature talks about a Pizarro believer, who entered to the Panama’s Catholic Cathedral to bless his Banner; Banner that have the image of “Santiago Apostol” in the back. In contrast, what was found in this research it is a Banner with any symbol beside to the Spanish kings, Banner that could not need the bless by a third person, if represent the own King who already bless it.

Finally, the combination of the positive dating results and negative results with the historical sources, give a certainty of the object movement: from a making in the Old World, a passage by a Conqueror to the New World and its final finding by the revolutionary army, to end as a precious, invaluable and unique object to be custody by the National Museum of Colombia as cultural heritage of humanity.

7. Proposed manufacture model for the Francisco Pizarro's Banner of Arms

Using the data collected in the previous chapters, and taken the knowledge gained with the analytical studies done to the Banner, it is possible to postulate the manufacture process done for the object as follows.

1. Three different areas of textile are woven in a plane way using no dyed degummed silk as threads. The textile is done in: two equal structures with a straight beginning and a convex curve ending (lateral areas of the Banner) and another one shorter with a straight beginning and concave curve ending.
2. The three areas are joint by a manual sewing using silk threads.
3. Two no dyed motif woven textiles (possibly with flowers motif) with the same dimensions of the previous textile are done. Each one will be a face of the final Banner.
4. By mean of green silk threads are joined the three layers of textile previously described (central plane textile and the two motif sheets) forming the Braid. At the same time, a previous made textile with metal threads in a regular patter [redacted]] is settled in the edges of the textile.
5. Two green textile lines are attached to the central fabric from the curve edge to the top of the future emblem in a vertical direction to give strength to the flag to support the future emblem.
6. A course textile is emplaced in the superior area of the Banner in a spherical way to let space for a future pole to hold the Banner.
7. The emblem previously manufactured is attached by manual sewing to the fabric.

The manufacture of the emblem could be follows the next process for its elaboration:

1. A rag paper is made from waste textiles, fabrics, and other materials.
2. Over the paper is drawn the emblem to elaborate with a carbon pencil.
3. Previously dyed silk is cut in the specific shape to be paste.
4. The rag paper is spread with animal glue and the coloured silk pasted.
5. The back face of the rag paper is spread with animal glue and pasted to a fabric of non-degummed, non-dyed silk.
6. The edges and areas of interest to be decorated (The towers, the lion shape, etc.) on the emblem are decorated with metal threads that are hand sewed with silk threads.
7. The full emblem is cut and pasted to the fabric previously done.

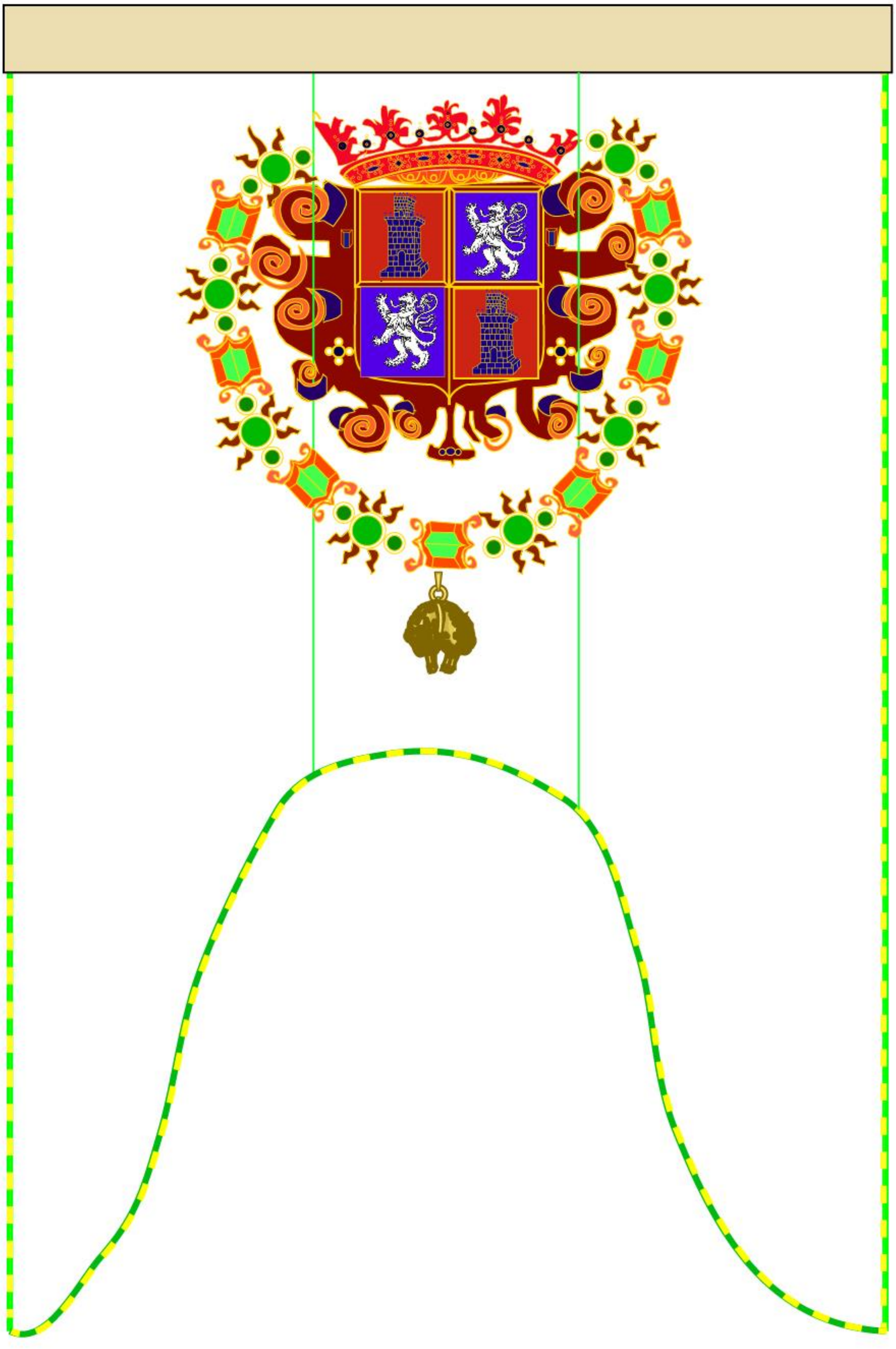


Figure 85 Suggested reconstruction for the Francisco Pizarro's Banner

8. Conclusions

The object studied under the name Francisco Pizarro's Banner, property of the National Museum of Colombia was characterized, being identified the different material components present in it.

The object presents several damage that needs its soon intervention to guaranty their prevalence among time for future generations. Their damage it is in the whole body of the object as in the whole material elements both as organic as inorganic components.

The visual inspection, microscopic observation and VP-SEM analysis, allowed to identify as Silk all the textile components of the Banner, except one cotton thread used probably to reattach some parts of the object. The major part of the Silk used in the manufacture of the Banner was degummed silk, being only non-degummed silk used on bottom of the emblem, down the rag paper. Only the silk on the emblem present dyeing. All the textile present degradation, fading, biotic attack and loos of structure.

The extraction process was successful, letting that through the liquid chromatographic analyses were confirm the use of natural dyes to color the emblem. Red (cochineal and Brazilian wood), blue (indigotin base plant), yellow (Weld and luteolin base plants) and green (mixture of blue and yellow dyes), were identified on different areas of the Banner emblem. The silk textile does not present any kind of dyeing but was identified the presence of amino acids coming from the degradation of the silk as coloring agents in the fading. All the fibers shown loose of tone, fading and some of them chemical degradation.

After the gas chromatography process was possible to evidence the use of animal glue in the manufacture of the Banner, as the use of rag paper based on a mixture of proteinaceous and lignin origin. The VP-SEM analysis of the rag paper allows determine that the paper present a handcraft origin with a broad matrix of components.

The analytical studies done over the object confirms the use of metal embroidery, based on the use of silver wires, coated with a fine gold layer and finally mechanically pressed, to form sheets that covered no dyed degummed silk threads. This metal threads were employed as decorative material for the edges of the image emblem, the Braid edge and possibly for the missed lamb in the Chain of the Order of the Golden Fleece. The metal thread presents a hug grade of corrosion, with a deep black layer of Silver Sulfide, with detaching crystals that fall on the textile.

By radiocarbon dating was possible determine that the manufacture of the object relies to the XV-XVI century, supporting the hypothesis of a Spanish origin. In the same way, was possible determine that the Banner suffered interventions through the time.

After the analytical study and combining it with historical data, it is postulated that the object labeled as Francisco Pizarro’s Banner, correspond truly to the Spanish Royal Banner that represent the Power and domain of the King Charles V and his kingdom in the new World, being used by Francisco Pizarro as conqueror item.

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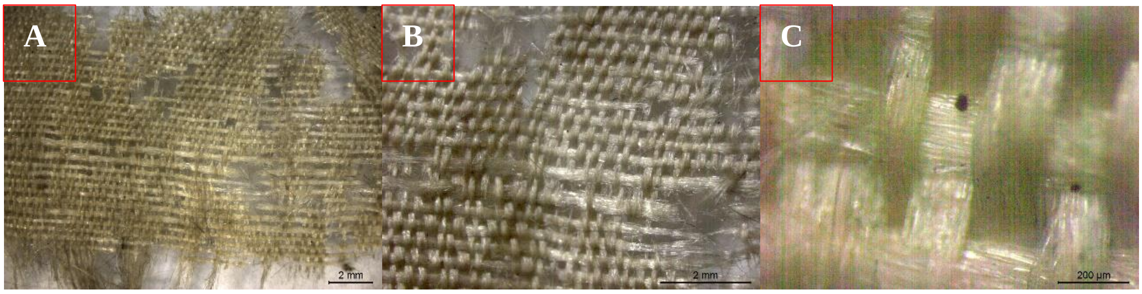
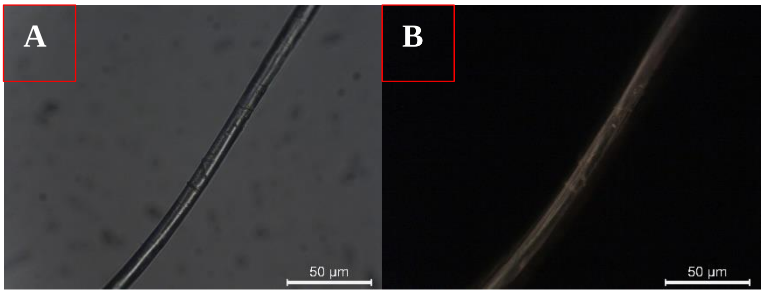
Appendix 1 Optical microscopy

Through a visual inspection under the microscope of each sample obtained from the Francisco Pizarro’s Banner of Arms it is possible gain a deeper knowledge of the Banner. On the following images the readers are invited to have a better understanding of each sample of the Banner and to internalize the knowledge coming from it and to have a better comprehension of the information given by the researchers in this study. First are presented the microphotographs taken under the stereomicroscope (SM) of the complete sample with different zooms. Then are presented the microphotographs from the different components (isolated) of interest of each sample under the Bright field microscope (BFM) and the Dark field microscope (DFM).

SM Sample 1

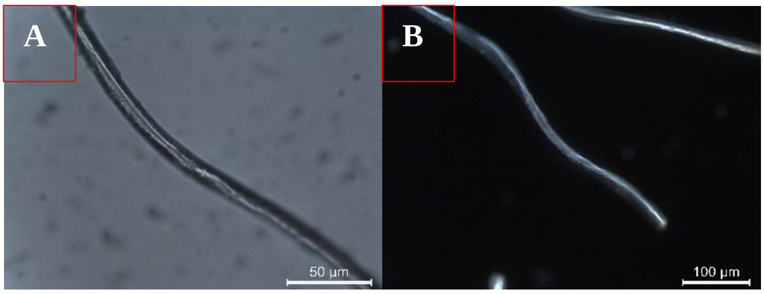


Sample 1A (Warp fiber)



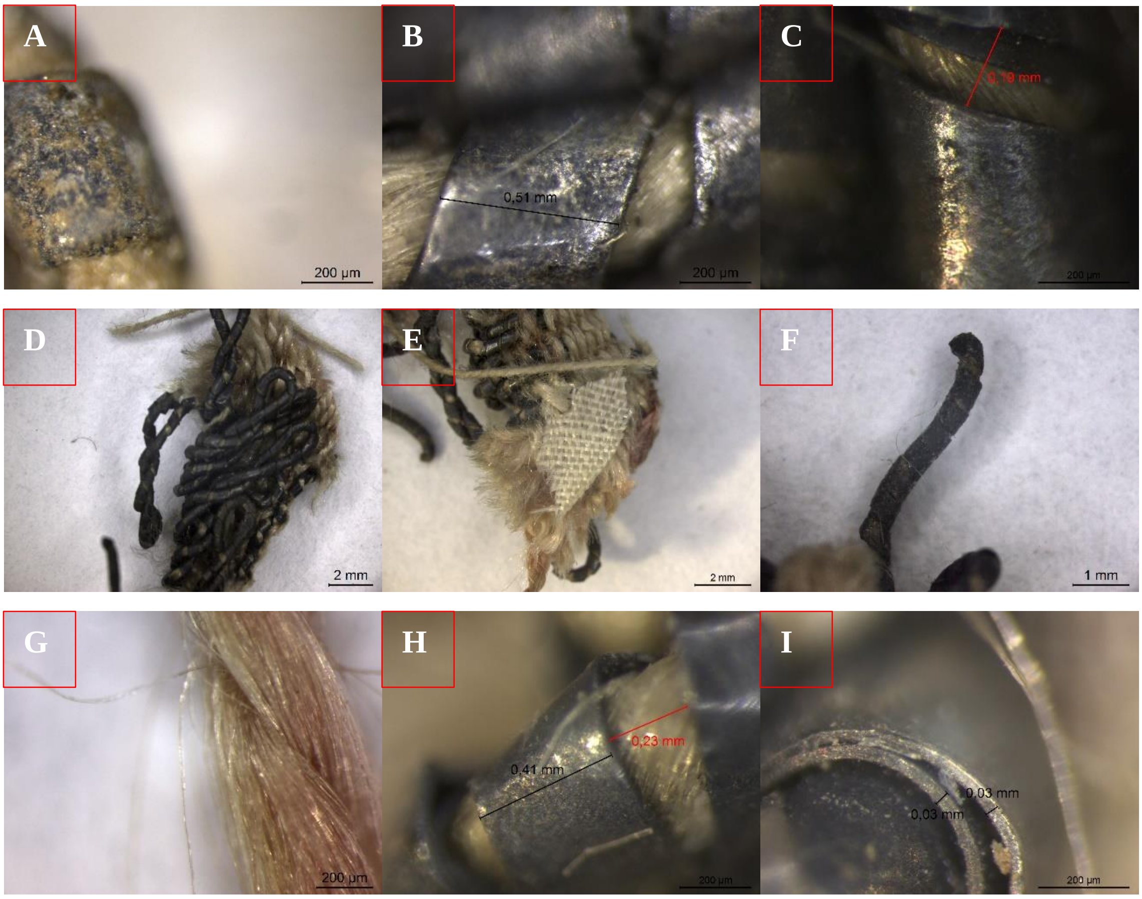
A) BFM B) DFM

Sample 1B (Weft fiber)

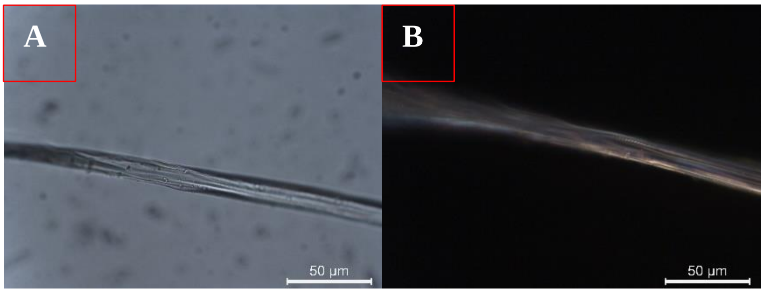


A) BFM B) DFM

SM Sample 2

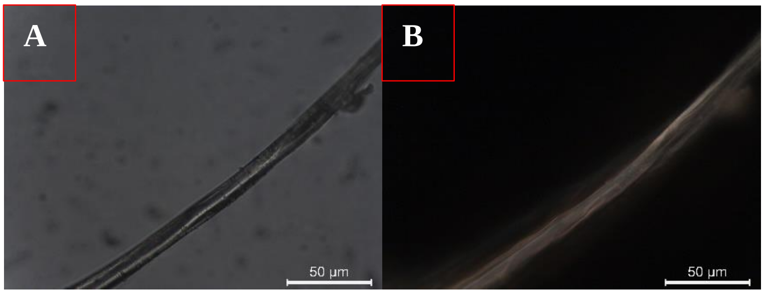


Sample 2A (warp fiber)



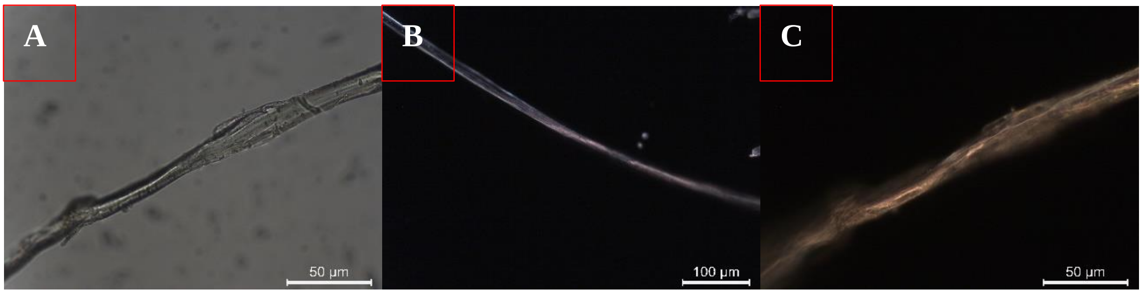
A) BFM B) DFM

Sample 2 (red weft fiber)



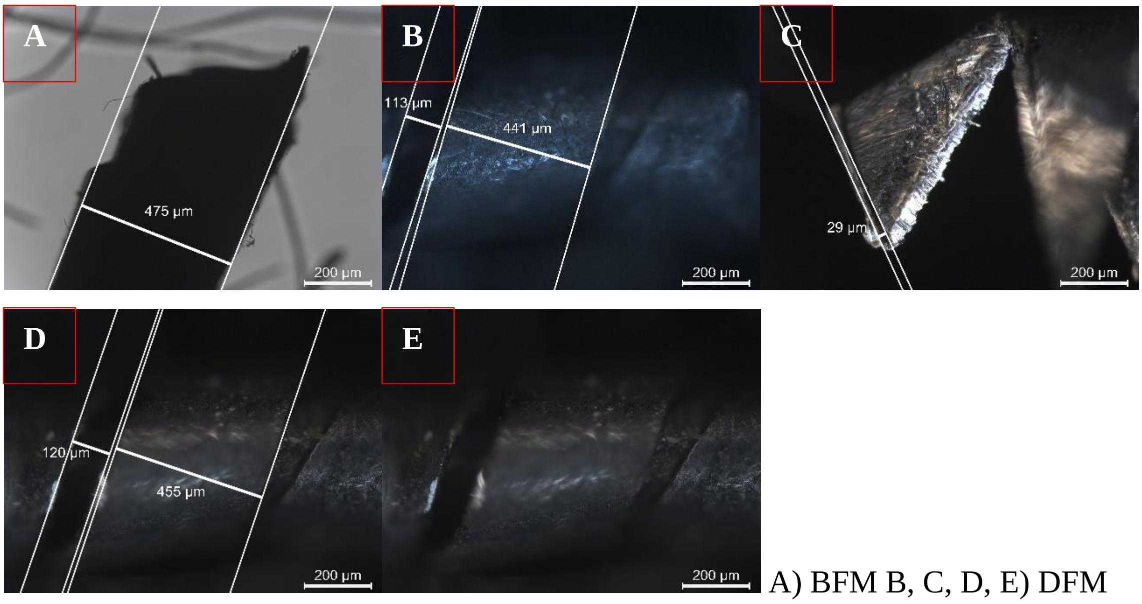
A) BFM B) DFM

Sample 2H (fiber from the sewing thread)



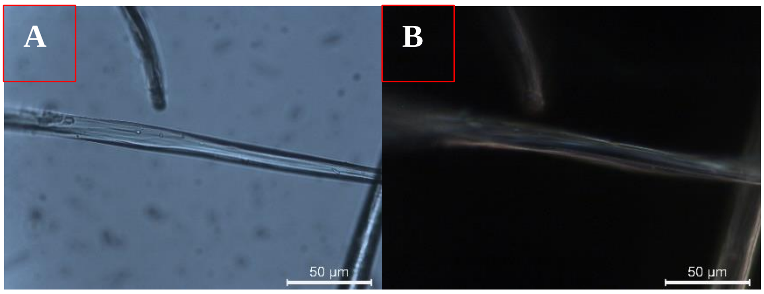
A) BFM B, C) DFM

Sample 2M (metal from the metal thread)



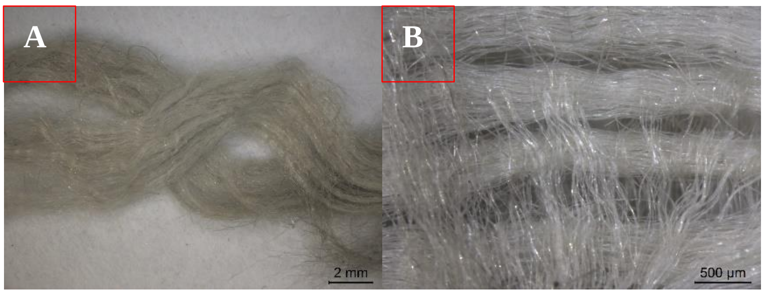
A) BFM B, C, D, E) DFM

Sample 2MF (fiber from the core of the metal thread)

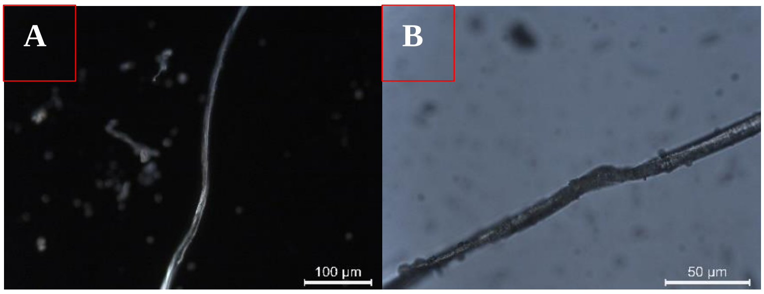


A) BFM B) DFM

SM Sample 3

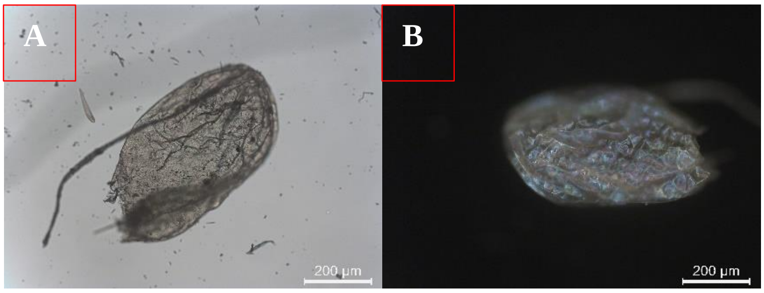


Sample 3 (fibers)



A) BFM B) DFM

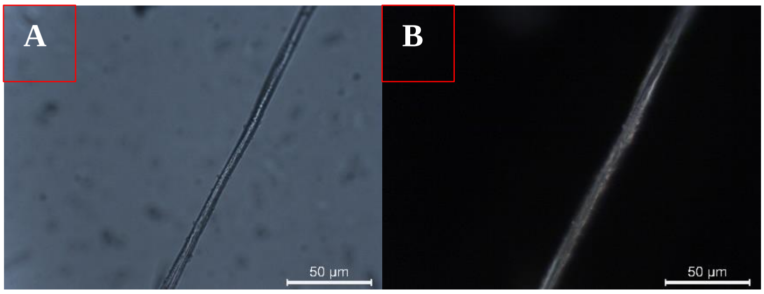
Sample 3 (Insect egg)



A) BFM B) DFM

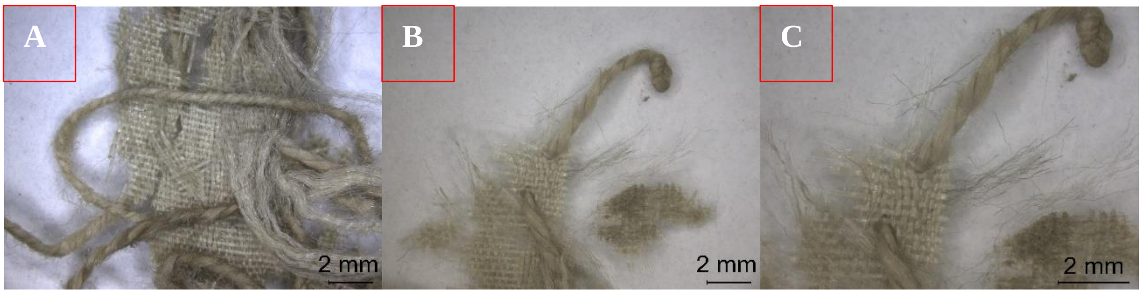
SM Sample 4

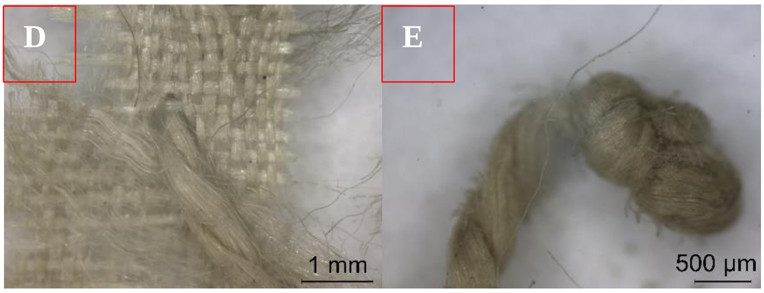
Sample 4H (fibers from the thread)



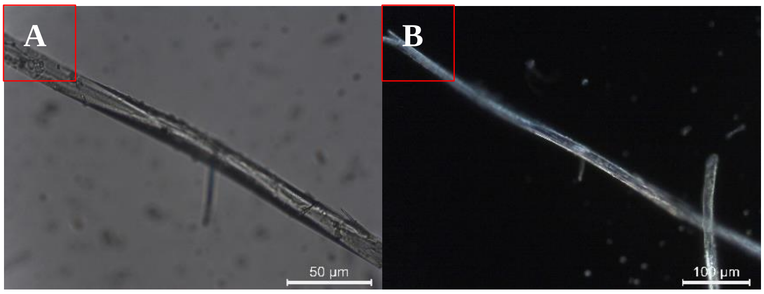
A) BFM B) DFM

SM Sample 5



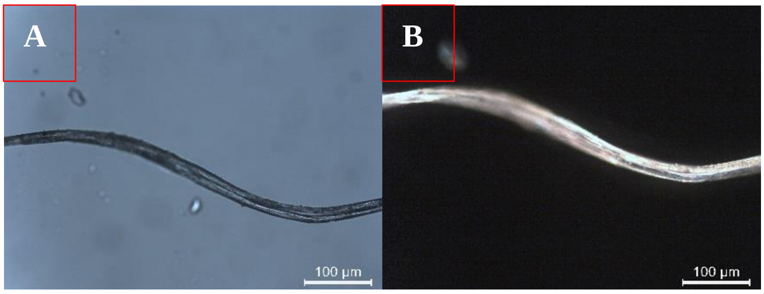


Sample 5A (warp)



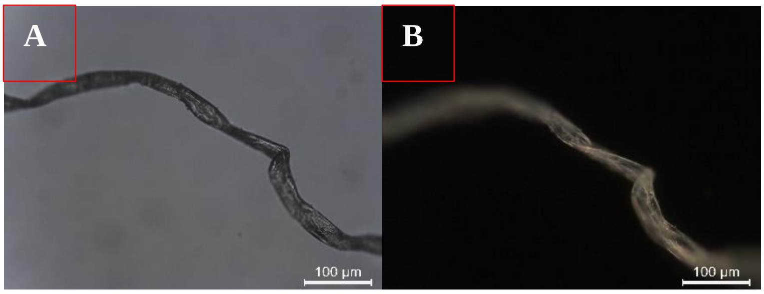
A) BFM B) DFM

Sample 5B (weft)



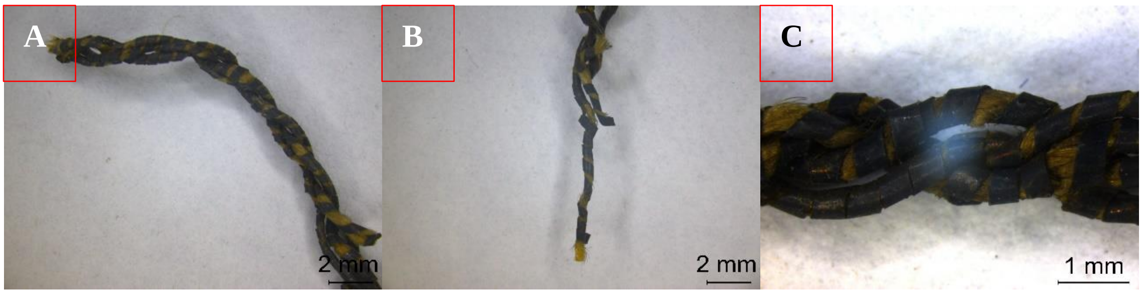
A) BFM B) DFM

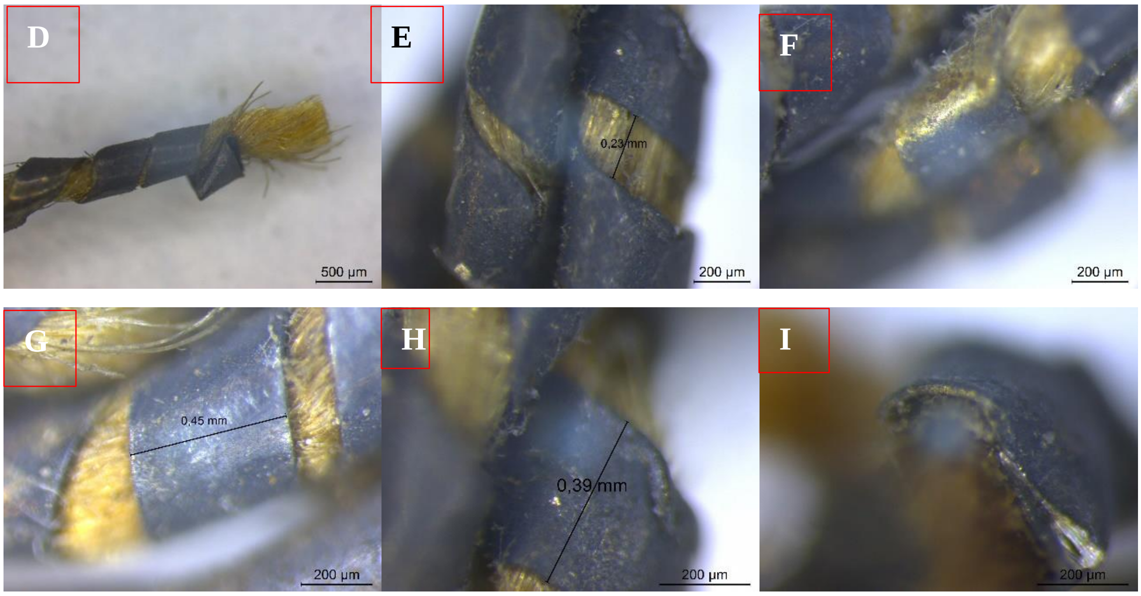
Sample 5H (Sewing thread)



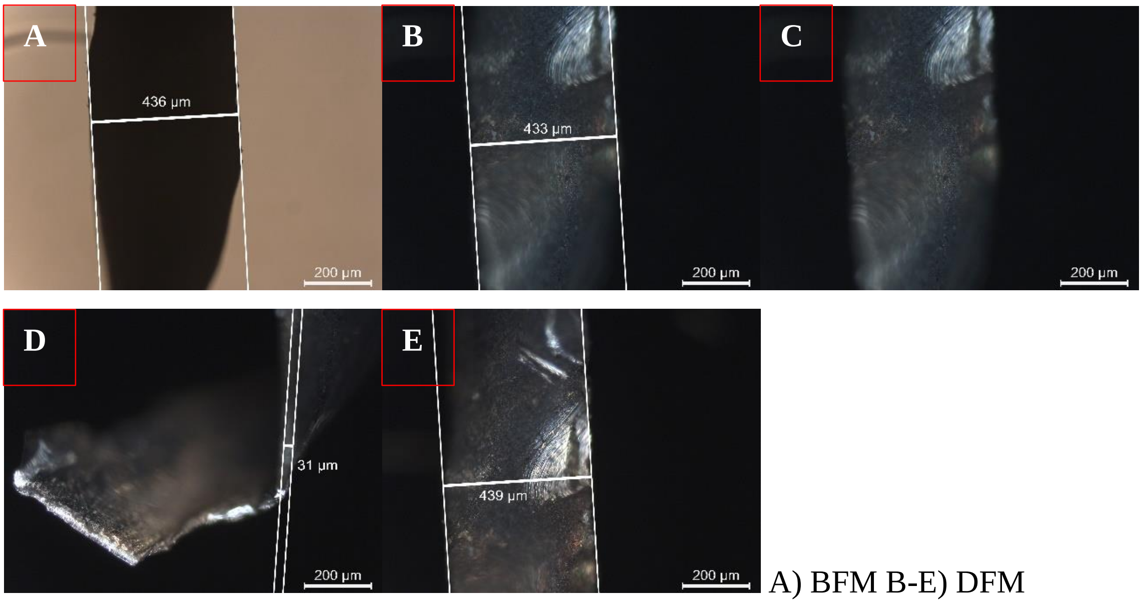
A) BFM B) DFM

SM Sample 6



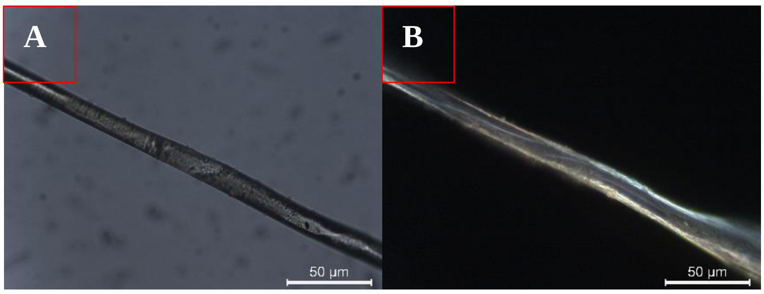


Sample 6M (metal from the metal thread)



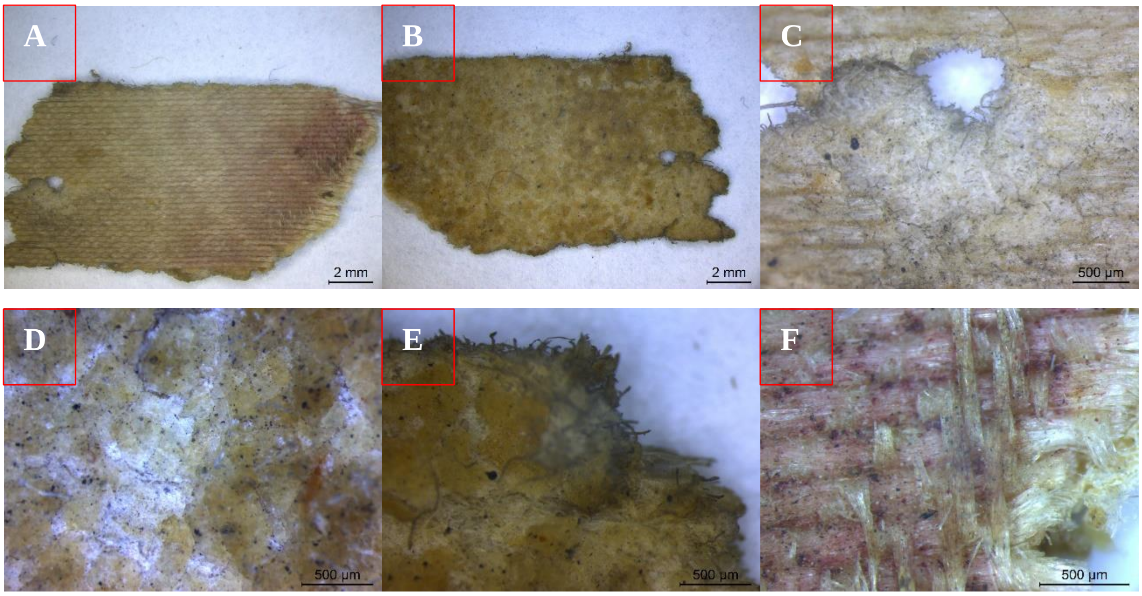
A) BFM B-E) DFM

Sample 6MF (Fiber from the core of the metal thread)

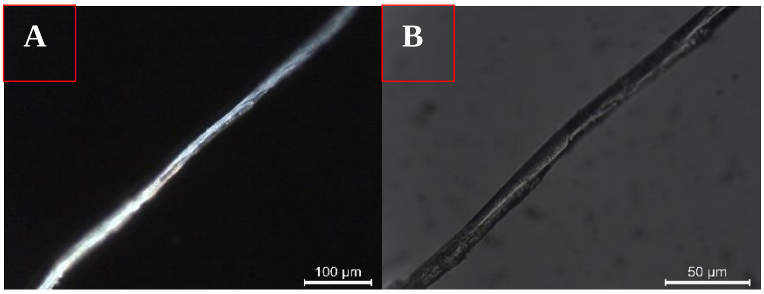


A) BFM B) DFM

SM Sample 7

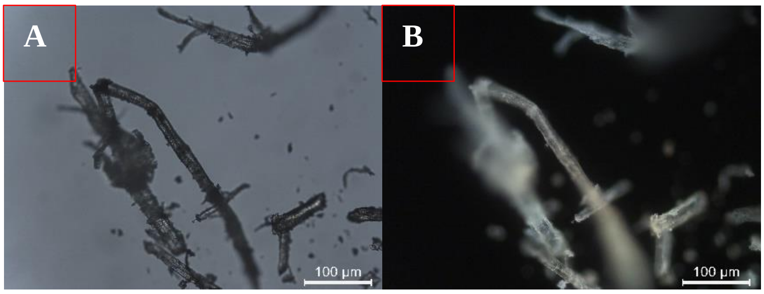


Sample 7F (fibers attached to the paper sample)



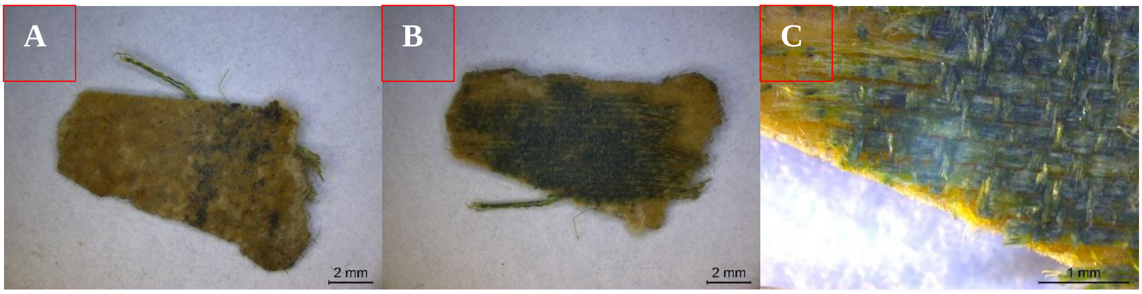
A) BFM B) DFM

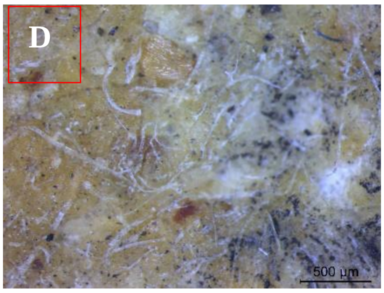
Sample 7PF (fibers from the inside of the paper)



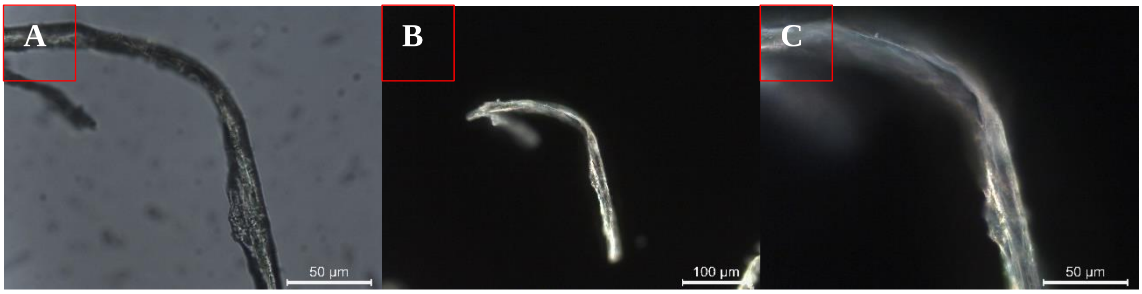
A) BFM B) DFM

SM Sample 8



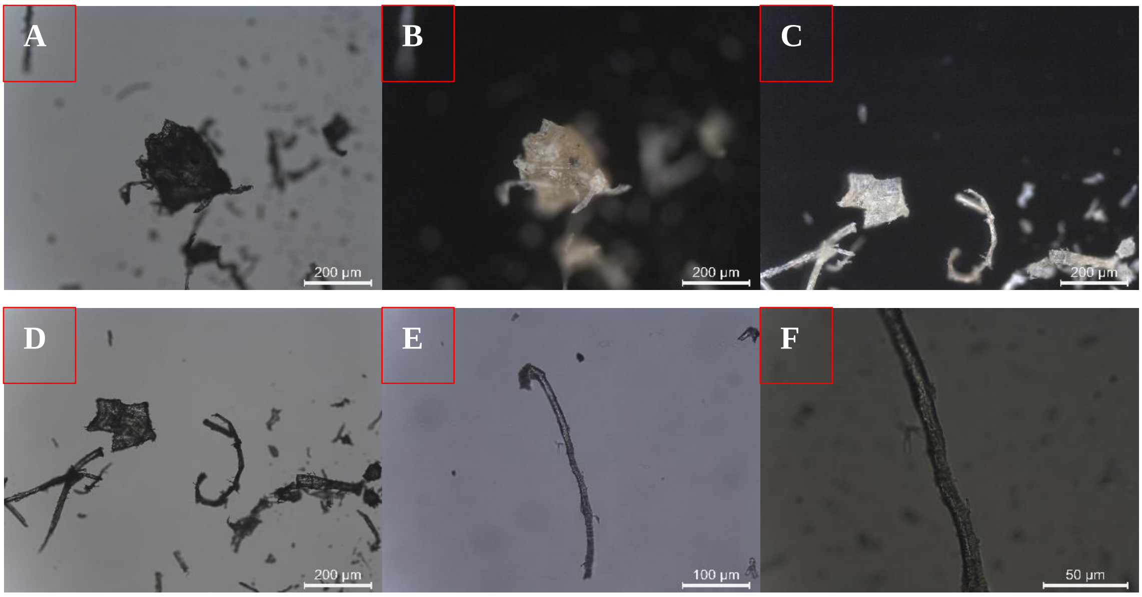


Sample 8F (fibers attached to the paper)



