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EVALUATION OF NOVEL AGI@AU TLC/SERS/μ-FTIR-ATR SYSTEM FOR THE IDENTIFICATION OF SYNTHETIC DYES IN CULTURAL HERITAGE

TESI DI LAUREA IN CHEMICAL METHODS OF EXAMINIG CULTURAL PROPERTY

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Marco Polo descrive un ponte, pietra per pietra.

- *Ma qual è la pietra che sostiene il ponte? – chiede Kublai Kan.*

- *Il ponte non è sostenuto da questa o quella pietra,* - *risponde Marco,* - *ma dalla linea dell'arco che esse formano.*

Kublai Kan rimane silenzioso, riflettendo. Poi soggiunge: - *Perché mi parli delle pietre? È solo dell'arco che m'importa.*

Polo risponde: - *senza pietre non c'è arco.*

Italo Calvino, *Le città invisibili*, October 1993

In memoriam Carolina Balbás Gómez

.

A México. 19-09-2017

A Isabel, Polo & Daniel: mi inspiración, fuerza y amor

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CULTURA
SECRETARÍA DE CULTURA

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ABSTRACT

The present thesis is focused in the evaluation of a methodology for the study of synthetic dyes by using Thin Layer Chromatography (TLC), μ-Fourier Transform Infrared Spectroscopy (μ-FTIR) and μ-Raman Spectroscopy (μ-Raman-SERS) techniques employing as support silver iodide nanoparticles over gilded glass (AgI@Au). For many years, the study of dyes has been conducted mainly with chromatographic techniques such as HPLC and GC in combination with spectroscopic methods such as FTIR and MS. The small amount of sample is one of the main improvements of the method proposed by the MA2D laboratory, same as the reduce sample pretreatment in order to obtain satisfactory results. Five dyes where studied: Acid Blue 74, Basic Violet 1, Basic Violet 3, Brilliant Green 1 and Acid Yellow 24. The same method was employed for the characterization of modern felt-tip pen inks by studying three pens from Stabilo® 68 series: 68/22, 68/41 and 68/55.

Key words: AgI@Au, synthetic dyes, μ-SERS, TLC, μ-FTIR

RESUMEN

La presente tesis se enfoca en la evaluación de un método de análisis para el estudio de colorantes sintéticos usando las técnicas de cromatografía de capa fina (TLC), μ-espectroscopia infrarroja por transformada de Fuorier (μ-FTIR) y μ-espectroscopia Raman (μ-Raman-SERS) usando como soporte nanopartículas de yoduro de plata aplicadas sobre un portaobjetos recubierto de oro. Durante muchos años el estudio de colorantes se ha realizado con métodos cromatográficos como HPLC y GC en combinación con técnicas espectroscópicas como FTIR y MS. La poca cantidad de muestra es una de las principales ventajas del método propuesto por el laboratorio MA2D, así como el reducido pre tratamiento que reciben las muestras, obteniendo buenos resultados. Cinco colorantes fueron estudiados: Acid Blue 74, Basic Violet 1, Basic Violet 3, Brilliant Green 1 y Acid Yellow 24. El mismo método de análisis se utilizó para la caracterización de tintas modernas empleadas en marcadores Stabilo® de la serie 68: 68/22, 68/41 y 68/55.

Palabras clave: AgI@Au, colorantes sintéticos, μ-SERS, TLC, μ-FTIR

ABSTRACT

La presente tesi è focalizzata nella valutazione della metodologia d'analisi per lo studio di coloranti di origine sintetica utilizzando cromatografia di strato sottile (TLC), μ-spettroscopia infrarossa per trasformata di Fourier (μ-FTIR) e μ-spettroscopia Raman (μ-Raman-SERS) con un supporto di nanoparticelle d'argento ioduro su vetrino dorato. Negli ultimi anni la caratterizzazione dei coloranti si realizza con metodi cromatografici come HPLC e GC in combinazione con tecniche spettroscopiche come FTIR e MS. La ridotta quantità di campione è uno dei principali vantaggi della metodologia sviluppata dal laboratorio MA2D, e anche il poco pretrattamento che riceve il campione, ottenendo risultati ottimi. Sono stati analizzati cinque coloranti sintetici: Acid Blue 74, Basic Violet 1, Basic Violet 3, Brilliant Green 1 e Acid Yellow 24. Lo stesso metodo è stato applicato allo studio d'inchiostri moderni di pennarelli Stabilo® della serie 68: 68/22, 68/41 e 68/55.

Parole chiave: AgI@Au, coloranti sintetici, μ-SERS, μ-FTIR

CONTENTS

Glossary

INTRODUCTION

> *"Alchemist of old spent their days and nights searching for gold, and never found the magic Proteus, though they chased him through all gases and all metals. If they had, indeed, we doubt much if the discovery had been as useful as this of Perkin's purple"*
>
> *Charles Dickens, All the year round, September 10, 1859.*

Dyestuffs are constantly present in our daily life since ancient times. The natural dyes were extensively used and some of them were highly appreciated, such as the Tyrian purple that reached a higher price than gold and was a symbol of royalty. Dyes were not only use for giving color to textiles but also for the production of lakes in order to be used for painting.

Fig. 1 Unicorn Tapestry, Cloisters, Metropolitan Museum of New York, USA

An important part of the aesthetic value of the Iranian carpets, paintings from the great masters and most renamed modern painters, Mayan textiles and medieval tapestries, is related to the color given by natural dyes. However, after the last part of the 19th century, a revolution in the manufacture of dyestuff appear thanks to the technological advances and the research in the field of chemistry, making available new hues for the artistic production.

Fig. 2 Women textile from Chiapas state. Museo Textil del Mundo Maya, San Cristóbal de las Casas, Mexico.

Museums such as the Victoria & Albert Museum in London, the Metropolitan Museum of New York, the Musee d'arts decoratifs in Paris, the Carpet Museum of Iran in Tehran, Museo Nacional de Historia in Mexico or the Museo Nacional del Traje in Madrid –just to mention some examples around the world- possess a great collection of dyed textiles that must be studied and preserved.

In this sense, the Science for the Conservation is important for what Salvatore Siano (2012, p. 15) have called "material reading"[1], which defines the interpretation of the complex material systems that form the object, and that is a complement for the "historic-stylistic reading"[2]. The material reading offers information of the materials deterioration, technological evolution and process of production, raw materials and important data that can be useful in the attribution and authentication of works of art.

The "material reading" also appears in the conservation methodology proposed by Barbara Appelbaum (2010, p. 10-11), inside the quadrant called "Object-specific information of the Material aspects" of the *Characterization grid* required for a full study of an object that must be treated for its conservation. In this methodology, each quadrant is as equal as important as the others are.

According to Appelbaum, even if the study of the material aspects of the objects are not focused on searching the artistic or historic value but the material aspects, it must never go separate of the non-material study of the object. The two aspects are important to obtain a holistic comprehension of it as the main conclusion, what we can call a complete diagnostic.

Thus, it is clear the importance of the research regarding synthetic dyes, not only for their characterization but also for the understanding of their degradation and conservation. The degradation is the main subject in the case of the synthetic dyes. Since many of them

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[1] Translated from the Italian *Lettura materica.*

[2] Translated from the Italian *Lettura storico-stilistica.*

present a very fast decay, the conservation of textiles, documents or paintings where they were used becomes a major problem for conservators.

In words of Marco Ciatti, director of the Opificio delle Pietre Dure in Florence, the conservators require the help of a scientist to understand the materials used by the artist and the possible phenomena of degradation linked to them. As Umberto Baldini highlighted in his theory of the Restoration, the conservation and its methodology have as the main support the theory and the material investigation (Siano, 2012, pp. 6-7).

As I mentioned before, dyes have a historic importance not only because they are present as constituent materials of many works of art and historic textiles, but because they are also the evidence of a historical period and the development of a huge industry.

In second place, the synthetic dyes, and in a greater way the early ones produced in the last part of the 19th century and the first decades of the 20th, are unstable and its degradation is fast. This not only damages its principal characteristic –the color- but also makes complicated their identification since many of them present degradation products similar to other dyes or they change completely their chemical structure.

On the other hand, some of these materials are still used in modern materials available for artist and, since it has been identified a problem of duration on time, their use in the elaboration of works of art must be well informed, considering that under certain condition the components will degrade. The selection of them should be followed by a preventive conservation plan in order to keep the qualities that incentivized their use.

These two statements evidence the main problem to be solved: to preserve the color –which is an important aspect of paintings and textiles- we have to be able to understand their chemical composition and identify them over the complex matrix where they are immersed (fiber-mordant-dye system, fiber-dye system or mordant-dye-binder-pigments system). In addition, we have to understand the mechanism of degradation and identify, if possible, the causes, to offer useful information to the conservator to determine the adequate treatment and defined the correct storage or exhibition conditions.

Recently chemists have considerably developed the study of these materials. Fortunately, the chemical composition of the synthetic dyes can be easy identified, since there is abundant bibliography respect to their production, which as conservation scientists we have to understand and disseminate (Brokerhof, 2015, p.8). Moreover, some of the mechanisms of degradation have been already studied because they are also of industrial interest. So, why to make a research project in this field?

The traditional techniques employed for the study of dyes are generally chromatographic (GC, HPLC) coupled to spectroscopic methods (FTIR, MS). However, these techniques required a certain amount of samples, which is destroyed. The latest development bet on the non-invasive techniques or the ones that required a smaller amount of sample. Thus, techniques such as Fiber Optics Reflectance Spectroscopy (FORS) have been developed; nevertheless, the data interpretation is complex and not always accurate since they present a high matrix effect and interpretation models must be established by analyzing mock-ups. Furthermore, not all the institutions have access to the instrumentation required to this kind of analysis.

This is the reason why, the development of a technique that allows the identification of dyes in a fast and simple way, with a small amount of sample and by using instrumentation that is common in laboratories and museums such as FTIR or Raman is an interest subject to explore.

The AgI@Au system, which stands for gold coated slide cover with silver iodide particles, was proposed by the Microchemistry and Microscopy Art Diagnostic Laboratory (M2ADL) from the Alma Mater Studiorum Università di Bologna. It allows the separation of the components of dye mixture by TLC and increase the capacity of identification of the molecules by enhancing the signal due to the use of silver nanoparticles.

Proposing a new method always requires a process of validation and evaluation, in order to identify the advantages and limitations, but more important to be sure that the quality of the information offered by it corresponds to the scientific standards of utility and reliability. As it generally happens in Analytical Chemistry, the requirements of the produced information are closely linked to the needs of the end-user of that information, in our case the conservators (van Zoonen, van't Klooster, Hoogerbrugge, Gort, & van de Wiel, 1998, p. 356).

In this sense, an analytical method can be described as a chain of decisions, actions and procedures funded into the initial problem that, in most cases, can be answered by the information produced by the new method (van Zoonen, van't Klooster, Hoogerbrugge, Gort, & van de Wiel, 1998, pp. 356-357).

Therefore, the evaluation of the method developed by the MA2D laboratory is the main goal of the present thesis, by taking into consideration the previous projects, analyzing different kinds of samples and evaluating the results obtained. The present project is part of the European project “Integrated Platform for the European Research Infrastructure ON Cultural Heritage” (IPERION CH) in which collaborates the M2ADL, under the direction of Prof. Rocco Mazzeo, supervisor of the present thesis.

The samples analyzed in this project were kindly donated by two of the co-partners; the Centre de Recherche et de Restauration des Musées de France that contributed with samples artificially aged, and the Cultural Heritage Agency of the Netherlands that gave the real sample coming from the book entitle *Tabellarische Uebersicht über die künstlichen organischen Farbstoffe*. The modern felt-tip pens samples were acquired by M2AD laboratory in order to analyzed the contemporary commercial materials available for artists, and the results were compared with the research developed by the Università degli studi di Bari Aldo Moro, Italy.

This project is still under development; however, the results obtained until now have shown the promising application. This research adds to a chain of investigation that has arranged part of the methodology.

The agenda of this thesis revolves around the improvement of the extraction method of the dyes from the fiber, the understanding of the interaction between some dyes and the AgI nanoparticles and the possibility to apply this methodology of analysis to real samples from the end of the 19th century.

The dyes selected were Basic Violet 1, Basic Violet 3, Brilliant Green 1, Acid Blue 74 and Acid Yellow 24. The same methodology was applied to modern materials, Stabilo® felt-tip pens from 68 series, which many of them contain in their formulations some early synthetic dyes such as Acid Blue 9 and Basic Violet 4.

The present document is structured in four chapters. The Chapter I presents the objective of the research. Then a general revision of the early synthetic dye industry and the state of art in the field of analysis of dyestuff is contained in Chapter II. The structure of the evaluation process and the experimental procedures conducted during this investigation are explained in Chapter III, meanwhile, the results obtain and the discussion constitutes Chapter IV. At the end are presented the concluding remarks of the project.

1. RESEARCH OBJECTIVES

The main objective of the research is to evaluate a methodology for the characterization of synthetic dyes used for the manufacture of objects of historical and artistic interest. It is focused in the dyes produce between 1854 and 1940, which are the early years of the synthetic dyes industry.

The method should be able to identify the analyte with a small amount of sample, reducing the sample pretreatment and by analyzing the same test case with different techniques such as μ-FTIR and μ-Raman.

The project evaluates the power of a novel system that combines the separation of components, in terms of Thin Layer Chromatography (TLC), with spectroscopic techniques such as μ-FTIR and μ-Raman.

As said above; the system was developed by the M2AD laboratory and in previous studies, some standards samples of early synthetic dyes and samples artificially aged have been studied; however the methodology has not be used for the study of real and contemporary samples, which is one of the main goals the present research.

The information produced by the investigation will help to continue with the progress in terms of establishing a methodology that offers information for the study and conservation of cultural property colored with early synthetic dyes and even other kinds of colorants, for instance, colorants of natural origin.

2. STATE OF ART. EARLY SYNTHETIC DYES: PRODUCTION, DEGRADATION, AND CHARACTERIZATION

"The starting point is the study of color and its effects on men"

Vasilij Kandinskij, Concerning the Spiritual in Art, 1912

2.1 The Development of Synthetic Dye Industry

Until the 19th century, dyeing was linked to tradition and transmission of knowledge during generations; learning how to use the natural dyes and varying the shades by choosing different mordants to colored the natural fabrics. In some cases, the dyehouses were even specialized in the use of one specific color. There was no control of chemicals concentration or chemical composition of the dyestuff, only the experience (Holme, 2006, p. 237).

The use of natural dyestuffs continued until 1854 and even during the First World War. However, by 1890, almost the 90% of all the dyestuff used in the dyeing industry were from synthetic origin (Holme, 2006, p. 237). The industrial production of synthetic dyes started during the 1860s but without great success due to some problems; mainly poor fastness to light and high cost because of the small-scale production. Still, they had promising characteristics, like brilliant hues and good tinctorial strength, which kept the interest of the chemists and industry in their development (Park & Shore, 1999, p. 159).

Fig. 1 Sir William Henry Perkin, by Sir Arthur Stockdale Cope, oil on canvas, 1923, National Portrait Gallery, London.

Fig. 2 Rabbit skin mask, dyed with picric acid.

One of the first dyes obtained from chemical reactions was the picric acid, discovered by Woulfe in 1771, and can be considered a pre-industrial synthetic dye. It was used as a dye during 1840-1850, mainly employed for dyeing silk by Guinon, Marnas & Co. in Lyon, France, their yellow silks were exhibited at the London Great Exhibition in 1851. Moreover, a purple dye, called murexide, obtained from the uric acid using the excrement of birds, imported from Peru to Europe, in the 1850s was compare to Roman purple (Ball, 2015, p. 218-219).

However, the United Kingdom was the place where the synthetic dye industry was born. The first synthetic dye to be produced was mauveine or aniline purple, it was discovered by William Henry Perkin who treated aniline sulphate with potassium dichromate and then extracted the precipitated with methanol, then the purple extract was employed for dyeing a piece of silk (Christie, 2015, p. 7).

Perkin & Sons was the first firm to be created. The first plant was stablished in Greenford Green in 1857 (Murmann, 1998, p. 9). Perkin's discovery was patented in 1863 after some modifications to the process to cover the requirements of the dyeing industry (Holme, 2006, p. 240). The second discovery of Perkin was safranine, which was obtained by oxidation of mauve with lead peroxide, it was useful for imparting color to silk and wool fibers but not to cotton, which required the addition of a mordant such as tannins or sodium stannite (Chatwal, 2009, p. 1.5).

Just after the discovery of mauveine other synthetic dyes were obtained, for example, fuchsine in 1956 and methyl violet in 1861. In 1871 fluorescein appeared and by chemical modification to it, red eosin was obtained in 1873. Two years later erythrosine G was synthesized from iodination of fluorescein. This kind of dyes not only were used for the textile industry but also as lakes in modern paints (de Keijzer, van Bommel, & Geldof, 2009) pen inks and even with medical proposes.

Since then, the production of synthetic dyes became a big industry and many other substances were synthesized, i. e. synthetic indigo, which was discovered by Adolf van Baeyer in 1880 and produced after 1897. Other synthetic dyes manufactured in the first decades of the 20th century were indanthrone blue and flavanthrone yellow, discovered by René Bohn in 1901, benzamidoanthraquinones by Robert Schmidt (1902-1905), Ciba Violet A (1908), etcetera (Park & Shore, 1999, p. 159).

The main raw material for the synthesis of dyes was coal. During the last part of the 19th century, the coal production was dominated by the United Kingdom and Germany was mainly a consumer of it. Moreover, the biggest textile industry was also in Britain, industry that demanded a great quantity of new and brilliant dyes (Murmann, 1998, p. 12).

According to Murmann (1998, pp. 9-10), Germany was the first country in the global production of dyes since 1870 until the First World War, followed by the United Kingdom, which its production decrease considerably after 1913. On the other hand, the United States failed in the development of this industry with a small production, around 1.9% of the world production, meanwhile, the German firms such as BASF, Hoechst, Bayer, AGFA, and Cassella controlled over the 90% of the production (see Table 1).

The production of dyes raised dramatically from 1862 to 1913, around 3800% in terms of value and 4000%[1] in terms of volume, according to the data collected by Murmann and Homburg (Murmann, 1998, p. 18).

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[1] From 3,500 tons in 1871 to 160,000 tons in 1913. (Murmann, 1998, p. 18)

Table 1. Estimated Dye Production and Consumption in 1913, taken from Murmann, 1998, p. 19

Country	Production in tons	Consumption in tons	Trade balance
Germany	1350,000	20,000	115,000
Switzerland	10,000	3,000	7,000
France	7,000	9,000	-2,000
United Kingdom	5,000	23,000	-18,000
USA	3,000	26,000	-23,000
Other producers	2,000	-	-
China	-	28,000	-
India	-	8,000	-
Italy	-	7,000	-
Russia	-	7,000	-
Japan	-	5,500	-
Canada	-	1,200	-
Mexico	-	600	-
Australia	-	500	-
Africa	-	1,000	-
Others in			
Europe	-	18,000	-
Asia	-	3,000	-
South America	-	1,200	-
Total	162,000	162,000	-

Fig. 3 Cotton plain weave with brocading in chenille by Alexander Morton & Co., ca.1926.