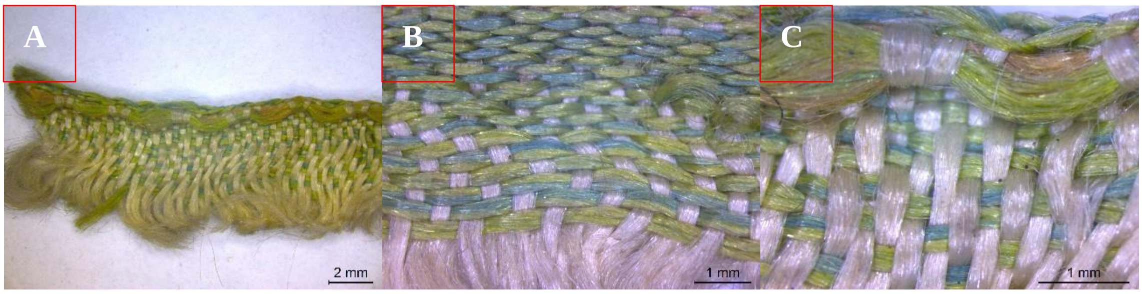
A) BFM B-C) DFM

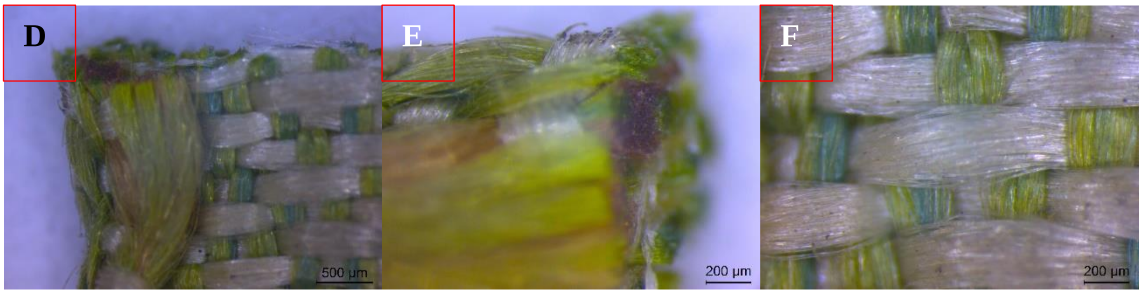
Sample 8PF (Fibers from inside of the paper)



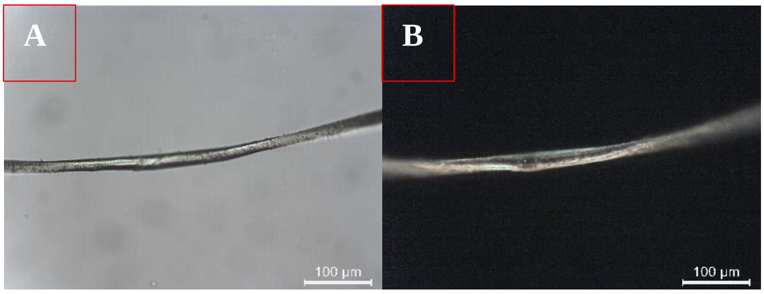
A, D, E) BFM B, C, F) DFM

SM Sample 9



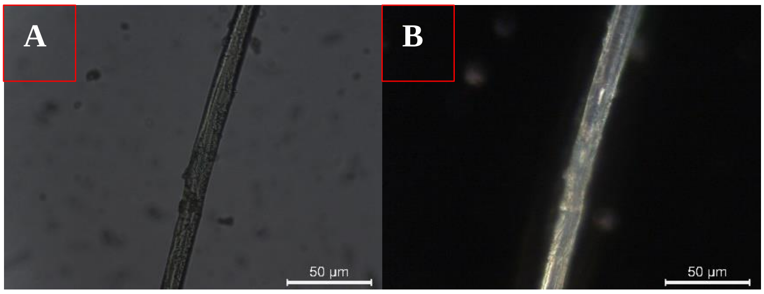


Sample 9A (White fiber from the warp)



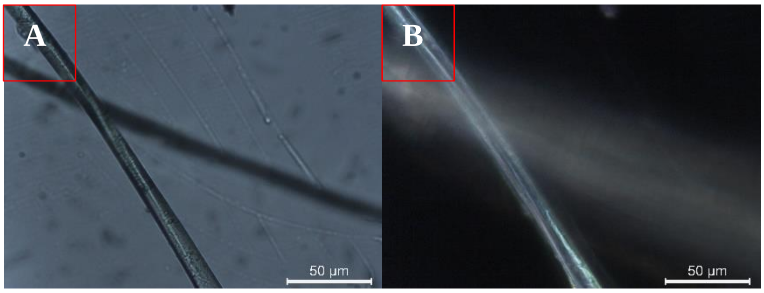
A) BFM B) DFM

Sample 9B (fiber of light green color of the weft)



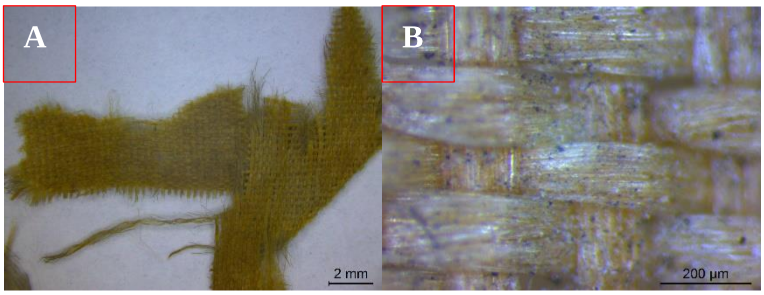
A) BFM B) DFM

Sample 9B (fiber of dark green color of the weft)

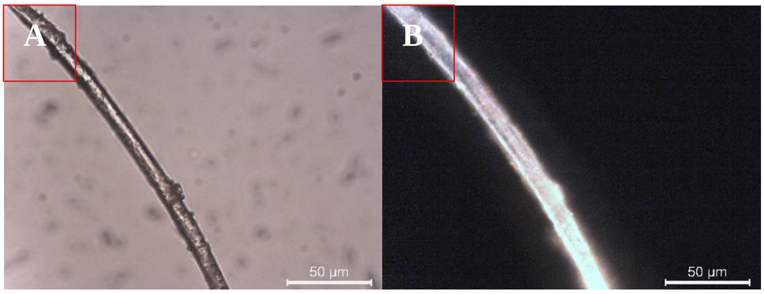


A) BFM B) DFM

SM Sample 10

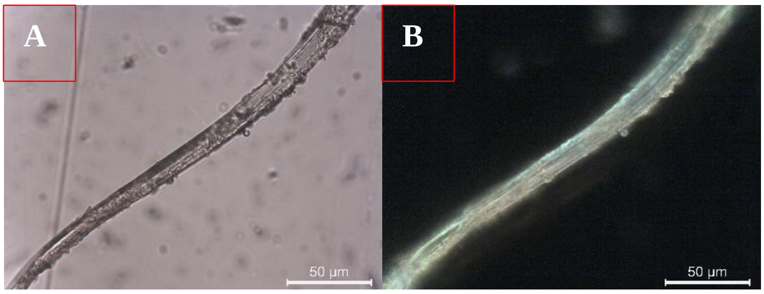


Sample 10A (warp)



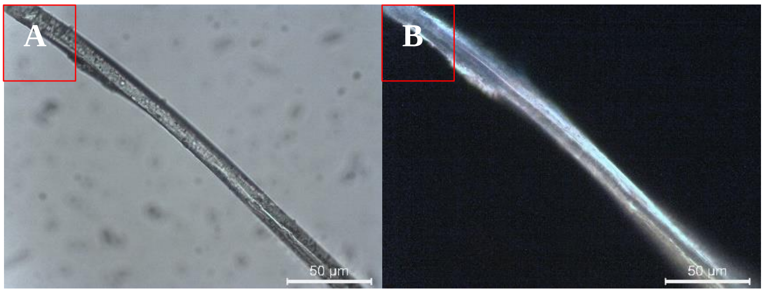
A) BFM B) DFM

Sample 10B (weft)



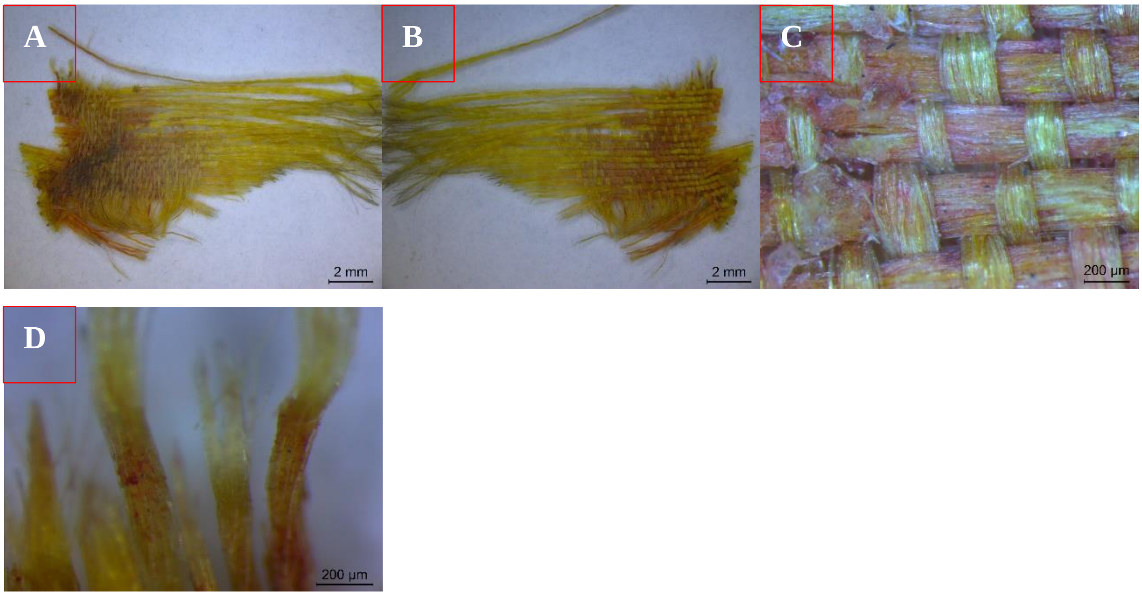
A) BFM B) DFM

Sample 10H (Sewing thread)

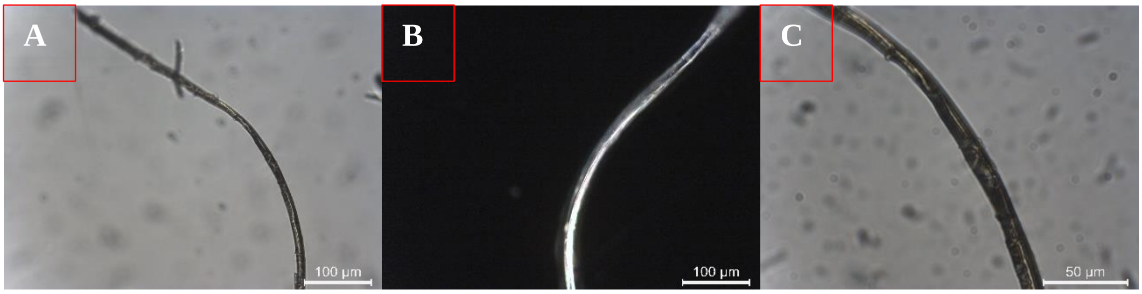


A) BFM B) DFM

SM Sample 11

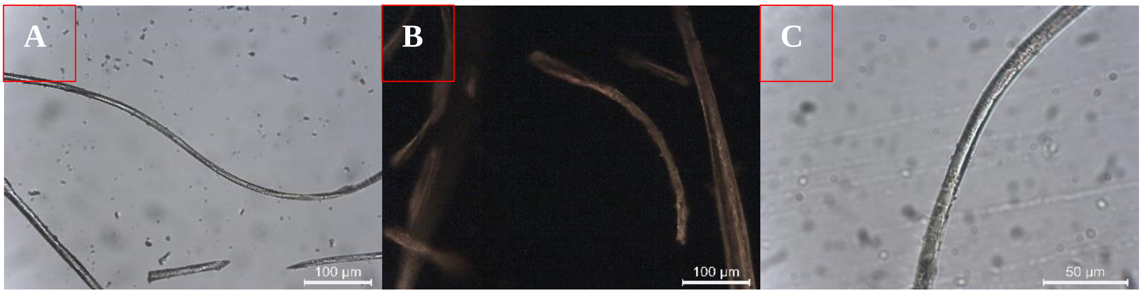


Sample 11A (warp)



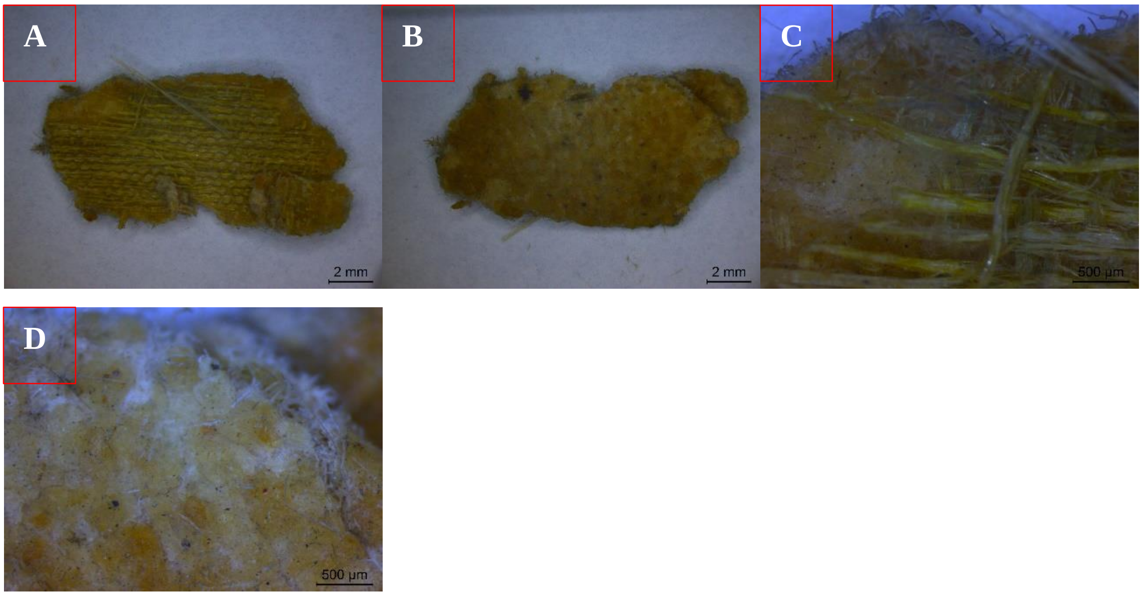
A, C) BFM B) DFM

Sample 11B (weft)

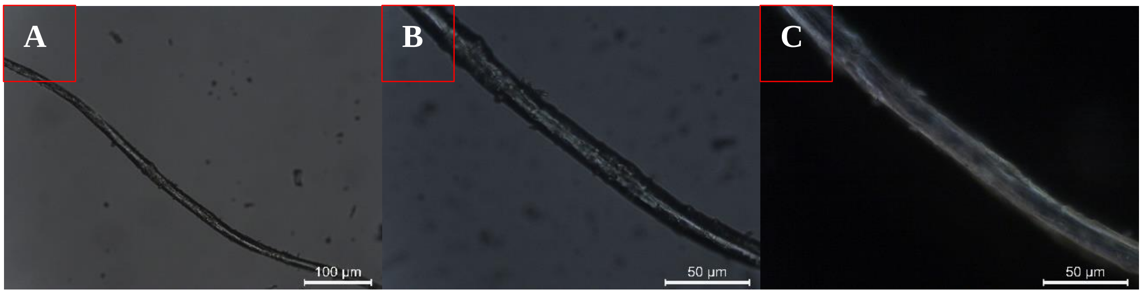


A, C) BFM B) DFM

SM Sample 12

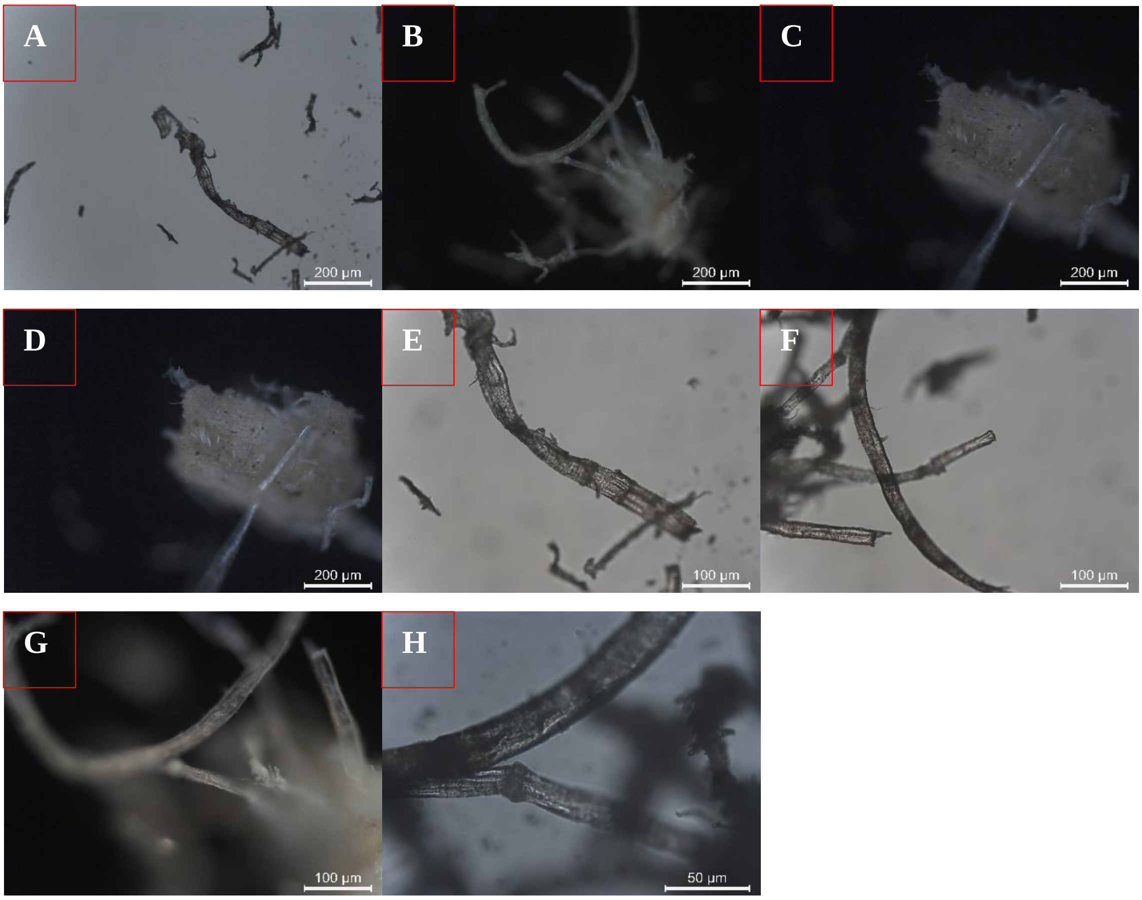


Sample 12F (fibers attached to the paper sample)



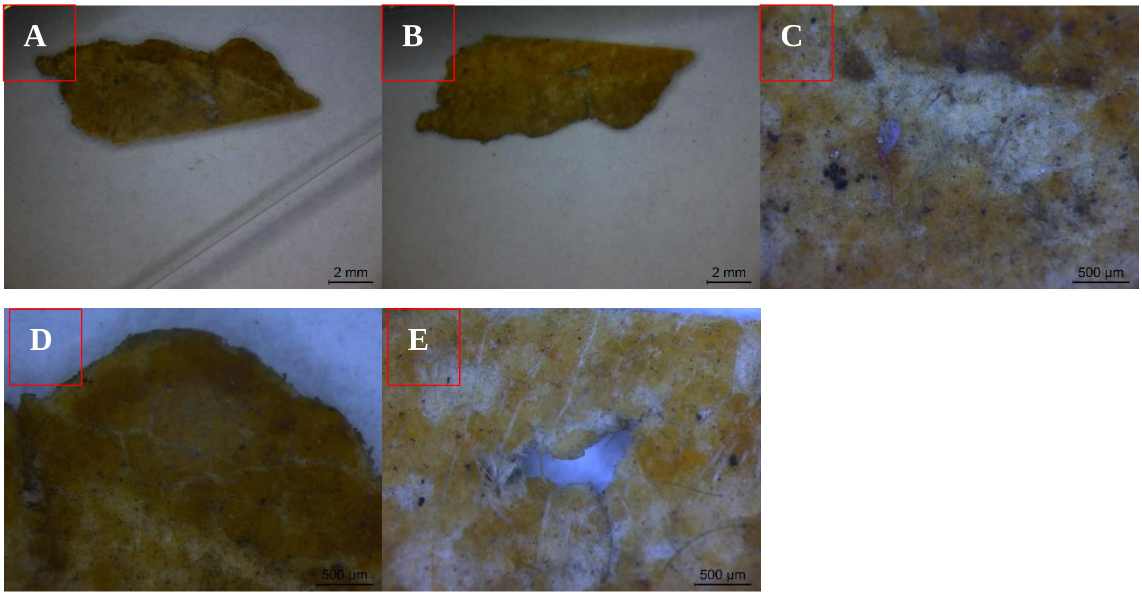
A,B) BFM C) DFM

Sample 12PF (fibers coming from the inside of the paper)

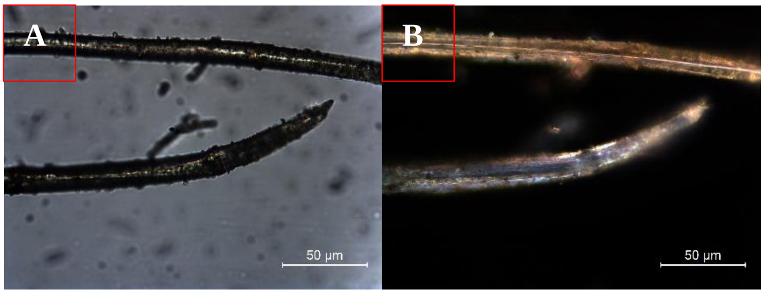


A, E, F, H) BFM B, C, D, G) DFM

SM Sample 13

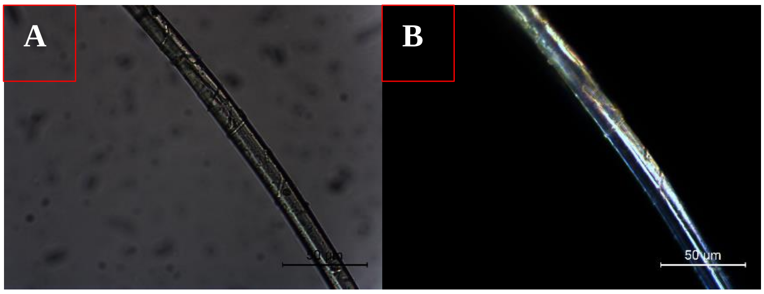


Sample 13F (fiber attached to the paper)



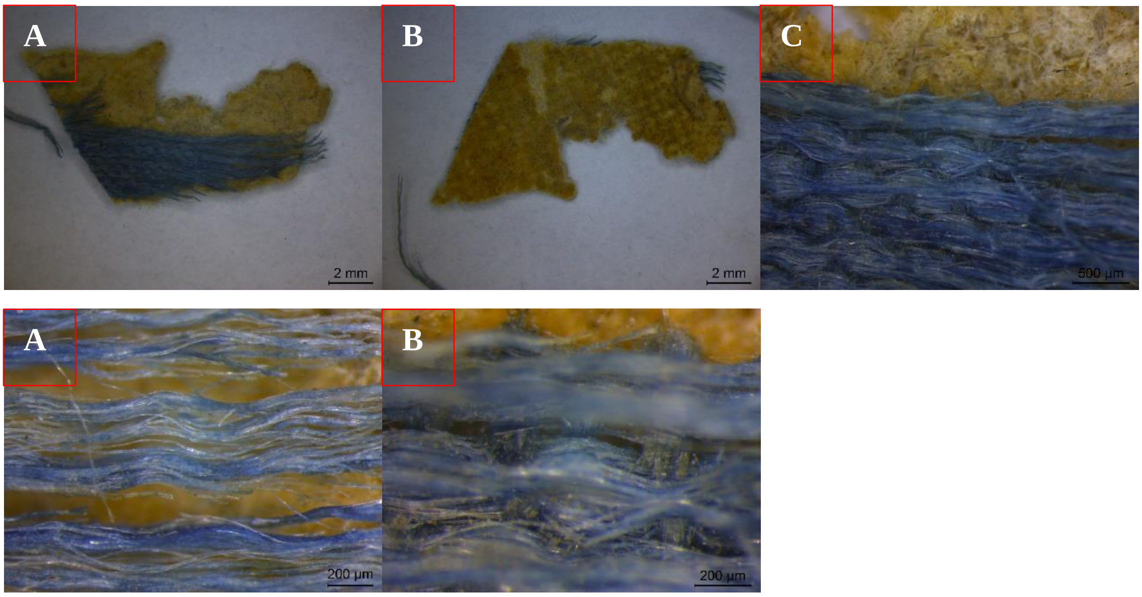
A) BFM B) DFM

Sample 13H (fiber form sewing thread)

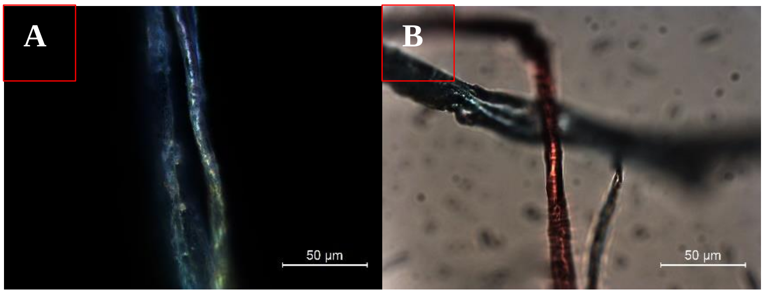


A) BFM B) DFM

SM Sample 14

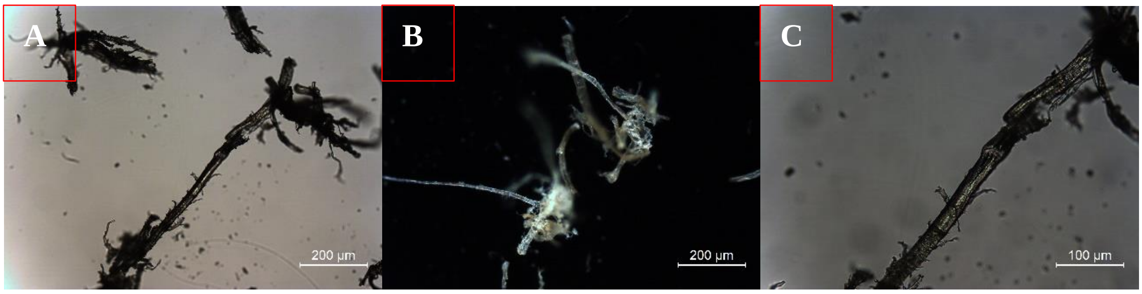


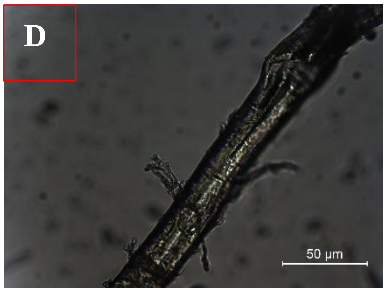
Sample 14F (Fiber attached to the paper)



A) BFM B) DFM

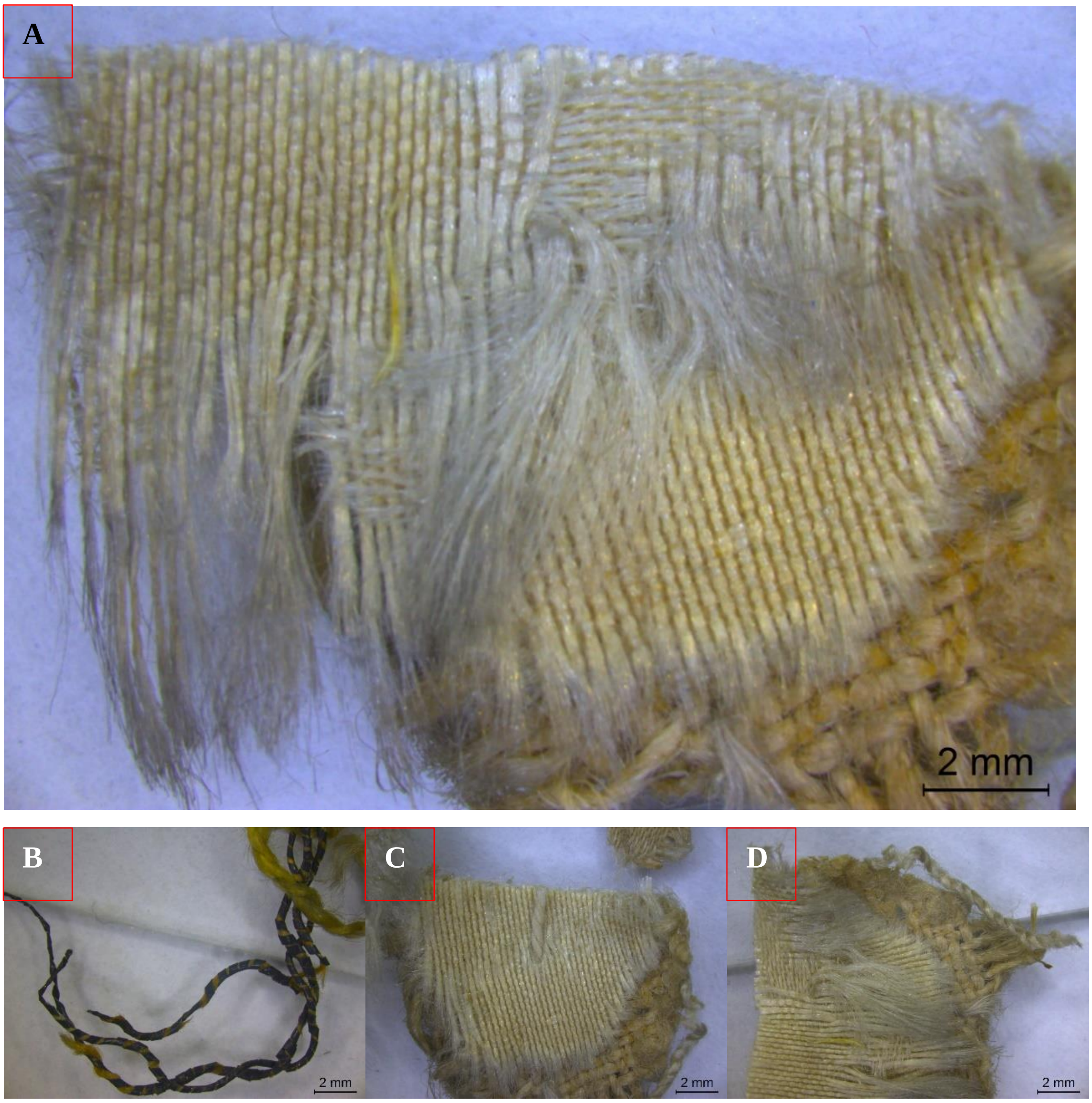
Sample 14PF (fiber from the inside of the paper)

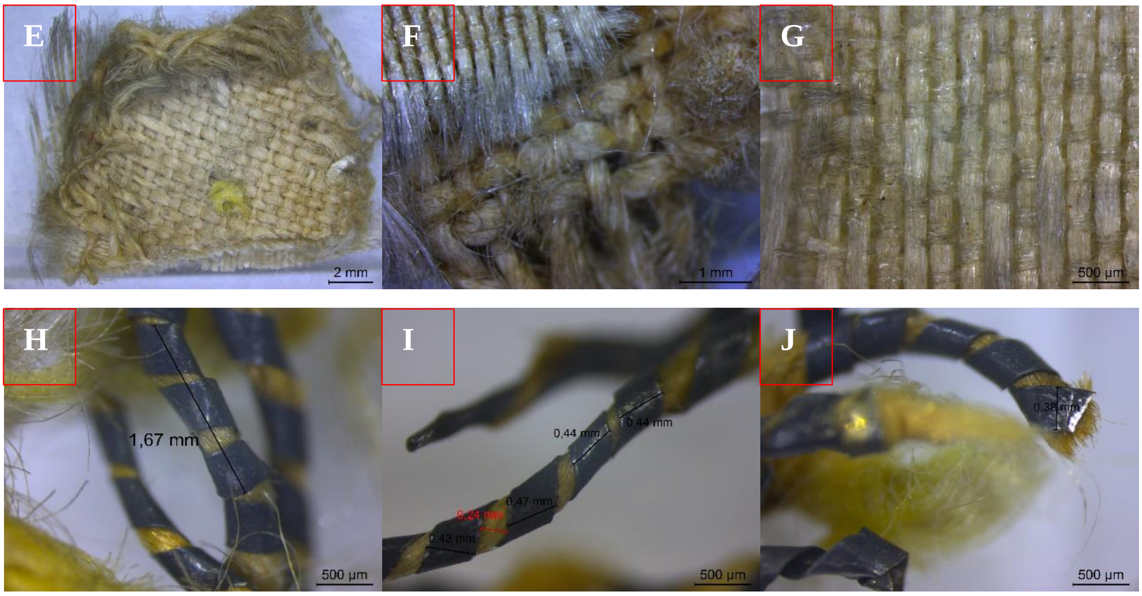




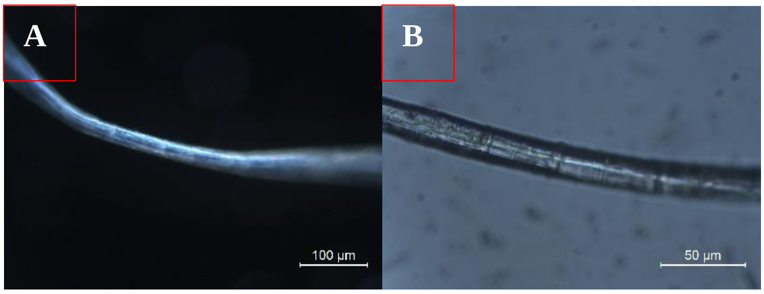
A, C, D) BFM B) DFM

SM Sample 15



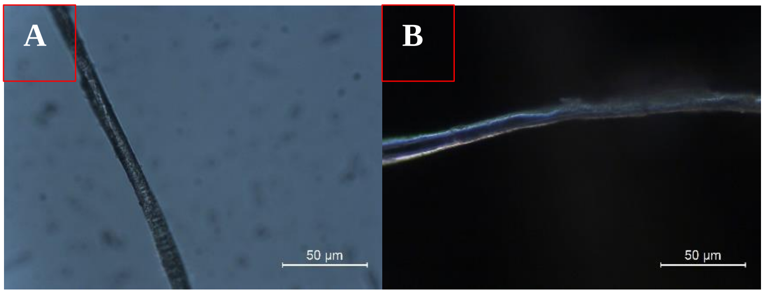


Sample 15 Coarse fiber A (warp) 1 layer



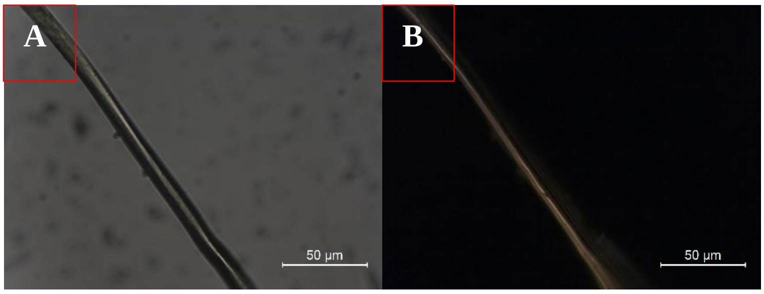
A) BFM B) DFM

Sample 15 Coarse fiber B (weft) 1 layer



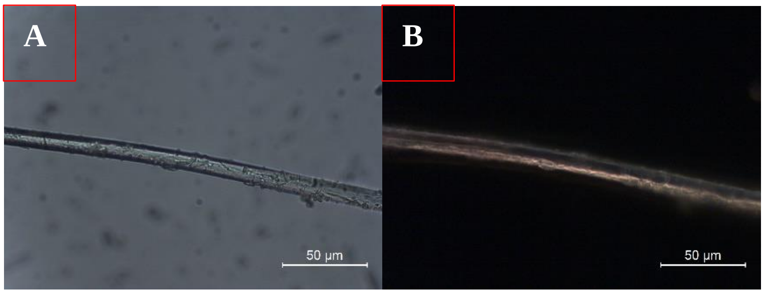
A) BFM B) DFM

Sample 15 medium fiber 2 layer



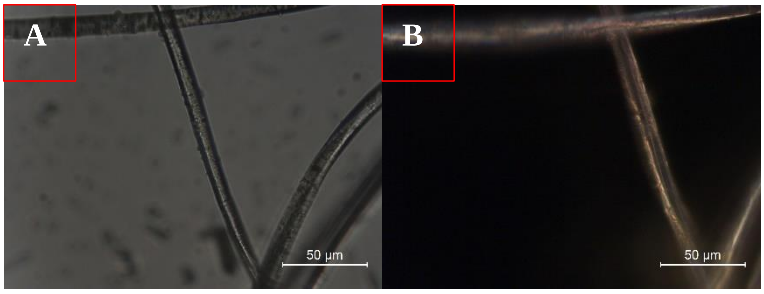
A) BFM B) DFM

Sample 15 soft fiber 3 layer



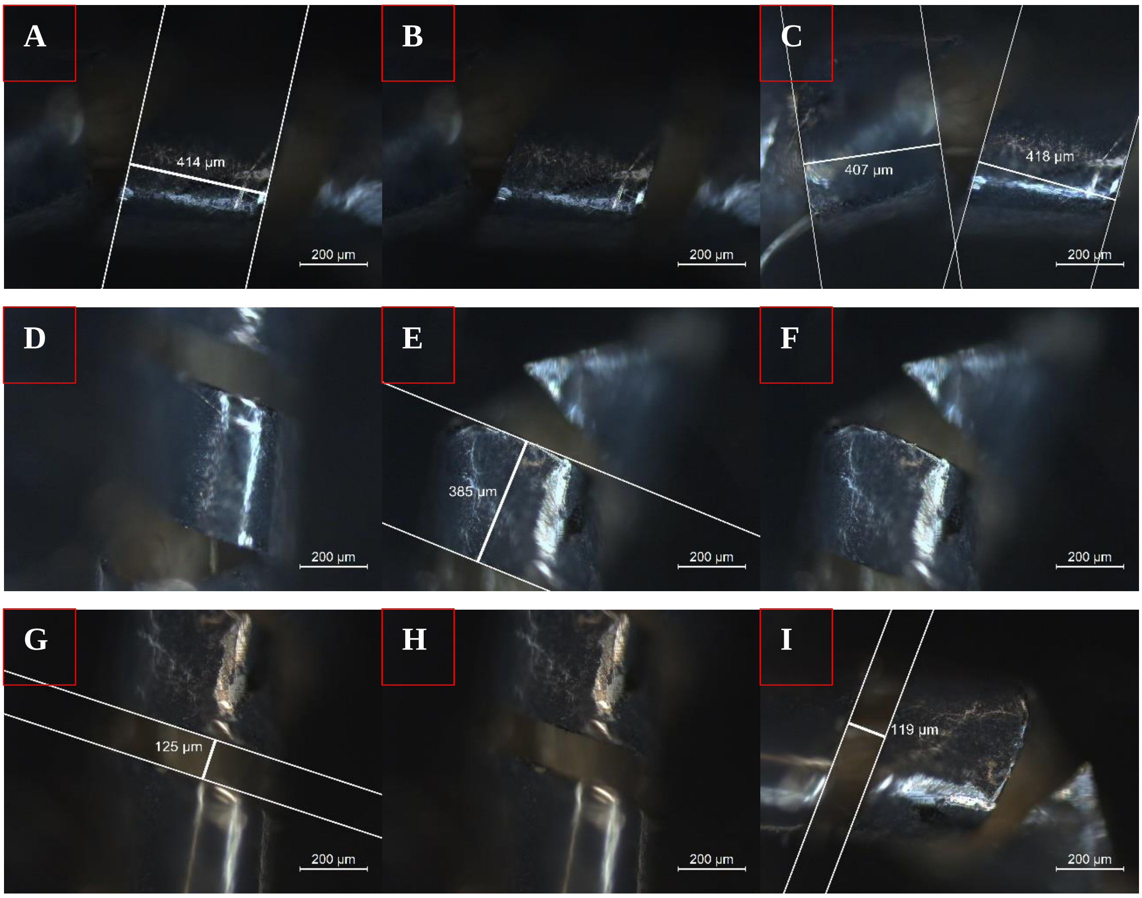
A) BFM B) DFM

Sample 15H (fiber form sewing thread)