However, the degradation of these new dyes was quickly identify and test samples in order to recognize the fastness resistant became a common practice between some of the producers. James Morton –who was the head of a dynasty of fabric designers- notice the degradation of some of the colorants employed in his velvet woven. He made some early experiments to determine the degradation of dyes in textiles by using several samples exposed to certain conditions in a greenhouse. The results of these experiments allowed Morton to select the more resistant synthetic dyes for his tapestries production (Park & Shore, 1999, p. 160), creating his own company called Sundour Fabrics in 1906 in collaboration with his son Alexander Morton, and offering unfadable fabrics (Jackson, 2002, p. 23).

Due to the difficulties caused by the beginning of the First World War (194-1918), Morton began to produce his own dyes such as indanthrone blue and flavanthrone yellow and after anthraquinone dyes. The latter, at the beginning, was not well accepted by dyers so the BASF company introduced the first color fastness label employed in objects manufacture just with that kind of dyes in order to promote its use (Park & Shore, 1999, p. 160).

Fig. 4 Paris, France, 1869-1870, Vignon, Ribbed silk trimmed with satin, faced with cotton, brass, Victoria & Albert Museum

Perkin’s discovery changed deeply the textile industry and many others such as printing. By 1956 more than 1,000 different synthetic dyes were available, including all the colors of the spectrum and their respectably shades, allowing, for example, the use of only one dye to obtain green and not anymore a mixture of yellow and blue dyes as it was done before. (Schriver, 1956).

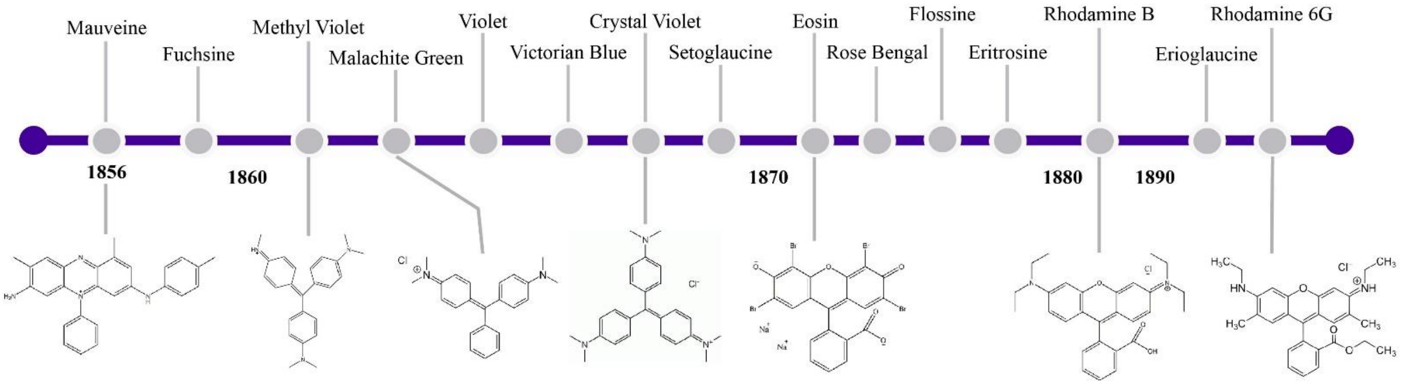


Fig. 5 Time line of some of the dyes synthetized from mauveine during the last decades of the 19th Century. Based on Ball, 2015, p.238.

The develop of synthetic dye industry during the las part of the 19th century was very important mainly in countries as England, Germany and in lower scale France and Switzerland, which had great advance in the chemical industry and research. Many companies were appearing and other disappearing due to the constant rearrangement of the industry. During this time, manuals with the information about the supplies required for the production of some synthetic dyes were available. According to Hesse:

> *"[…] by 1912 Germany and Switzerland were net exporters of dyes and Britain a net importer. Germany was also exporting to Asia (24% of total exports) and North America (23%). In Europe her main markets after England were Austria, Italy, Belgium, France and the Netherlands.*" (cited by Baker, 2011, p. 37)

This big growth of the dye industry affected the society of the time. The new middle class that appeared after the Industrial Revolution found in the synthetic dyes and its use in textiles and the artistic field interesting goods to acquire, however, there were also philosophical ideas that encourage the use of natural products. The interest for the new dyestuffs was reflected in the Exhibition where many of these new substances were shown in areas such as textile, pharmaceutic and chemicals. This interest is also illustrated in the articles published during this time, where a positive reaction of the public to the synthetic dyes was shown. (Baker, 2011, p. 44-49).

Contrary to these enthusiastic opinions, others such as the painter Jean Georges Vibret (1840-1902), considered the use of these new materials a "catastrophe for art" due to the high attention to the brilliance of the color and not to their stability (Kirby, 2005, p. 69).

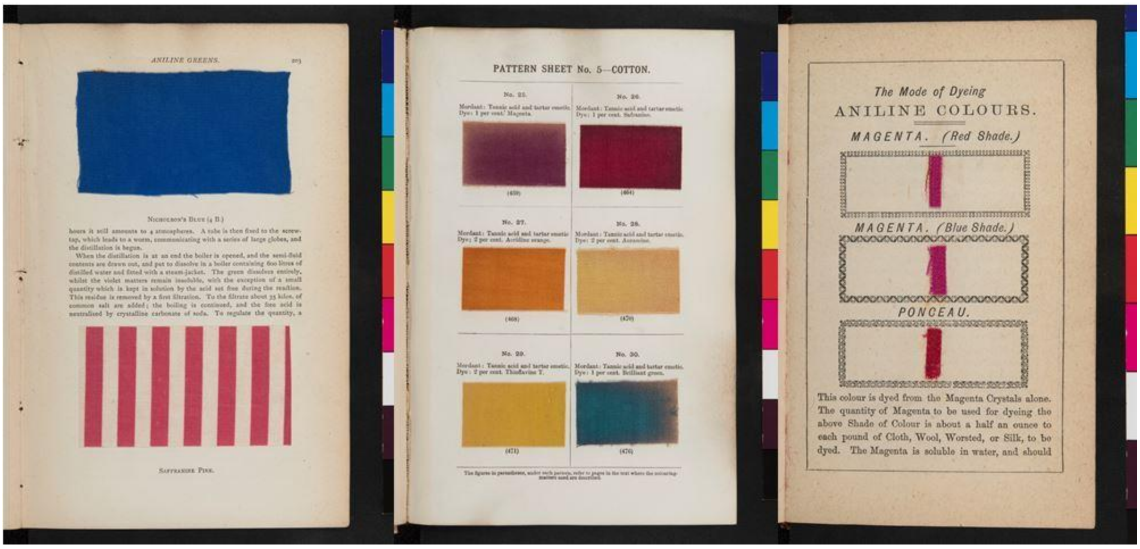
The use of the synthetic dyes penetrated completely in the daily life of people. The new materials were also use as inks for pens, such as the phtalocyanines, methyl violet, alkali blue, Victorian blue and Rhodamine B, which were very cheap and were used in different mixtures in order to obtain a specific ink colors (Crown, Conway, & Kirk, 1961, p. 339).

During the XX century, the group of phtalocyanines was discovered and became the most important group of organic pigments especially for the blue and green. In the last part of the century, the introduction of new dyes declined due to the cost of introducing a new product in the market and the increase in the toxicological controls. The production of focused on the so-called "functional dyes" which performed a specific function, as in the case of chlorophyll (Christie, 2015, pp. 13-17).

Pattern books and dyeing manuals

Two of the real samples come from the pattern book published in 1893 by Verlag von Julius Springer in Berlin entitled *Tabellarische Uebersicht über die künstlichen organischen Farbstoffe*, it is a case of pattern book that contains samples of the different dyes offered for the textile industry, in this case wool samples.

Julius Springer founded a bookstore in 1842. At the beginning the publication were political caricatures and treatises of Germany's *Vormärz* period, but later started publishing specialized literature in the scientific field, engineering and technical disciplines. It is possible to say that the book from where the samples studied in the present research come is an example of this kind of publications when the industrialization was fast and a big number of scientific innovations appeared, as the synthetic dyes (Sarkowski, 1996).



This colour is dyed from the Magenta Crystals alone. The quantity of Magenta to be used for dyeing the above Shade of Colour is about a half an ounce to each pound of Cloth, Wool, Worsted, or Silk, to be dyed. The Magenta is soluble in water, and should

Fig. 6 Examples of dye samples used in the Dye-versity project (L-R: Samples from William Crookes' Dyeing and Calico-Printing (LRA Store 32264) , Samples from Edmund Knecht, Christopher Rawson, and Richard Loewenthal's A Manual of Dyeing (LRA Store 32323-32325), Samples from David Smith's A Dyers Instructer (Sp Coll RB 5094).) Taken from McDonald, 2017

As Anita Quye mentioned, "the dyed samples were a way of sharing skills that until then had been closely guarded secrets by individuals for centuries". The first publication of this type was done by James Napier in 1855 (McDonald, 2017).

As Danilo Craveia has highlighted, the big diversity of this kind of books requires the establishment of a proper classification, ever since many of them are completely diverse. According to the period of production, the kind of samples and the support to which they are attached. According to the author, a pattern book constitutes a commercial instrument in which a group of industrial products is presented to the potential client (Craveia, 2011).

The importance of these books resides in the utility for the study of dye degradation, the identification of the dye with more sensitivity to certain factors and planning strategies for the exhibition and storage of textile collections (McDonald, 2017).

Felt-tip pens

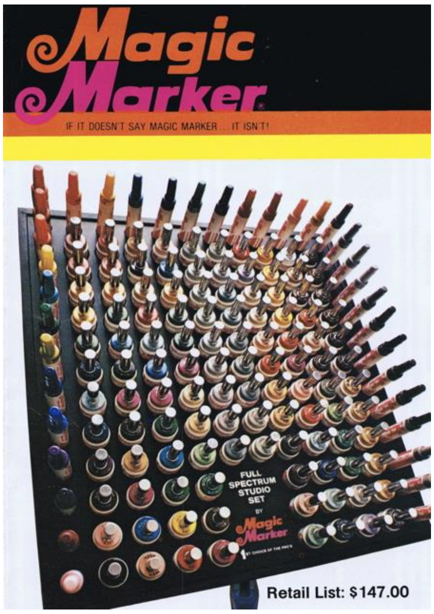


Fig. 7 Magic Marker® Advertisment

From the 1940's a felt-tip markers were commonly used for labeling and artistic proposes, however it was in 1953 when Sidney Rosenthal invented the first felt-tip pen by using a bottle full of ink and placing a wool felt wick at the end of it, he started the marketing of this new kind of pen calling it the "Magic Marker". Since then, this kind of products became popular. Later, in 1962 was invented the modern fiber-tip pen, by Yukio Horie from the Tokyo Stationery Company (Bellis, 2016).

Felt-tip pens consist of a plastic body and an ink reservoir made of polyester. The tip at the beginning was made of wool, but with the evolution of the production methods, it became from synthetic origin. It is generally produced with a powder of some material, mixed with water, molded in order to give it the cylindrical shape and the baked (Advameg, Inc., 2017).

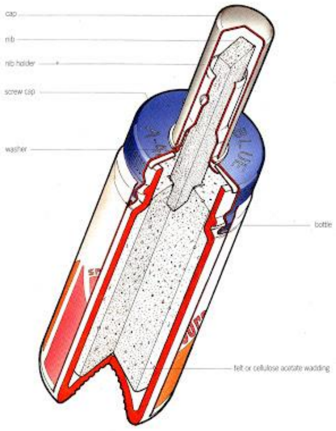


Fig. 8 Magic Marker felt-tip pen structure scheme

The tip has a different composition according to the two major manufacturers' countries. In Japan, the tips are made of compacted fibers added with a binder, a piece of bamboo wood and felt. On the other hand, in the United States, tips are made of synthetic fibers fused or bonded and the other kind is constituted of a compressed mass of tiny plastic beads. (522)

The ink of these pens flows into the tip by capillarity. It is constitute by a mixture of dye, 1-10% by weight of water, a solvent like an alkyl or alkylene carbonates –at the beginning was used xylol or tulol but they were substituted due to their toxicity- some additives such as nonyphenylpolyglycol ether, fatty alcohol ehoxalates and preservatives, for instance, orthophenolphenyl (Advameg, Inc., 2017).

The present research studies three felt-tip pens from the Stabilo® 68 series. The Stabilo company started in 1865 when Gustav Schwanhäusser bought Grossberger und Kurz company. The company known as Swam Pencil Factory started the mass production of pencils in 1904 but interrupted due to the World War I (Schwanhäusser Industrie Holding GmbH & Co. KG, 2015).

In 1925, the company was reestablished and acquired the name of Stabilo®, the World War II interrupted its activity again due to the destruction of the factory, however, in 1948 the Bavarian plant was stablished. During the 1960's the company expanded its production and started to manufacture ballpoint pens, felt-tip pens, and fiber-tip pens. Around 1966 the 68 series was one of the most popular products due to the quick-drying inks and ten colors available (Schwanhäusser Industrie Holding GmbH & Co. KG, 2013).

Fig. 9 Fabrizio Tosi. Kurt Cobain portrait, Stabilo 68 series pens over paper.

Nowadays the Stabilo® 68 pen has a tip of 1mm width, it possesses a water-based ink and is available in 40 colors, 6 fluorescent colors and various ranges that can be acquired in a single way or in different packing sets.

Dyes classification

The big amount of new dyes makes complicated its classification and identification, thus the nomenclature and their classification become an important issue to consider. Nowadays there are around 3600 different dyes that are used commercially and different ways to classifications. In the commercial nomenclature, the names are constituted generally by the name of the class followed by words, letter or number that describe some of the characteristics of the dye. The following table shows some examples.

Table 2 Examples of dye nomenclature components

Shade of the dye	Type of dye, fastness property or temperature of dyeing Consumption in tons	
Y or G= Yellow	S=Acid dye	D= Direct dye for cotton
R= red	F= Fastness to specific agents	C= Cold bran reactive dye
B= Blue	L= Light fastness	H= hot brand reactive dye
O= Orange	I= Vat dye	I_λ= dyeing in cold or normal temperature

Different to the commercial nomenclature, a more precise system to identify the dyes is the Color Index (C.I.) A naming system which is published by the Society of Dyers and Colourists (SDC) in U.K. and the American Association of Textile Chemist and Colorist (AATCC) in the USA. The first C. I. list was published in 1924 by the SDC. In this nomenclature, each dye possesses two numbers, one relative to the class and the other relative to the dyeing method. Nowadays the C.I. list is constituted of 11,685 fingerprints of dyes and contains 44,810 commercial names. Since it is the most accurate nomenclature, it is used in present research.

The classification can be done by the use or by the chemical composition of dyestuffs, the latter is the one that will be followed in the present work. The dye groups are Azo dyes, Anthraquinones, Vat dyes, Indigoid dyes, Polymethine dyes, Ary-carbonium dyes, Phthalocyanine dyes, Nitro dyes, and Miscellaneours dye Classes. Table 3 presents the classification of the dyes studied in the present research.

Table 3 Classification of dyes studied in the present research

Dye class	C.I. Name	C.I. Number	IUPAC Name	Other names
Tri-aryl Methines	Acid Blue 9 (AB9)	42090	diazanium;2-[[4-[ethyl-[(3-sulfonatophenyl)methyl]amino]phenyl]-[4-[ethyl-[(3-sulfonatophenyl) methyl]azaniumylidene]cyclohexa-2,5-dien-1-ylidene] methyl]benzenesulfonate	Brilliant blue, Blue No.1, brilliant blue FCF
Indigoid	Acid Blue 74 (AB74)	73015	3,3′-dioxo-2,2′-bisindolyden-5,5′-disulfonic acid disodium salt	Indigo Carmine, Food Blue 1, C Blue 2, Sicovit Indigotin 85E 132, Indigotine, Brilliant Indigo4 G
Tri-aryl Methines	Basic Green 1 (BG1)	42040	[4-[[4-(diethylamino)phenyl]-phenylmethylidene]cyclohexa-2,5-dien-1-ylidene]-diethylazanium;hydrogen sulfate	Brilliant Green, Pigment green 1, Diamond green G, Fast Green J.
Tri-aryl Methines	Basic Violet 1 (BV1)	42535	N-(4-(bis(4-(dimethylamino) phenyl)methylene)cyclohexa-2,5-dien-1-ylidene)methanaminium chloride	Methyl Violet 2B, Methyl VioletMethyl rosanilinium chloride, Hexamethyl parosanilinium chloride
Tri-aryl Methines	Basic Violet 3 (BV3)	42555	Tris(4-(dimethylamino)phenyl) methylium chloride	Crystal Violet, Gentian Violet, Methyl violet 10B
Tri-aryl Methines	Basic Violet 4 (BV4)	42600	[4-[bis[4-(diethylamino)phenyl] methylidene]cyclohexa-2,5-dien-1-ylidene]-diethylazanium;chloride	Ethyl Violet, Ethyl Violet Chloride, Ethyl purple 6B
Nitro	Acid Yellow 24 (AY24)	10315	2,4-Dinitronaphthalen-1-ol	Martius Yellow, Saffron Yellow, Naphthylen yellow

2.2 Dye Classes

In the following section are explained the four different dye classes of the colorants studied in the present research considering their general chemical properties.

Arylcarbonium Ion Colorants

This was the first group of synthetic dyes to appear. The dyes that are considered in this group present different chemical structures. The majority are cationic but some of them are also neutral or ionic. The general structure of these molecules is a central carbon attached to either two or three aromatic rings, so they can be divided into di or triarylmethine, the last ones are generally the most stable (Christie, 2015, p. 155). The presence of the aromatic rings and their resonance are the main reason why this kind of colorants possess a brilliant color (Chatwal, 2009, p. 187).

There are different ways to obtain these dyestuffs; Chatwal (2009, p. 187) describes the process as the introduction of groups as NH_2, NR_2 or OH into a para position of the benzene ring of the triphenylmethane. Other authors describe the process as an aromatic substitutions reactions between a C_1 electrophile with an aromatic system activated by a strong electron-releasing group. This can occur in one operation and in some cases; an oxidation reaction can be required in order to obtain the final product (Christie, 2015, p. 158).