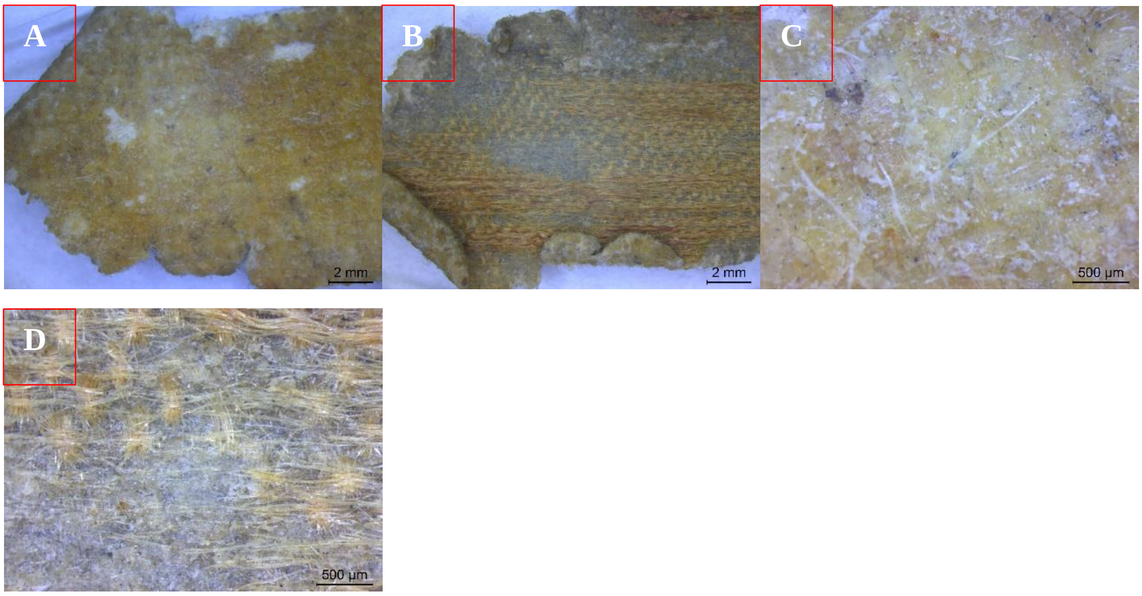
A) BFM B) DFM

Sample 15M (metal form the metal thread)

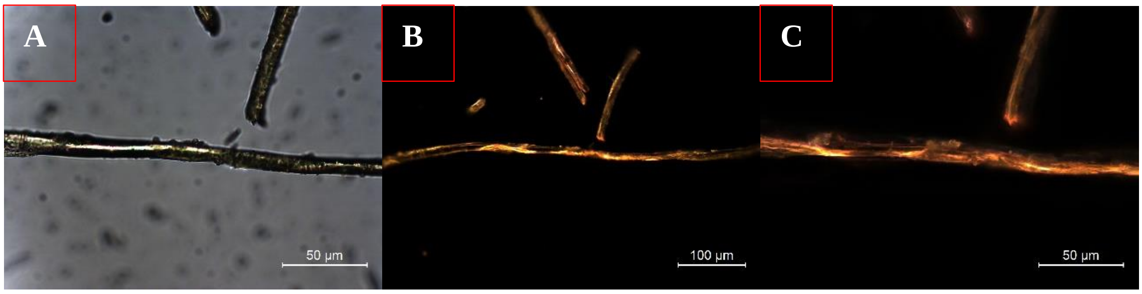


A-I) DFM

SM Sample 16

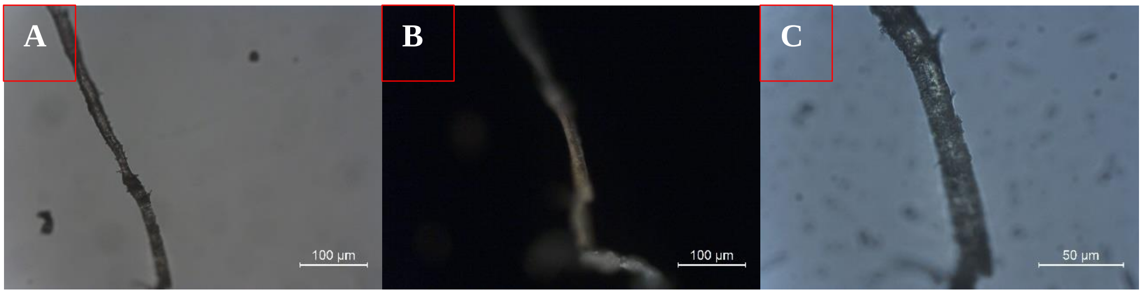


Sample 16F (fibers attached to the fiber sample)



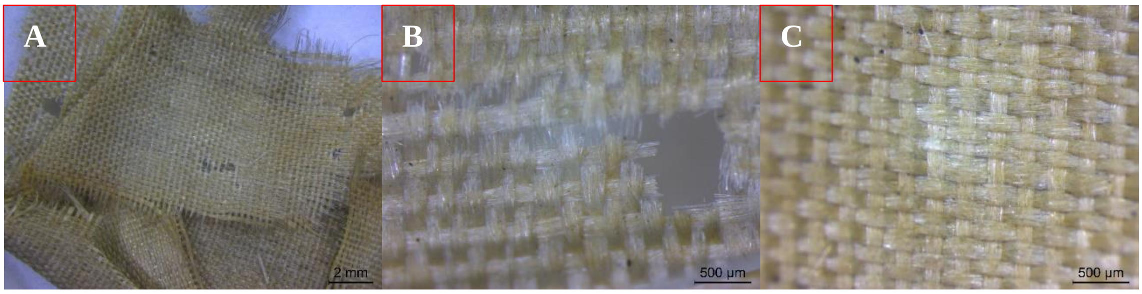
A) BFM B-C) DFM

Sample 16PF (fibers from the inside of the paper)

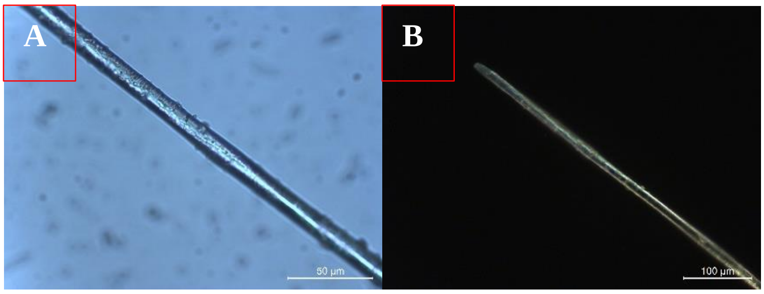


A, C) BFM B) DFM

SM Sample 17

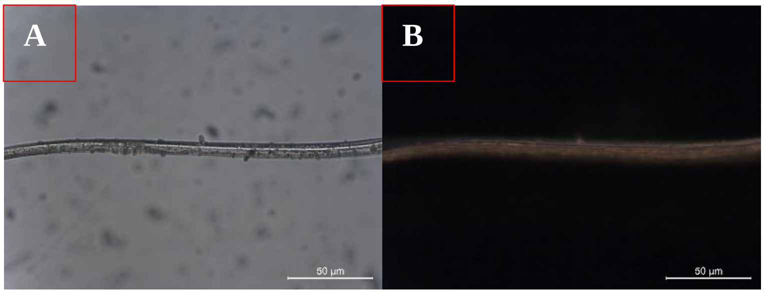


Sample 17A (warp)



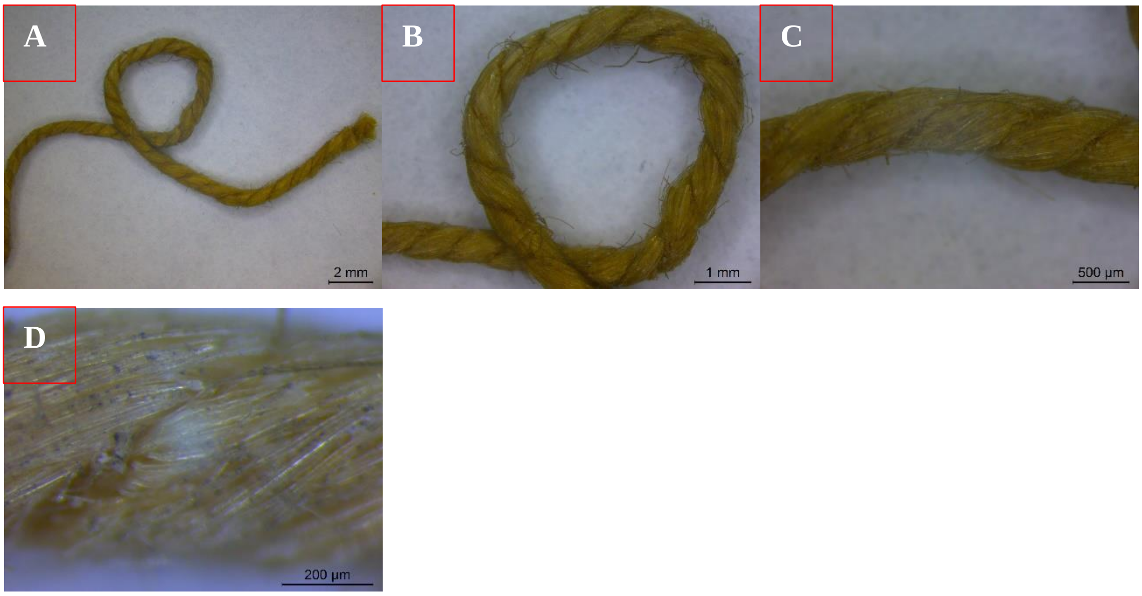
A) BFM B) DFM

Sample 17B (weft)

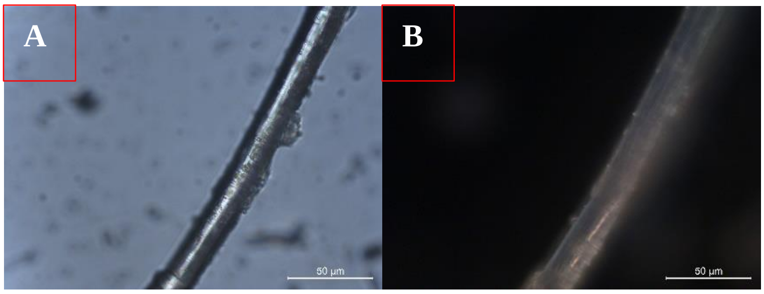


A) BFM B) DFM

SM Sample 18

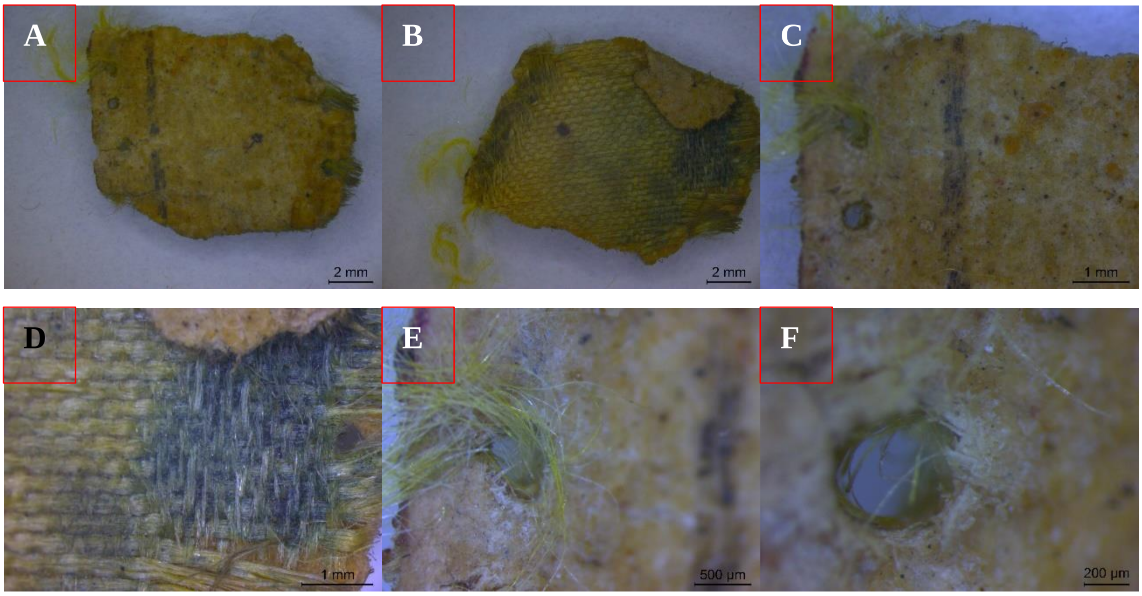


Sample 18H (fibers from the thread)

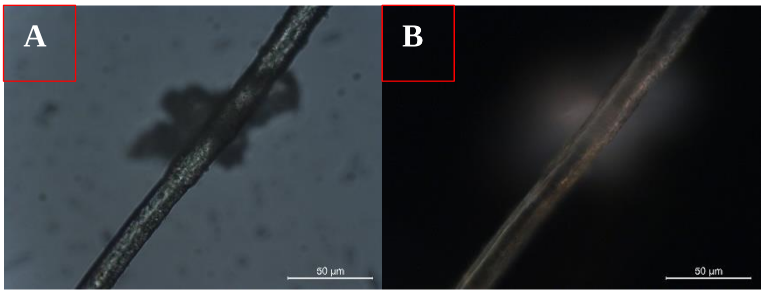


A) BFM B) DFM

SM Sample 19

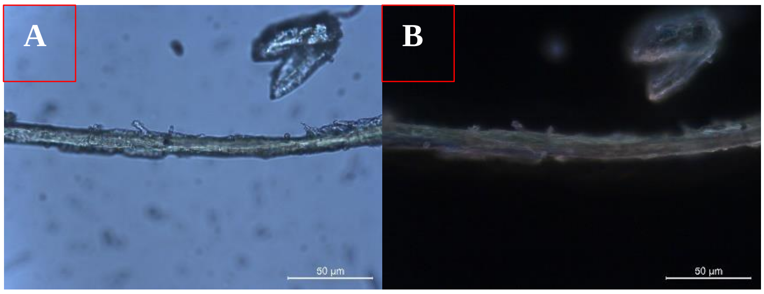


Sample 19F (fibers attached to the paper)



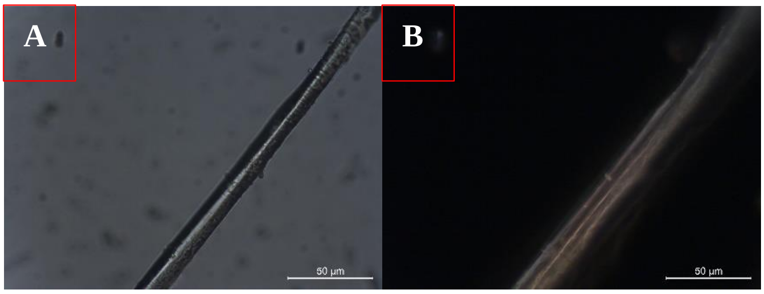
A) BFM B) DFM

Sample 19PF (fibers from the inside of the paper)



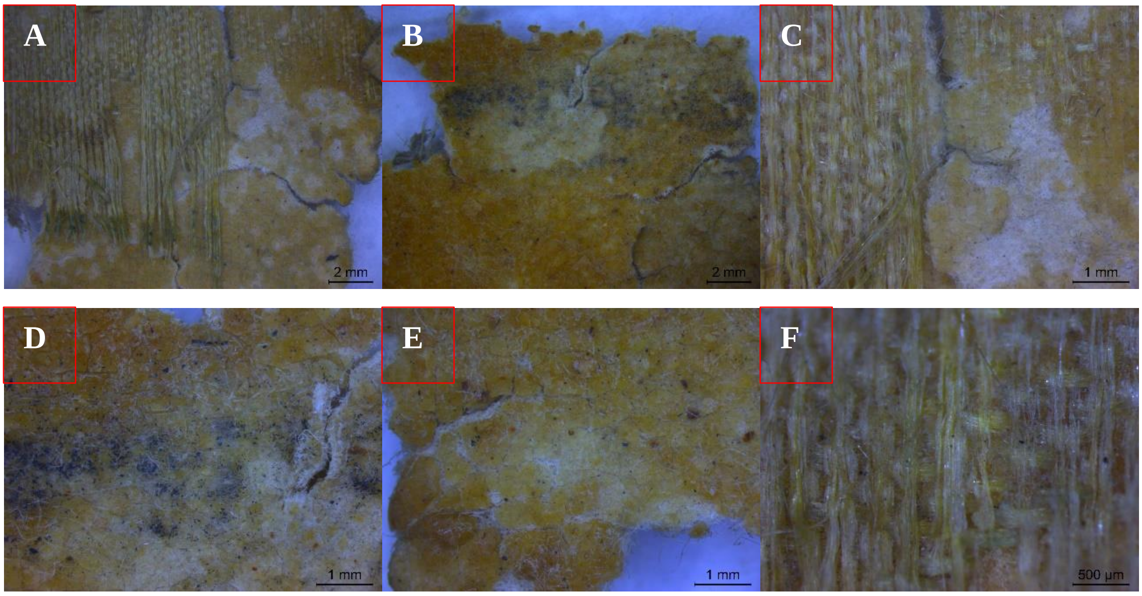
A) BFM B) DFM

Sample 19YT (fibers yellow from the sewing thread)

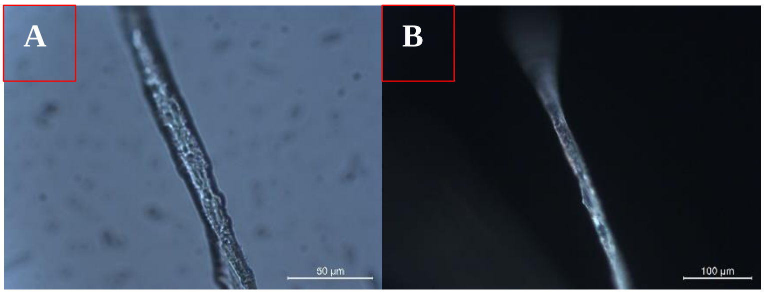


A) BFM B) DFM

SM Sample 20

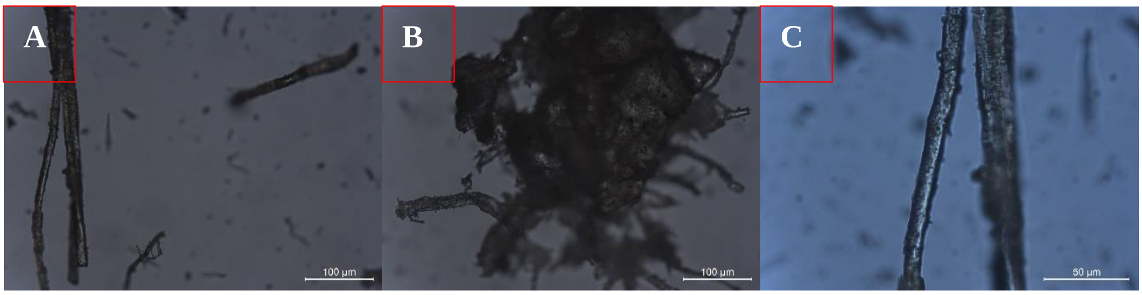


Sample 20 F (fibers attached to the paper)



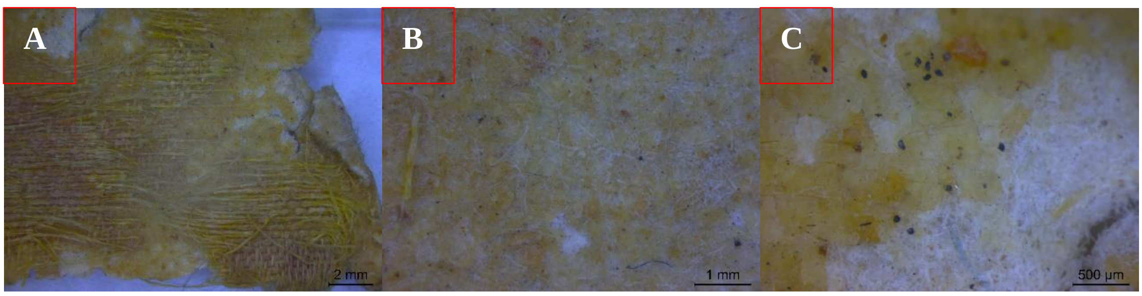
A) BFM B) DFM

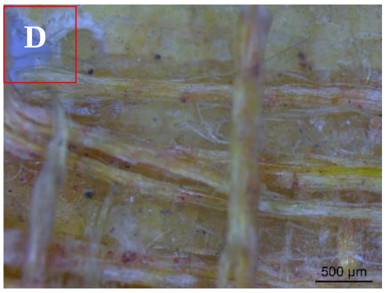
Sample 20PF (fibers from the inside of the paper)



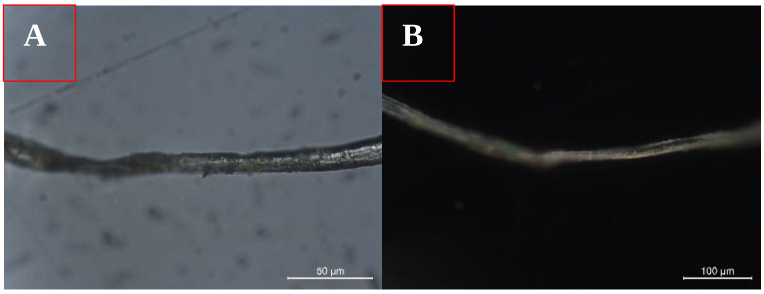
A-C) BFM

SM Sample 21

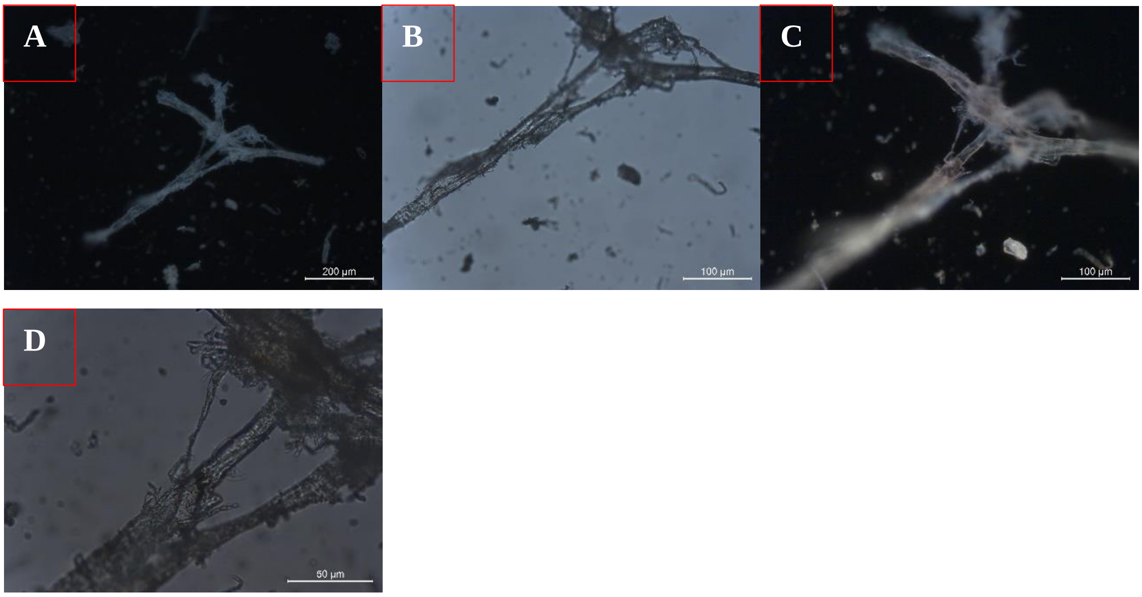




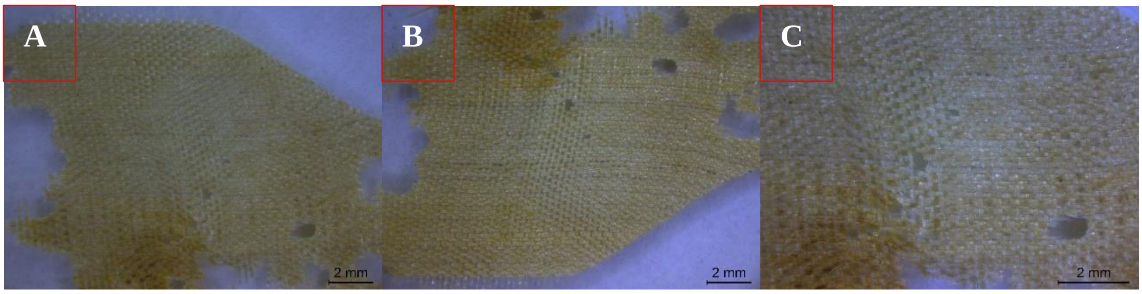
Sample 21F (fibers attached to the paper)

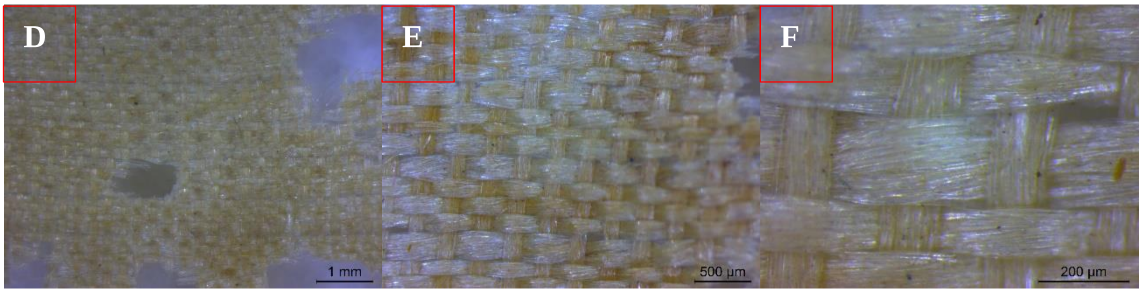


Sample 21PF (fibers from the inside of the paper)

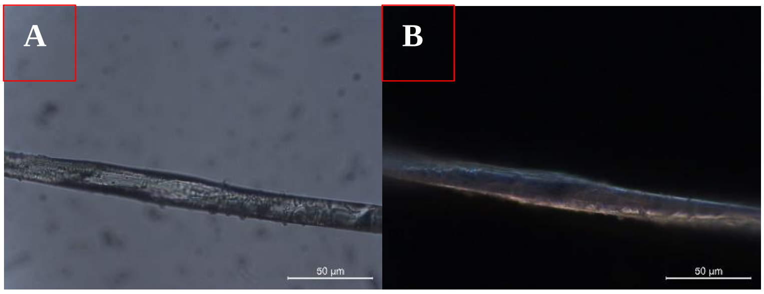


SM Sample 22

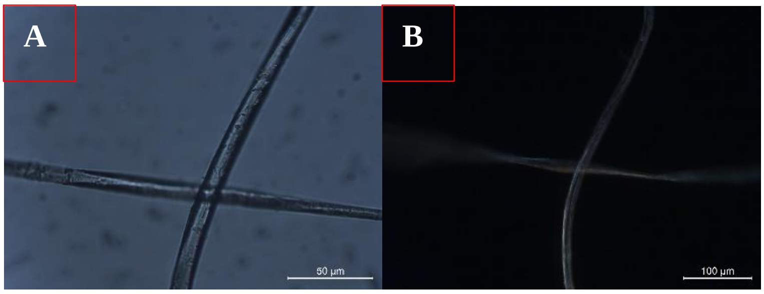




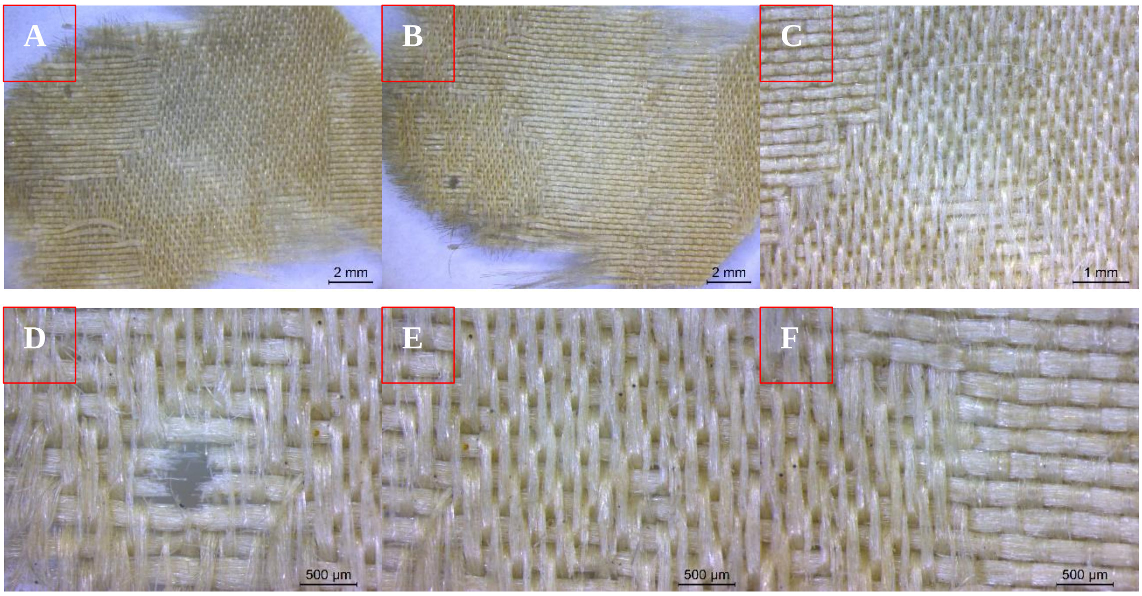
Sample 22A (warp)



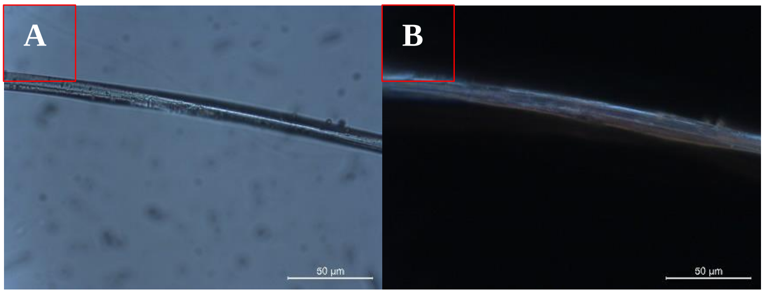
Sample 22B (weft)



SM Sample 23

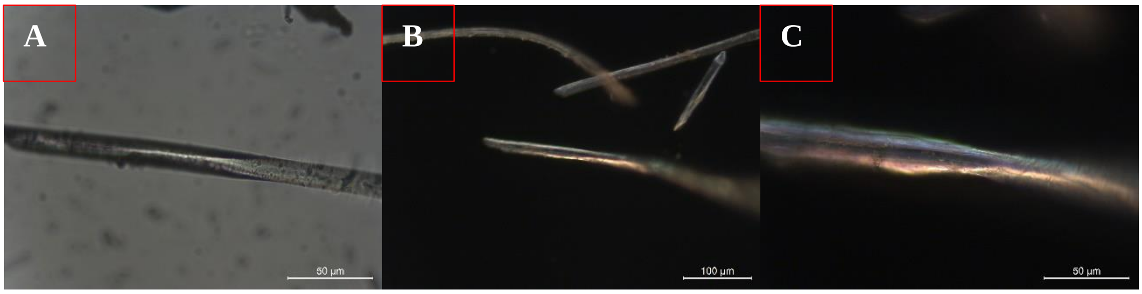


Sample 23A (warp)



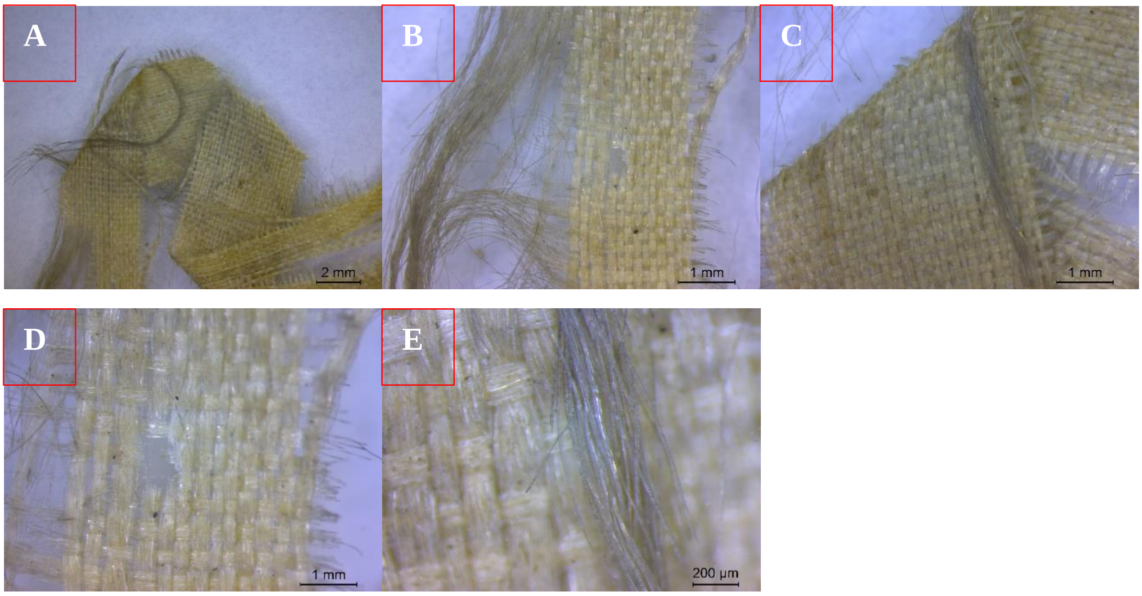
A) BFM B) DFM

Sample 23B (weft)

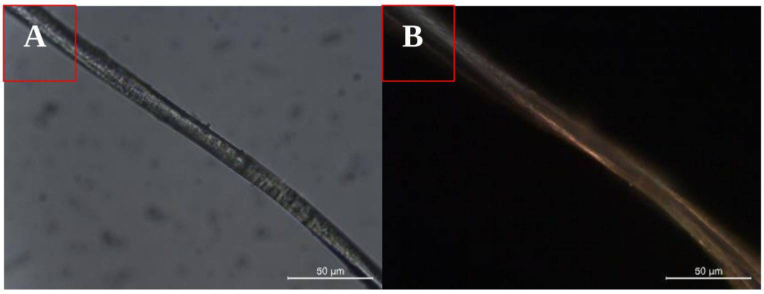


A) BFM B, C) DFM

SM Sample 24

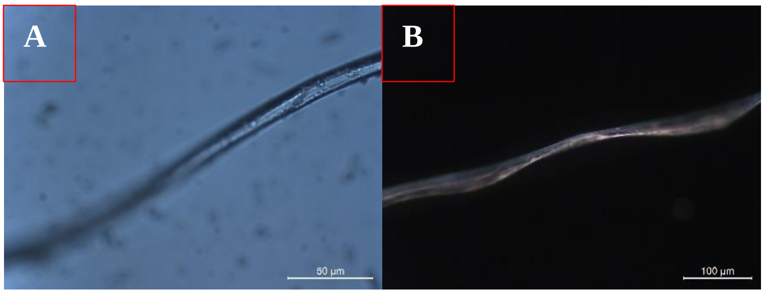


Sample 24A (warp)



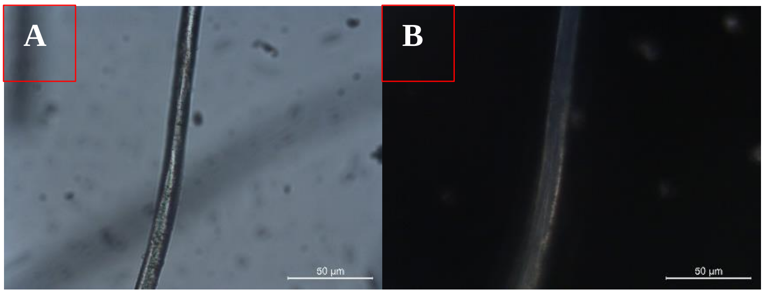
A) BFM B) DFM

Sample 24B (weft)



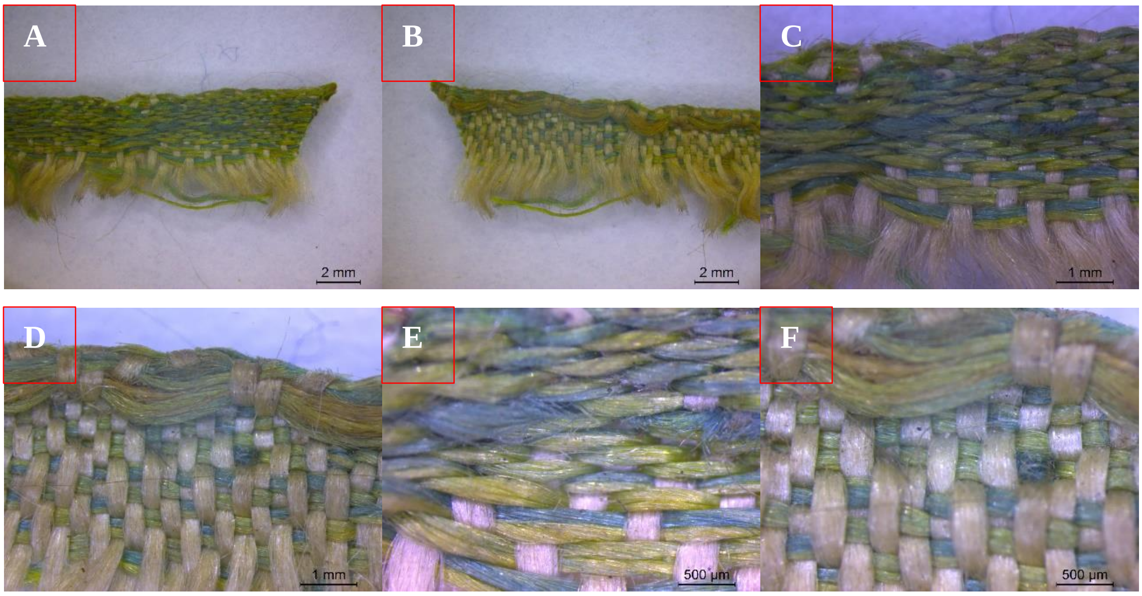
A) BFM B) DFM

Sample 24H (fiber form sewing thread)

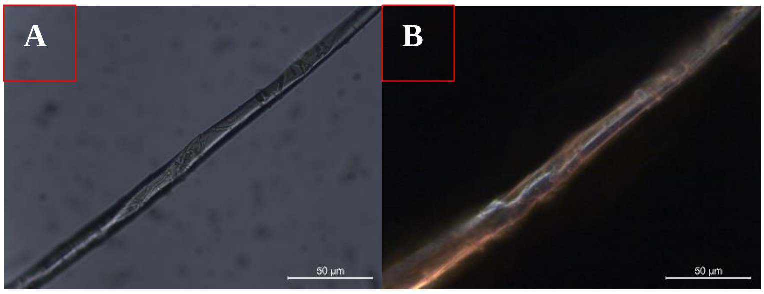


A) BFM B) DFM

SM Sample 25

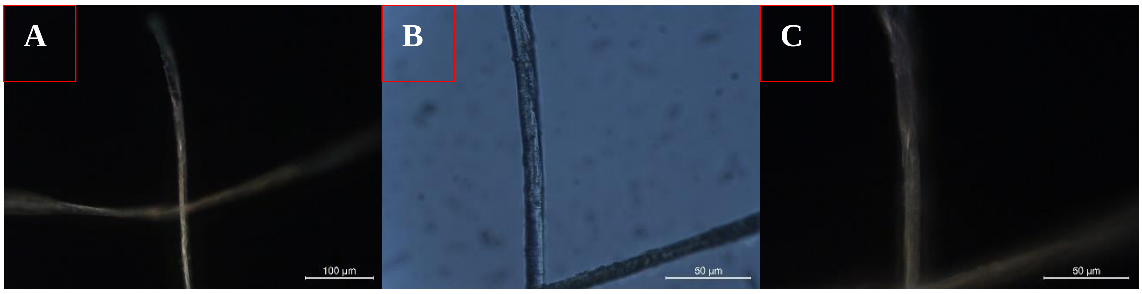


Sample 25A (warp white)



A) BFM B) DFM

Sample 25 B (weft green)



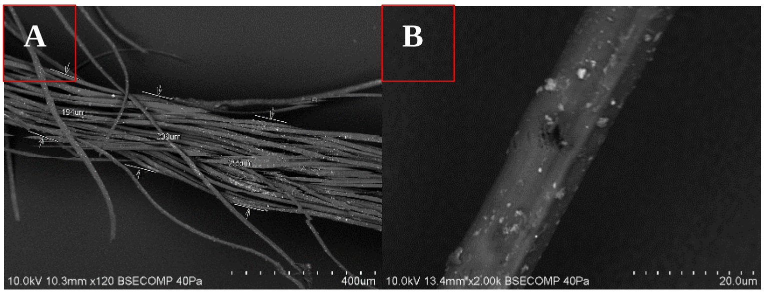
B) BFM A, C) DFM

Appendix 2 VP-SEM

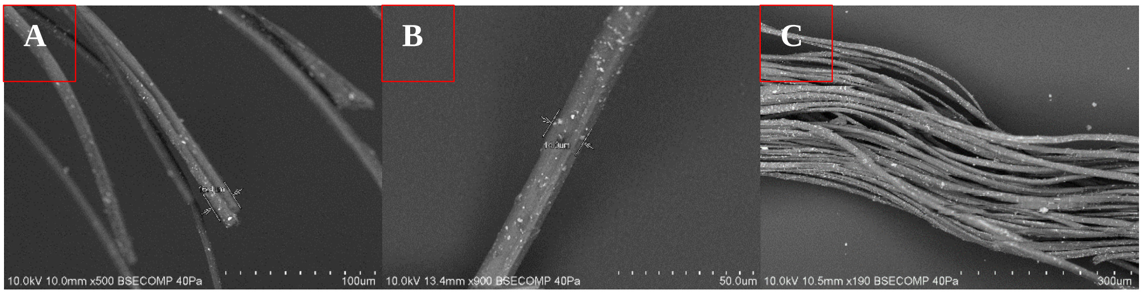
Below are presented the images taken under the VP-SEM from the analysis of the different components isolated of each sample from the Francisco Pizarro's Banner of Arms, with the aim to present more information to others researchers hoping that will be useful as tool for future discussions. With this analytical data is expected that the readers gain a better understanding from the actual state of the Banner and obtain a complementary view from the explained by the author on the results chapter.

Sample 1

Sample 1A (warp)

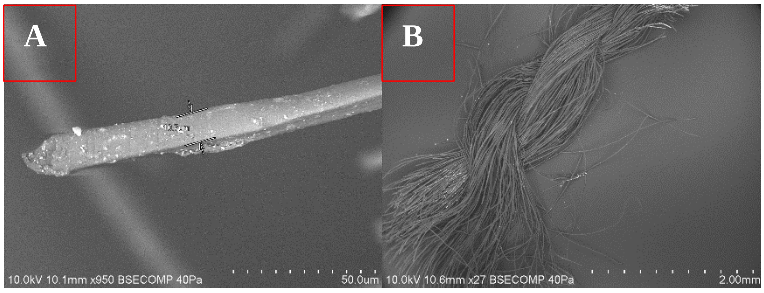


Sample 1B (weft)

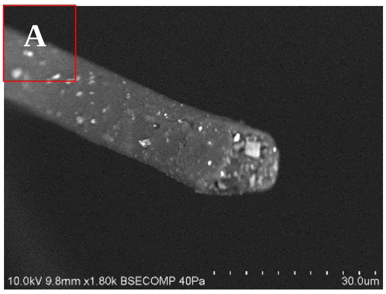


Sample 2

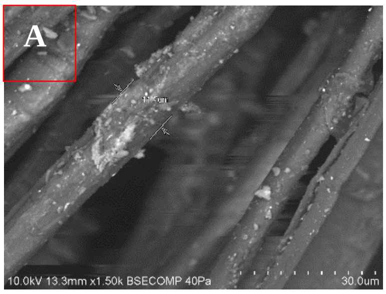
Sample 2A (warp)



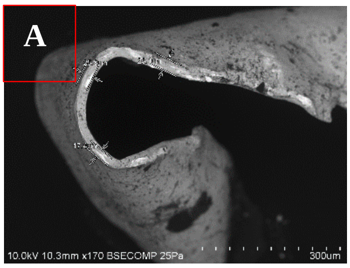
Sample 2B (weft)



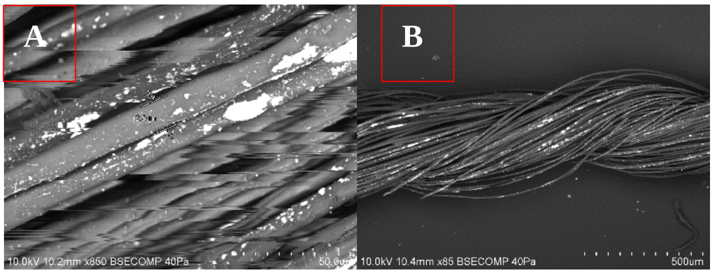
Sample 2H (fibers from the sewing thread)



Sample 2M (metal thread)

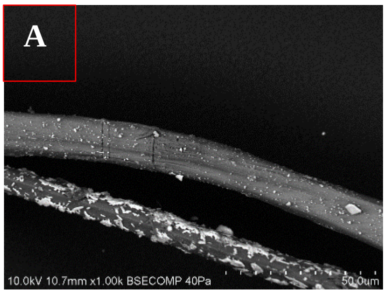


Sample 2MF (fibers from the core of the metal thread)

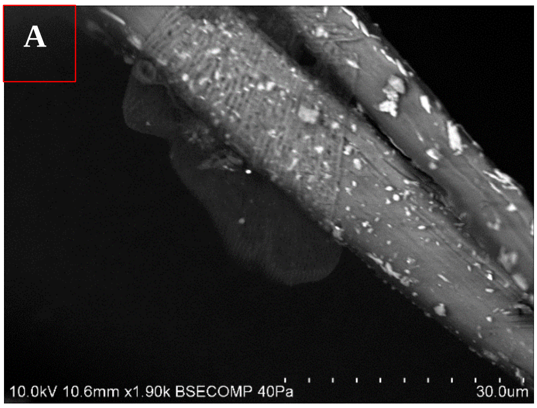


Sample 3

Sample 3A (warp)

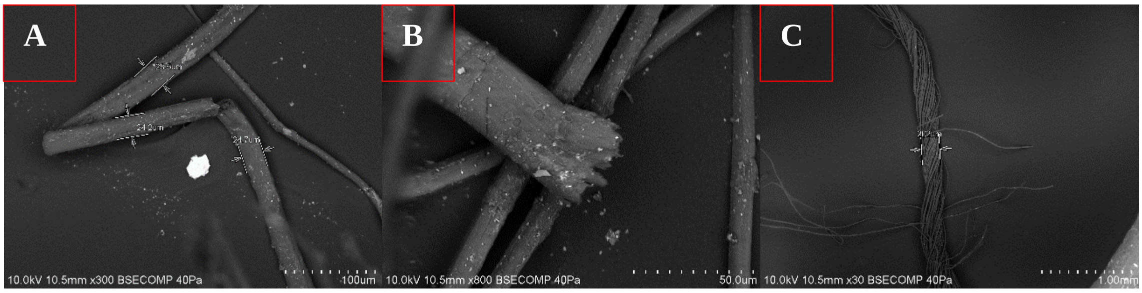


Sample 3A (warp fiber with insect egg)



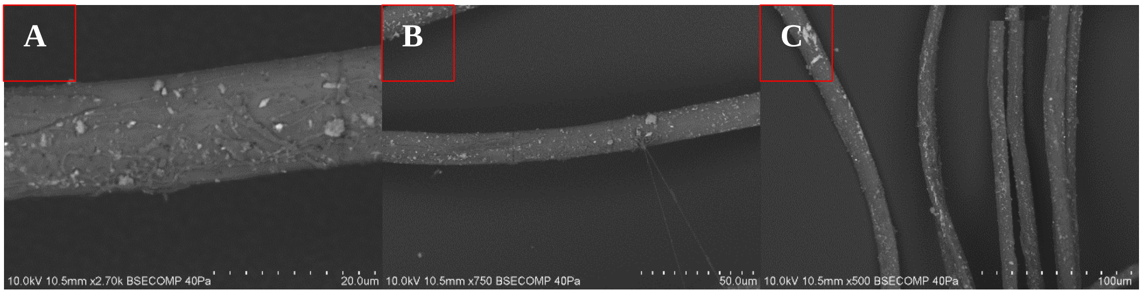
Sample 4

Sample 4A (warp)

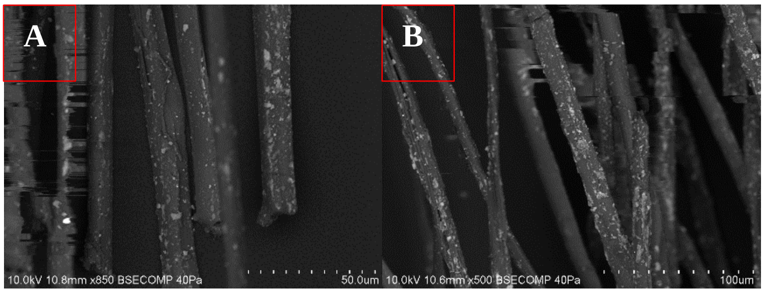


Sample 5

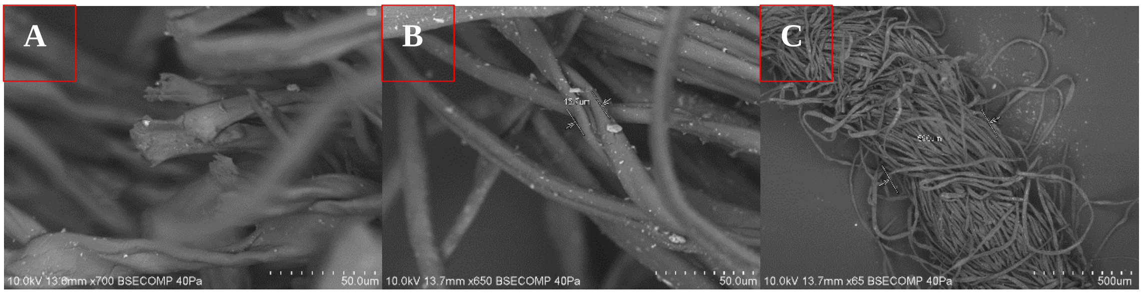
Sample 5A (warp)



Sample 5B (weft)

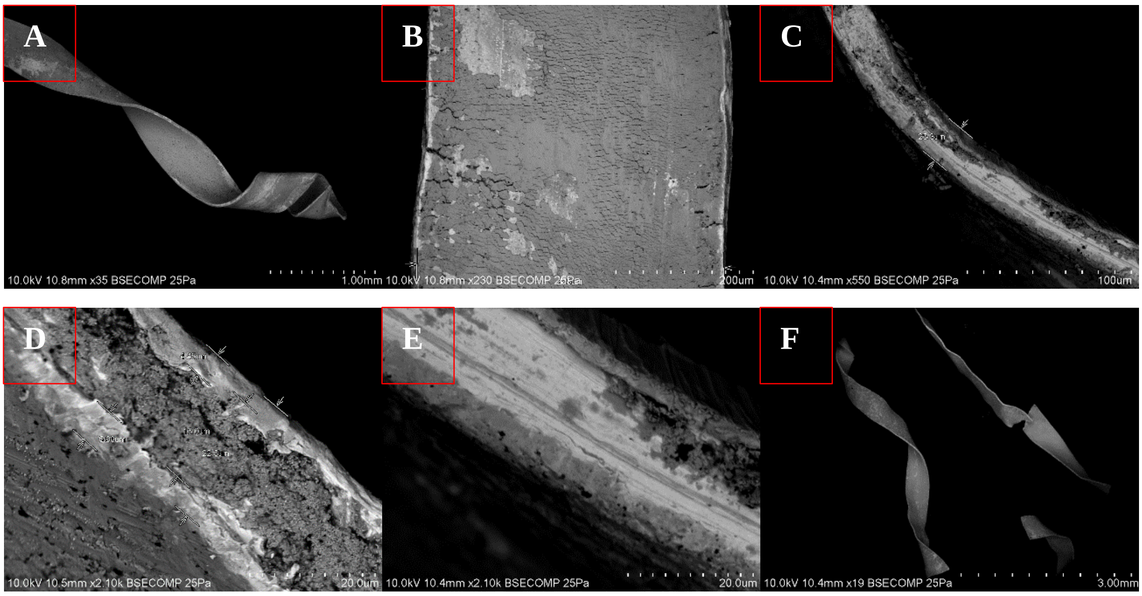


Sample 5H (fibers from the sewing thread)

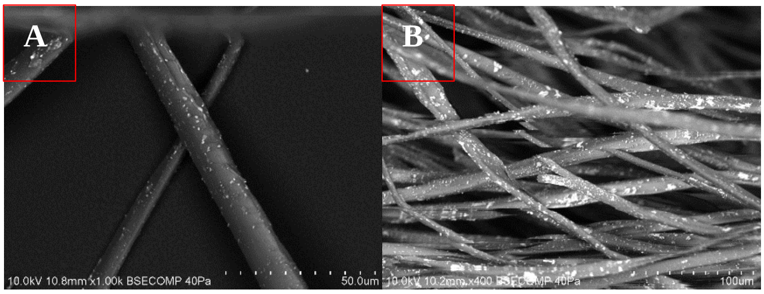


Sample 6

Sample 6M (metal from the metal thread)

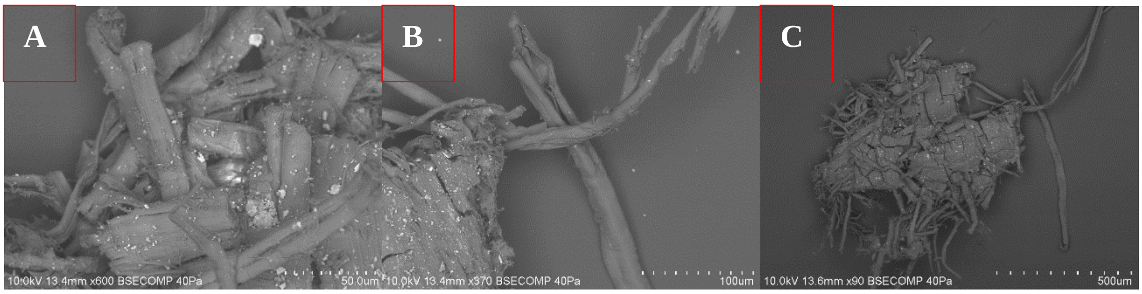


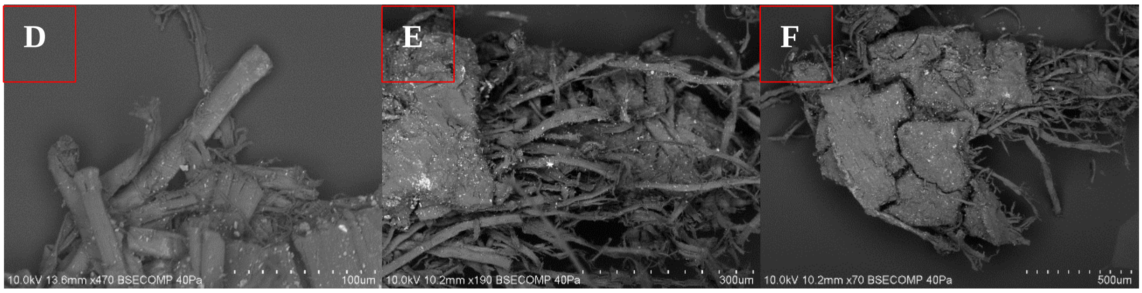
Sample 6MF (fibers from the core of the metal thread)



Sample 7

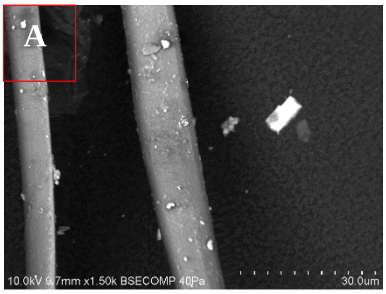
Sample 7P (paper)



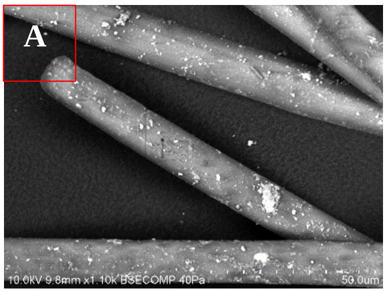


Sample 9

Sample 9 (green fiber)

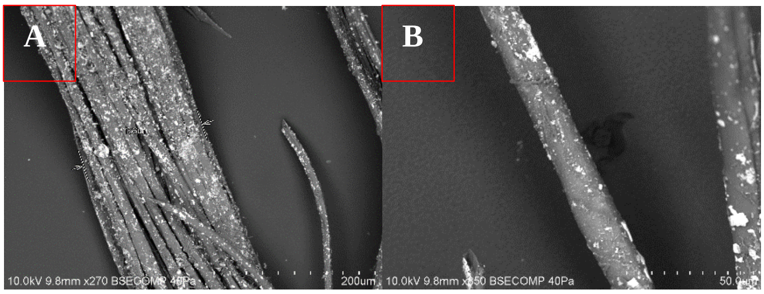


Sample 9 (white fiber)

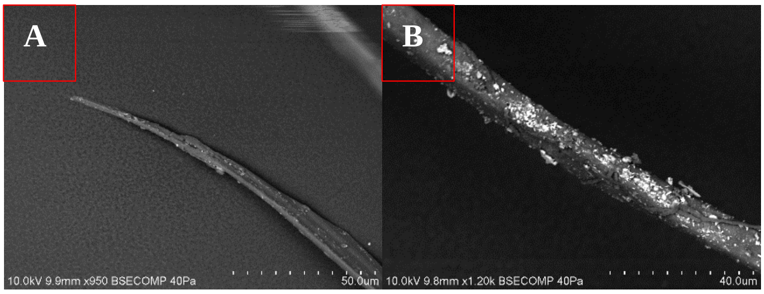


Sample 10

Sample 10A (warp)

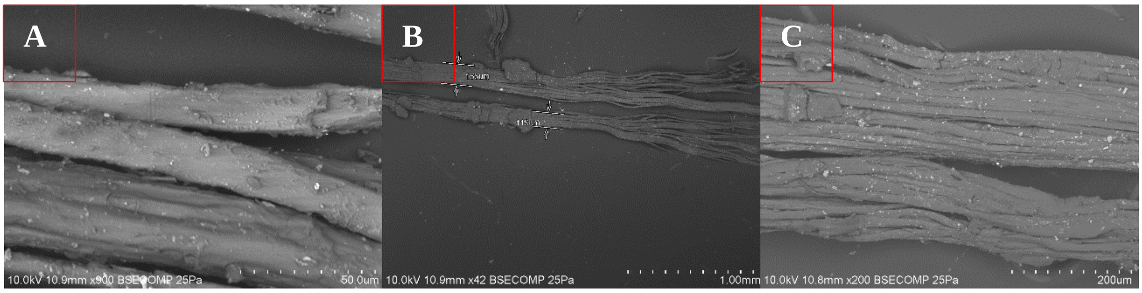


Sample 10H (fiber of sewing thread)

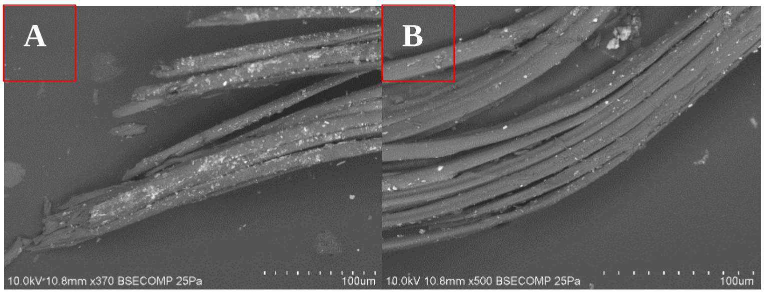


Sample 11

Sample 11A (warp)

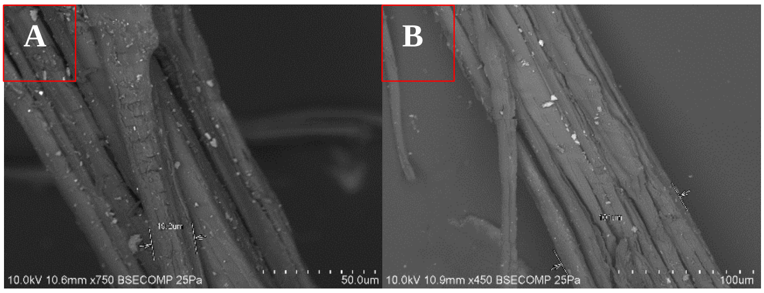


Smple11B (weft)

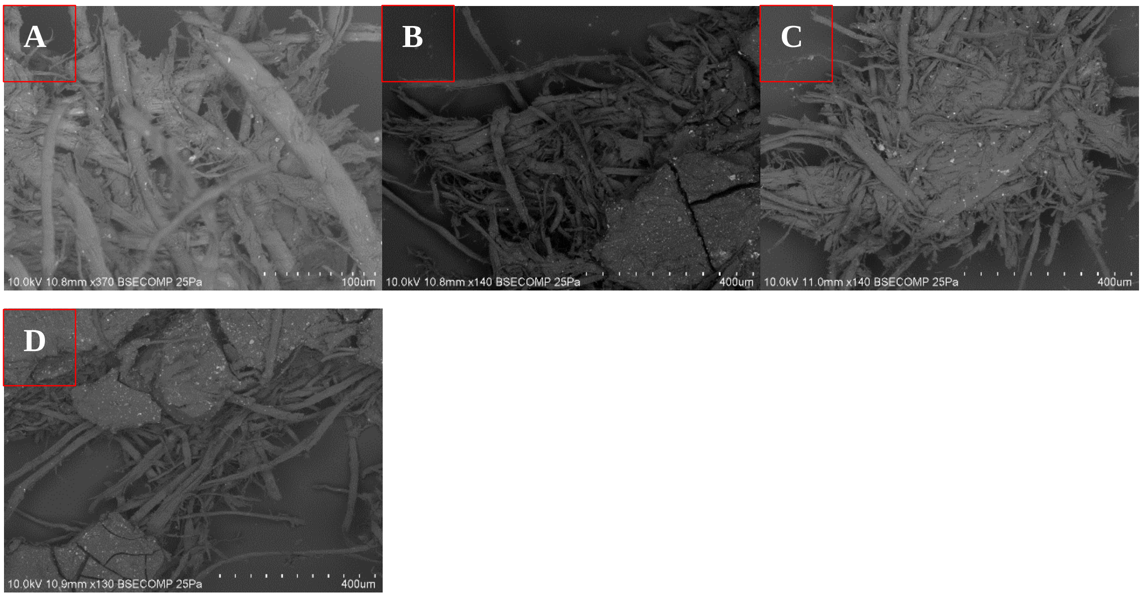


Sample 12

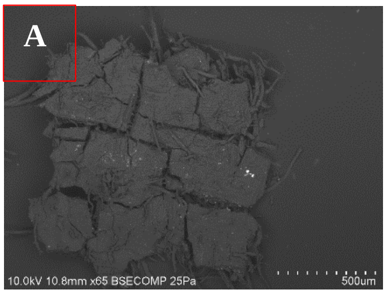
Sample 12F (fiber attached to the paper)



Sample 12P (detail of the paper)

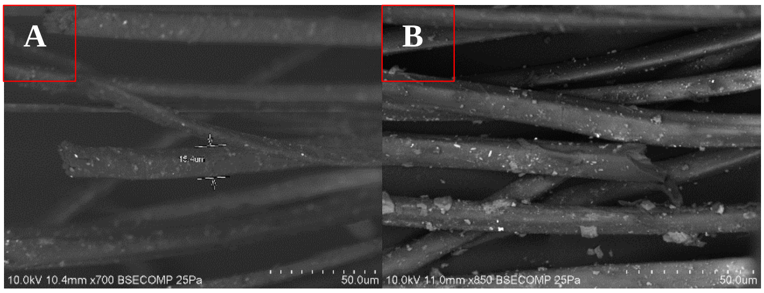


Sample 12G (detail of the adhesive over the paper)



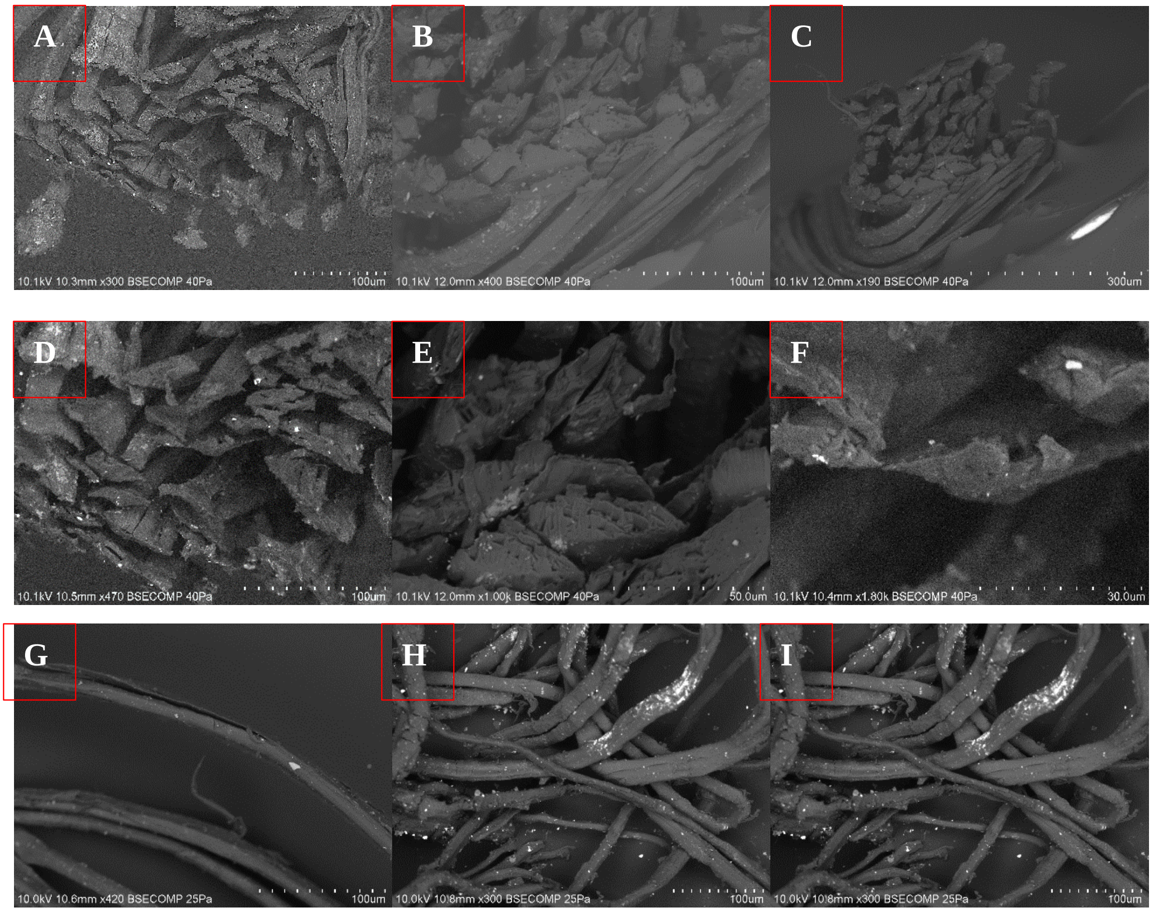
Sample 13

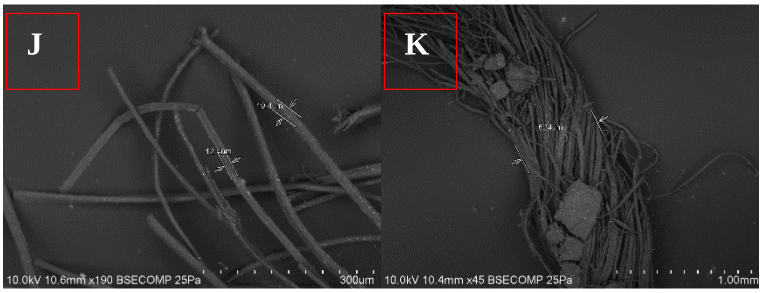
Sample 13H (fibers of sewing thread)



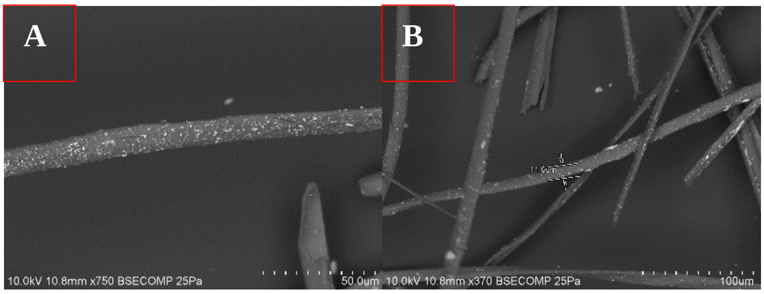
Sample 15

Sample 15CF (fibers from the coarse textile 1 layer)

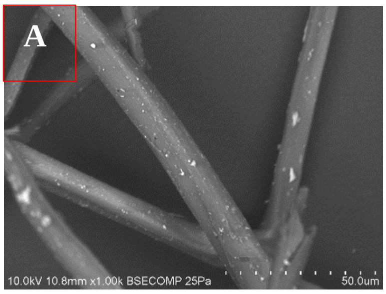




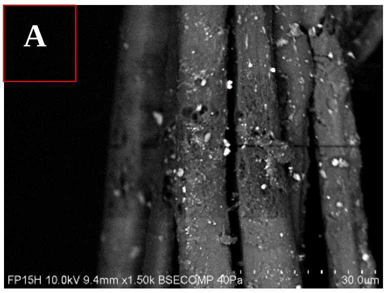
Sample 15MF (fiber from the core of the metal thread)



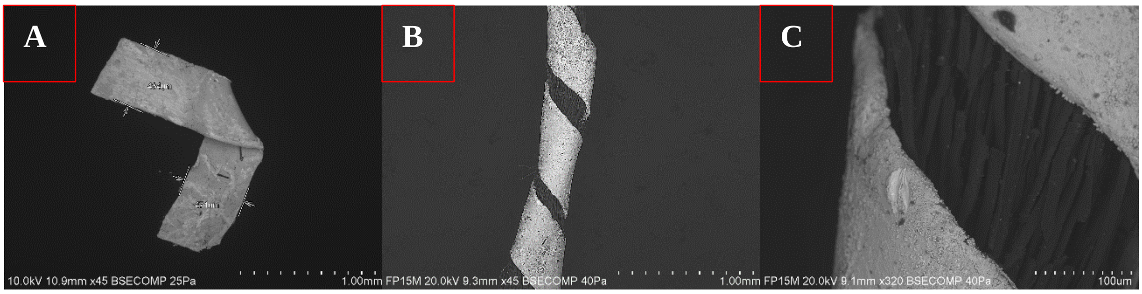
Sample 15SF (fibers from the soft fabric 2 layer)

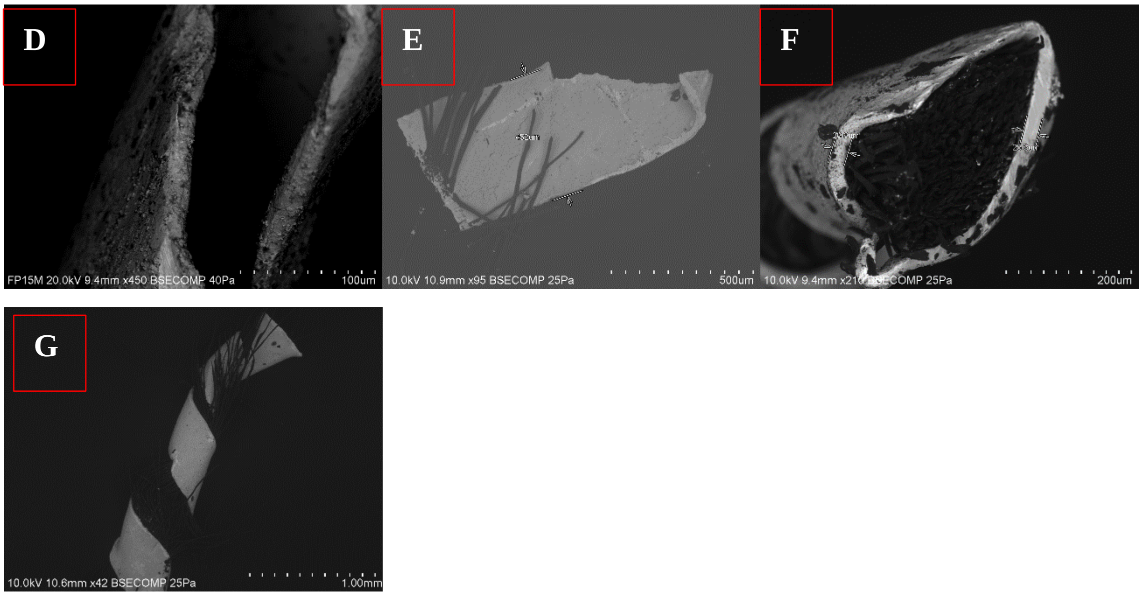


Sample 15H (fibers from sewing thread)



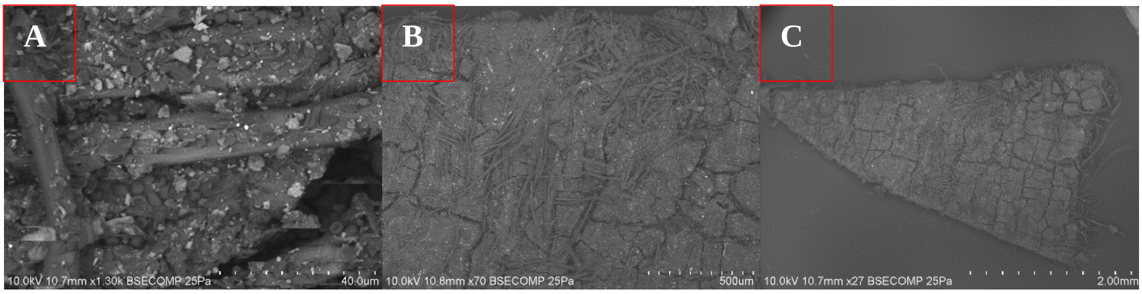
Sample 15M (metal from the metal thread)





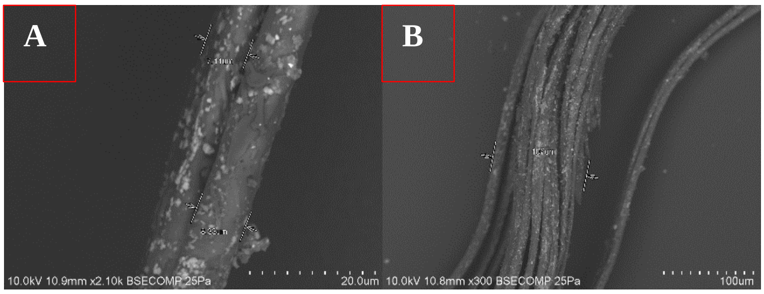
Sample 16

Sample 16P (detail of paper)

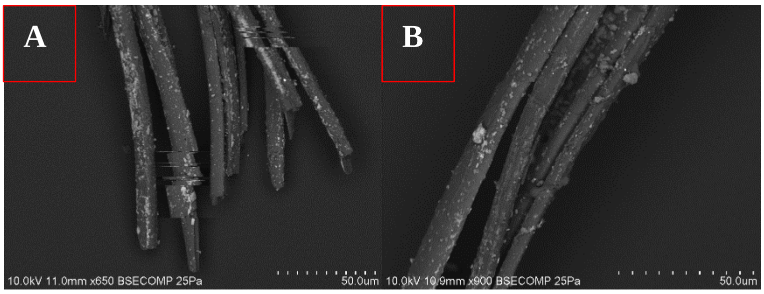


Sample 17

Sample 17A(warp)

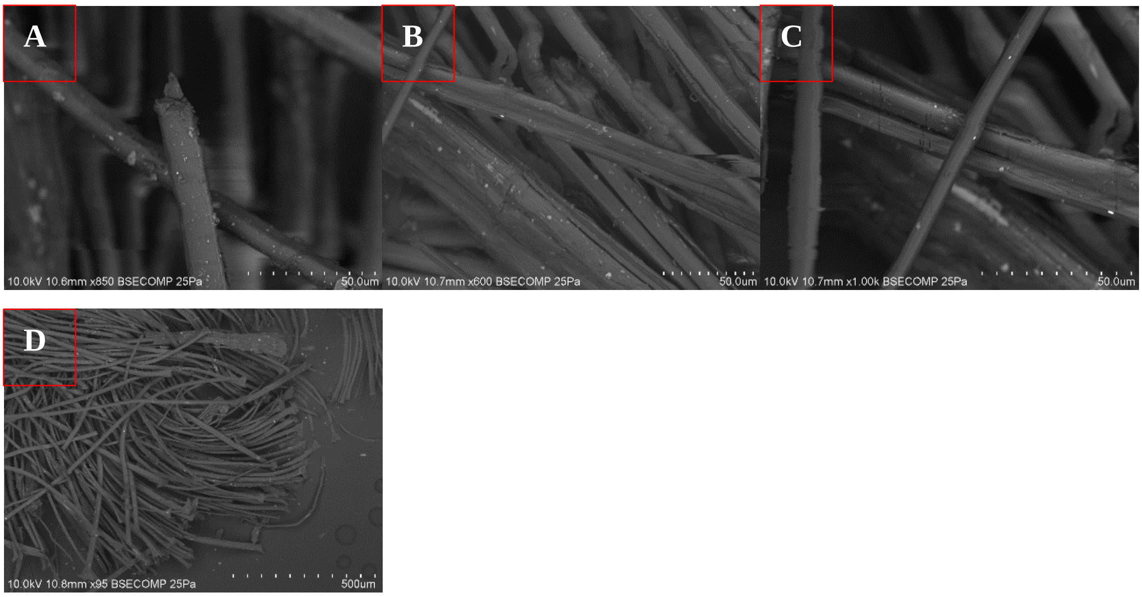


Sample 17B (weft)

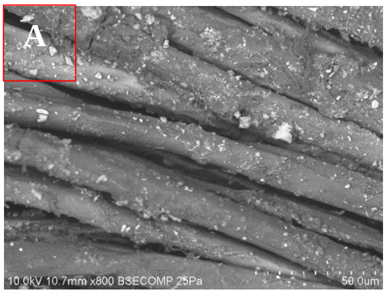


Sample18

Sample 18H (fiber from sewing thread)

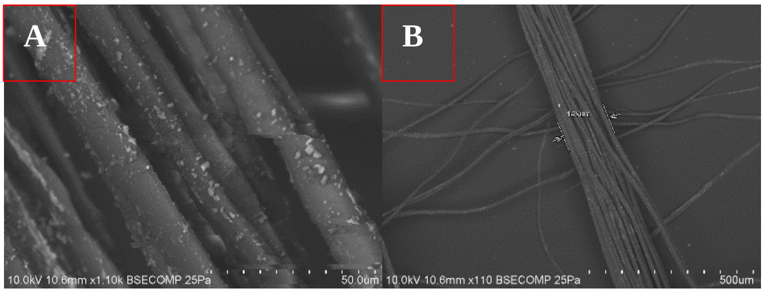


Sample 19

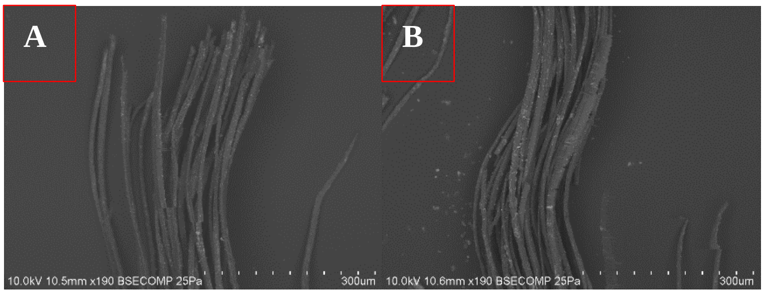


Sample 22

Sample 22A (warp)

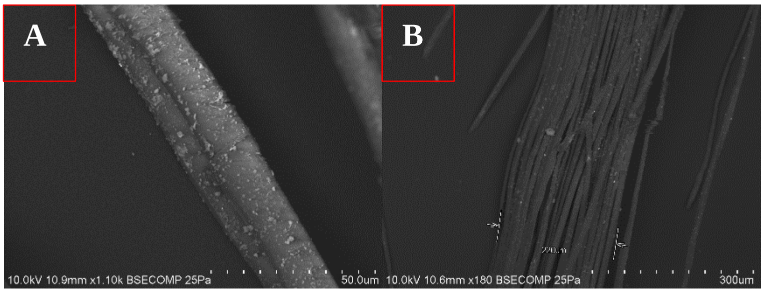


Sample 22B (weft)

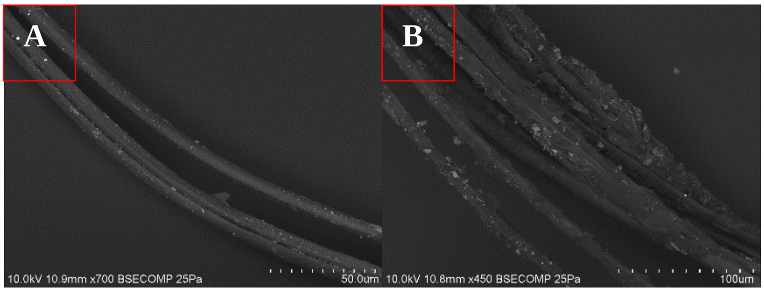


Sample 23

Sample 23A (warp)

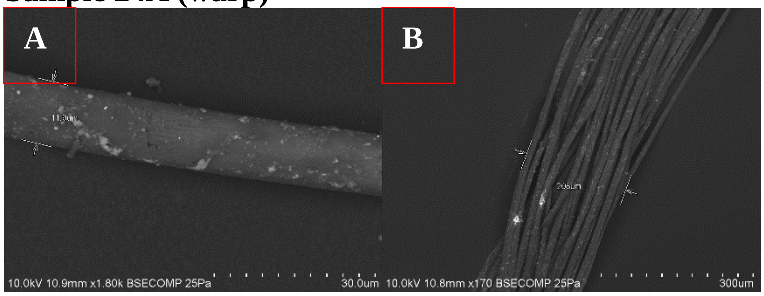


Sample 23B (weft)

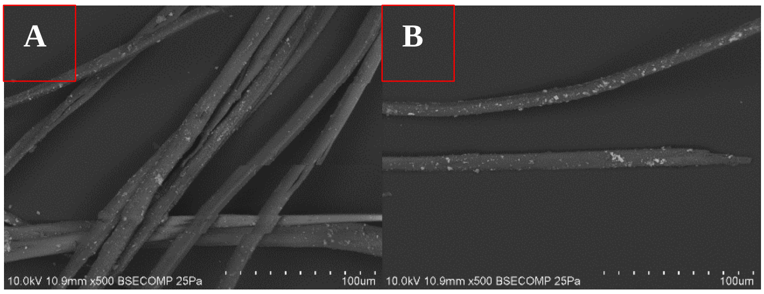


Sample 24

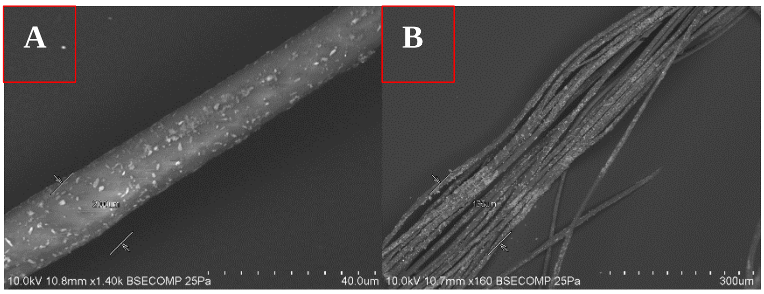
Sample 24A (warp)



Sample 24B (weft)

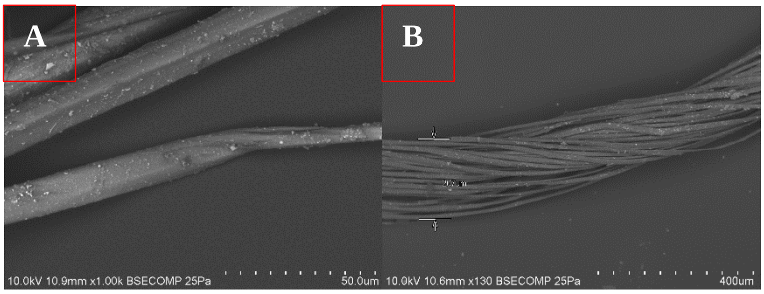


Sample 24H (fibers from sewing thread)

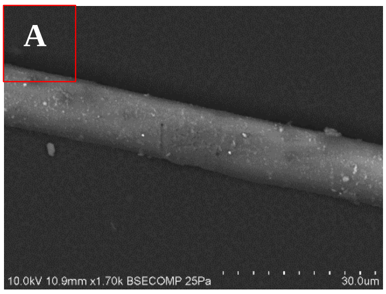


Sample 25

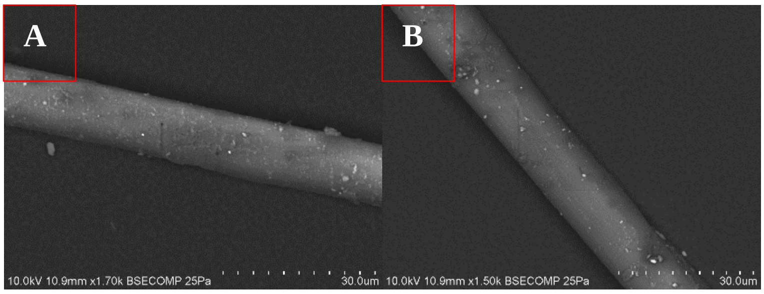
Sample 25GD (fibers with dark green color)



Sample 25GL (fibers with light green color)



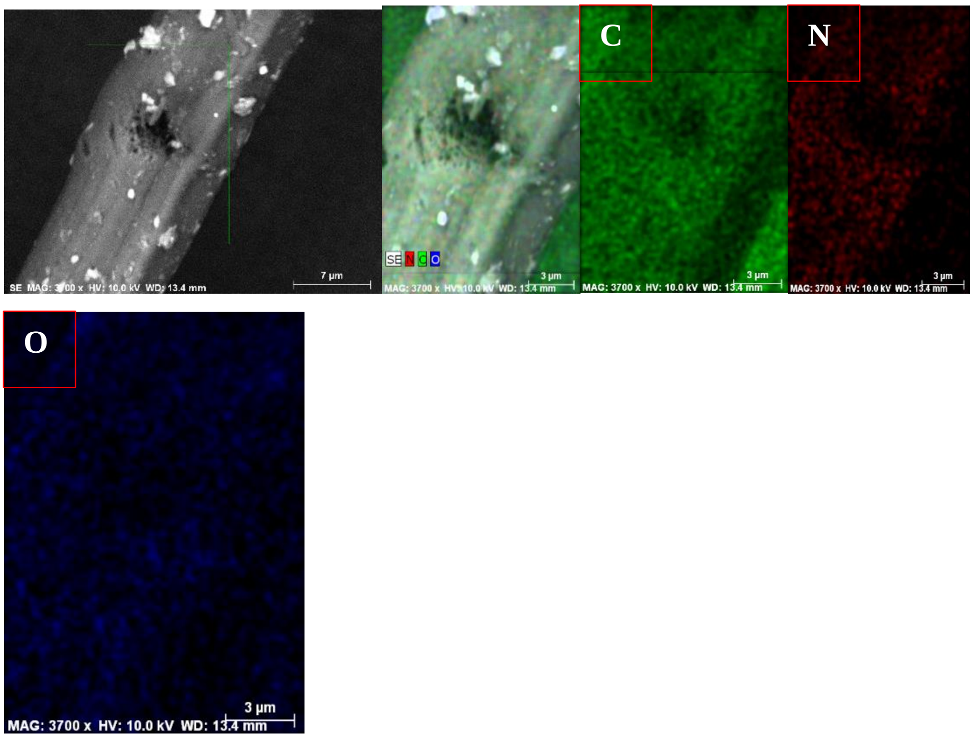
Sample 25W (fibers without color)



Appendix 3 EDS

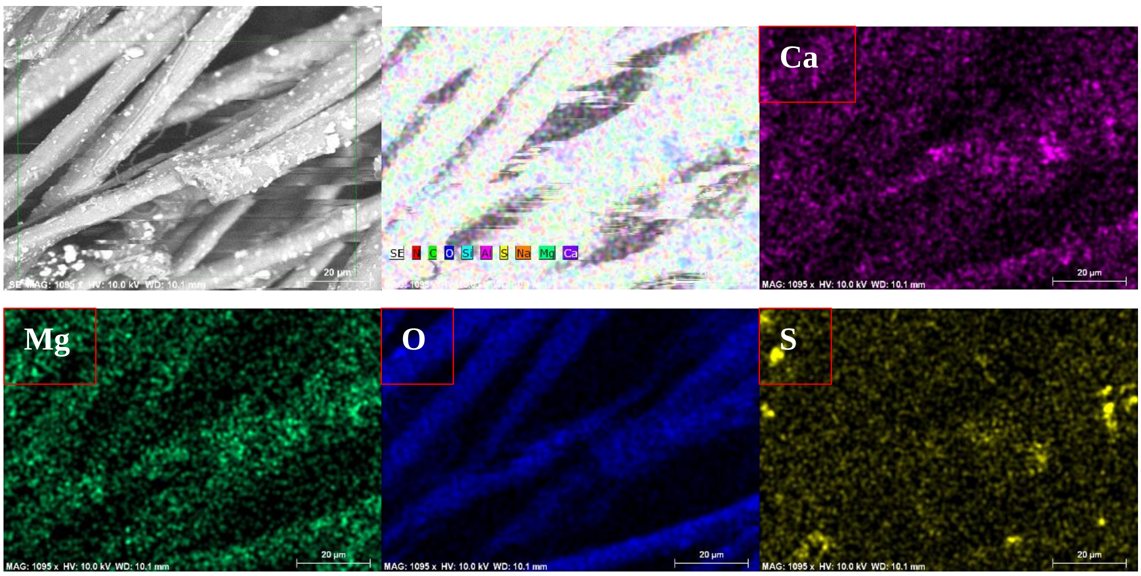
With aims to offer a better understanding to the readers about the results gained on this research, next are presented a more complete data obtained by the EDS analysis from the different components isolated of each sample from the Francisco Pizarro's Banner of Arms. Mapping and EDS spectra of the different areas of interest are shown.