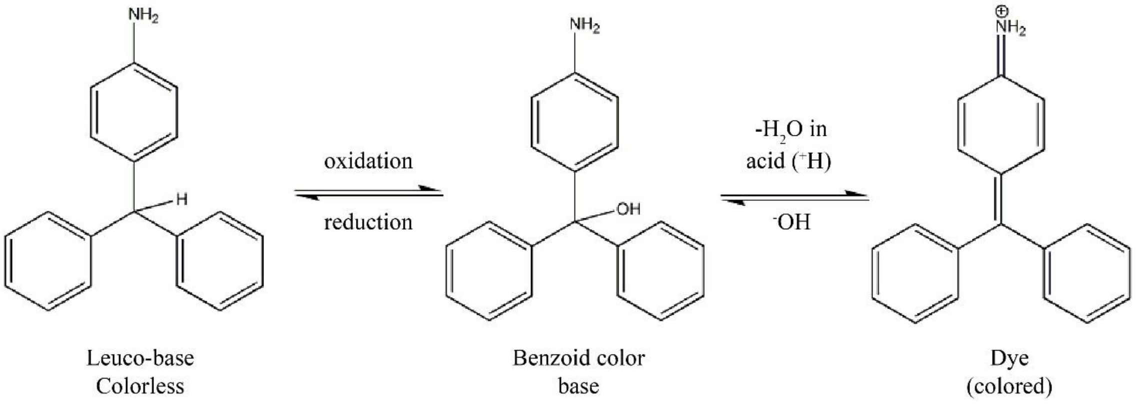


Fig. 10 Synthesis reaction according to Chatwal, 2009.

Nowadays these dyes are still used but in a smaller scale, they are mainly of historical importance because they were largely used during the last part of the 19th century and the first half of the 20th. Some of the colorants that are part of this groups are Mauveine, Rhodamine B, Rhodamine 6G, Fluorescein, Auramine O, Malachite Green, Crystal Violet, Methyl Violet, etcetera.

a) The Tri-aryl Methines Dyes Series

This group of dyes, also known as tri-aryl carbonium, is the oldest class of synthetic dyes. Chemically speaking they have a similar structure to cyanine dyes. All the dyes from this class are derived from the same basic structure composed of three aromatic rings (Gordon & Gregory, 1987, pp. 242-243). They are still used but in smaller scale in comparison with another kind of synthetic dyes. Mainly are employed as basic colorants to dye acrylic fibers and papers and as pigments and inks (Christie, 2015, p. 155).

The tri-aryl methane dyes are divided into two series: Rosaniline and Malachite. The first group began with the synthesis of fuchsine, and during the 1860s the number of colorants of this series increased due to the synthesis of Regina purple (1860), methyl violet (1861) and Hofmann’s Violet (1863) and after the experiments of Nicholson in 1862 other kind of blue dyes were synthesized (de Keijzer, van Bommel, & Hofmann-de Keijzer, 2011).

On the other hand, the Malachite series appeared at the end of the 1870s and contains different green colorants such as Malachite green (1877), brilliant green (1879), Victorian green 3B (1883) and after 1888 the sulfonated blue members of this series appeared (de Keijzer, van Bommel, & Hofmann-de Keijzer, 2011).

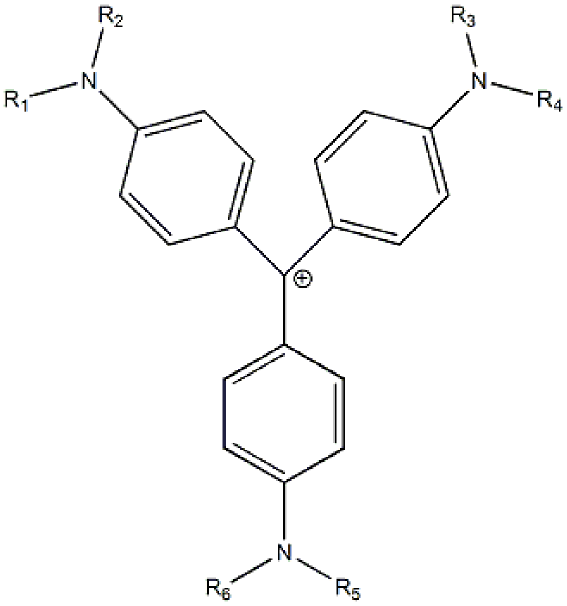


Fig. 11 General molecule of the triarylmethines dyes.

The main structure of this class of dyes is a central carbon atom attached to three aromatic rings, this kind of arylcarbonium colorant are the most stable than the ones that possess two aromatic rings (diphenylmethane) reason why have been used more. Even if they are commonly called triphenylmethanes the correct name is tri-aryl methines, which indicates that the central C atom is sp^2 (Christie, 2015, p. 155).

As described before the synthesis of this kind of dyes is conducted by a C_1 electrophile reaction with an aromatic system, which is activated through an electrophilic attack by the presence of an electron-releasing group. Depending on the kind of molecules employed in the reaction, in some cases, an oxidation is required to obtain the final product (Christie, 2015, pp. 158-159).

The donor group defines the color of the arylcarbonium dyes. According to Gordon and Gregory (1987, p. 246), “the weaker the donor group, the more hypsochromic the dye”. For instance, the Crystal Violet is less hypsochromic[2] than Pararosaline due to the presence of an amino group in the first one.

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[2] Hypsochromic shift: a change in the absorption of a molecule, produced by a substitution or solvent effect, from a longer to a shorter wavelength and thus a change in the color.

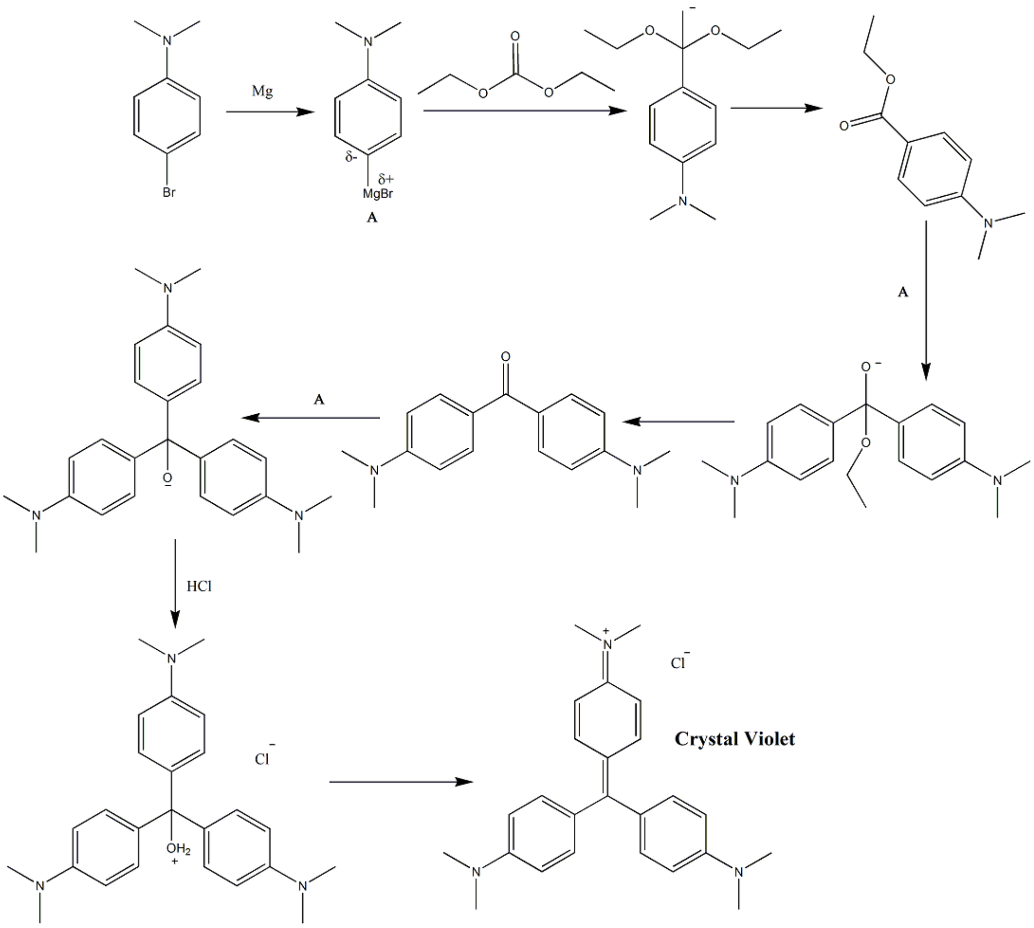

Fig. 12 Mechanism of synthesis of Crystal Violet by Grignard reactions.

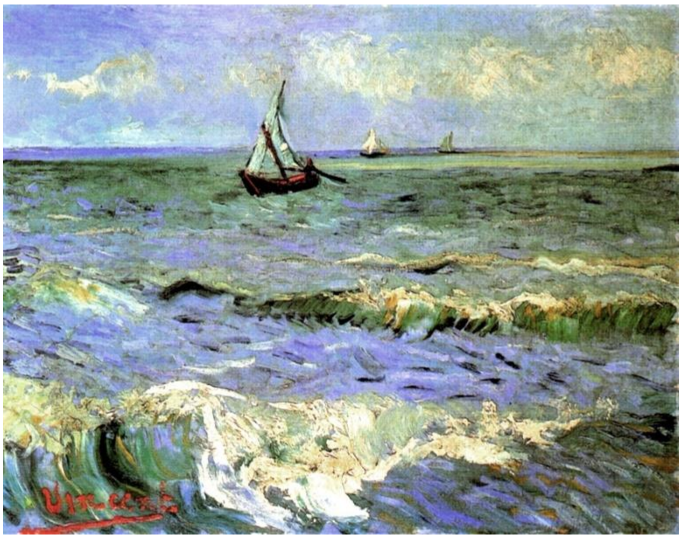

Fig. 13 Seascape at Saintes-Maries, oil on canvas, by Vincent van Gogh, 1888. Van Gogh Museum, Amsterdam

The use of the triphenylmethane dye series is wide. They can give color to fibers and be employed as lakes by precipitation of the colorant on coordination metals, such as Aluminum (Al) or Lead (Pb), which produce a very bright orange to blue pigments. An example of its use are the paintings *Glass with Roses* (1886) and *Seascape at Saintes-Maries* (1888) by Vincent van Gogh, which were painted using a lake of Crystal Violet (de Keijzer, van Bommel, & Geldof, 2010).

Synthetic dyes are also employed in the preparation of writing inks. The use of inks constituted by synthetic dyes increased considerably with the large consumption of modern pens, ballpoint mainly, which represent a great innovation in the writing tools. Some of these modern inks contain a mixture of synthetic dyes with a similar chemical structure and form system vehicle-dyes. For instance, a blue ink can be constituted by phthalocyanine blue, methyl violet, and Victoria blue (Crown, Conway, & Kirk, 1961, p. 338). Artists used these for writing letter or modifying documents, therefore they can be present as components of the Cultural Heritage as happened with the menu with some notes done by Vincent van Gogh. These dyes are also present in the inks of modern markers such as Stabilo® ones, which were also analyzed in the present research.

Nitro Dyes

This class of dyes represents one of the simplest molecule structures constitute commonly in two or more aromatic rings and at least one nitro group in *ortho*-position and one donor group, such as an amino or a hydroxyl group. This class has a historical importance since the first synthetic substance used to dye –picric acid- forms part of it (Gordon & Gregory, 1987, pp. 27, 253). They have a deep yellow to brown color and possess good properties for dyeing polyester fibers because the molecule is small (Zollinger, 2003, pp. 161-162).

Some other important historical nitro dyes are the Martius Yellow –Acid Yellow 24- and the Acid Yellow 1 (Gordon & Gregory, 1987, p. 253). Carl Alexander von Martius (1838-1920) who founded a synthetic dyes company in Berlin in 1867 synthesized the AY1 for the first time. AY 24 is obtained from the sulphonation in concentrated sulfuric acid (98%) and a later nitration in nitric acid of p-naphthol, avoiding the combination of both acids in order to elude the breaking of the aromatic rings (Caberoy, 2014).

Acid Yellow 1, also called Naphthol Yellow, was discovered by Caro in 1879, and it is the only hydroxynitro dye that still in use since it does not present toxic effects, even if it present poor fastness properties. It produces a green yellow color (Gordon & Gregory, 1987, p. 253). The yellow dyes were highly demanded since they were used for obtaining green shades by combining them with blue before the green synthetic dyes were obtained.

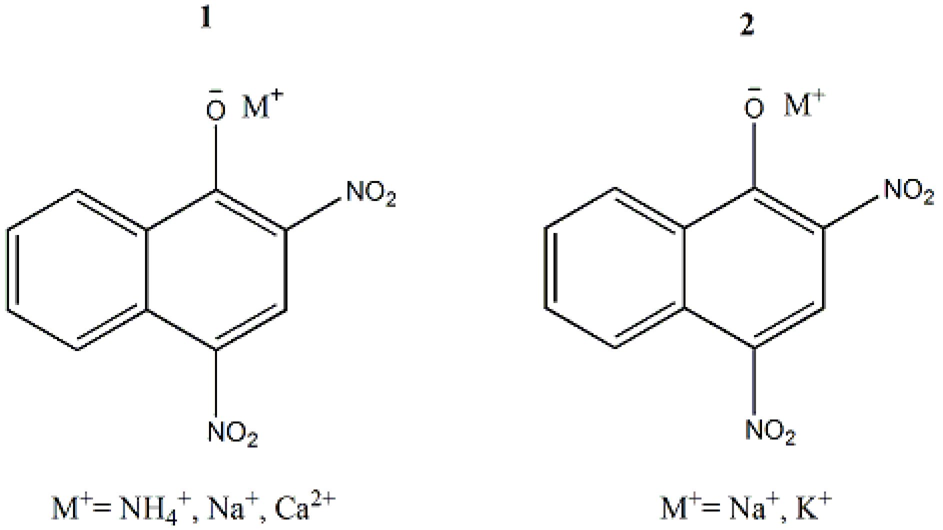

Fig. 14 Acid Yellow 24 or Martius Yellow molecule (1) and Acid Yellow 1 or Napthol Yellow molecule (2)

Indigoid class

The indigoid dyes class is one of the oldest know dyes series, it contains the natural blue dye indigo extracted from *Indigofera tinctorea* and *Isatis tinctoria*, but nowadays it is obtained mostly synthetically. Its use was reduced at the beginning of 20th century and recovered during the 1960s due to the denim used for blue jeans (Christie, 2015, pp. 105-106).

There were many studies about indigo during the times, yet the distillation of indigo was already known, von Baeyer obtained, in 1869, indole from the reduction of Indigo, allowing him to understand better the chemical structure of it. In 1897 K. Heumann discovered the commercially viable route to obtain indigo in a synthetic way (Gordon & Gregory, 1987, pp. 13-14).

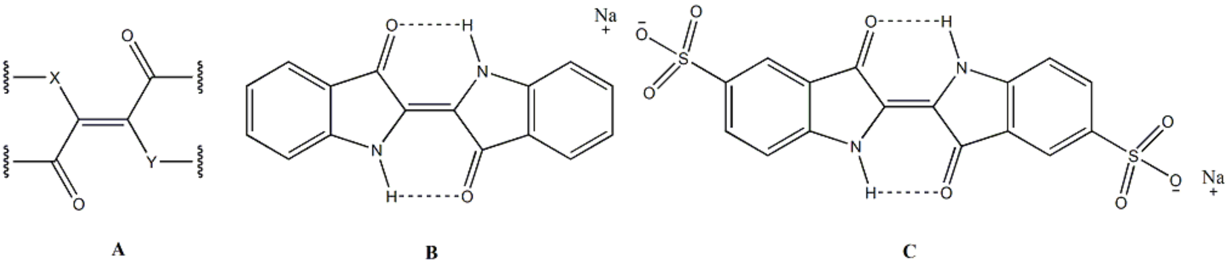

Fig. 15 A: Basic structure of indigoids B: Indigo molecule C: Indigo carmine molecule

Fig. 16 Denim jeans advertisement, 1975

The reaction for obtaining synthetic indigo consist in seven steps. The process was constantly modified and a broken thermometer that released mercury induced part of the success accidentally. Even if the reactions are complex, the cost of synthetic indigo is lower than the natural one. The synthetic dye is purer than the natural one (Gordon & Gregory, 1987, pp. 14-15).

Thus, the use of synthetic indigo increased after the establishment of the industrial synthesis process. Since then, it was greatly used for the textile production. The denim fashion, which used indigo for obtaining the characteristic blue color, launched the consumption of this dye.

2.3 Degradation of Synthetic dyes

Since when studying cultural heritage samples, they present chemical modifications due to aging, it is important to understand the chemical changes in order to have an idea of the possible molecules that can be found and which of them correspond to degradation products of the dyes of interest. This is the reason why in this section contents a revision of the knowledge about the degradation of the dyes of our interest.

The Degradation of Tri-aryl Methines Dyes

As said before, since the beginning of the synthetic dyes industry, some problems related to the stability of these new products was noticed. In comparison with another kind of synthetic dyes such as anthraquinone or vat dyes, the aryl-carbonium class present a poor light fastness, especially when used for dyeing fibers like wool, silk, and cotton; however, this characteristic is improved when used for dyeing polyacrylonitrile fibers (Gordon & Gregory, 1987, p. 292). The same problem has been noticed in inks and lakes produces with the same class of colorants. The inks used by artists such as van Gogh show fading and discoloration.

It has been seen that water and oxygen have a large effect in this type of colorants (Gordon & Gregory, 1987, p. 292). The fading, which leads to changes in color, i.e. from violet to brown, and the loss of information, have been largely observed. Moreover, until now it is not well understood the reactivity mechanisms in the dye-substrate or dye-mordant-substrate systems due to the degradation, also activated by light or humidity (Confortin, Brustolon, Franco, Neevel, & van Bommel, 2010).

Two mechanisms are responsible of the degradation of this class of dyes: decomposition by demethylation and oxidation. The first one consist in the removal of methyl groups from the molecule, for instance, according to Favaro, et al. (Favaro, Confortin, Pastore, & Brustolon, 2012) the demethylated products of Crystal Violet can be monodemethylated, bisdemethylated, tridemethylated, tetrademethylated, pentademethylated, p-rosaniline and Michler’s ketone and its demethylated derivatives.