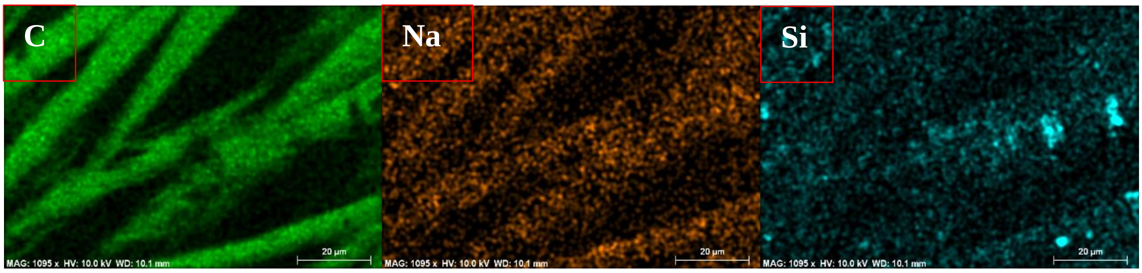
Sample 1



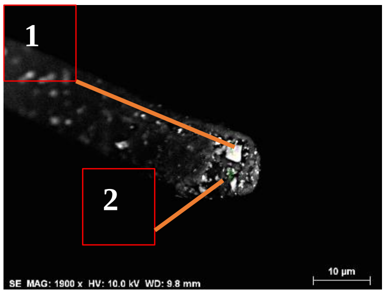
Sample 2

Sample 2A (warp)



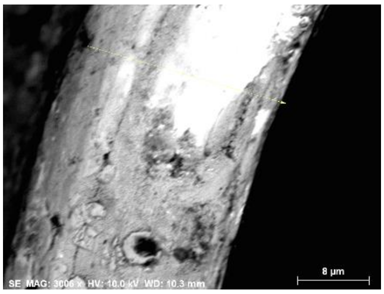


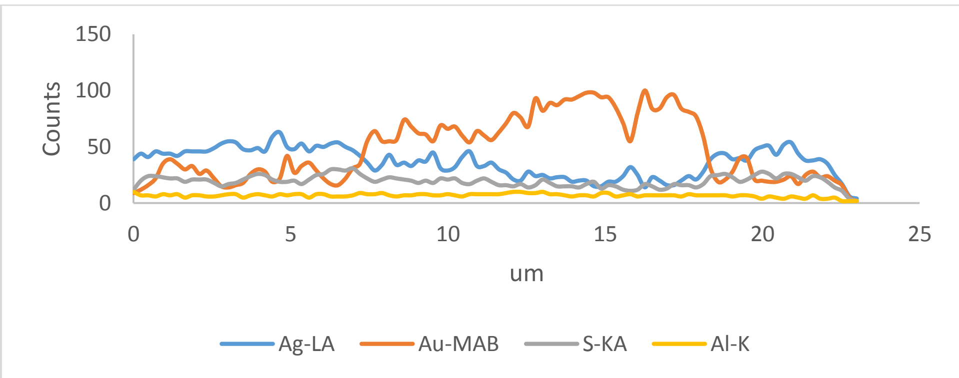
Sample 2B (weft)

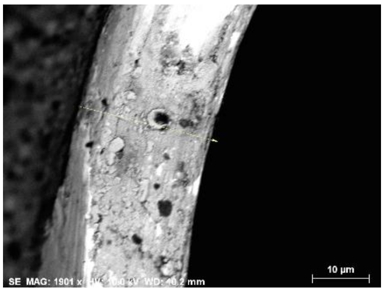


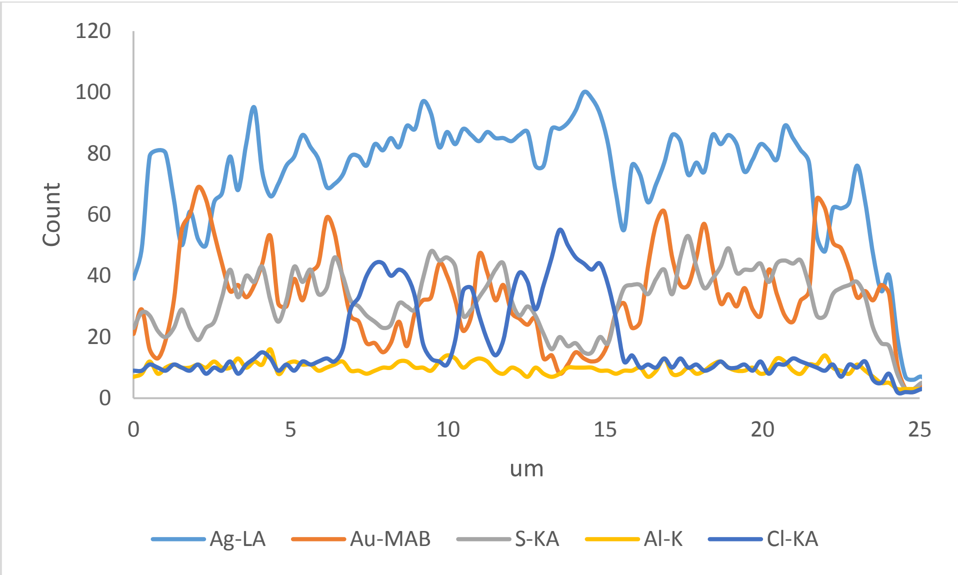
Mass percent (%)										
Spectrum	C	O	Na	Mg	Al	Si	K	Ca	Fe	Tl
1	22.37	44.47	-	2.43	6.65	10.93	1.1	1.03	11.02	-
2	66.9	26.83	0.48	-	1.18	2.32	0.63	1.03	-	0.63
Mean value:	44.64	35.65	0.48	2.43	3.91	6.63	0.86	1.03	11.02	0.63
Sigma:	31.49	12.47	0	0	3.87	6.09	0.33	0	0	0
Sigma mean:	22.26	8.82	0	0	2.73	4.31	0.23	0	0	0

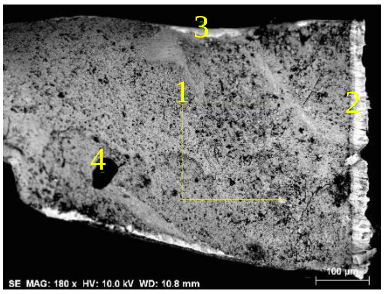
Sample 2M (metal)

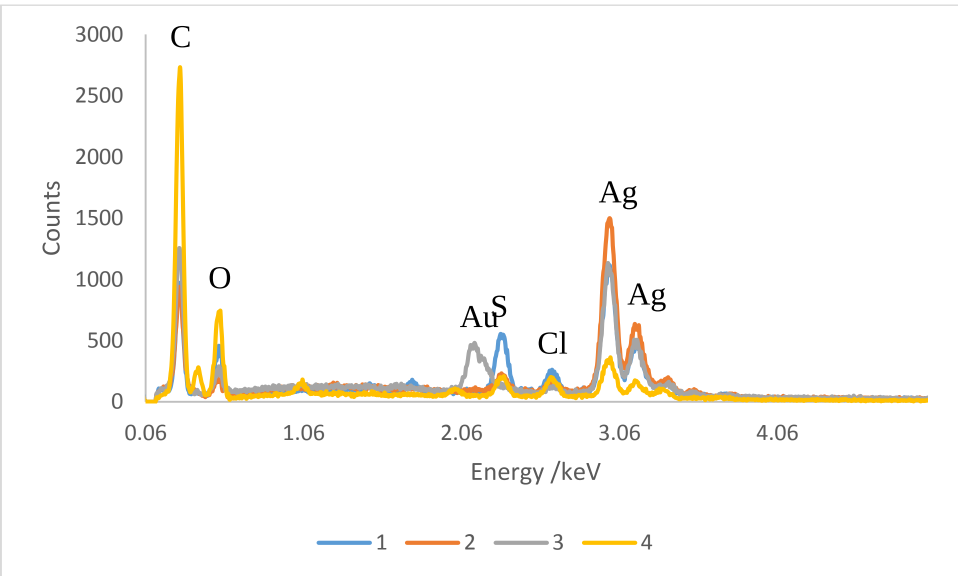





10 µm

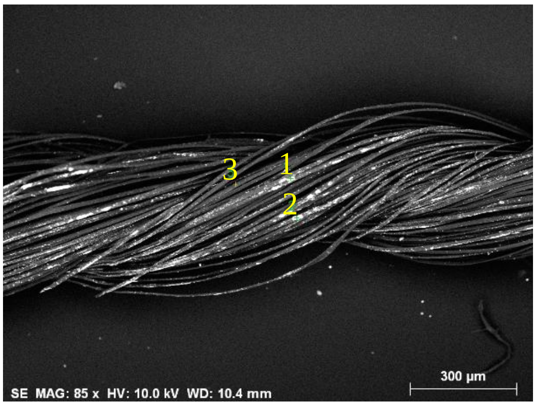

120
100
80
60
40
20
0
Count
0
5
10
15
20
25
um
Ag-LA
Au-MAB
S-KA
Al-K
Cl-KA

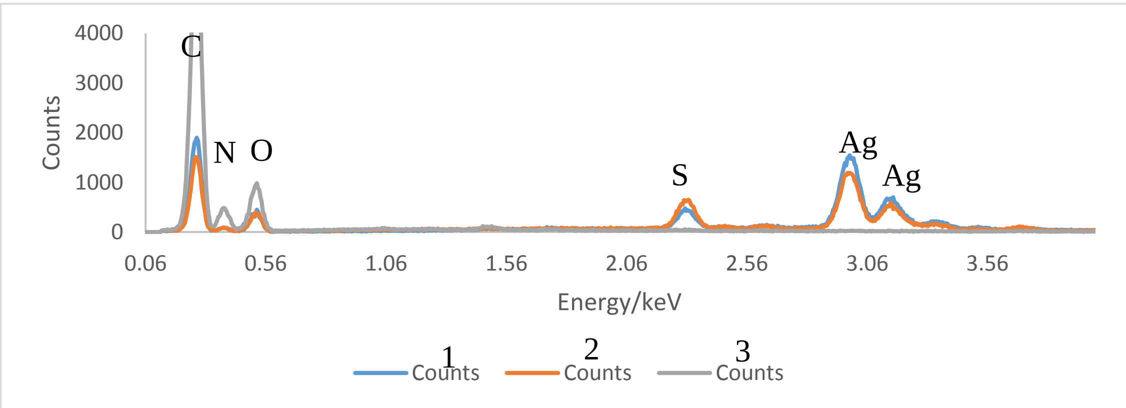

3
1
2
4
SE MAG: 180 x HV: 10.0 kV WD: 10.8 mm
100 µm


3000
2500
2000
1500
1000
500
0
Counts
C
O
Au
S
Cl
Ag
Ag
0.06
1.06
2.06
3.06
4.06
Energy /keV
1
2
3
4

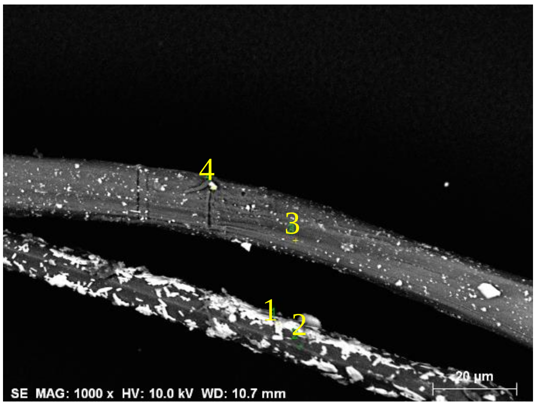
Spectrum	C	N	O	Na	Mg	Al	Si	P	S	Cl	Ag	Au
1						0.76	1.48		10.26	3.31	84.20	
2					0.66				2.30		97.04	
3											79.21	20.79
4	38.38	10.24	18.97	1.25		0.05		0.84	2.95	3.32	24.01	
Mean value:	38.38	10.24	18.97	1.25	0.66	0.40	1.48	0.84	5.17	3.31	71.12	20.79
Sigma:	0.00	0.00	0.00	0.00	0.00	0.50	0.00	0.00	4.42	0.00	32.29	0.00
Sigma mean:	0.00	0.00	0.00	0.00	0.00	0.25	0.00	0.00	2.21	0.00	16.15	0.00

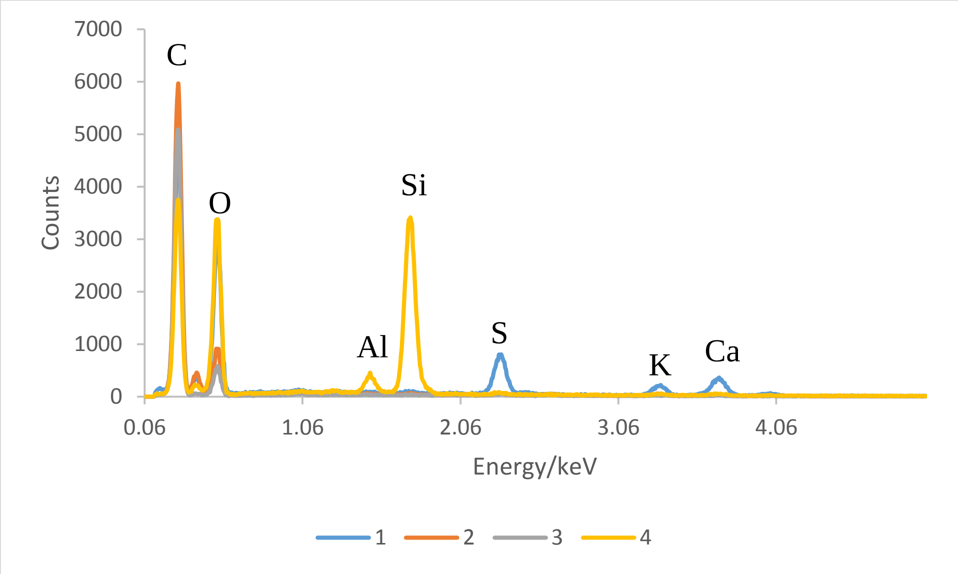
Sample 2MF (fiber form the core of the metal thread)





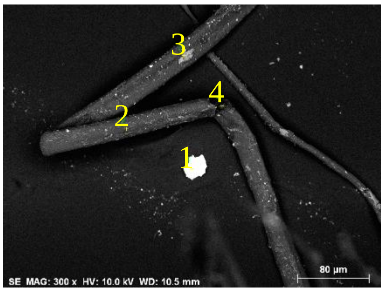
Sample 3

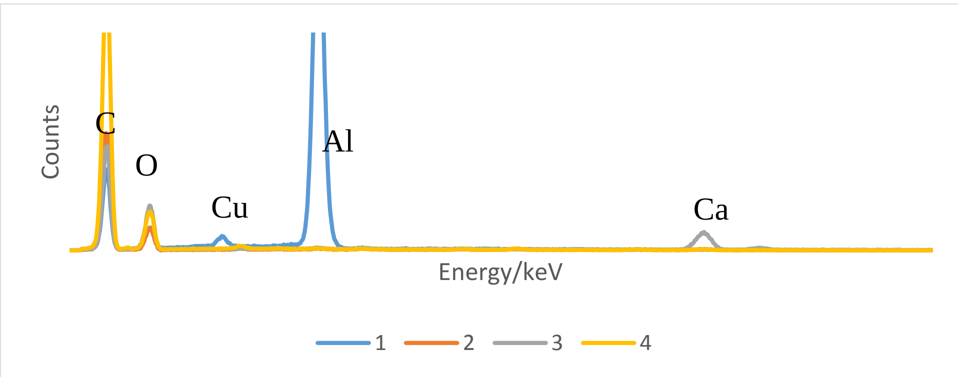




Mass percent (%)								
Spectrum	Na	Mg	Al	Si	S	Cl	K	Ca
1	2.1	1.14	-	1.08	34.3	-	16.64	44.73
2	8.47	7.52	-	6.68	13.6	9.91	24.96	28.86
3	12.85	-	2.74	5.65	28.7	-	19.5	30.6
4	-	0.47	5.55	88.1	1.41	-	1.58	2.88
Mean value:	7.81	3.04	4.14	25.4	19.5	9.91	15.67	26.77
Sigma:	5.4	3.89	1.99	41.9	14.9	0	10.01	17.44
Sigma mean:	2.7	1.95	0.99	21	7.45	0	5	8.72

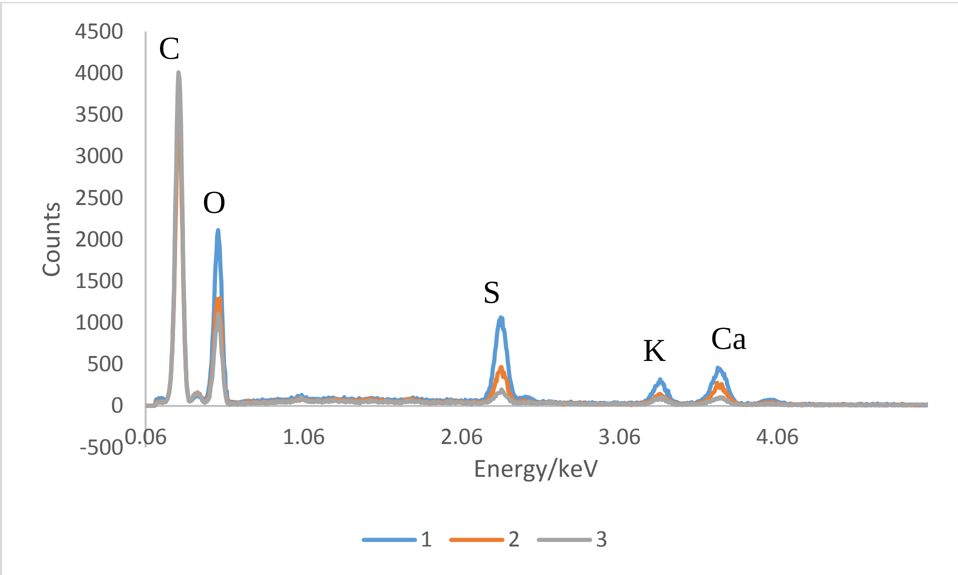
Sample 4





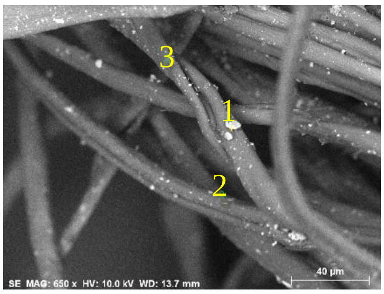
Spectrum	Na	Mg	Al	Si	S	Cl	K	Ca	Cu
1			94.30						5.70
2	7.17	2.37	6.64	10.53	6.65	18.18	14.49	33.97	
3	0.94		1.46	2.16				95.44	
4	25.57		8.45	7.87	6.93	14.68	10.75	25.75	
Mean value:	11.23	2.37	27.71	6.86	6.79	16.43	12.62	51.72	5.70
Sigma:	12.81	0.00	44.49	4.28	0.20	2.48	2.64	38.09	0.00
Sigma mean:	6.40	0.00	22.25	2.14	0.10	1.24	1.32	19.04	0.00

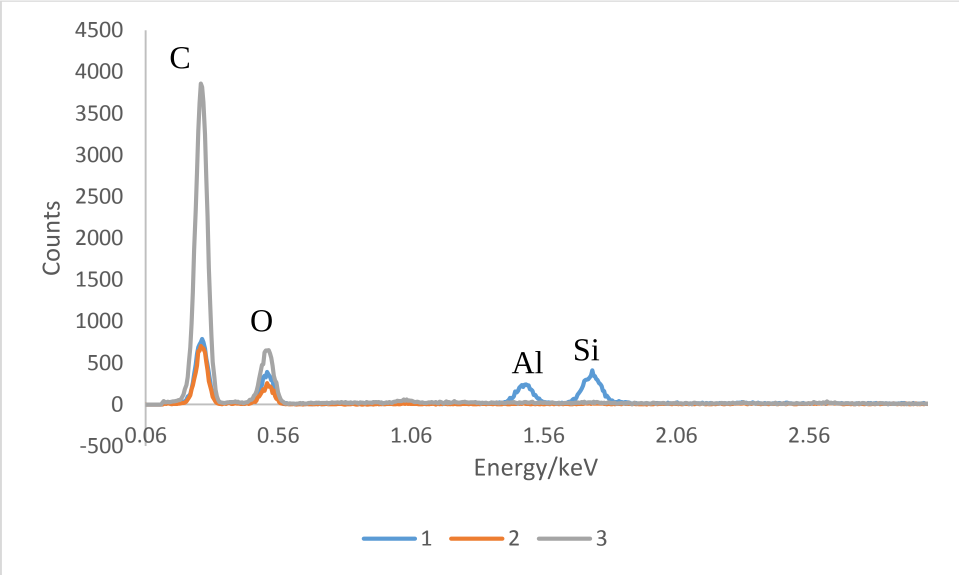
Sample 5B (weft)



Spectrum	Na	Al	Si	S	K	Ca
1	1.14	0.32		34.87	18.28	45.39
2	1.87	1.18	1.68	29.09	15.68	50.49
3	5.18	1.39	2.32	24.01	24.43	42.66
Mean value:	2.73	0.96	2.00	29.32	19.46	46.18
Sigma:	2.15	0.57	0.45	5.43	4.50	3.98
Sigma mean:	1.24	0.33	0.26	3.14	2.60	2.30

Sample 5H (fibers from sewing thread)

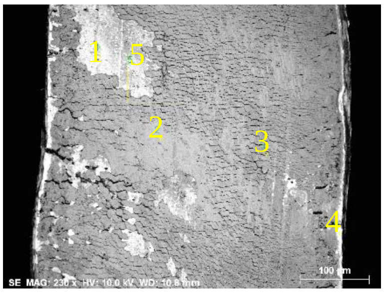


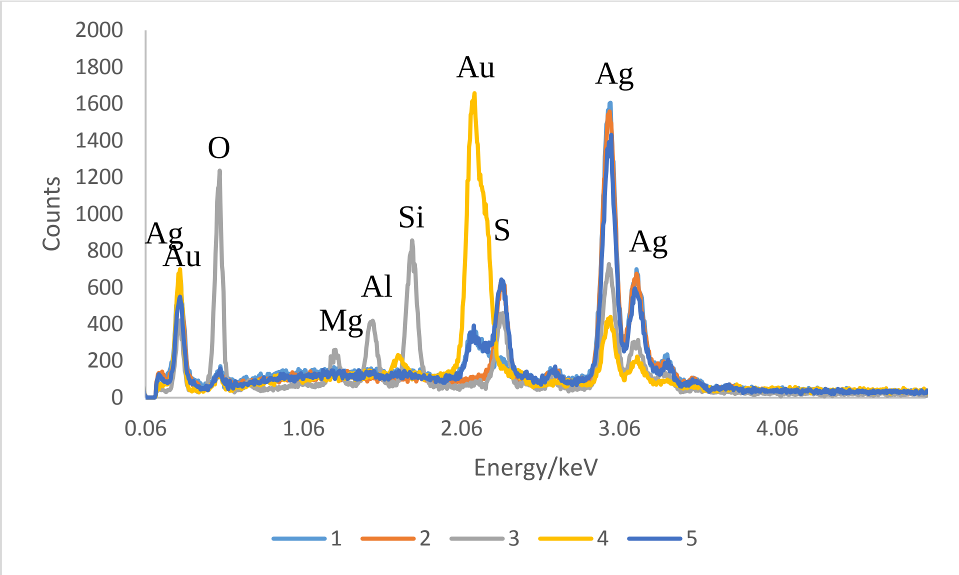


Spectrum	Na	Al	Si	Cl	K	Ca
1	0.00	26.54	73.46			
2	4.34		4.18	15.61	31.60	44.28
3	25.10		8.58	17.52	48.80	
Mean value:	9.81	26.54	28.74	16.57	40.20	44.28
Sigma:	13.42	0.00	38.79	1.35	12.16	0.00
Sigma mean:	7.75	0.00	22.40	0.78	7.02	0.00

Sample 6

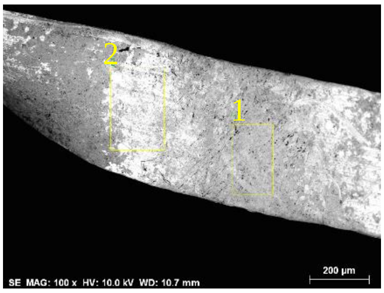
Sample 6M (surface of the metal)



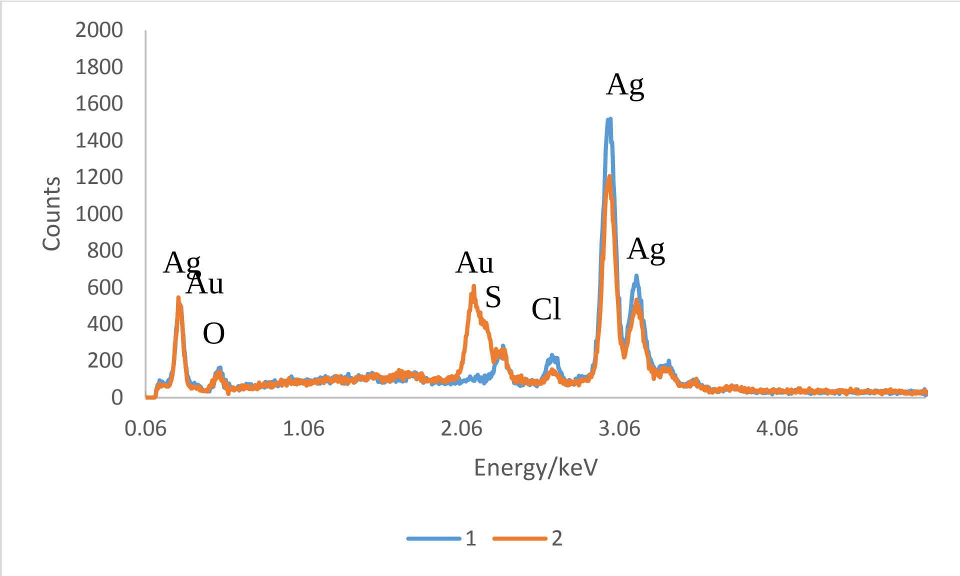


Spectrum	Mg	Al	Si	S	Fe	Ag	Au
1						88.86	11.14
2				8.72		91.28	
3	2.83	5.77	16.88	9.27	6.64	58.61	
4						25.73	74.27
5		0.14		9.01		80.11	10.74
Mean value:	2.83	2.96	16.88	9.00	6.64	68.92	32.05
Sigma:	0.00	3.99	0.00	0.27	0.00	27.36	36.56
Sigma mean:	0.00	1.78	0.00	0.12	0.00	12.24	16.35

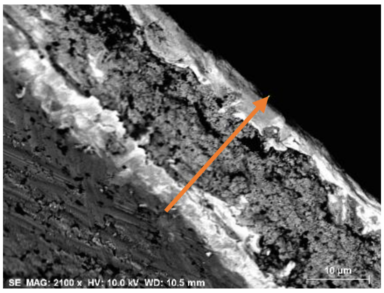
Sample 6M (metal external face)

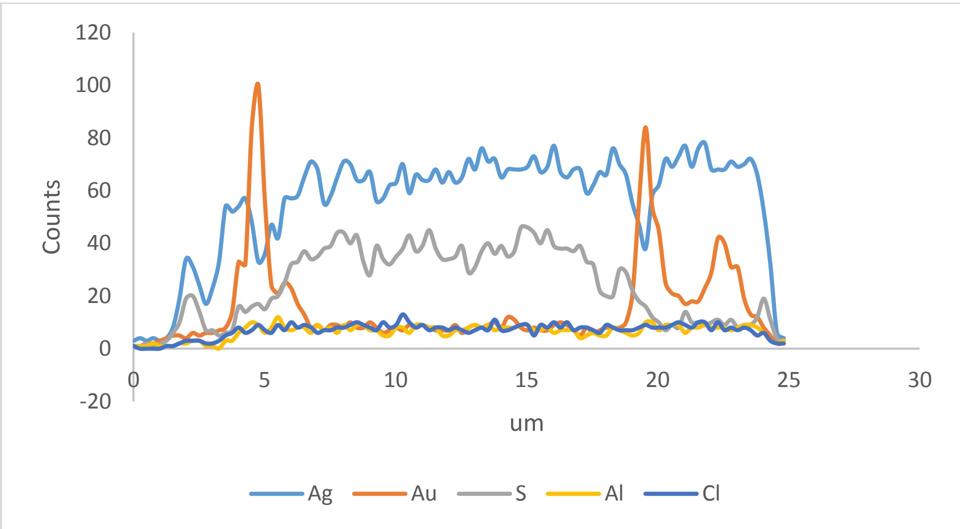


Spectrum	Al	Si	S	Cl	Ag	Au
1	0.31	0.52	2.89	1.41	94.88	
2					76.27	23.73
Mean value:	0.31	0.52	2.89	1.41	85.57	23.73
Sigma:	0.00	0.00	0.00	0.00	13.16	0.00
Sigma mean:	0.00	0.00	0.00	0.00	9.30	0.00

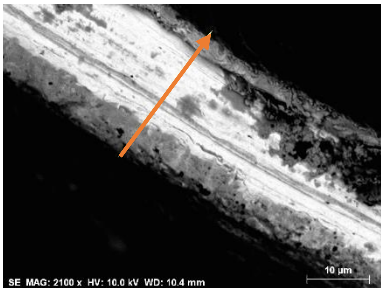


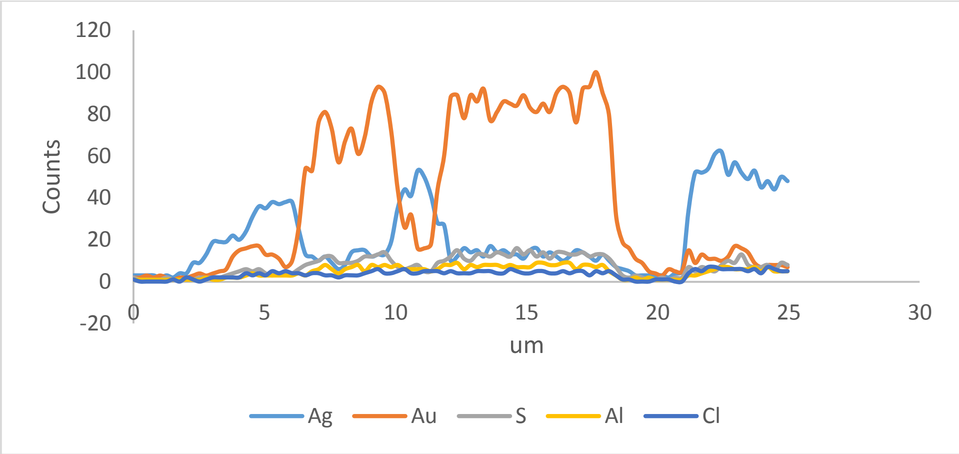
Sample 6M (edge of the metal thread no cleaned)



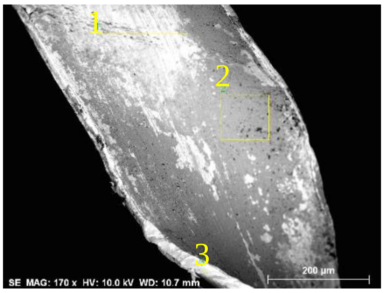


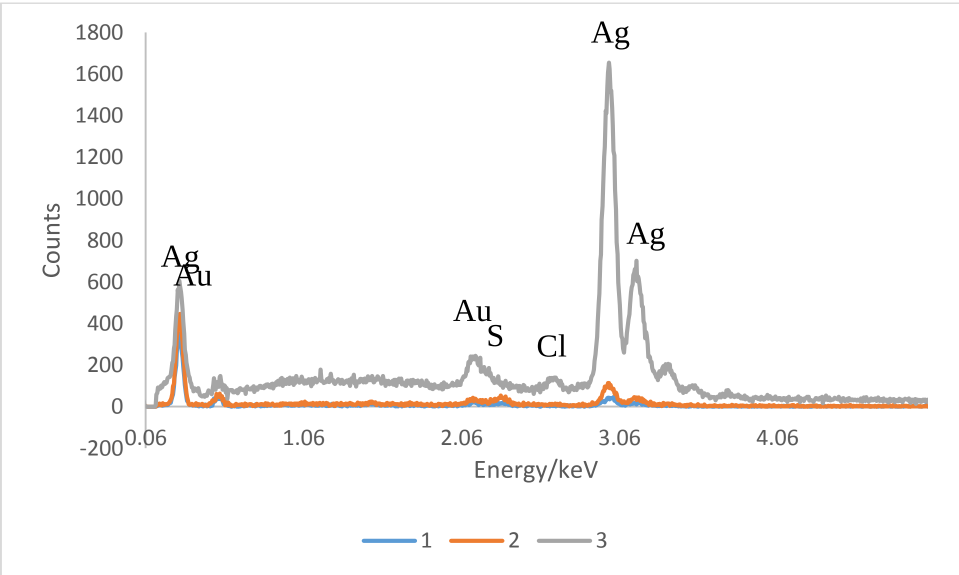
Sample 6M (edge of the metal thread cleaned)



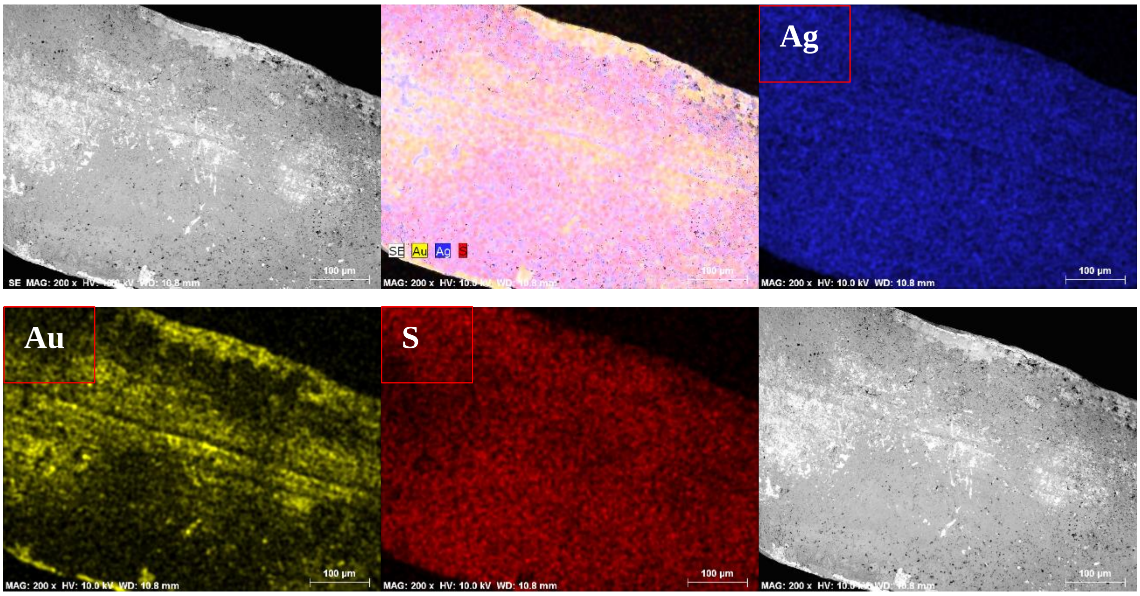


Sample 6M (metal internal face)



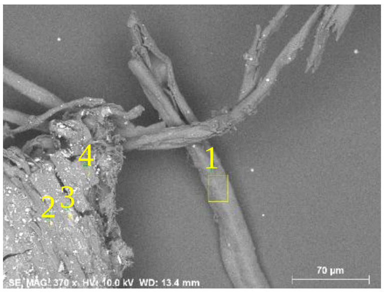


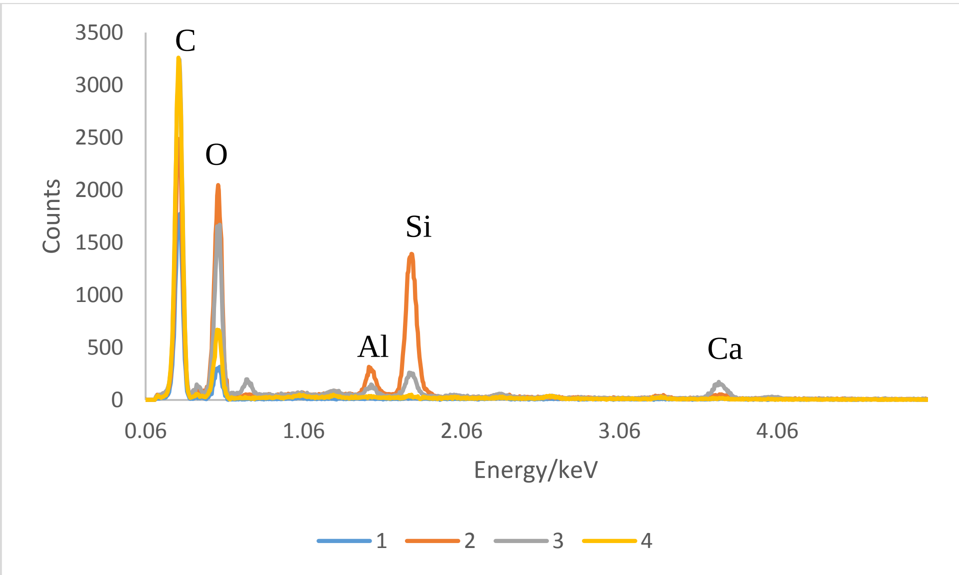
Spectrum	Al	S	Ag	Au
1	2.64	7.21	71.95	18.20
2	2.26	8.70	73.38	15.66
3			93.94	6.06
Mean value:	2.45	7.95	79.75	13.31
Sigma:	0.27	1.05	12.31	6.40
Sigma mean:	0.16	0.61	7.10	3.70