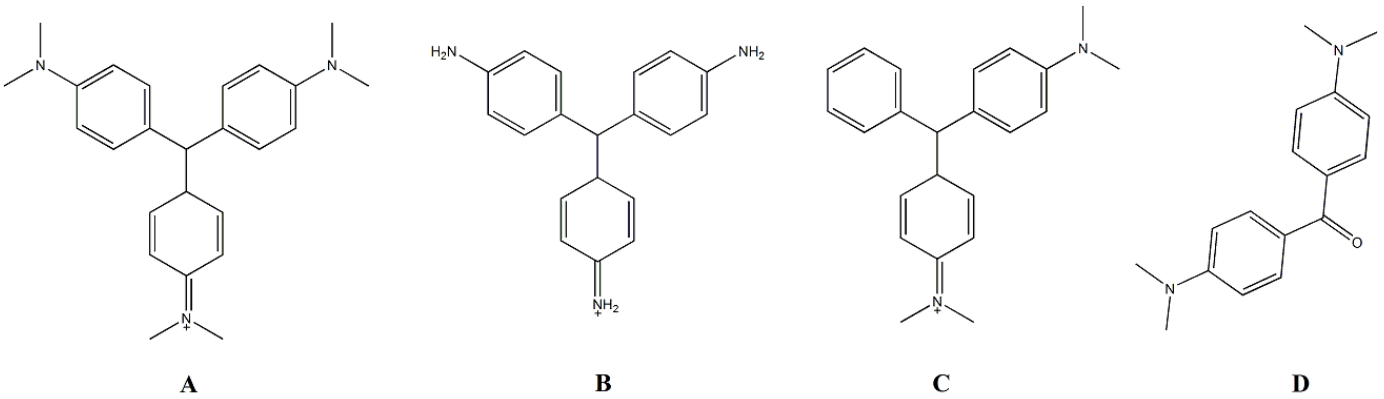

Fig. 17 A: Crystal Violet, B: p-rosalniline, C: diamond Green (basic green 4), D: Michler’s ketone. (Confortin, Brustolon, Franco, Neevel, & van Bommel, 2010)

It is important to highlight that some of the degradation products correspond to other dyes such as mono-demethylated Crystal Violet, which is penta-methylated pararosaniline and bis-demethylated Crystal Violet that is tetra-methylated pararosaniline, while tri-demethylated Crystal Violet corresponds to tri-methylated pararosaniline and finally tetrademethylated Crystal Violet is bis-methylated pararosaniline. All these compounds were found in samples exposed to UV light (365 nm) for 115hours (Confortin, Brustolon, Franco, Neevel, & van Bommel, 2010).

The presence of Michler's ketone is explained by the authors as remain of the synthesis of Crystal Violet or as a degradation product of it or other dyes such as methyl violet. Its presence also accelerates the degradation (Confortin, Brustolon, Franco, Neevel, & van Bommel, 2010).

Moreover, the deamination of Crystal Violet was also identified, by the loss of the –N$(CH_3)_2$ groups. According to the analysis of lakes over paper, the temperature and relative humidity are not involved in the fading process (Confortin, Neevel, van Bommel, & Reissland, 2013, p. 83). On the other hand, when one of the methyl groups linked to a N atom is substituted by oxygen, N-oxides are formed (Favaro, Confortin, Pastore, & Brustolon, 2012, p. 1662-1663).

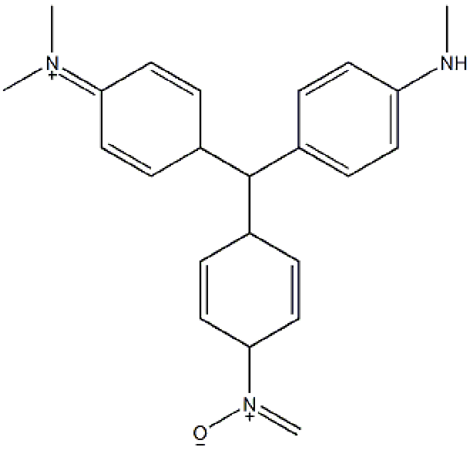

Fig. 18 N-imidine oxide structure proposed (Favaro, Confortin, Pastore, & Brustolon, 2012, p. 1664)

The oxidation process can produce different molecules. It has been identified the formation of a N-imidine oxide in combination with other O containing compounds where the nitrogen atom possess a lone pair of electrons available for conjugation. In addition, other compounds where one of the methyl groups is substituted by an OH group also were found. It seems that this group is responsible for the bathochromic effect (change in color) during the degradation the dyes. The oxidation of the central carbon leads to the formation of the Michler's ketone, which seems to accelerate the degradation of the dye (Favaro, Confortin, Pastore, & Brustolon, 2012, p. 1663-1664).

The Michler's ketone has an important role in the degradation of these dyes. It is present during the synthesis and, as it was mentioned, it catalyzes the degradation. The energy absorbed by it is transfer to the dye molecule producing the so-called indirect fading. Moreover, it can produce the triplet-triplet energy transfer increasing the photodegradation of the molecules.

As mentioned by Gordon and Gregory (1987, pp.292-293) another mechanism that affects this kind of dyes is the fragmentation mainly in the carbinol base, probably produced by the formation of radicals.

The degradation of this dyes have produced several damages in cultural properties, mainly in documents that were written with inks containing this kind of materials. As an example can be mentioned the *Menu* (1886) and the *Montmajour* (1888) drawing from Vincent van Gogh.

Other artists such as Paul Gaugin also used the new dyestuff as inks for writing and drawing and as a lake in their paintings. For example in the painting *L'appel*, from 1902 is evident the use of the new violet colorants available in that moment (The Art Institute of Chicago, The Metropolitan Museum of Art, 1959, p. 60) however, in the paintings the colors seem to be more stable. The research about the degradation mechanism of the Crystal Violet indicates that the sunlight has the similar effect than the artificial aging with UV light.

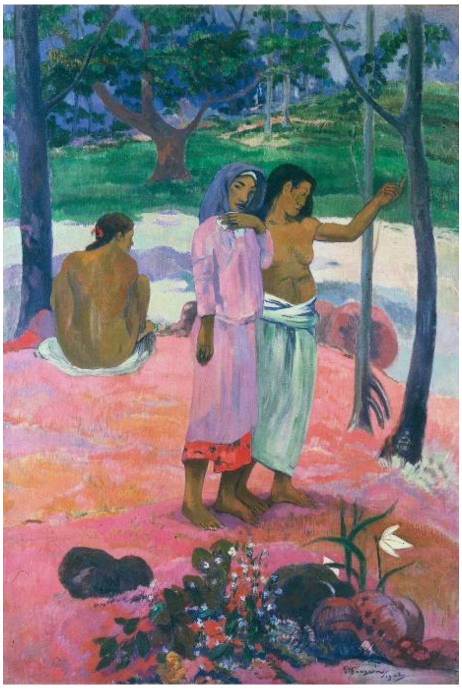

Fig. 19 L'appel, oil on canvas by Paul Gaugin, 1902.Cleveland Museum of Art.

Degradation of nitro dyes

There are no many studies about the degradation of this kind of dyes in Cultural Heritage. Studies in the field of treatment of water polluted with dyes as Martius Yellow have been done in order to stablished effective way to remove remains of dye after textile coloration.

It has been noticed that the nitro group can undergo a reduction in anaerobic situation. Nitro group can also suffer oxidation by attack of the ring by hydroxyl groups, and under certain conditions can produce nitric acid by reacting with hydroxyl groups. Another path of degradation is the abstraction of hydrogen atoms but at a slower rate (Singla, Grieser, & Ashokkumar, 2009).

It has been also identified the denitration and decarboxylation of the chromophoric ring and producing cinnamic acid, molecule that can produce further degradation and the formation of oxalic acid (Singla, Grieser, & Ashokkumar, 2009, p. 32).

The light is a factor that damages considerably the yellow dyes, effect that is confirmed with the artificially aged samples as it will present later in the results of the colorimetric analysis. As in many cases, light can induce photooxidation reactions of this kind of molecules, always in the presence of hydroxyl groups.

Finally, some biological activity can also produce degradation of this kind of dyes, for instances, it has been noticed that cyanobacteria can be responsible for discoloration of dye in textiles (Dellamatrice, Silva-Stenico, Beraldo de Moraes, Fiore, & Rosim Monteiro, 2017).

Degradation of indigoid dyes

The degradation of indigoid dyes has been of interest of conservation research since is a very common dye present in the textile and paintings collections. Moreover, the use of Indigo Carmine still very important in the industry for dyeing denim, this is why its degradation has been studied for the environmental protection.

As Poulin (2007, p. 49) mentioned, the factors related to the degradation of the Indigoid are of physical nature and due to the presence of oxygen, which can cause oxidation reaction even in absence of light.

The oxidation of indigoid molecules results in the formation of smaller molecules such as isatin, isatoicanhydride, and anthranilic acid (2-aminobenzoic acid); however, the fastness is not always present or evident in the textiles. The small size of these compounds can produce its evaporation and deposition over close surfaces, a reason why not always are identified during the analysis of fiber extracts, until now nine degradation products have been identified (Poulin, 2007, pp. 49-50).