Sample 7

Sample 7F (fibers attached to the paper)

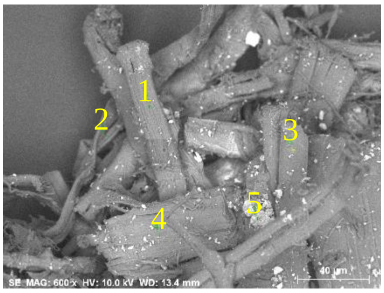


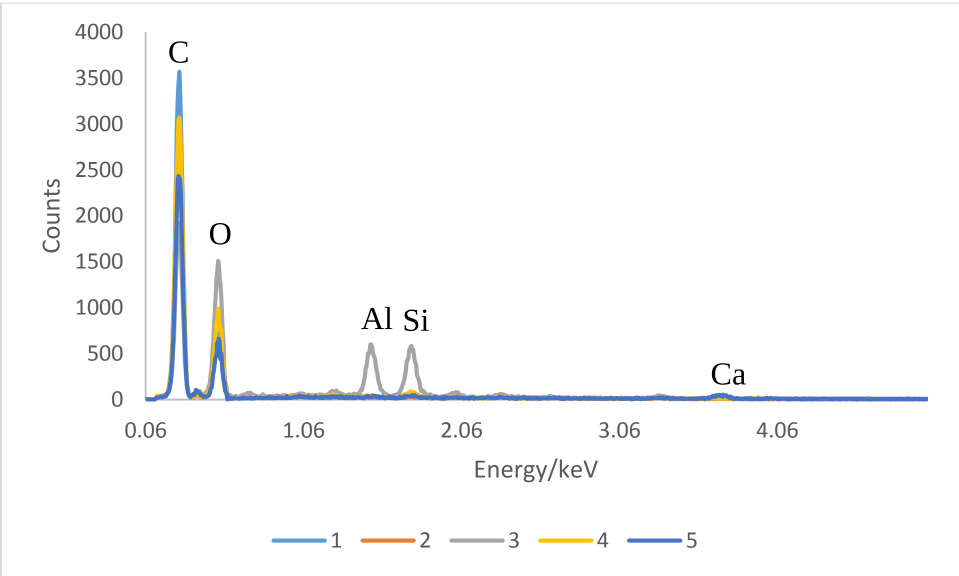


Spectrum	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Tl
1	9.17		0.00	5.36		21.36			44.00	20.11	
2		1.07	9.34	79.39				3.10	7.09		
3		2.48	4.25	13.42	0.86			1.10	25.05	48.76	4.08
4	12.24	9.19		12.35			23.57	22.38	20.27		

Mean value:	10.71	4.25	4.53	27.63	0.86	21.36	23.57	8.86	24.10	34.43	4.08
Sigma:	2.17	4.34	4.68	34.69	0.00	0.00	0.00	11.75	15.28	20.26	0.00
Sigma mean:	1.08	2.17	2.34	17.35	0.00	0.00	0.00	5.88	7.64	10.13	0.00

Sample 7P (fibers from inside of the paper)

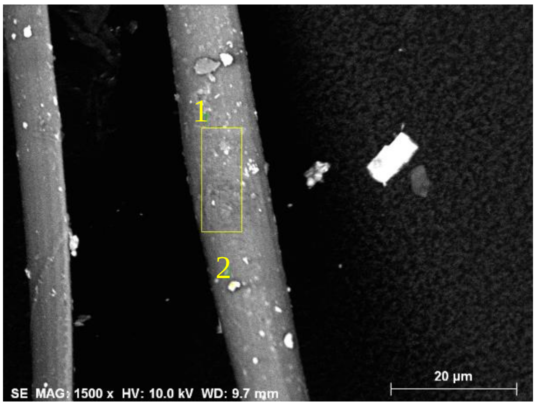


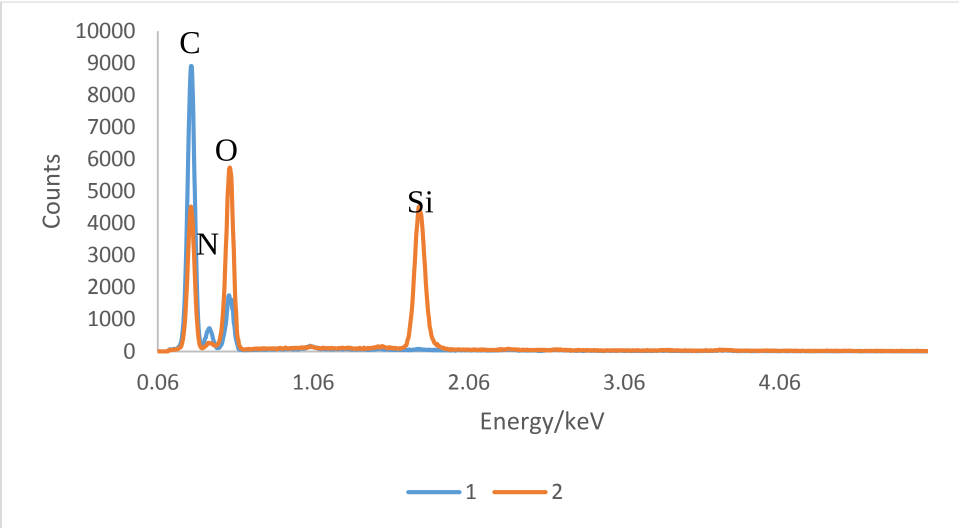


Spectrum	C	N	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe
1				8.50	9.84	5.10	15.74		12.04	18.16	12.96	17.65	
2	65.88	4.52	29.60										
3					2.26	24.42	38.72	3.68			3.68	7.66	13.02
4					12.07	9.13	41.02				17.23	20.55	
5	55.45		37.94	0.15		0.15	0.56				0.84	4.92	
Mean value:	60.66	4.52	33.77	4.33	8.06	9.70	24.01	3.68	12.04	18.16	8.68	12.69	13.02
Sigma:	7.37	0.00	5.90	5.91	5.14	10.48	19.36	0.00	0.00	0.00	7.70	7.57	0.00
Sigma mean:	3.30	0.00	2.64	2.64	2.30	4.69	8.66	0.00	0.00	0.00	3.44	3.39	0.00

Sample 9

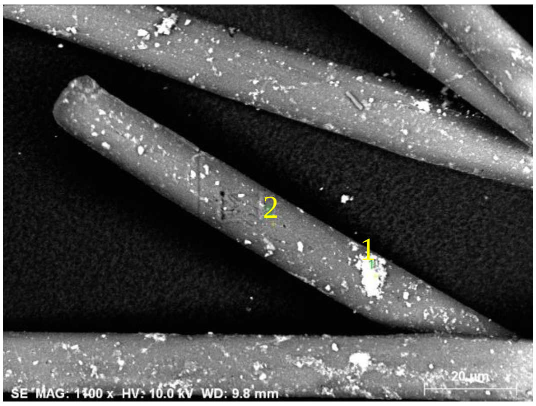
Sample 9 (fiber of green color)

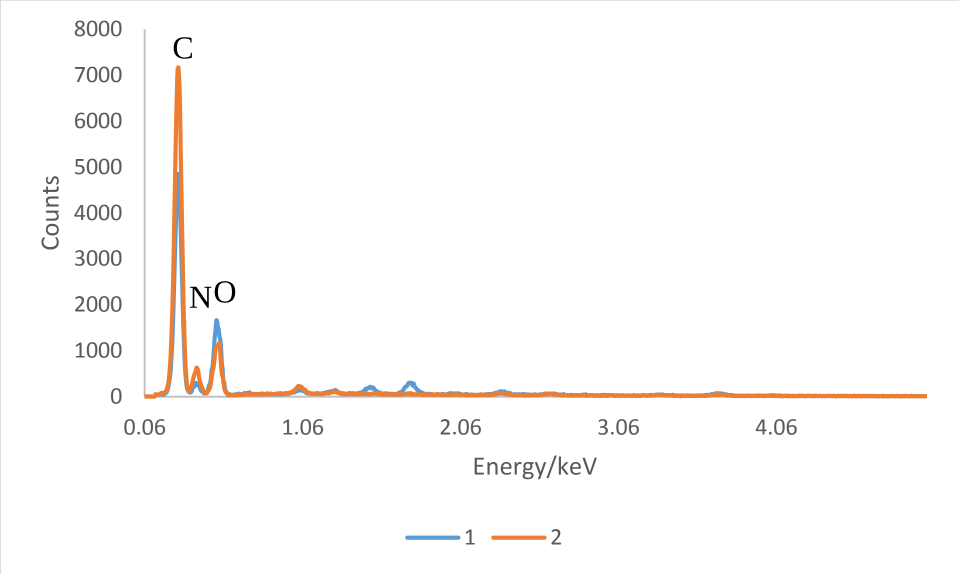




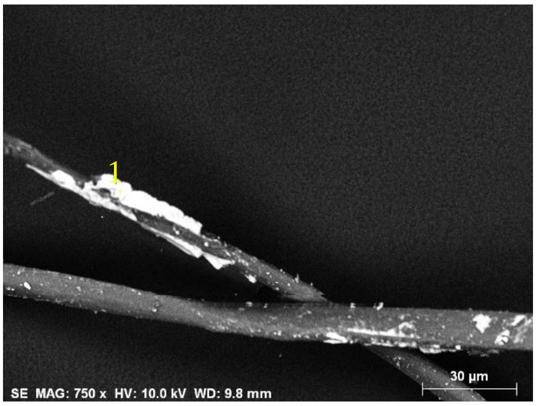
Spectrum	C	Na	Al	Si	S	Cl	Ca
1	97.06	0.95	0.15	0.20	0.28	0.43	0.94
2		0.68		97.65			1.67
Mean value:	97.06	0.81	0.15	48.92	0.28	0.43	1.31
Sigma:	0.00	0.19	0.00	68.91	0.00	0.00	0.52
Sigma mean:	0.00	0.13	0.00	48.73	0.00	0.00	0.36

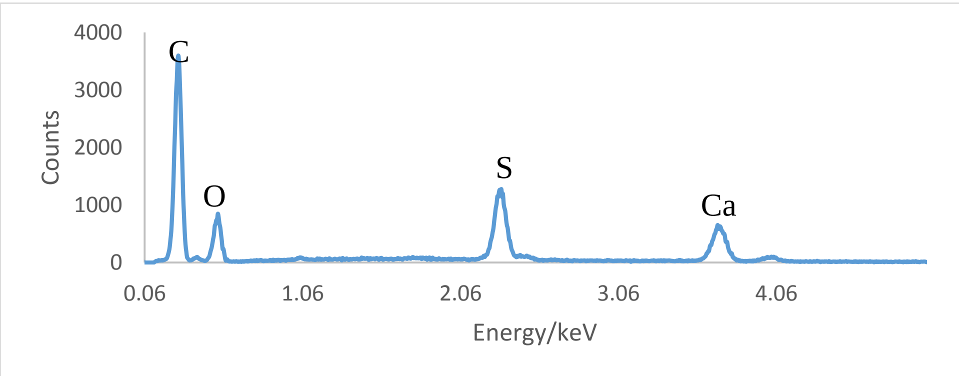
Sample 9 (fiber of white color)



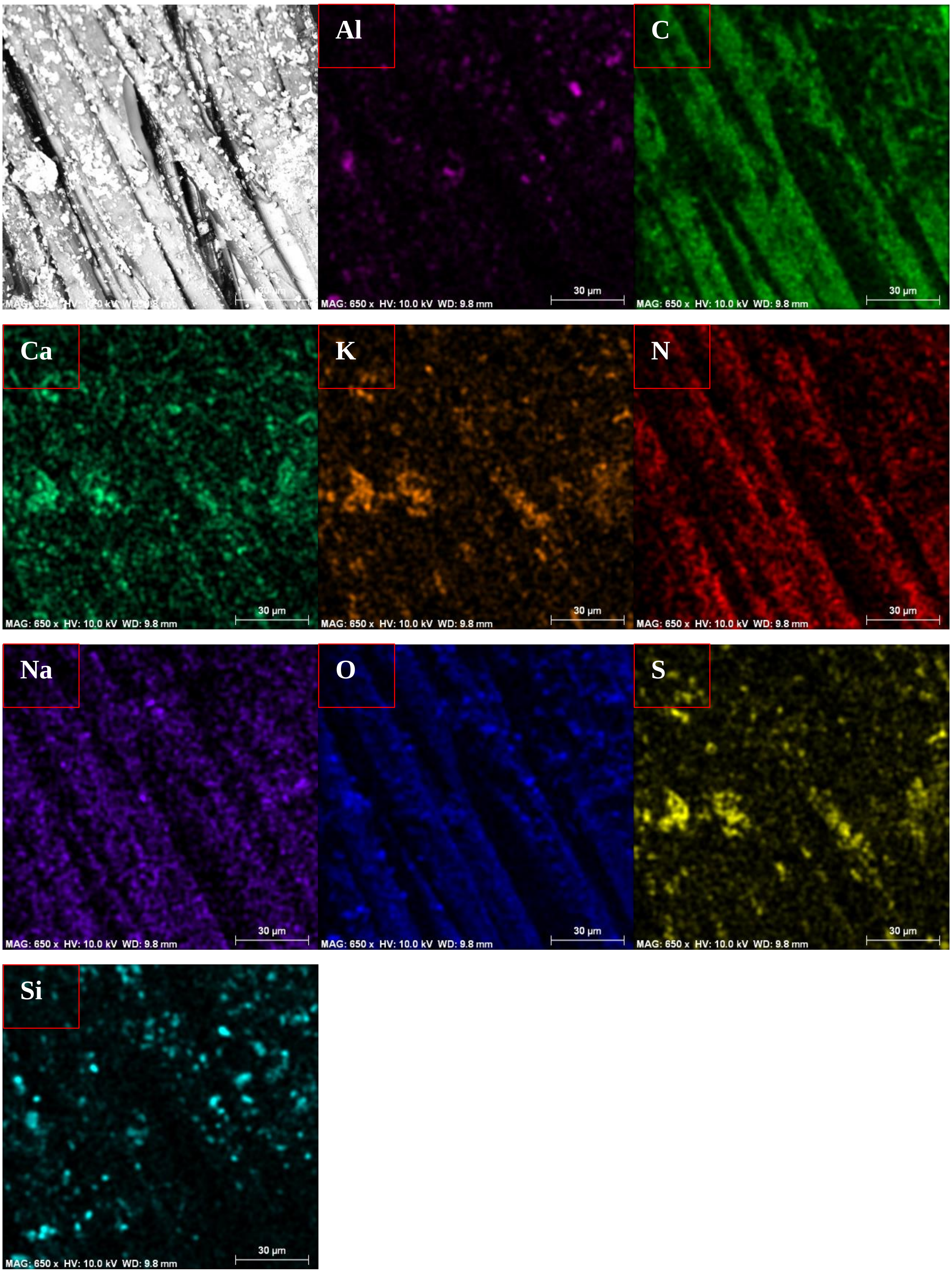


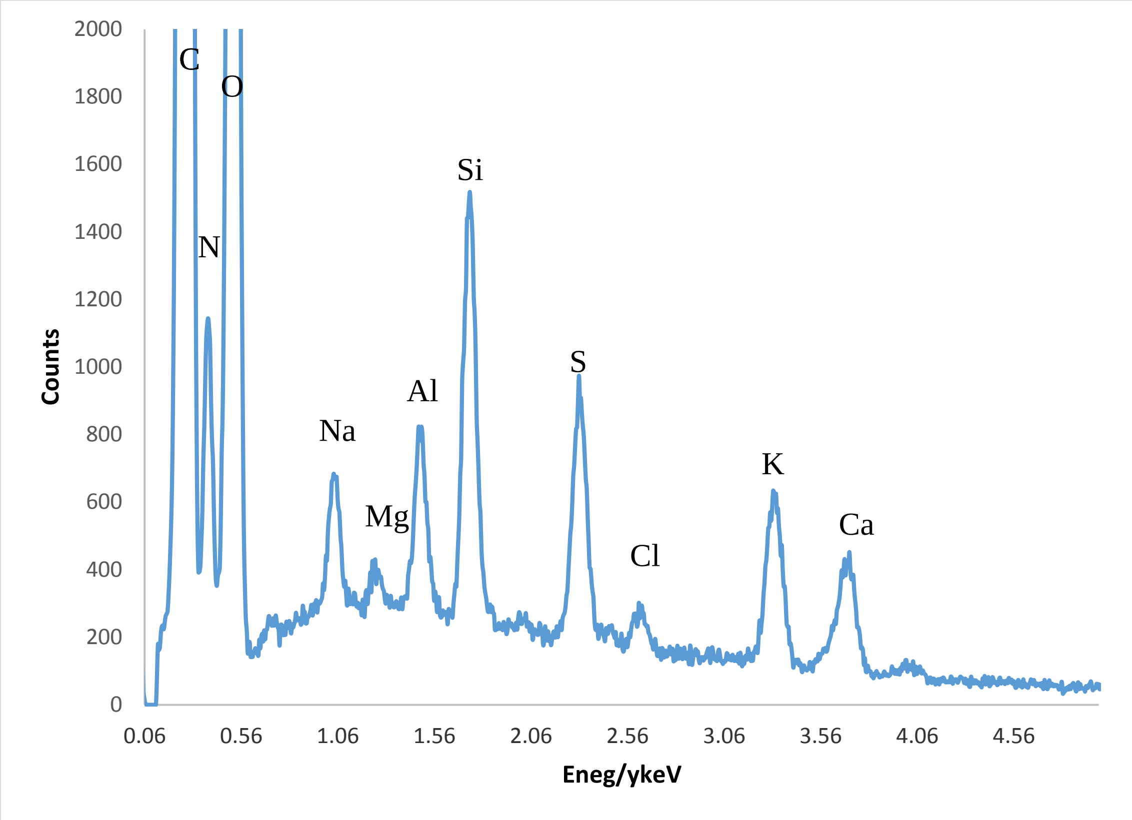
Spectrum	C	N	O	F	Na	Mg	Al	Si	P	S	Cl	K	Ca
1	49.09	6.89	35.50	0.46	0.53	0.26	0.93	2.53	0.00	0.68	0.40	0.38	2.36
2	52.70	16.75	26.88		1.42	0.30				0.33	0.38	0.30	0.95
Mean value:	50.89	11.82	31.19	0.46	0.97	0.28	0.93	2.53	0.00	0.50	0.39	0.34	1.66
Sigma:	2.55	6.97	6.10	0.00	0.63	0.03	0.00	0.00	0.00	0.25	0.02	0.05	0.99
Sigma mean:	1.81	4.93	4.31	0.00	0.44	0.02	0.00	0.00	0.00	0.18	0.01	0.04	0.70





Sample 10

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400
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1.06
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2.06
2.56
3.06
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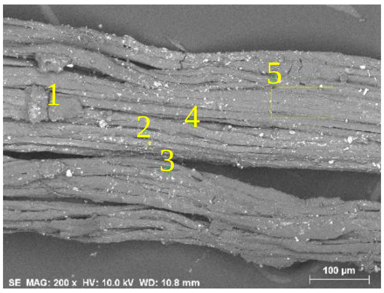
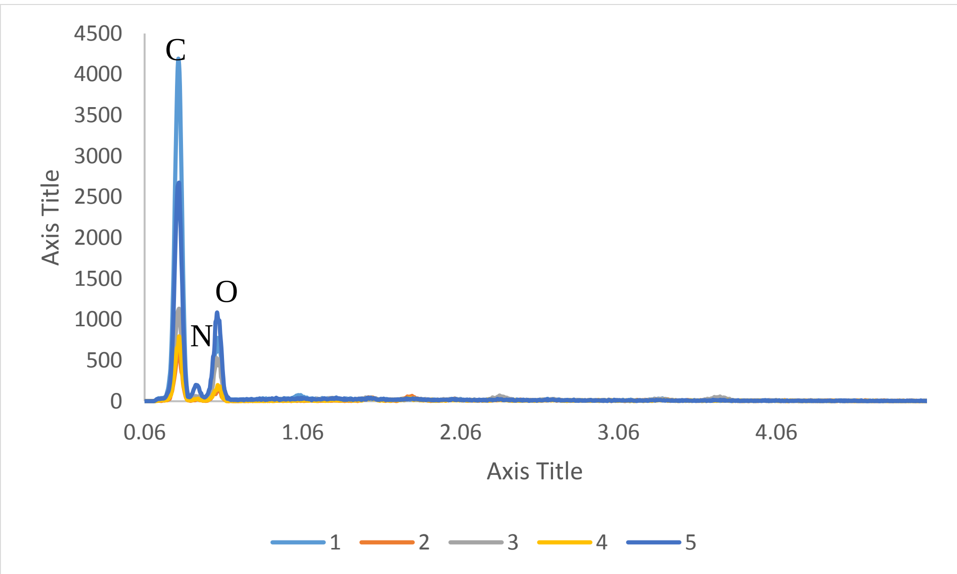
4.56
Eneg/ykeV
C
O
N
Si
S
Al
Na
Mg
K
Ca
Cl

Sample 11


1
2
3
4
5
100 µm
SE MAG: 200 x HV: 10.0 kV WD: 10.8 mm


Axis Title
4500
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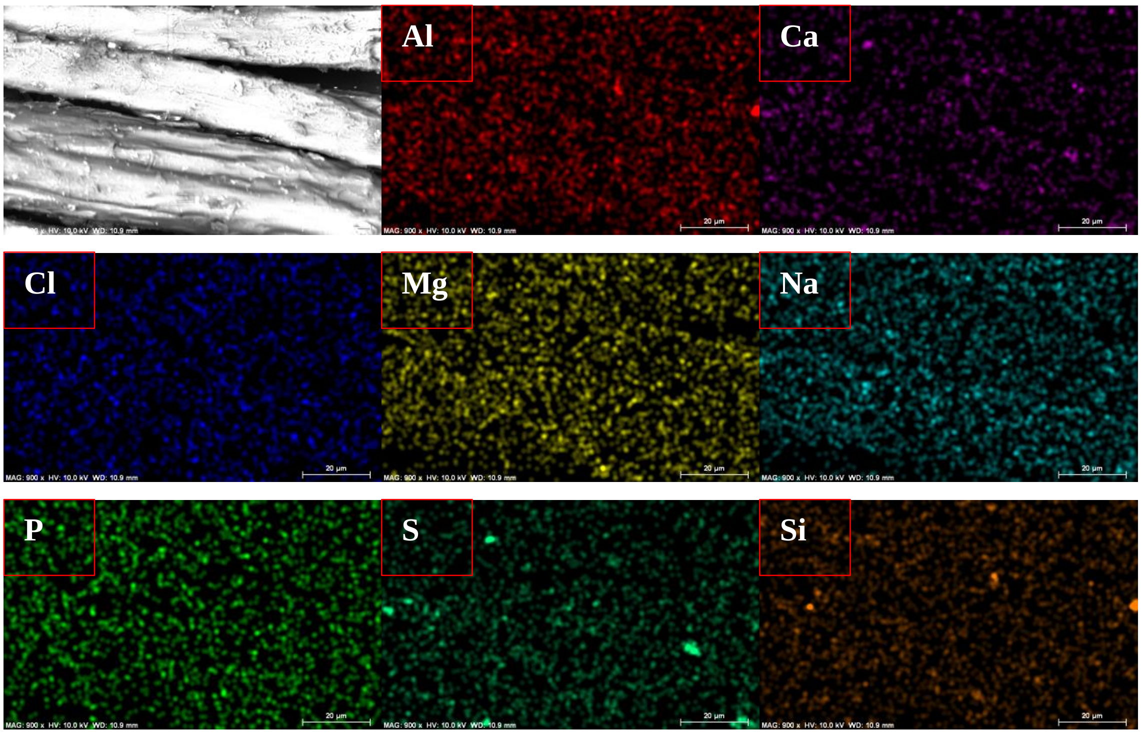
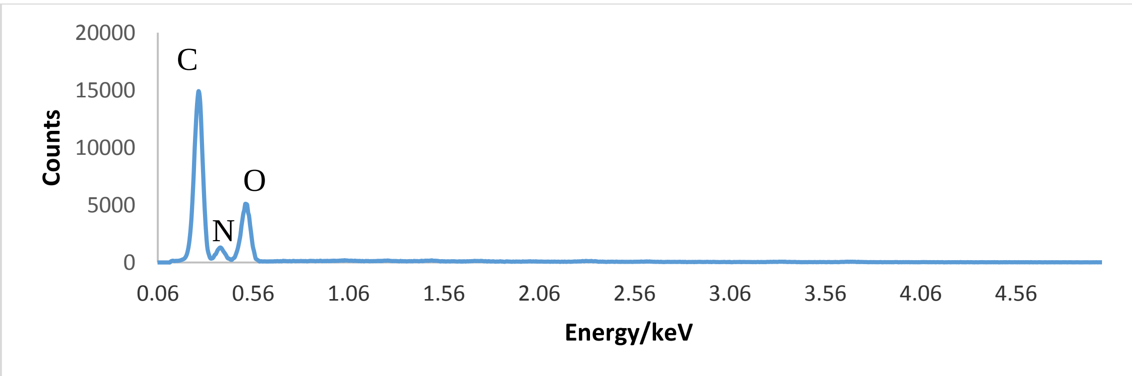
1000
500
0
0.06
1.06
2.06
3.06
4.06
Axis Title
C
N
O
1
2
3
4
5

Appendix 3 EDS

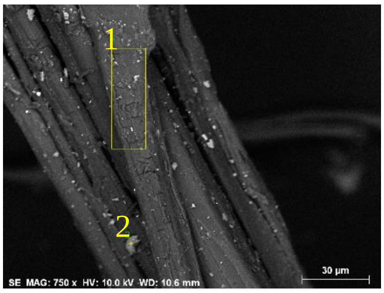
Spectrum	C	N	O	Na	Al	Si	P	S	Cl	K	Ca	Fe	Mo
1	67.11		30.51	0.66	0.07		0.08		0.28	1.06			0.23
2	54.47		25.43		1.69	4.49	0.38			2.87	2.61	8.07	
3	45.17		43.24		0.14			1.59		1.83	8.03		
4	60.88	8.48	27.87		0.79	1.42		0.57					
5	45.79	10.52	42.99		0.20	0.20				0.30			
Mean value:	54.68	9.50	34.01	0.66	0.58	2.03	0.23	1.08	0.28	1.52	5.32	8.07	0.23
Sigma:	9.52	1.45	8.51	0.00	0.69	2.21	0.21	0.72	0.00	1.09	3.84	0.00	0.00
Sigma mean:	4.26	0.65	3.80	0.00	0.31	0.99	0.09	0.32	0.00	0.49	1.72	0.00	0.00

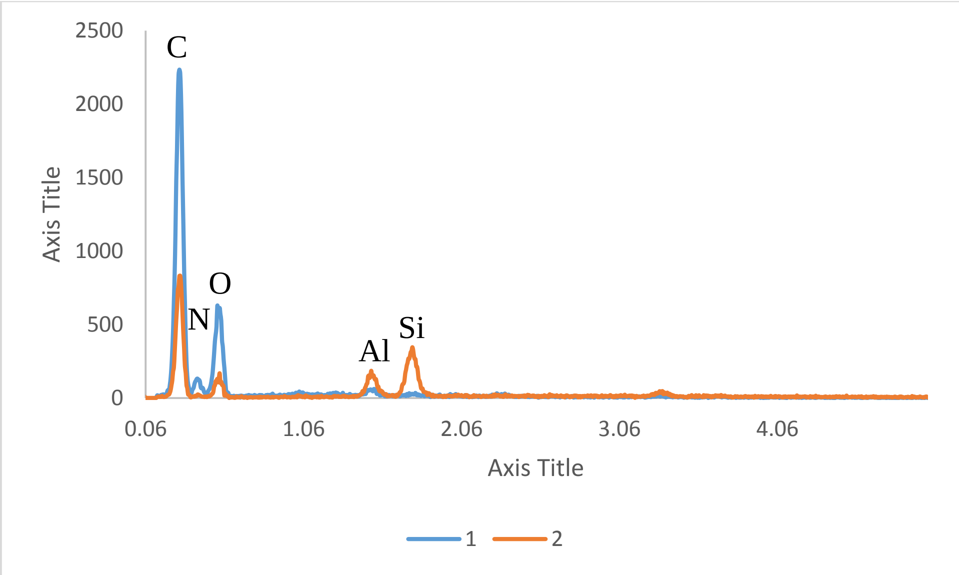




Sample 12

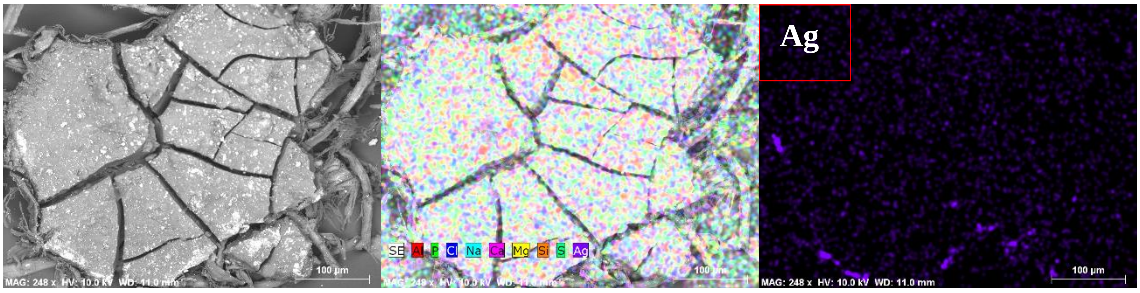
Sample 12F (fiber attached to the paper)



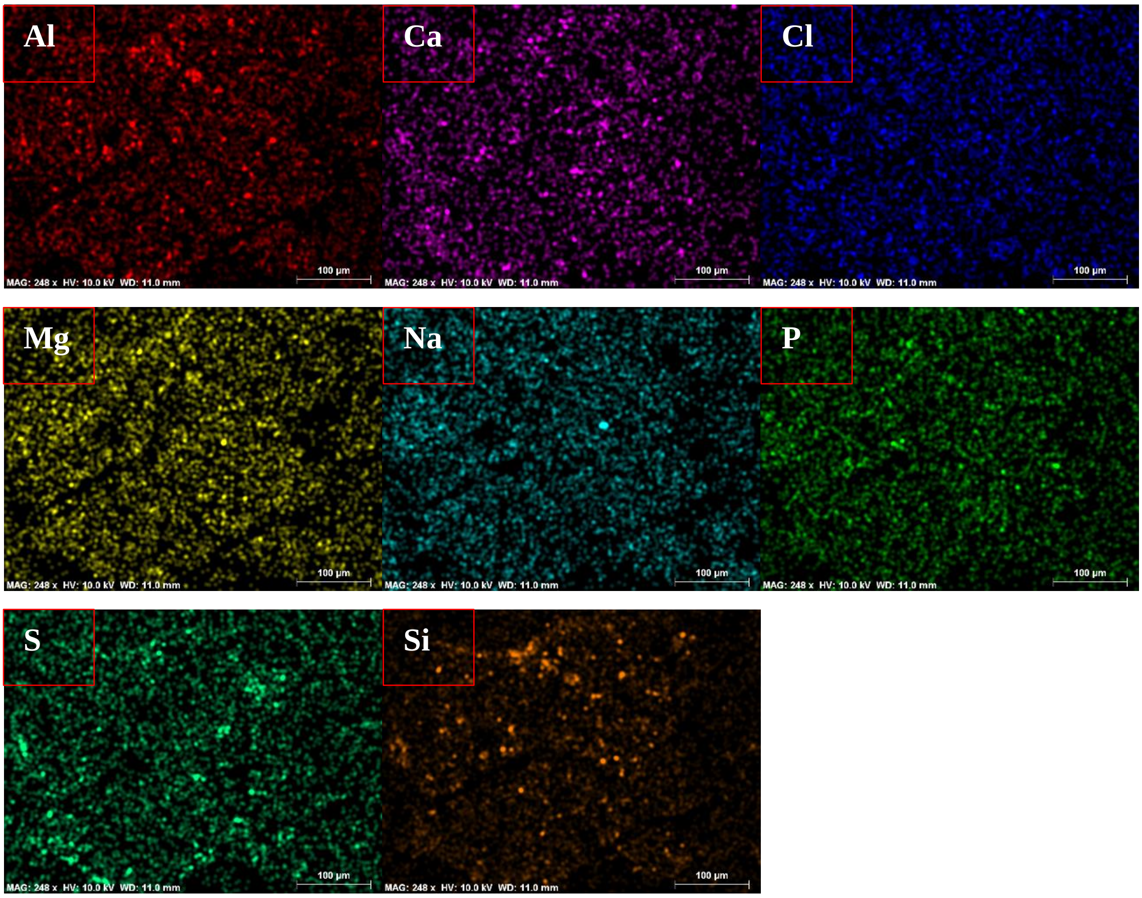


Spectrum	C	N	O	Na	Mg	Al	Si	S	K	Fe
1	52.79	10.10	34.78	0.29	0.14	0.71	0.17	0.42	0.61	
2	58.36		12.96	0.00		5.49	17.86		2.13	3.20
Mean value:	55.57	10.10	23.87	0.15	0.14	3.10	9.02	0.42	1.37	3.20
Sigma:	3.94	0.00	15.43	0.21	0.00	3.38	12.51	0.00	1.08	0.00
Sigma mean:	2.79	0.00	10.91	0.15	0.00	2.39	8.84	0.00	0.76	0.00

Sample 12P (detail of the op of the paper)



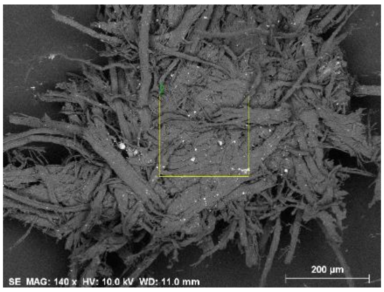
Appendix 3 EDS

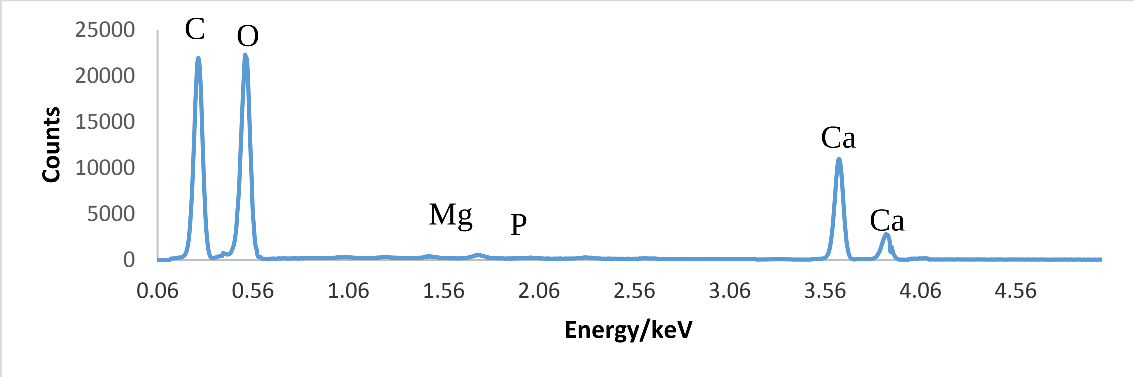


Element	AN	series	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in wt.% (1 Sigma)
Carbon	6	K-series	24.75	23.03	34.57	3.37
Oxygen	8	K-series	48.85	45.46	51.21	6.51
Magnesium	12	K-series	0.09	0.09	0.06	0.04
Phosphorus	15	K-series	0.19	0.18	0.10	0.04
Calcium	20	K-series	33.57	31.24	14.05	1.19
		Sum:	107.46	100	100	

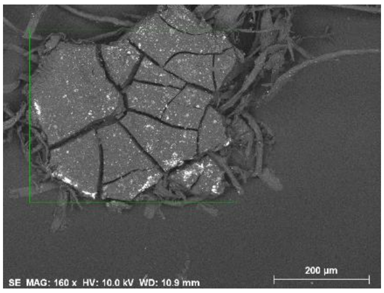
Element	AN	series	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in wt.% (1 Sigma)
Magnesium	12	K-series	0.35	13.74	18.13	0.06
Aluminium	13	K-series	0.26	9.98	11.87	0.05
Silicon	14	K-series	0.65	25.05	28.62	0.08
Potassium	19	K-series	0.48	18.62	15.28	0.07
Calcium	20	K-series	0.84	32.61	26.10	0.10
		Sum:	2.58	100.00	100.00	

Sample 12P (detail of bottom of the paper)



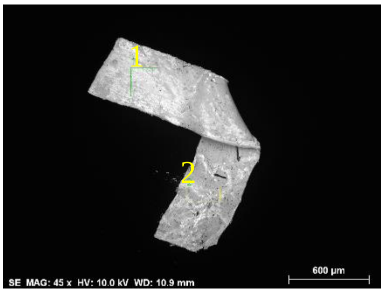


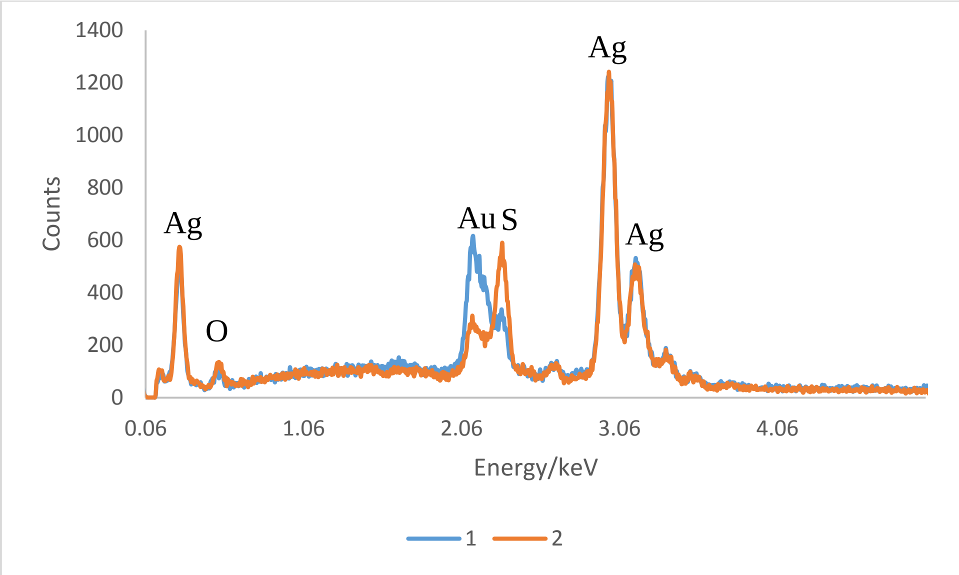
Sample 12 (detail of the adhesive surface)



Sample 15

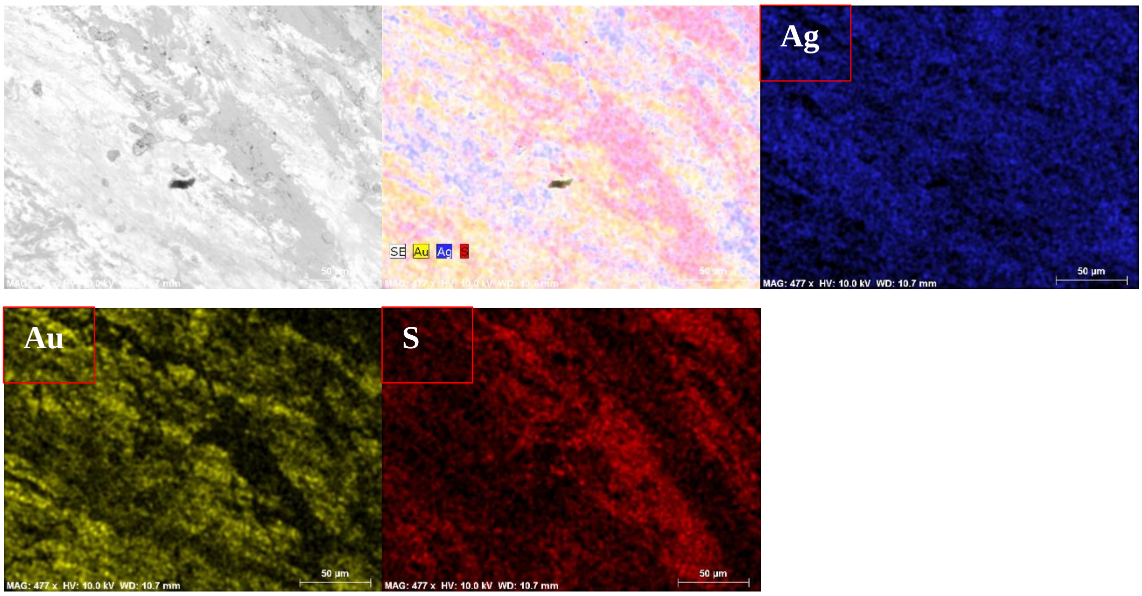
Sample 15M (metal from the metal thread)



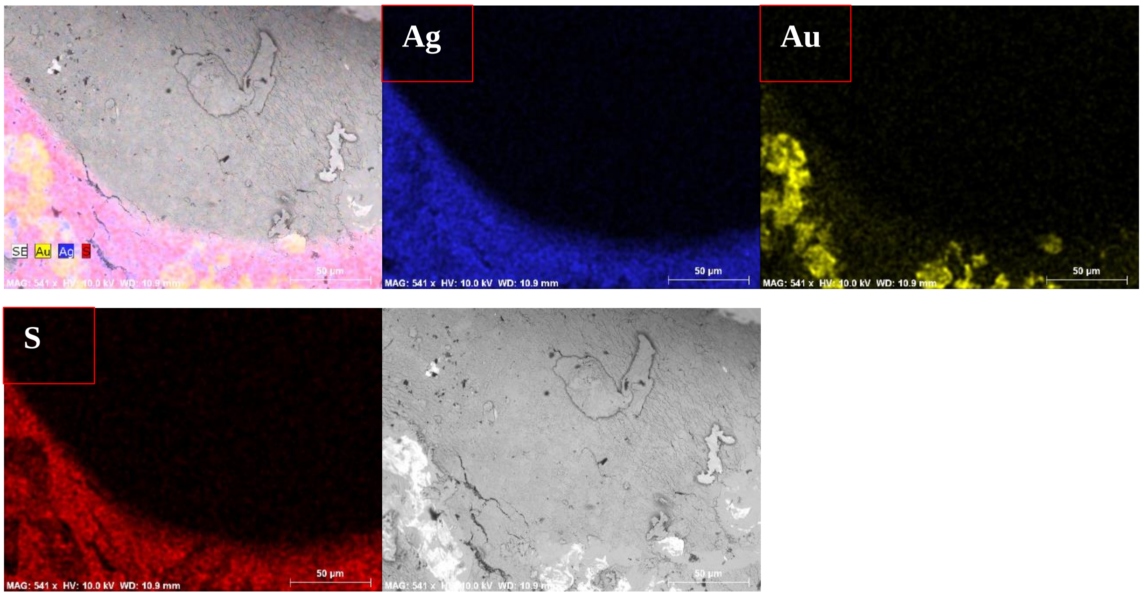


Spectrum	Al	S	Ag	Au
1		4.01	73.07	22.93
2	0.15	9.05	80.44	10.35
Mean value:	0.15	6.53	76.75	16.64
Sigma:	0.00	3.56	5.22	8.89
Sigma mean:	0.00	2.52	3.69	6.29

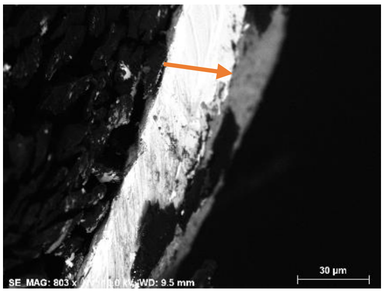
Sample15M (External face)

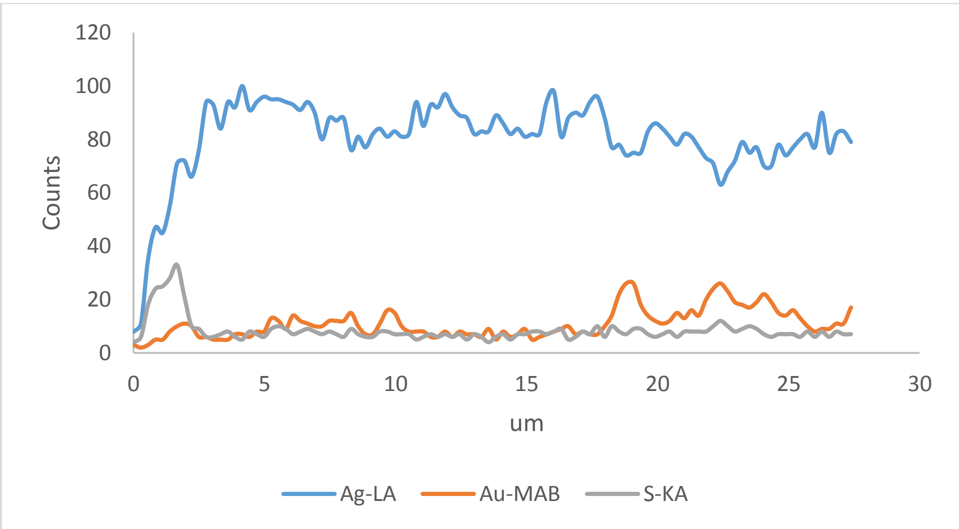


Sample15M (Internal face)

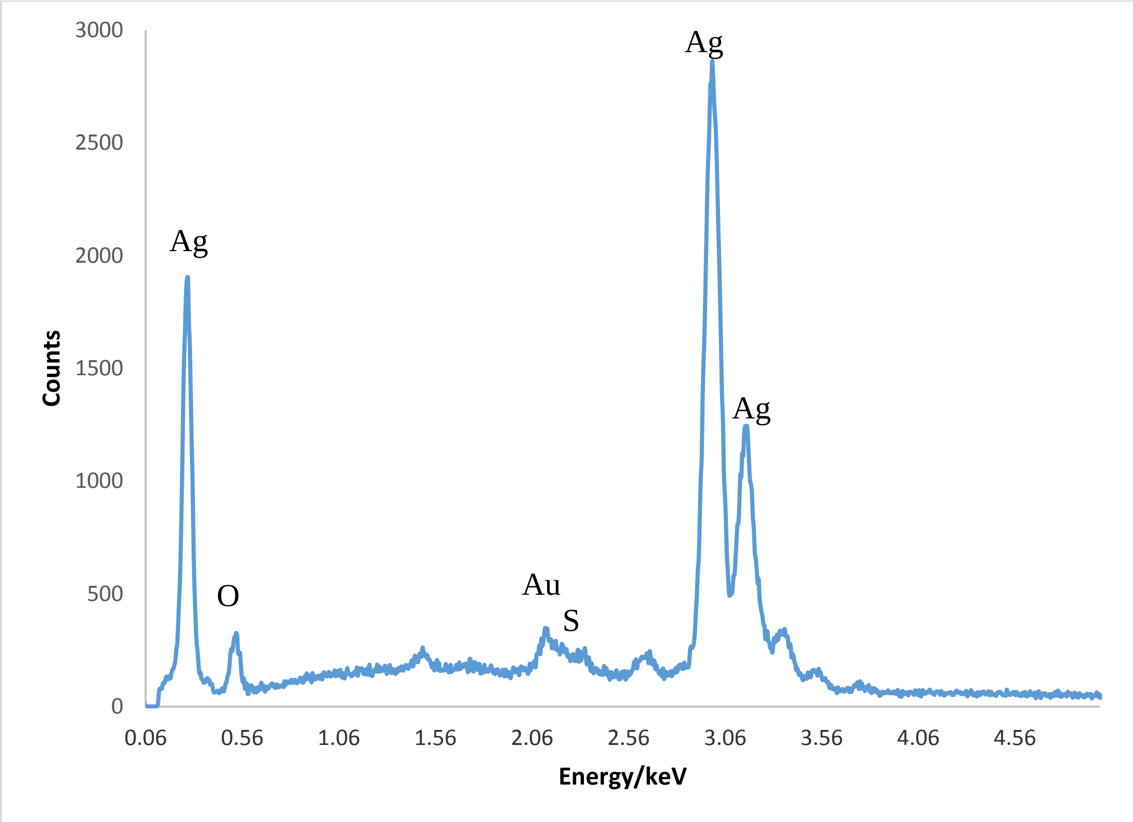


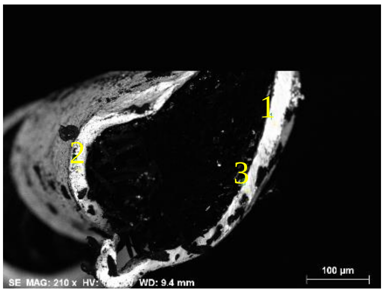
Sample 15M (cross section)

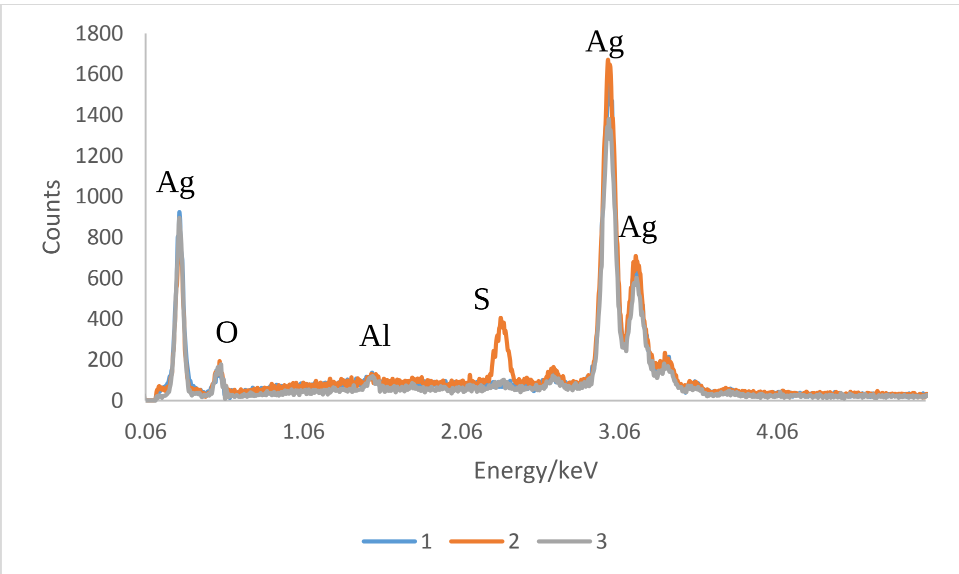




Appendix 3 EDS

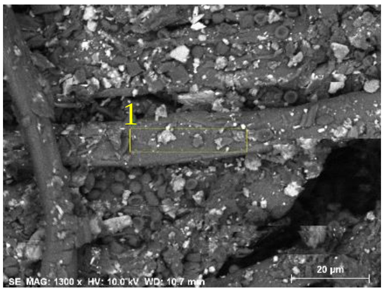


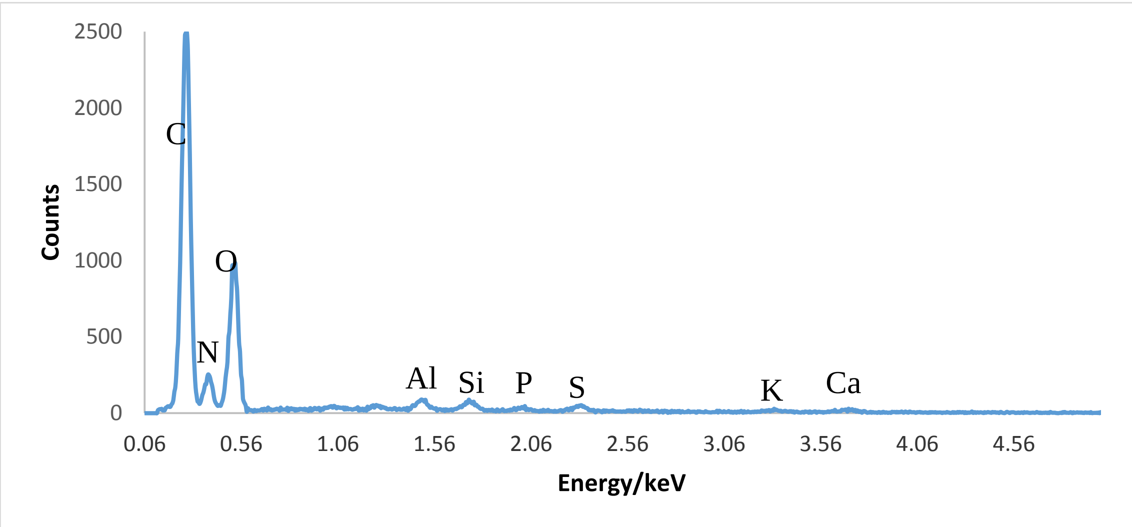




Spectrum	Al	Si	S	Ag
1	0.50		0.12	99.38
2	0.20		5.04	94.76
3	0.72	0.00		99.28
Mean value:	0.47	0.00	2.58	97.81
Sigma:	0.26	0.00	3.48	2.64
Sigma mean:	0.15	0.00	2.01	1.53

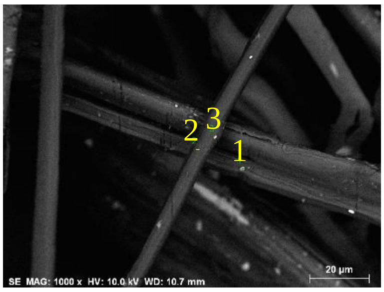
Sample 16

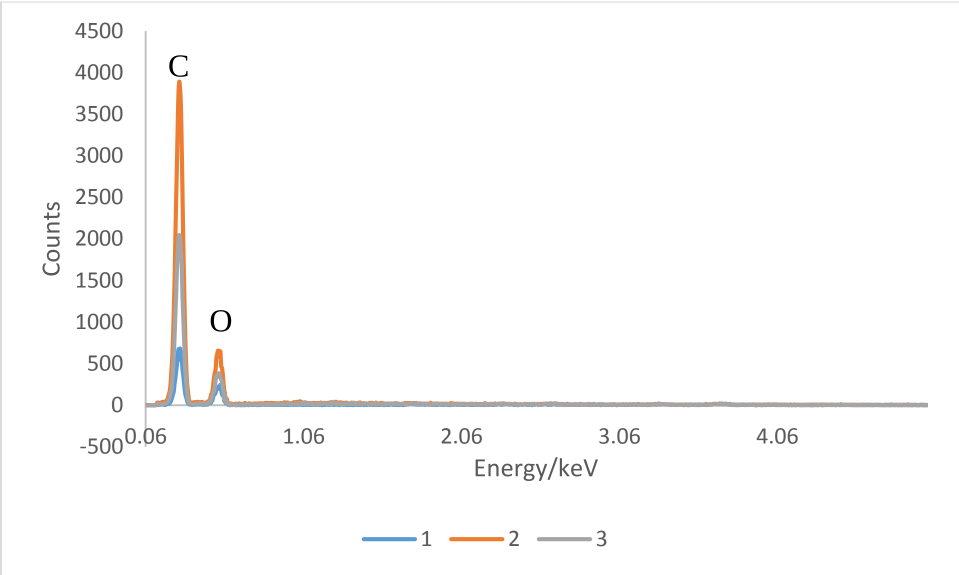




Element	series	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in wt.% (1 Sigma)
Sodium	K-series	1.08	7.61	9.87	0.13
Magnesium	K-series	1.11	7.83	9.61	0.12
Aluminium	K-series	2.46	17.26	19.07	0.18
Silicon	K-series	2.91	20.43	21.69	0.19
Phosphorus	K-series	1.24	8.69	8.37	0.11
Sulfur	K-series	2.15	15.09	14.04	0.15
Potassium	K-series	1.27	8.91	6.80	0.11
Calcium	K-series	2.02	14.18	10.55	0.16
	Sum:	14.23	100.00	100.00	

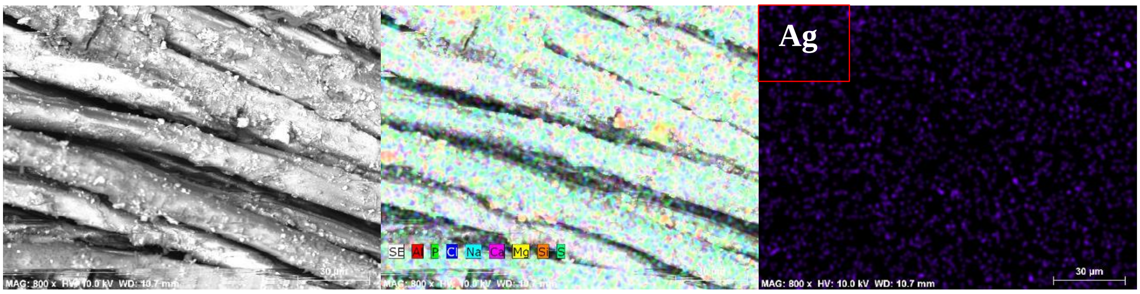
Sample 18H (fiber from the sewing thread)

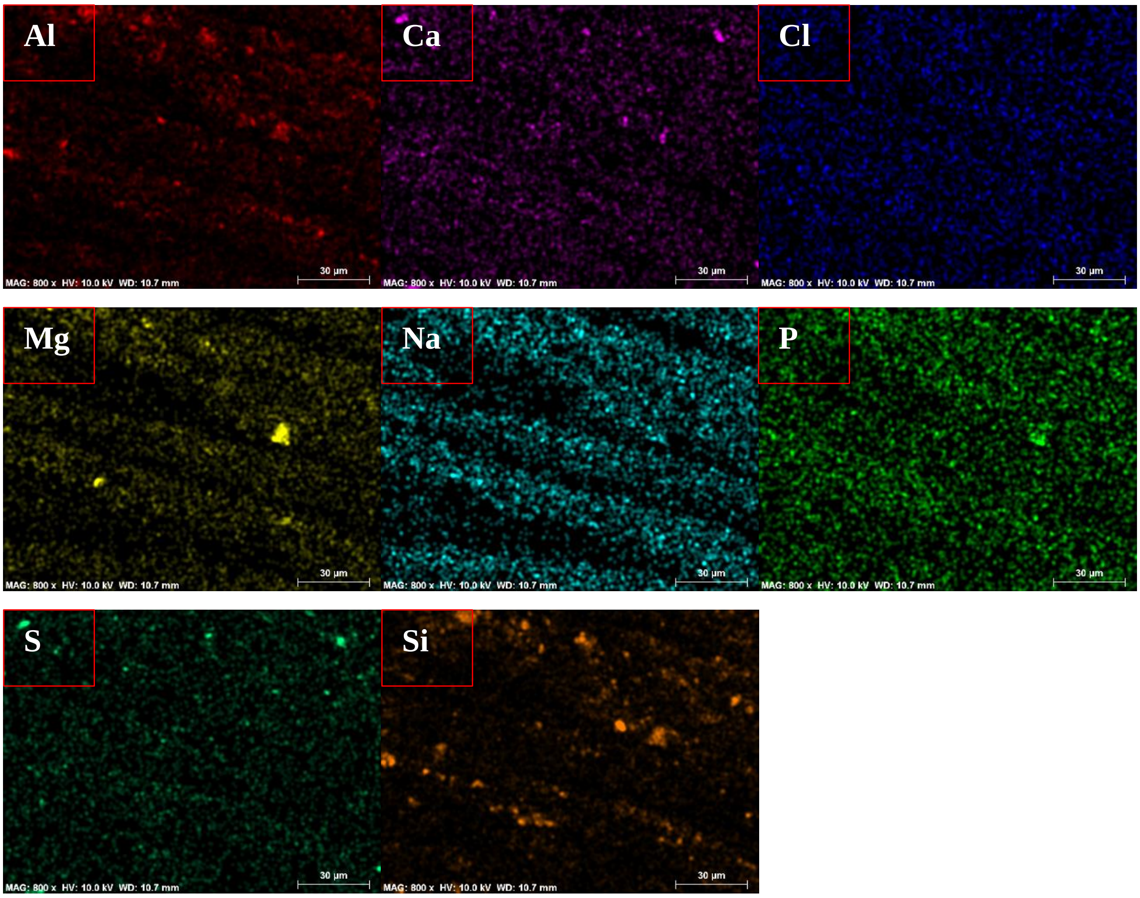




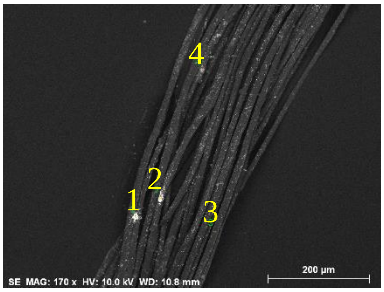
Spectrum	C	O	Na	Si	Cl	K	Ca
1	53.30	41.45		1.17		1.42	2.66
2	71.91	27.09	0.32				0.67
3	70.32	28.19			0.37		1.12
Mean value:	65.18	32.24	0.32	1.17	0.37	1.42	1.48
Sigma:	10.32	7.99	0.00	0.00	0.00	0.00	1.04
Sigma mean:	5.96	4.61	0.00	0.00	0.00	0.00	0.60

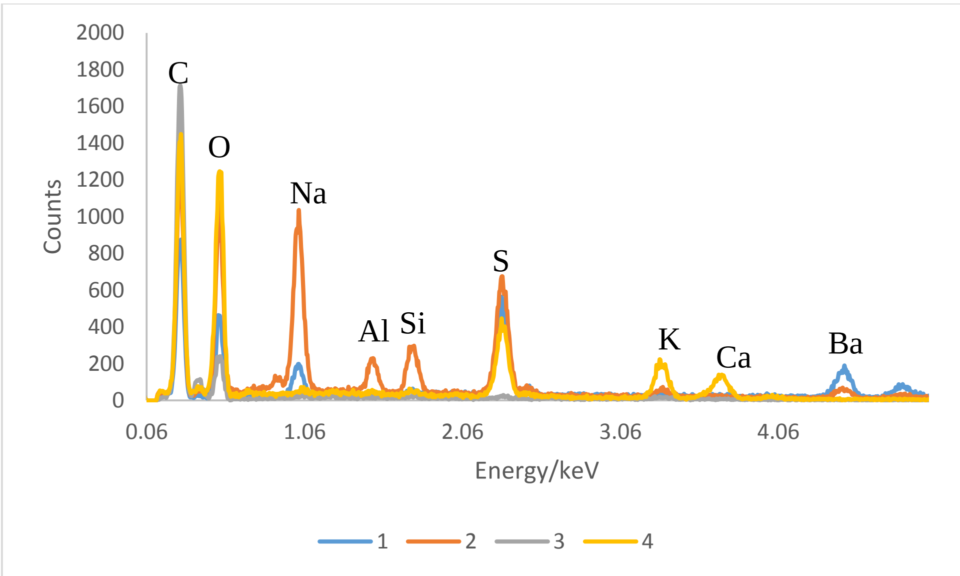
Sample 19





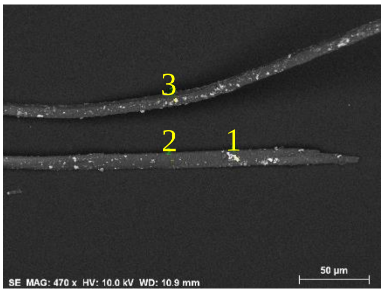
Sample 24A (warp)

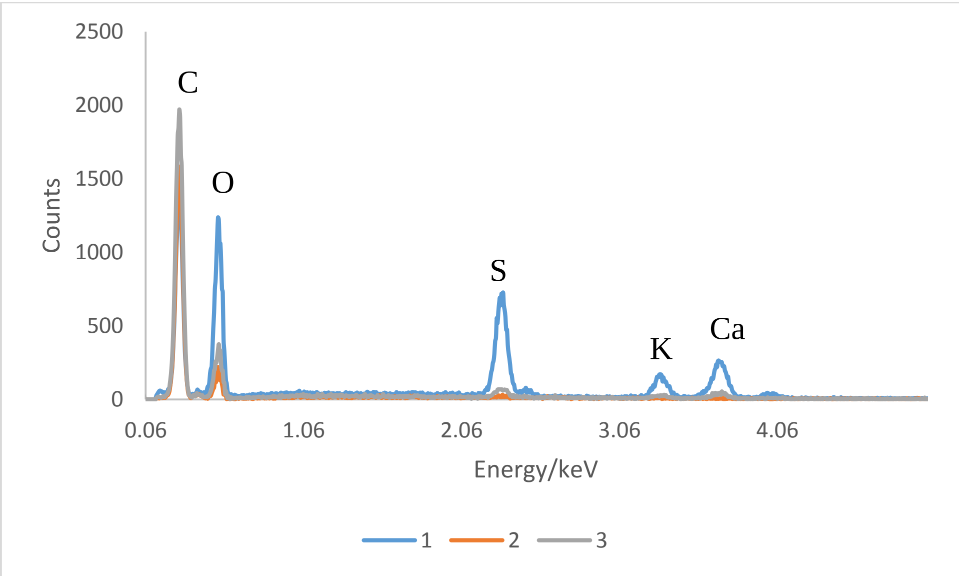




Spectrum	C	N	O	Na	Al	Si	S	K	Ca	Fe	Zn	Ba
1	29.52		12.56	0.00	0.00	0.00	22.15	0.00			0.80	34.97
2	34.32		24.66	1.61	0.00	1.31	11.15	1.71			13.87	11.37
3	57.21	15.90	24.83	0.21			0.57	1.28				
4	29.79		42.99	0.00		0.00	3.69	9.49	10.89	3.15		
Mean value:	37.71	15.90	26.26	0.46	0.00	0.44	9.39	3.12	10.89	3.15	7.33	23.17
Sigma:	13.18	0.00	12.55	0.78	0.00	0.76	9.60	4.31	0.00	0.00	9.24	16.69
Sigma mean:	6.59	0.00	6.27	0.39	0.00	0.38	4.80	2.15	0.00	0.00	4.62	8.34

Sample 24B (weft)

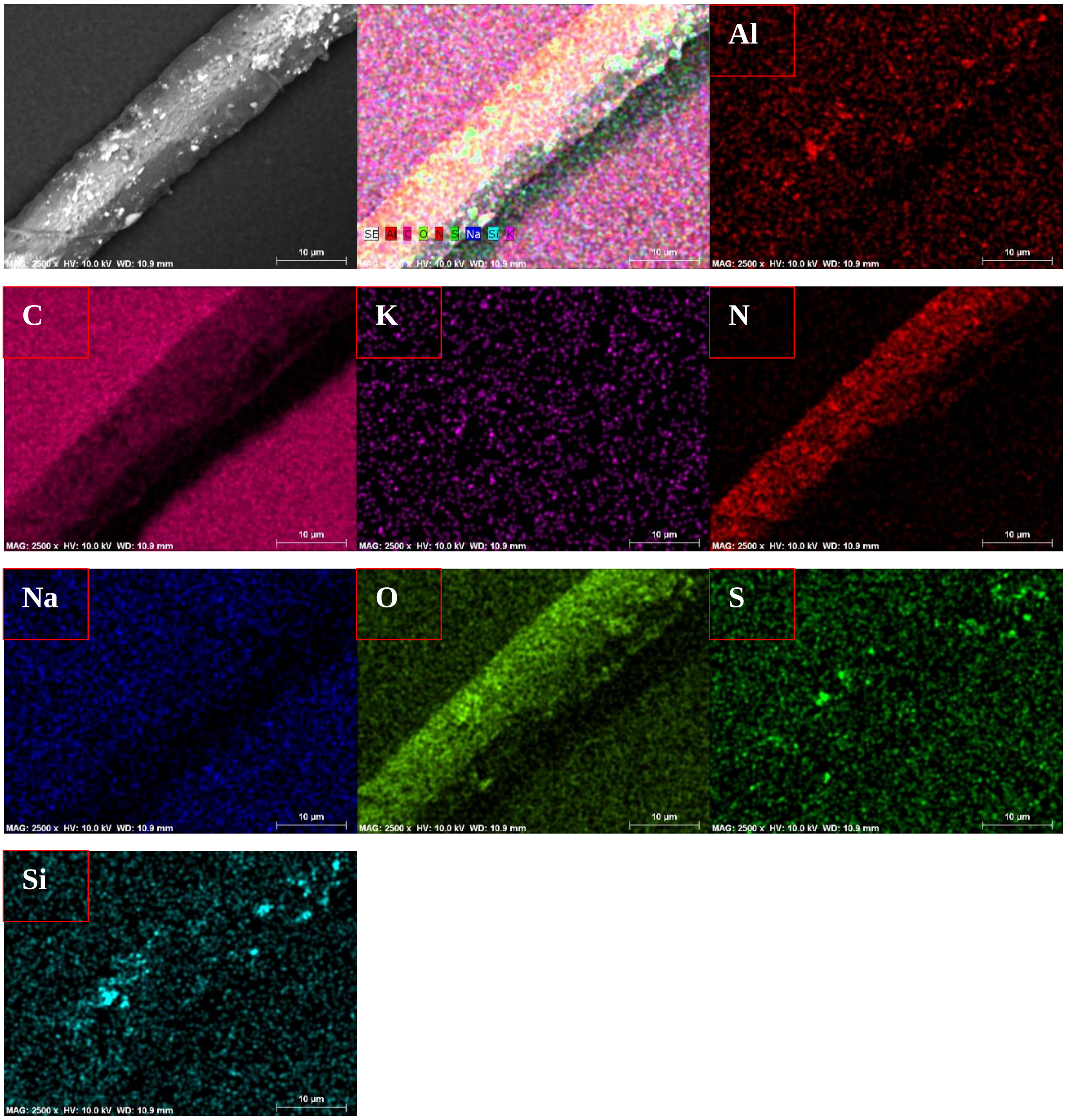




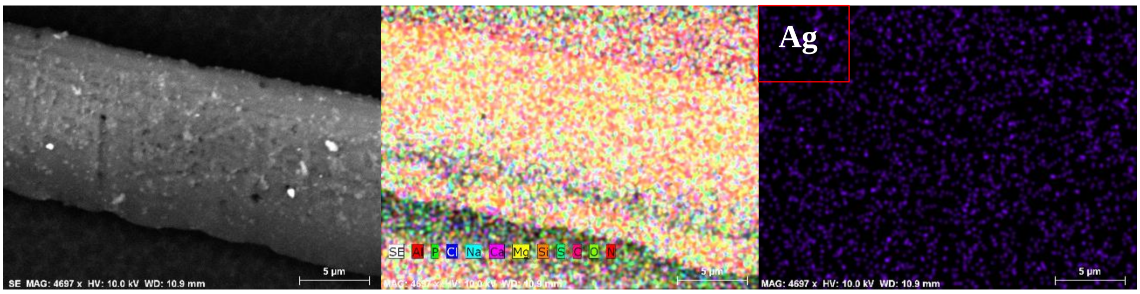
Spectrum	Na	S	K	Ca
1		38.90	17.01	44.09
2	2.53	97.47		
3		27.44	18.35	54.21
Mean value:	2.53	54.60	17.68	49.15
Sigma:	0.00	37.57	0.95	7.15
Sigma mean:	0.00	21.69	0.55	4.13

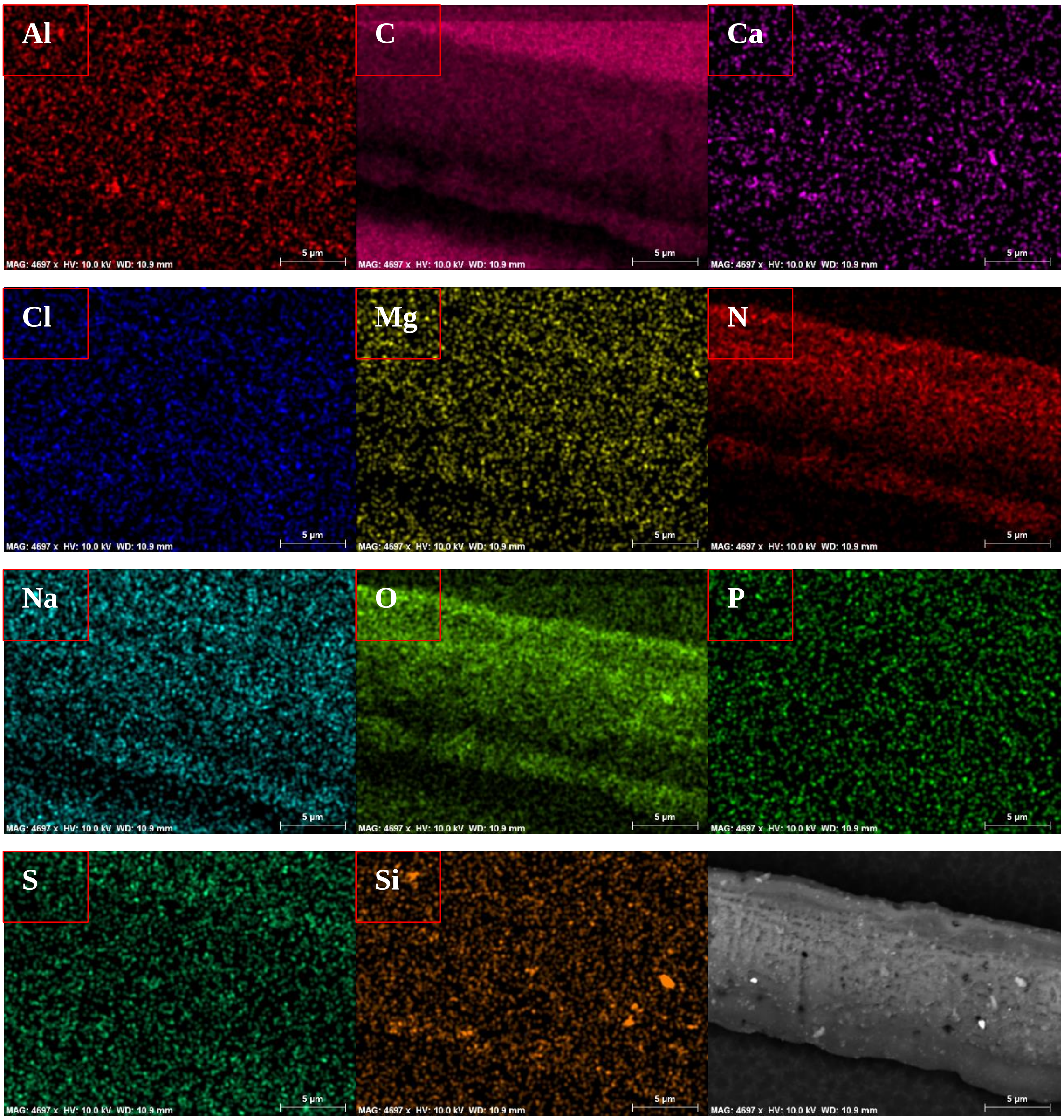
Sample 25

Sample 25 (fiber of dark green color)



Sample 25 (fiber of light green color)




Al
C
Ca
Cl
Mg
N
Na
O
P
S
Si
MAG: 4697 x HV: 10.0 kV WD: 10.9 mm
5 µm

Appendix 4 HPLC-PDA-MS

With aims to offer a better understanding to the readers about the results gained on this research, next are presented the complete data obtained by HPLC-PDS-MS after the extraction process on the samples from the Francisco Pizarro's Banner of Arms.

Color	**Sample**	**r.t. /min**	**UV/ Vis**	***m/z*** **+**	**-**	**Identification**	**Possible dye source**
Blank	11E1	2.20	242	**293.01,** 315.03		Solvents	No dye
		23.19	260	141.40, **302.30**, 346.31, 390.34,			
Silk	1E	13.14	241, 275	**509,** 566, **593, 637,** 694, 765, 781	**507**, 591, **635,** 692, 763, 779	Silk peptide degradation	
		14.17	254	**537, 665**	**535, 663**		
		14.90	243, 275	635, 693	165, 633, 691		
		15.71	239, 246, 276	186, 247			
	5E	13.14	241, 275	**509,** 566, **593, 637,** 694, 765, 781	**507**, 591, **635,** 692, 763, 779		
		14.17	254	**537, 665**	**535, 663**		
		14.90	243, 275	635, 693	165, 633, 691		
		15.71	239, 246, 276	186, 247			
	9E3	13.14	241, 275	**509,** 566, **593, 637,** 694, 765, 781	**507**, 591, **635,** 692, 763, 779		
		14.17	254	**537, 665**	**535, 663**		
		14.90	243, 275	635, 693	165, 633, 691		
		15.71	239, 246, 276	186, 247			
	10E	13.14	241, 275	**509,** 566, **593, 637,** 694, 765, 781	**507**, 591, **635,** 692, 763, 779		
		14.17	254	**537, 665**	**535, 663**		
		14.90	243, 275	635, 693	165, 633, 691		

		15.71	239, 246, 276	186, 247			
	17E	13.14	241, 275	**509,** 566, **593, 637,** 694, 765, 781	**507**, 591, **635,** 692, 763, 779		
		14.17	254	**537, 665**	**535, 663**		
		14.90	243, 275	635, 693	165, 633, 691		
		15.71	239, 246, 276	186, 247			
	22E	13.14	241, 275	**509,** 566, **593, 637,** 694, 765, 781	**507**, 591, **635,** 692, 763, 779		
		14.17	254	**537, 665**	**535, 663**		
		14.90	243, 275	635, 693	165, 633, 691		
		15.71	239, 246, 276	186, 247			
	23E	13.14	241, 275	**509,** 566, **593, 637,** 694, 765, 781	**507**, 591, **635,** 692, 763, 779		
		14.17	254	**537, 665**	**535, 663**		
		14.90	243, 275	635, 693	165, 633, 691		
		15.71	239, 246, 276	186, 247			
	24E	13.14	241, 275	**509,** 566, **593, 637,** 694, 765, 781	**507**, 591, **635,** 692, 763, 779		
		14.17	254	**537, 665**	**535, 663**		
		14.90	243, 275	635, 693	165, 633, 691		
		15.71	239, 246, 276	186, 247			
	25EW	13.14	241, 275	**509,** 566, **593, 637,** 694, 765, 781	**507**, 591, **635,** 692, 763, 779		
		14.17	254	**537, 665**	**535, 663**		
		14.90	243, 275	635, 693	165, 633, 691		
		15.71	239, 246, 276	186, 247			
Yellow	20E	14.1	254	**537, 665**	**535, 663**	Silk degradation	Weld

		14.88	248, 394	585, **565**	563		
		15.45	255, 353	465, 611	609	Luteolin di-O-glucoside	
		15.62	268, 341	611, 655, 465	609, 653, 463	Luteolin 3,7'-di-O-glucoside	
		15.82	268, 341	465	463		
		16.05	255, 353	625, 595	623, 593		
Red	16E	14.07	245	299	315		Brazil-Wood
		14.64	245,278	287, 432	178, 285, 303		
		14.77	248, 278	476, 428, 344, 285	426, 344, 283		
		15.19	245, 276	285	344, 283, 153		
		15.74	246, 280	305, 285,	303, 283		
		16.41	245, 276, 444	285	283	Brazilin	
		16.91	285, 305	245	243	Type C Compound	
Red	2E	14.07	245	299	315		Brazil-Wood
		14.64	245,278	287, 432	178, 285, 303		
		14.77	248, 278	476, 428, 344, 285	426, 344, 283		
		15.19	245, 276	285	344, 283, 153		
		15.74	246, 280	305, 285,	303, 283		
		16.41	245, 276, 444	285	283	Brazilin	
		16.91	285, 305	245	243	Type C Compound	
Orange	9ER	14.10	245	299	315		Brazil-Wood
		14.65	245,278	287, 432	178, 285, 303		
		14.77	248, 278	476, 428, 344, 285	426, 344, 283		
		15.21	245, 276	285	344, 283, 153		
		15.78	246, 280	305, 285,	303, 283		

		16.32	245, 276, 444	285	283	Brazilin	
		16.92	285, 305	245	243	Type C Compound	
Orange	25ER	14.13	244		343, 315, 239		Brazil-Wood + Weld
		14.52	243, 319	611	609	Luteolin di-O-glucoside	
		15.08	244, 320	611	609	Luteolin 3,7'-di-O-glucoside	
		15.86	248, 356	449	447	Luteolin 7-O-glucoside	
		16.58	245, 440	431, 449	431, 447	Luteolin 7-O-glucoside	
		16.93	258, 307, 333	449	243, 447, 495	Type C Compound	
Red	7E	14.11	233, 253		345, 191		Cochineal
		14.65	231, 247, 271	493, 149	491, 344		
		14.92	245, 275, 493	493	491	Carminic Acid	
Red	11E2	14.9	245, 275, 493	493	491	Carminic Acid	Cochineal + luteolin base
		15.42	255, 353	611	609	Luteolin di-O-glucoside	
		15.59	253, 342, 469	625, 595, 493	623, 593, 491		
		16.29	248, 270, 469	493	491		
Red	21E	14.9	245, 275, 493	493	491	Carminic Acid	Cochineal + luteolin base
		15.42	255, 353	611	609	Luteolin di-O-glucoside	
		15.59	253, 342, 469	625, 595, 493	623, 593, 491		
		16.03	248, 270, 469	493	491		
Blue	14E	14.25	253		239		"Woad"

		15.77	242, 293	241	239		
		18.6	247, 299		333, 311, 239, 162		
		18.92	246		322, 239		
		23.89	249, 285, 608	374, 330			
		24.52	290, 542	330, 356		Indigotin	
Blue	8E	15.5	248, 353	611	609	Luteolin di-O-glucoside	“Woad”+ luteolin base
		18.6	247, 299		333, 311, 239, 162		
		18.92	246		322, 239		
		23.89	249, 285, 608	374, 330			
		24.52	290, 542	263		Indigotin	
Green	9E1	14.53	246, 267, 334	611	609	Luteolin di-O-glucoside	Woad + Weld
		15.07	246, 266, 337	611	609	Luteolin 3,7’-di-O-glucoside	
		15.85	248, 348	449	447	Luteolin 7-O-glucoside	
		16.57	267, 336	449, 433	431, 447	Apigenin 7-O-glucoside + Luteolin 4’-O-glucoside	
		16.87	246, 266, 336	449, 433	431, 447	Apigenin 7-O-glucoside + Luteolin 4’-O-glucoside	
		23.82	247, 285, 608	263		Indigotin	
Green	9E2	14.53	246, 267, 334	611	609	Luteolin di-O-glucoside	Woad + Weld
		15.07	246, 266, 337	611	609	Luteolin 3,7’-di-O-glucoside	
		15.85	248, 348	449	447	Luteolin 7-O-glucoside	
		16.57	267, 336	449, 433	431, 447	Apigenin 7-O-glucoside +	

						Luteolin 4'-O-glucoside	
		16.87	246, 266, 336	449, 433	431, 447	Apigenin 7-O-glucoside + Luteolin 4'-O-glucoside	
		23.82	247, 285, 608	263		Indigotin	
Green	25EG	14.53	246, 267, 334	611	609	Luteolin di-O-glucoside	Woad + Weld
		15.07	246, 266, 337	611	609	Luteolin 3,7'-di-O-glucoside	
		15.85	248, 348	449	447	Luteolin 7-O-glucoside	
		16.57	267, 336	449, 433	431, 447	Apigenin 7-O-glucoside + Luteolin 4'-O-glucoside	
		16.87	246, 266, 336	449, 433	431, 447	Apigenin 7-O-glucoside + Luteolin 4'-O-glucoside	
		23.82	247, 285, 608	263		Indigotin	

Appendix 5 Py-GC-MS

With aims to offer a better understanding to the readers about the results gained on this research, next are presented the complete list of compounds identified after the Py-GC-MS process on the samples from the Francisco Pizarro's Banner of Arms.

1- Adhesive

RT(min)	Chemical Name	Source
2.5442	>Cyclopentanone	
2.6267	>Propanoic acid, 2-oxo-, methyl ester	lipids
2.7925	>1-germa-2-silabutane	
2.9442	>1-Deoxy-2,4-methylene-3,5-anhydro-d-xylitol	carbohydrate
3.0542	>1,4-DIOXADIENE	carbohydrate
4.23	>2-Furancarboxaldehyde	carbohydrate
4.7525	>2-Acetyltetrahydrofuran	carbohydrate
4.7567	>2-Acetyltetrahydrofuran	carbohydrate
5.0992	>1-Deoxy-2,4-methylene-3,5-anhydro-d-xylitol	carbohydrate
5.1358	>ANILINE-1-(13)C	protein
5.1567	>ANILINE-1-(13)C	protein
5.5908	>Ethane, 1,2-bis[(4-amino-3-furazanyl)oxy]-	carbohydrate
5.6583	>2-Cyclopenten-1-one	
5.7075	>Furfural	carbohydrate
5.7567	>Butanoic acid, 2-hydroxy-, methyl ester	lipids
6.1358	>Glycine, N,N-dimethyl-, methyl ester	protein
6.1683	>3-Methoxy-2-propenal	
6.4642	>1H-Pyrrole, 3-methyl-	protein
6.7667	>iso-VALERIC ACID	lipids
6.7842	>Butanoic acid, 3-methyl-	lipids
7.1033	>1H-Pyrrole, 3-methyl-	protein
7.4467	>Disulfide, dipentyl	
7.5183	>2-Furanmethanol	carbohydrate
7.565	>2-Butanone	
7.73	>Ethylbenzene	carbohydrates
8.4642	>2-Propanone, 1-(acetyloxy)-	carbohydrates
9.11	>Protoanemonine	
9.48	>Styrene	protein
9.5783	>[2-(N,N-Dimethyl)]-1,2-propanediamine	protein
9.6042	>Methylephedrine	
9.87	>1,2-Propanediol,3-methoxy-	carbohydrates
10.0108	>Glutaraldehyde	

10.2817	>Cyclopentane, bromo-	
10.345	>2-Cyclopenten-1-one, 2-methyl-	
10.6058	>Ethanone,1-(2-furanyl)-	carbohydrate
10.6167	>Butanoic acid, 4-hydroxy-	lipids
10.6967	>2(5H)-Furanone	carbohydrate
10.7017	>2(5H)-FURANONE	carbohydrate
10.9125	>Benzene, methoxy-	carbohydrates
11.2383	>1,2-Cyclopentanedione	
11.4625	>Hexanoic acid, methyl ester	lipids
11.6175	>2,5-Hexanedione	
12.0033	>5-Hydroxy-2-heptanone	
12.0425	>2(5H)-Furanone, 5-methyl-	carbohydrate
13.0283	>4-Methyl-2-hydroxycyclopent-2-en-1-one	
13.1433	>2-Furancarboxaldehyde, 5-methyl-	carbohydrate
13.1617	>Furan, 2-methyl-	carbohydrate
13.17	>2-Cyclopenten-1-one, 3-methyl-	
13.245	>1-Acetoxy-2-propionoxyethane	
13.2517	>1-Acetoxy-2-propionoxyethane	
13.3983	>2-Butanone, 1-(acetyloxy)-	
13.7408	>Methyl2-furoate	carbohydrate
13.79	>4,5-dihydrofuran-3-carbaldehyde	carbohydrate
13.8408	>4(1H)-Pyrimidinone, 6-methyl-	protein
14.0808	>Phenol	carbohydrates
14.2283	>2-Hydroxy-gamma-butyrolactone	
14.3075	>Pentanoic acid, 4-oxo-, methyl ester	lipids
14.4383	>Cyclohexanol,2,3-dimethyl-	carbohydrate
14.6525	>2,3-Dimethyl-2-cyclopenten-1-one	
14.7683	>(E)-3,4-Dimethyl-3-hexene	
14.8275	>Pyridine, 3-methoxy-	protein
15.0558	>Butanoic acid, anhydride	lipids
15.1533	>1H-Pyrrole, 2-ethyl-4-methyl-	protein
15.5483	>Benzene, 1-methoxy-4-methyl-	carbohydrates
15.5533	>Benzene, 1-methoxy-4-methyl-	carbohydrates
15.7767	>2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	
16.115	>Butanedioic acid, dimethyl ester	lipids
16.2642	>2-Cyclopenten-1-one, 2,3-dimethyl-	
16.4142	>4-Methyl-5H-furan-2-one	carbohydrate
16.445	>Benzeneacetaldehyde	carbohydrates
16.5592	>Benzenemethanamine, N,N-dimethyl-	carbohydrates/protein
16.5942	>Cyclopentene, 3,5-dimethoxy-	
16.8775	>3,5-DIMETHYL CYCLOPENTENOLONE	

16.915	>Phenol, 2-methyl-	carbohydrates
17.1083	>mesifuranne	carbohydrate
17.1875	>3,5-Octadien-2-one	
17.385	>TRANS-CYCLOPENTEN-3,4-DIOL	carbohydrates
17.5575	>3,4-DIMETHYL CYCLOPENTENOLONE	
17.65	>Phenol, 4-methyl-	carbohydrates
17.6875	>2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	
18.1358	>Phenol, 2-methoxy-	carbohydrates
18.1667	>Benzenamine, N,N-dimethyl-	protein
18.2142	>1-Hexyn-3-ol	carbohydrates
18.3633	>2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	
18.6025	>2(1H)-Pyridinone	
18.8967	>4H-Pyran-4-one, 3-hydroxy-2-methyl-	
19.1042	>Methyl pyrrole-2-carboxylate	
19.1375	>2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	
19.4458	>Pentane, 1-bromo-5-methoxy-	
19.9542	>Cyclohexanone, 2-acetyl-	
20.0717	>Benzene, 1,2-dimethoxy-	carbohydrates
20.1283	>Phenol, 3,4-dimethyl-	carbohydrates
20.6125	>2-Ethyl-3-methoxy-2-cyclopentenone	
20.6408	>Benzene, 1,4-dimethoxy-	carbohydrates
21.0042	>2,3-Dimethoxytoluene	
21.1875	>2,6-Piperidinedione	
21.3483	>(S)-(+)-2',3'-Dideoxyribonolactone	
21.7833	>Benzaldehyde, 3-methoxy-	
22.0475	>1,4:3,6-Dianhydro-à-d-glucopyranose	
22.305	>Mequinol	carbohydrates
22.3575	>2,4-Imidazolidinedione, 3,5,5-trimethyl-	protein
22.3933	>3,4-Anhydro-d-galactosan	
22.5775	>2-Furancarboxaldehyde, 5-(hydroxymethyl)-	carbohydrate
23.3158	>Benzene, 1,4-dimethoxy-2-methyl-	carbohydrates
23.8033	>1,3-Dioxane	
24.0367	>Hydroquinone	
24.2658	>1H-Inden-1-one, 2,3-dihydro-	
24.635	>Indole	protein
25.1217	>Benzene, 1,2,3-trimethoxy-	carbohydrates
25.1967	>2-Methoxy-4-vinylphenol	
25.5358	>3-Acetyl-2,5-dimethylthiophene	
25.8017	>Phenol, 3,4-dimethoxy-	carbohydrate
25.8967	>L-Proline,1-methyl-5-oxo-,methylester	protein
25.9783	>1,4-Benzenediol,2-methyl-	carbohydrates

26.2	>Phenol,2,6-dimethoxy-	carbohydrates
26.2317	>3,4-Anhydro-d-galactosan	
26.6142	>Benzene,4-ethenyl-1,2-dimethoxy-	carbohydrates
26.72	>1,2,4-Trimethoxybenzene	carbohydrates
26.7833	>L-Proline,5-oxo-,methylester	protein
27.235	>á-d-Allopyranoside,methyl6-deoxy-2-O-methyl-	
27.4542	>1,4-Benzenediol,2-methoxy-	carbohydrates
28.3525	>Benzene,1,2,3-trimethoxy-5-methyl-	carbohydrates
28.665	>Octanedioic acid,dimethyl ester	lipids
29.5975	>á-D-Glucopyranose,1,6-anhydro-	
31.1867	>Nonanedioic acid, dimethyl ester	lipids
31.7517	>2-Pyrrolidone-5-carboxylic acid, N-methyl, methyl ester	protein/lipid
31.9333	>L-Proline, 1-methyl-5-oxo-, methyl ester	protein
33.3075	>L-Proline, 5-oxo-, methyl ester	protein
33.81	>2,2'-Dipyridyl	
35.0583	>L-Proline, 1-methyl-5-oxo-, methyl ester	protein

2- Rag paper

RT(min)	Chemical Name	Source
2.7783	>1-Propanamine	
2.8958	>1-Deoxy-2,4-methylene-3,5-anhydro-d-xylitol	carbohydrate
3.3925	>Cyclopentene,3-methoxy-	
5.045	>1-Deoxy-2,4-methylene-3,5-anhydro-d-xylitol	carbohydrate
5.7133	>3-Cyclopentene-1-acetaldehyde,2-oxo-	
5.7183	>2-Cyclopenten-1-one	
5.7683	>Butanoic acid, 2-hydroxy-, methyl ester	lipids
6.095	>N-Aminopyrrolidine	protein
6.3925	>Glycine, N,N-dimethyl-, methyl ester	
6.525	>Furan, 2-(methoxymethyl)-	
7.9033	>2-Propenoic acid, 2-methyl-, (tetrahydro-2-furanyl)methylester	lipids
8.11	>2-Propylfuran	
8.3192	>1,3-Butadiene,1,4-dimethoxy-, (Z,Z)-	
8.7558	>2-Methyl-2,4-dimethoxybutane	
9.8333	>2,4(1H,3H)-Pyrimidinedione	
9.8875	>N-tert-Butylmethylamine	
10.1325	>4-methoxy-3-buten-2-one	
10.3692	>2-Cyclopenten-1-one, 2-methyl-	
10.6358	>Ethanone,1-(2-furanyl)-	
10.64	>2-ACETYL FURAN	
10.695	>Butyrolactone	
10.8233	>2(5H)-FURANONE	
10.9042	>Benzene,methoxy-	carbohydrates

11.26	>3-Pentanone, 2,4-dimethyl-	
11.5575	>1,3-Butadiene, 1,4-dimethoxy-, (E,E)-	
12.1717	>3-Hexanone, 2-methyl-	
12.9575	>Benzaldehyde	
13.1558	>2-Furancarboxaldehyde,5-methyl-	
13.2258	>2-Cyclopenten-1-one, 3-methyl-	
13.6883	>2-methoxycarbonyl-1-aza-cyclopropane	
13.7075	>Fructofuranose,2,6-anhydro-1,3,4-tri-O-methyl-, á-d-	
13.7625	>2-(1-methylhydrazino)-3-methylbutanamide	
14.0717	>Phenol	carbohydrate
14.4542	>2-Norpinanol,3,6,6-trimethyl-	carbohydrate
14.835	>N,N'-di-t-Butylethylenediamine	
15.0692	>Butanoic acid, anhydride	lipids
15.5308	>Benzene, 1-methoxy-3-methyl-	carbohydrates
15.7567	>1,2-Cyclopentanedione, 3-methyl-	
16.0317	>Cyclopentene, 3,5-dimethoxy-	
16.1167	>Butanedioic acid, dimethyl ester	lipids
16.2508	>Cyclopentene, 3,5-dimethoxy-	
16.5883	>Cyclopentene, 3,5-dimethoxy-	
16.85	>1,3,5-Trimethylhexahydro-1,3,5-triazine	
16.93	>Cyclohexanecarboxaldehyde,4-methoxy-	
17.3333	>Butane, 1,2,4-trimethoxy-	
17.6092	>(S)-4-Hexanolide	
17.665	>Phenol, 3-methyl-	carbohydrate
17.6908	>2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	
17.7233	>Isopropylimidazole-2-thione	
17.9458	>Cyclopropanecarboxylic acid, 2-methylene-, methyl ester	
18.1317	>Phenol, 2-methoxy-	carbohydrate
18.1633	>N,N,N-TRIMETHYL-N-PHENYLAMMONIUMCHLORIDE	
18.3425	>Benzoic acid, methyl ester	lipids
18.3642	>1,2-Cyclopentanedione, 3-methyl-	
18.4683	>4-hydrazino-5-methoxypyrimidine	
18.8142	>Furan, 2-(methoxymethyl)-	
19.3283	>3H-Pyrazol-3-one,2,4-dihydro-2,4,5-trimethyl-	
19.5358	>1H-Tetrazaborole, 4,5-dihydro-1,4,5-trimethyl-	
20.0442	>6-Methylheptane-2,5-dione	
20.0683	>Benzene,1,2-dimethoxy-	carbohydrates
20.1675	>1-Methoxy-1-cyclopropylpentane	
20.3325	>Hepta-2,4-dienoic acid, methyl ester	lipids
20.6167	>2-Ethyl-3-methoxy-2-cyclopentenone	
20.6367	>Benzene, 1,4-dimethoxy-	carbohydrates
21.0025	>2,3-Dimethoxytoluene	protein
21.4358	>Methylene-(4-trimethylsilylphenyl)-amine	
21.78	>Benzaldehyde,3-methoxy-	
22.0467	>1,4:3,6-Dianhydro-à-d-glucopyranose	

22.295	>Mequinol	carbohydrate
22.9592	>2,3-Dimethoxytoluene	protein
23.0575	>CIS-1,2-DIMETHOXYCYCLOPROPANE	
23.0625	>CIS-1,2-DIMETHOXYCYCLOPROPANE	
23.1758	>Phenol, 3,5-dimethoxy-	carbohydrate
23.3058	>Benzene,	carbohydrates
23.31	>Benzene,	carbohydrates
23.8008	>(R)-3,3-Dimethyl-1,2-butanediol	carbohydrate
24.0242	>3-Hydroxy-4-methoxybenzoicacid	lipids
24.8175	>3-methoxy-5-methylbenzaldehyde	
24.8767	>3-Methoxyacetophenone	
25.1192	>1,2,3-Trimethoxybenzene	carbohydrates
25.5317	>Phenol, 3,4-dimethoxy-	carbohydrate
25.7975	>Phenol, 3,4-dimethoxy-	carbohydrate
25.9033	>Mepivacaine metabolite	
26.2	>Phenol,2,6-dimethoxy-	carbohydrate
26.72	>1,2,4-Trimethoxybenzene	carbohydrates
26.7917	>3-Mercapto-2(1H)-pyridinone	
27.14	>Benzaldehyde, 2,3-dimethoxy-	
27.4083	>Benzene, 1,2,3-trimethoxy-5-methyl-	carbohydrates
27.8108	>Benzene, 1,2,3-trimethoxy-5-methyl-	carbohydrates
28.35	>Benzene, 1,2,3-trimethoxy-5-methyl-	carbohydrates
28.7283	>1,2,3,4-Tetramethoxybenzene	carbohydrates
29.0717	>2,4(1H,3H)-Pyrimidinedione, dihydro-1,3,5-trimethyl-	
29.1767	>Benzoic acid, 3,4,5-trimethoxy-	lipids
29.4383	>1,6-Anhydro-á-D-glucopyranose(levoglucosan)	
29.595	>VARATRALDEHYDE	
31.0367	>Tetrahydro-3,4,5-trimethoxy-6-methoxymethyl-2H-pyran-2-one	
31.2842	>3-Hydroxymandelicacid,dimethyl ether, methyl	ester
31.6758	>2',4'-Dimethoxyacetophenone	
31.9	>2-Pyrrolidone-5-carboxylicacid,N-methyl,methylester	protein
32.31	>Benzoic acid, 3,4-dimethoxy-, methyl ester	lipids
34.6325	>2-Ethyldimedone	
35.0492	>L-Proline,1-methyl-5-oxo-, methyl ester	
36.4758	>Benzoic acid, 3,4,5-trimethoxy-, methyl ester	lipids
38.7358	>METHYL-3,6-ANHYDRO-2,4-DI-O-METHYL-à-D-GLUCOPYRANOSIDE	
39.485	>Hexadecanoic acid, methyl ester	lipids
43.3267	>Methyl stearate	

Appendix 6 Radiocarbon dating AMS

UNIVERSITÀ DEL SALENTO

Dipartimento di Matematica e Fisica "Ennio De Giorgi"

CEDAD

CEntro di DAtazione e Diagnostica

Dr. Nick Schiavon
Universidad De Évora
Portogallo
Lecce, 21 Luglio 2016
Rif.CEDAD: 2016_0141

OGGETTO: *Risultati delle datazioni con il radiocarbonio.*

Tabella 1. Elenco del materiale analizzato e relativo codice identificativo.

Codice	*Codice CeDaD*	*Provenienza*
FP 1	LTL16550A	
FP15C	LTL16551A	
FP15F	LTL16552A	
FP15M	LTL16553A	
FP16	LTL16554A	
FP17	LTL16555A	
FP22	LTL16556A	

I campioni indicati in Tabella 1 sono stati sottoposti a datazione con il metodo del radiocarbonio mediante la tecnica della spettrometria di massa ad alta risoluzione (AMS), presso il Centro di Datazione e Diagnostica (CEDAD) dell'Università del Salento.

I macrocontaminanti presenti nei campioni, sono stati individuati mediante osservazione al microscopio ottico e rimossi meccanicamente.

Il trattamento chimico di rimozione delle contaminazioni dal campione è stato effettuato sottoponendo il materiale selezionato ad attacchi chimici alternati acido-alcalino-acido.

Il materiale estratto è stato successivamente convertito in anidride carbonica mediante acidificazione, e quindi in grafite mediante riduzione. Si è utilizzato H_2 come elemento riducente e polvere di ferro come catalizzatore.

La quantità di grafite estratta dai campioni è risultata sufficiente per una accurata determinazione sperimentale dell'età.

La concentrazione di radiocarbonio è stata determinata confrontando i valori misurati delle correnti di ^{12}C e ^{13}C, e i conteggi di ^{14}C con i valori ottenuti da campioni standard di Saccarosio C6 forniti dalla IAEA.

La datazione convenzionale al radiocarbonio è stata corretta per gli effetti di frazionamento isotopico sia mediante la misura del termine $\delta^{13}C$ effettuata direttamente con l'acceleratore, sia per il fondo della misura.

Campioni di concentrazione nota di Acido Ossalico forniti dalla NIST (National Institute of Standard and Technology) sono stati utilizzati come controllo della qualità dei risultati. Per la determinazione dell'errore sperimentale nella data al radiocarbonio è stato tenuto conto sia dello scattering dei dati intorno al valore medio, sia dell'errore statistico derivante dal conteggio del ^{14}C. La Tabella 2 riporta la datazione al radiocarbonio (non calibrata) per i campioni con l'indicazione dell'errore assoluto della misura.

Tabella 2. Valore misurato della radiocarbon age.

Campione	*Radiocarbon Age (BP)(*)*	*$\delta^{13}C$ (‰)(**)*	*Note*
LTL16550A	**384 ± 40**	**-21.5 ± 0.5**	
LTL16551A	**394 ± 45**	**-25.3 ± 0.5**	
LTL16552A	**80 ± 35**	**-23.1 ± 0.4**	
LTL16553A	**290 ± 40**	**-27.9 ± 0.3**	
LTL16554A	**325 ± 40**	**-26.8 ± 0.3**	
LTL16555A	**85 ± 35**	**-23.1 ± 0.3**	
LTL16556A	**203 ± 45**	**-26.0 ± 0.3**	

(**) Il valore riportato del termine di frazionamento isotopico degli isotopi stabili del carbonio ($\delta^{13}C$) si riferisce a quello misurato con il sistema AMS. Tale valore, pertanto, può differire dal termine di frazionamento naturale e da quello misurato mediante IRMS.

(*) Con BP si intende qui una datazione convenzionale al radiocarbonio non calibrata il cui calcolo implica (cfr. M. Stuiver, H.A. Polach, Radiocarbon, Vol. 19, No.3, 1977, 355-363):

- L'uso del tempo di dimezzamento di Libby (5568 anni) rispetto al valore corretto di 5730 anni;
- L'anno 1950 come anno di riferimento.
- L'utilizzo diretto o indiretto dell'acido ossalico come standard di riferimento.

(**) Vengono convenzionalmente indicati come "Moderni" i campioni con una datazione convenzionale al radiocarbonio minore di 200 anni BP.

La datazione al radiocarbonio per i campioni è stata quindi calibrata in età di calendario utilizzando il software OxCal Ver. 3.10 basato sui dati atmosferici [Reimer PJ, et al. 2013 *Radiocarbon* 55 No. 4-1869-1887]. Il risultato della calibrazione è riportato nei grafici e nelle Tabelle seguenti.

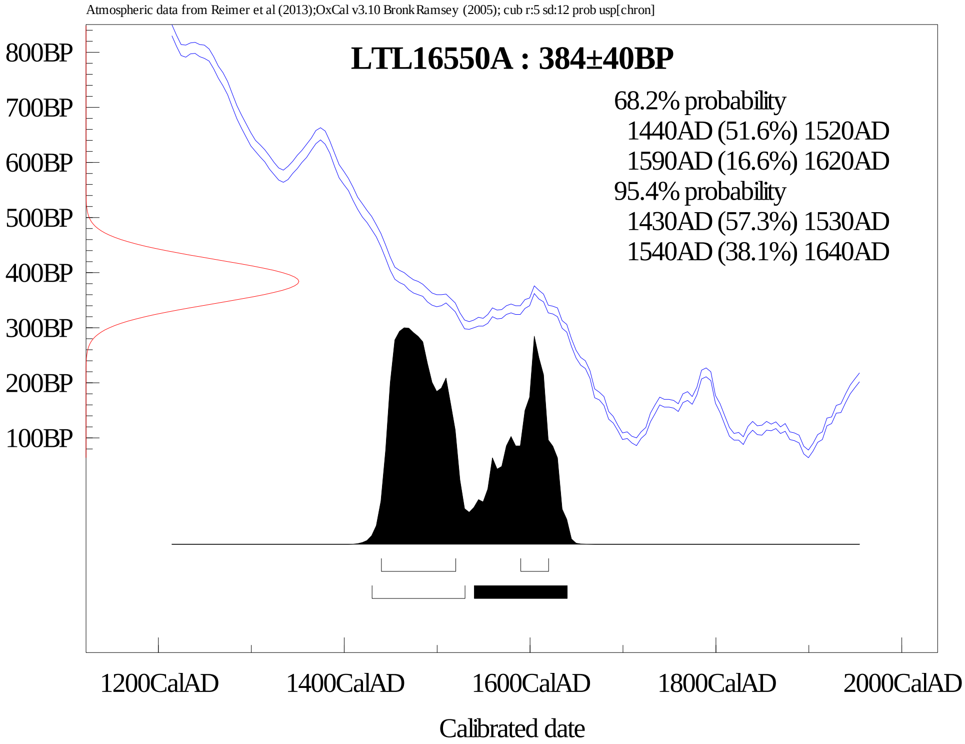


Figura 1. Calibrazione della data convenzionale al radiocarbonio del campione LTL16550A

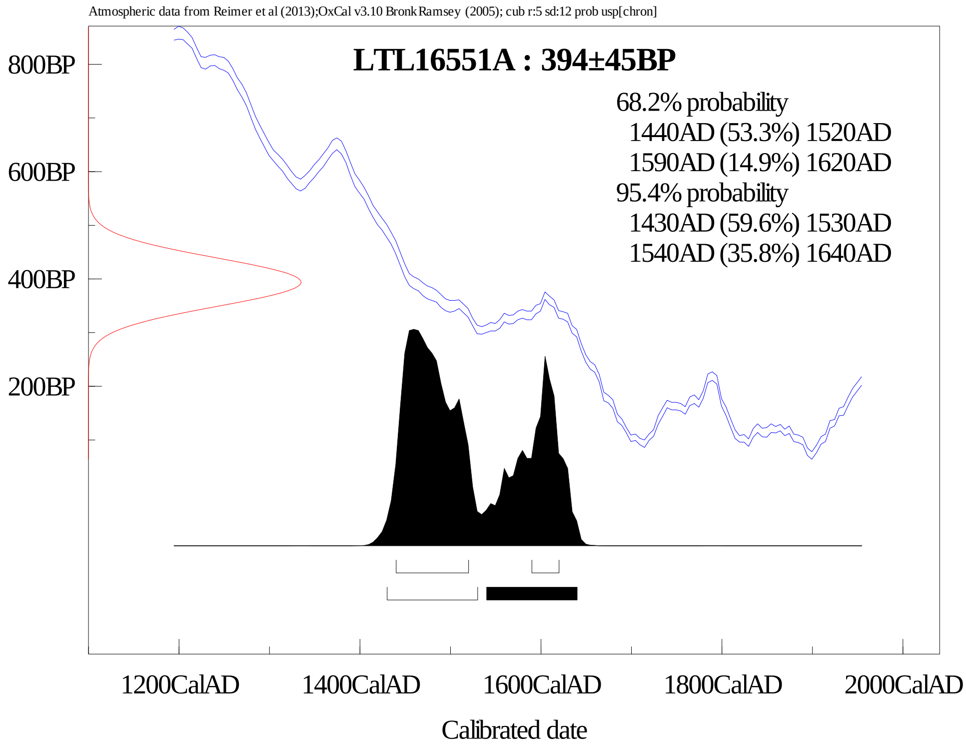


Figura 2. Calibrazione della data convenzionale al radiocarbonio del campione LTL16551A

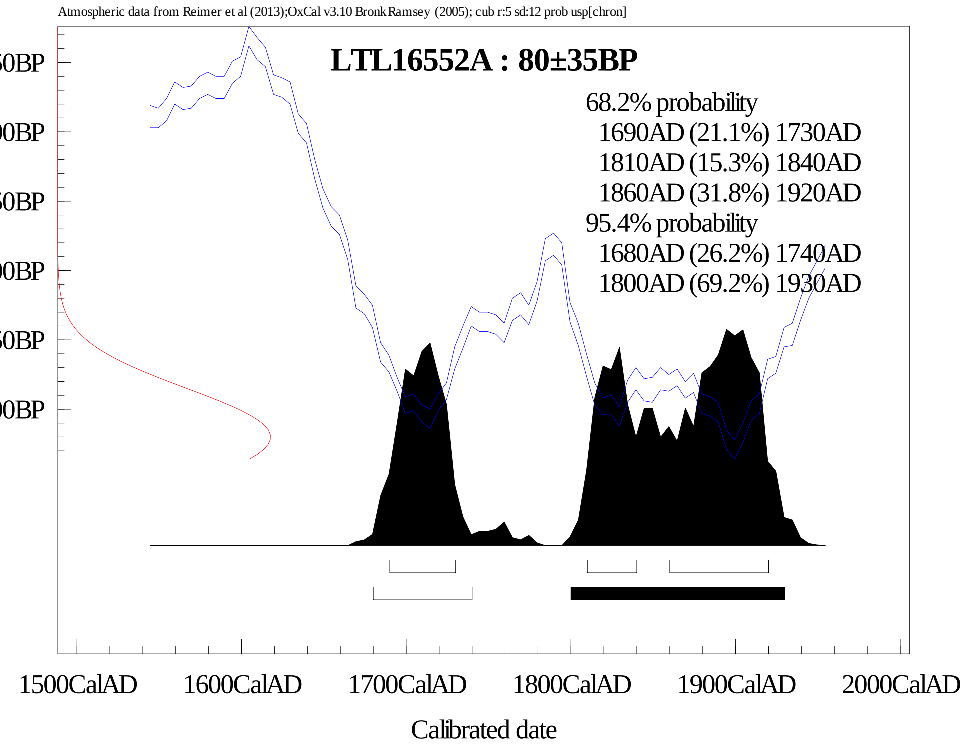


Figura 3. Calibrazione della data convenzionale al radiocarbonio del campione LTL16552A

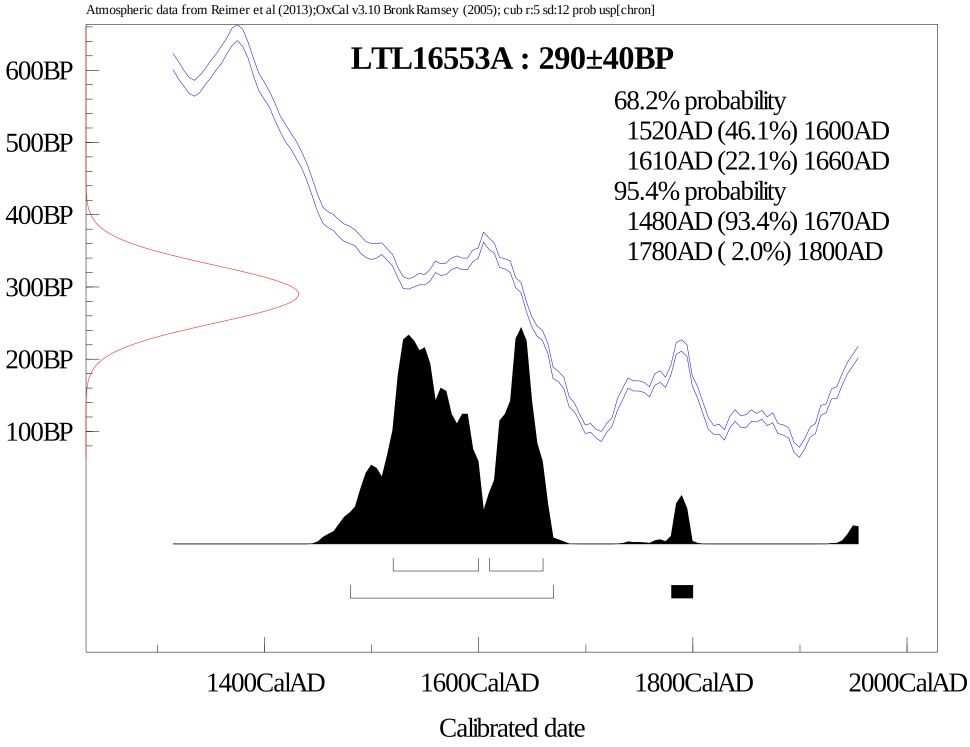


Figura 4. Calibrazione della data convenzionale al radiocarbonio del campione LTL16553A

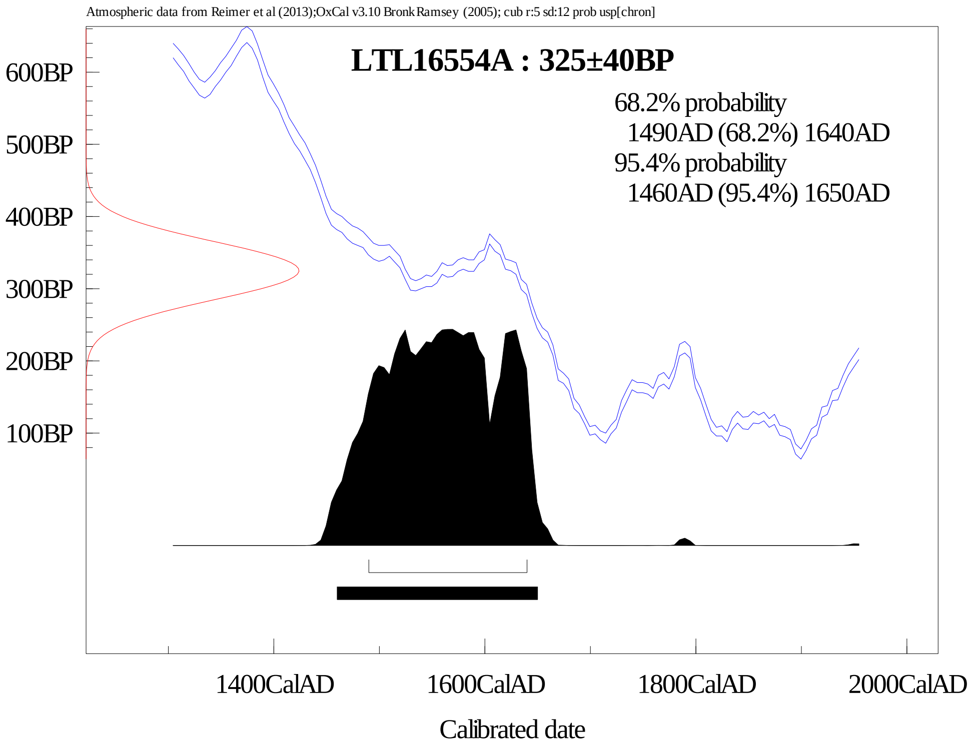


Figura 5. Calibrazione della data convenzionale al radiocarbonio del campione LTL16554A

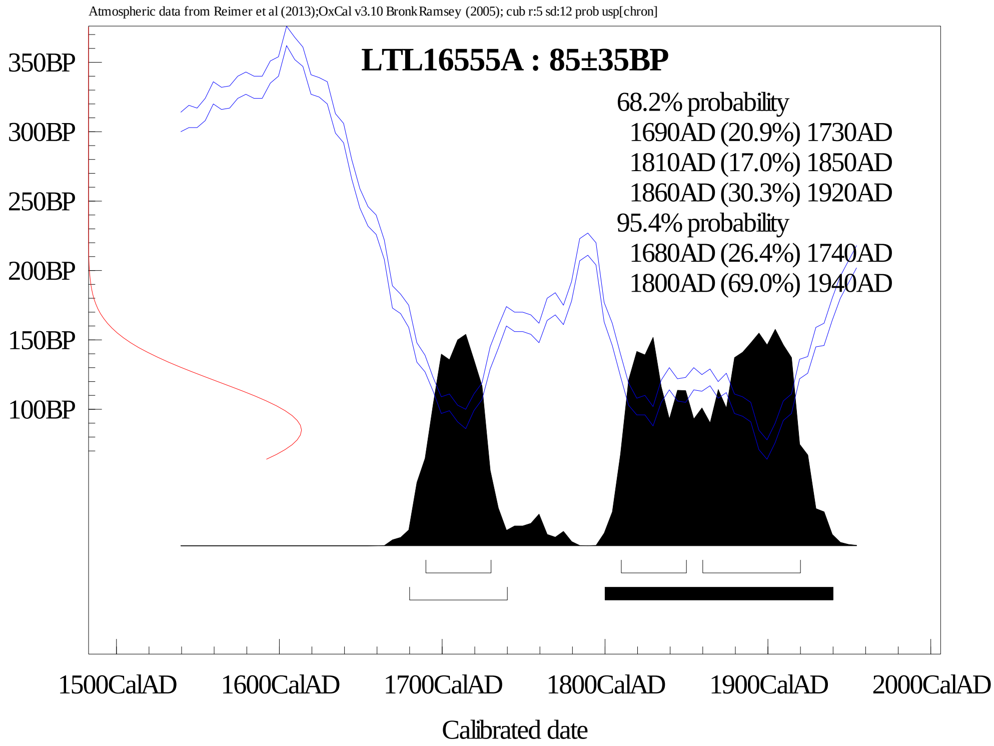


Figura 6. Calibrazione della data convenzionale al radiocarbonio del campione LTL16555A

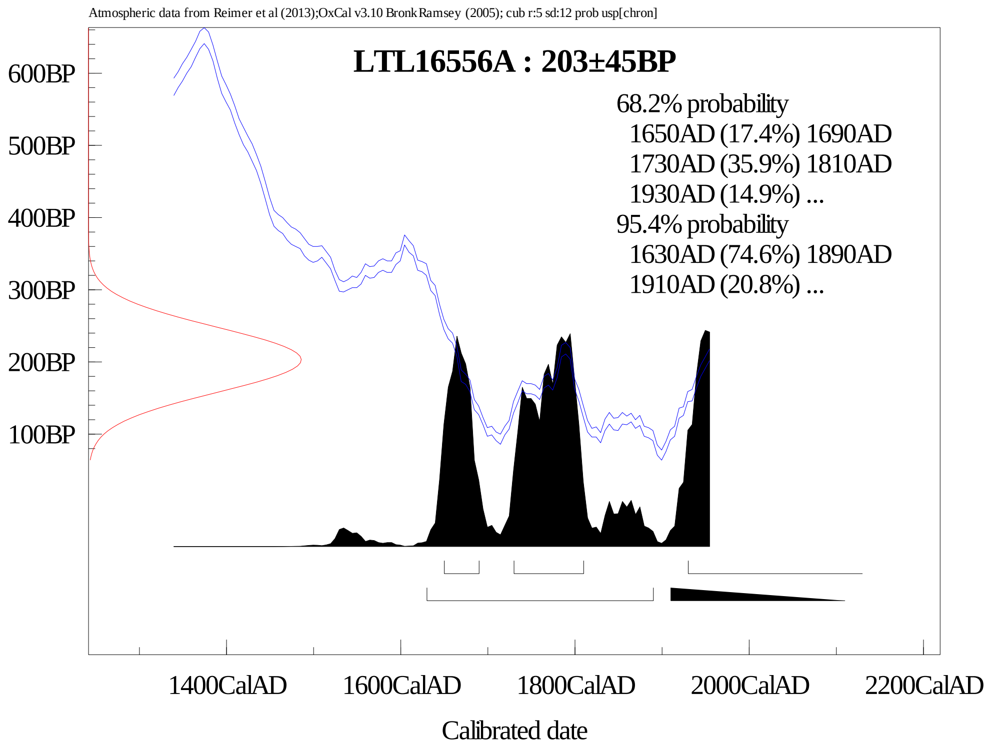


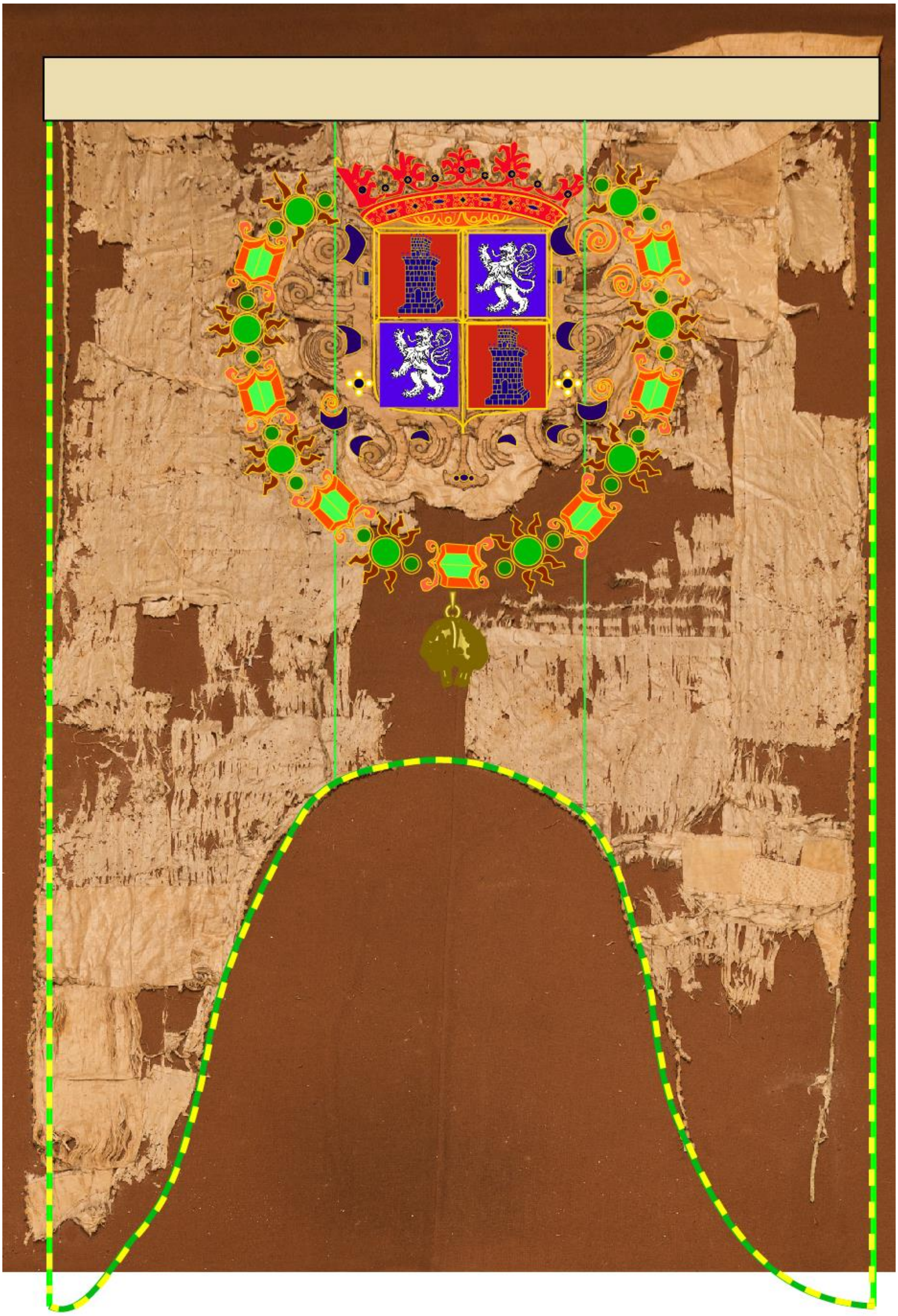
Figura 7. Calibrazione della data convenzionale al radiocarbonio del campione LTL16556A

CODICE CEDAD	CAMPIONE	DATAZIONE CALIBRATA (LIVELLO DI CONFIDENZA 2σ)
LTL16550A	FP 1	1430AD (57.3%) 1530AD 1540AD (38.1%) 1640AD
LTL16551A	FP15C	1430AD (59.6%) 1530AD 1540AD (35.8%) 1640AD
LTL16552A	FP15F	1680AD (26.2%) 1740AD 1800AD (69.2%) 1930AD
LTL16553A	FP15M	1480AD (93.4%) 1670AD 1780AD (2.0%) 1800AD
LTL16554A	FP16	1460AD (95.4%) 1650AD
LTL16555A	FP17	1680AD (26.4%) 1740AD 1800AD (69.0%) 1940AD
LTL16556A	FP22	1630AD (74.6%) 1890AD 1910AD (20.8%) 1950AD

TABELLA 3. Riepilogo delle datazioni calibrate per i campioni

Cordiali Saluti, Prof. Lucio Calcagnile Direttore, Centro di Datazione e Diagnostica dell'Università del Salento

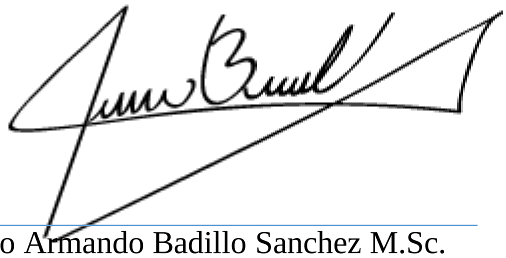
CEDAD - CEntro di DAtazione e Diagnostica Dipartimento di Matematica e Fisica "Ennio de Giorgi", Università del Salento c/o Cittadella della Ricerca, S.S. 7 per Mesagne, Km. 7 +300, 72100 Brindisi Tel. +39 0832 295050 FAX +39 0832 295058 e-mail: cedad@unisalento.it web: www.cedad.unisalento.it



Cristina Dias Ph.D.

Nicola Schiavon Ph.D.

Ana Manhita Ph.D.



Diego Armando Badillo Sanchez M.Sc.

Date:
September 27, 2016

Grade:
17/20