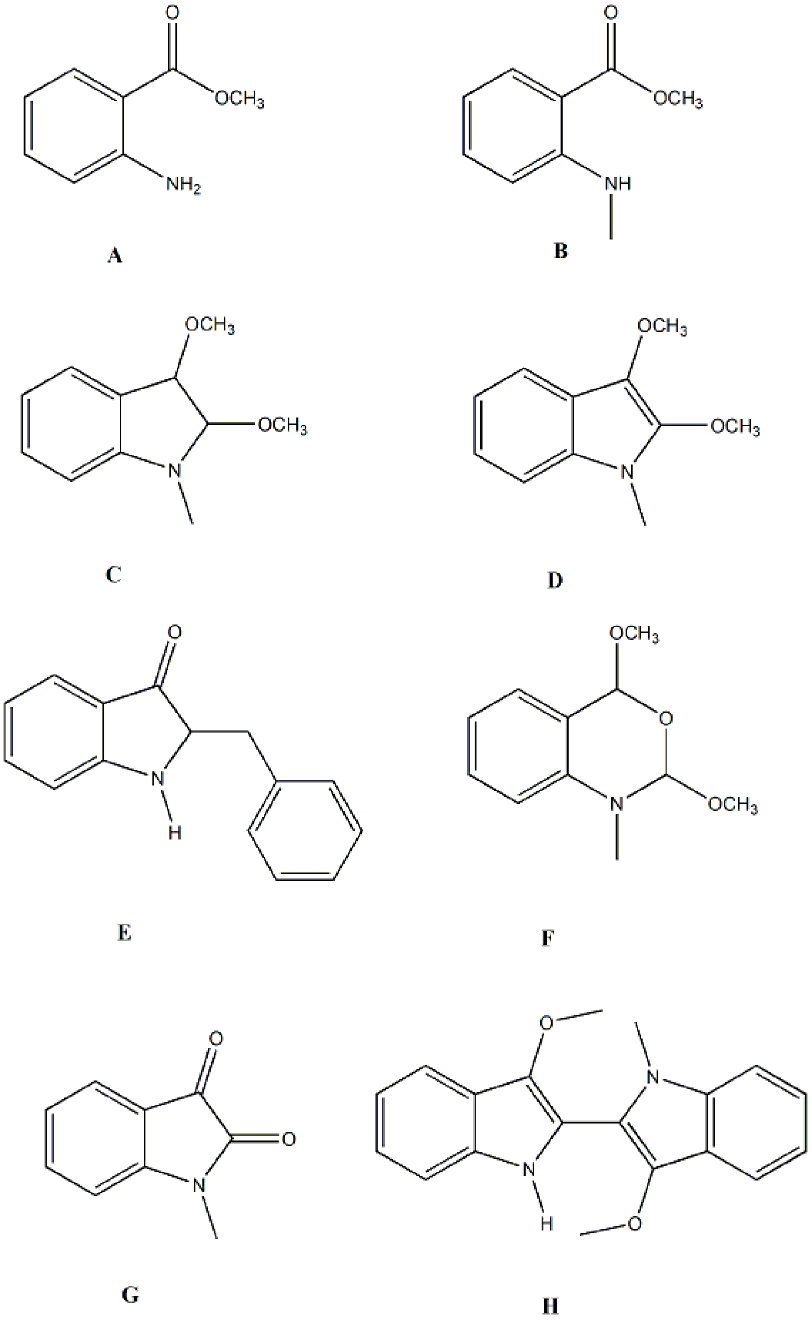

Fig. 20 Degradation products of indigo. A: anthranilic acid, methyl ester, B: N-methyl anthranilic acid, methyl ester, C: 2,3-dihydro-2,3-dimethoxy-1-methyl-indole (isomers) D: 22,3-dimethoxy-1-methyl-indole, E:2-benzyl-3-indolinone F: 1,2-duhydroxy-2,4-dimethoxy-1-methyl-3,1-benzoxazine, G: N-methyl isatin, H: 2-bis-(N-methylindole-3-methoxy)

2.4 The Characterization of synthetic dyes of historical and artistic interest

Since synthetic dyes are one of the materials that present many problems of conservation especially the light fastness, its characterization represents an important factor for conservators and historians in order to understand better the object that are studying or preserving. Thus, many techniques have employed to identify them. Their complexity and because they form part a complex matrix, the separation techniques have been the most used. In this section is presented a brief overview of the analytical techniques.

Chromatographic and spectroscopic techniques commonly employed in the identification of dyes (HPLC, GC, LC, MS)

Studies with High-Performance Liquid Chromatography (HPLC) and Gas Chromatography (GC) are commonly used for the characterization of dyes. These techniques have been improved by coupling them with detection systems, for instance, Mass Spectrometry (MS), and Diode-Array detector (DAD). To improve the results factors such as the mobile phase have been modified, solvents such as water, methanol, acetonitrile, and TFA have been proposed. Examples of these methodologies are the publications of Saltzman (1992), Halpine (1996), of course the extend work of Tibor Cserháti, who published the book entitled *Liquid Chromatography of natural pigments and synthetic dyes* in 2007 and the further researches such as Petroviciu, et al. (Petroviciu, Vanden Berghe, Cretu, Albu, & Medvedovici, 2011).

Improvements in the methodology of the study of dyes with HPLC was done, for natural ones, by Wouters and for the synthetic ones by Wegener, employing a reverse-phase HPLC. The amount of sample required correspond to around 100µl of extraction solution, and the pretreatment involves at least five steps, adding different solvents before the injection into the column (Halpine, 1996, p. 80).

In order to reduce the time of analysis and the amount of solvent employed, the Ultra High-Performance Liquid Chromatography (UHPLC) has been also applied to the study of colorants. This technique has a higher resolution but it still requires the sample preparation and in some cases, the amount sample is relatively big, as for the case of cochineal and kermes, due to detection problems (Serrano, van Bommel, & Hallett, 2013, p. 103).

In the other hand, the Gas Chromatography (GC) is a suitable technique that can offer good results for the characterization of dyes due to its capacity to make a better separation, nevertheless, the sample preparation is one of the main drawbacks since it requires the derivation of molecules in order to make them volatile.

The pyrolysis-GC-MS is a suitable option that allows the reduction of sample amount, and avoids the off-line sample pretreatment. This methodology has been employed for the identification of samples of historical textiles, giving a good result for the characterization of indigo dye (Degani, Riedo, & Chiantore, 2015, p. 1697).

The study of synthetic dyes in the field of Cultural Heritage research was already done with Py-GC-MS methodology in combination with derivatization techniques. The study performed by the Scienze Ambietali laboratory of Unibo have shown the suitability of identification of anthraquinoid and indigoid dyes dispersed in complex mixtures using this methodology (Fabbri, Chiavari, & Ling, 2000). The main drawback of this method is the need of sofisticate equipment not always available for all the institutions and the long process that requiere the sample treatment.

Non-invasive techniques (FORS, SERS)

As it can be seen, these techniques have been used for many years, however, since these methods required the extraction of the analyte from the fibers, which means the removal of some fibers from the object in order to perform the extraction of the dyes. This operation is not as simple as it can appear since the interaction between the analyte –which is already degradaded- and the fiber and mordant can create some incoveniences during this procedure. This is why recently the application of non-invasive techniques have been increasing.

As Gulmini, *et al*. have pointed the use of spectroscopic techniques in a non-invasive way have been developed in the recent decades, such as Fibre Optics Reflectance Spectroscopy (FORS) in the visible and NIR regions. The research of the authors have shown that this approach can be useful for the identification of some natural dyes, however, they have highlighted the drawbacks of this technique. The concentration of the dye is a determinant factor in the identification since a low and high quantity of dyes avoid the identification of characteristic bands in vis-FORS (Gulmini, *et al.*, 2013, p.144). The complexity of the matrix make also complicated the identification of the analytes.

To this problem has to be added the need for a complete database, which has to be stablished in order to have enough information for the comparison between the real samples and standards. Moreover, as it has been mentioned before, in many cases the molecular composition of some dyes are similar, making complicated to differentiate between them.

Due to the complicated interpretation of the data of non-invasive techniques, the micro-invasive methods have gained more acceptance in the Conservation Science field. This technique require a small amount of sample and reduce the matrix effect or interference. Tecniques such as Surface Enhanced Raman Spectroscopy (SERS) have been used.

The direct on the fiber SERS analysis has the advantage of no need of sample and no pretreatment, however it has technical incovenients such as the difficulty to obtain a homogeneous Ag nanoparticles coating over the fiber and the identification of the best area to perform the analysis. In order to maximized this technique, it has been coupled with Scanning Electron Microscope (SEM) for selecting the best area to performed the analysis, improving the results obtained from the SERS analysis (Prikhodko, *et al.*, 2015, p. 633).

Table 4 Summary of techniques commonly employed for the identification of dyes

Analytical techniques for dye characterization			
Type of technique	Characteristics	Separation techniques	Detection techniques
Invasive	-Requires sampling	Thin Layer Chromatography	Diode-array Detection
	- Sample pretreatment is necessary	Liquid Chromatography	Mass Spectrometry
	- Coupling of different techniques is necessary	High-Performance Liquid Chromatography and Ultra High-Performance Liquid Chromatography	Fourier transform Infrared Spectroscopy
	- Long time of analysis	Gas Chromatography	Raman Spectroscopy
Non-Invasive	-No sampling required	-	Fibre Optics Reflectance Spectroscopy
	- High matrix effect		Surface Enhanced Raman Scattering or Spectroscopy

Brief revision of the techniques employed in the present research

Thin-Layer Chromatography

As other chromatographic techniques, the Thin-Layer Chromatography (TLC) separates differents components of a given sample. The system is constituted by a coated plate, where the sample is applied, with a stationary phase. Once the sample is deposited on the plate, it is put into a sealed vessel, in order to maintain a saturated atmosphere, with the mobile phase, generally a mixture of solvents (Striegel & Hill, 1996, p. 5).

Thanks to the interaction of the sample molecules and both the stationary phase and the mobile phase, the different components are separated. When the time of analysis is finished, which depends on the kind of sample and solvents and has to be determined after some trials and constant inspection, some spots can be identified by the plate. The pattern obtained correspond to the different components that constitute the sample and it is called chromatogram (Striegel & Hill, 1996, p. 5).

The TLC plates are constituted by different materials, however, the most common is silica. For the present research, the sample was deposited over a plate constituted by a glass slide coated with Au and covered with AgI nanoparticles, this system was developed by the M2AD laboratory from the Unibo, and it is called AgI@Au. The separation of the sample is done by the interaction between the sample with the AgI nanoparticles, and the solubility of the analyte in the mixture of solvents.

The main advantages of the TLC technique in comparison with other chromatographic methods is that in general is simple, fast and inexpensive, nonetheless the identification of the components depends on the simple observation, in some cases with the help of radiations, and it is coupled with other techniques is not as easy as in HPLC or GC.

According to Striegel and Hill (1996, p.7), the amount of sample that can be studied with TLC is between 1mg to 500μg. The new advances, as the use of AgI nanoparticles as stationary phase, has decreased the amount sample to around 1μl of extraction solution. However, the sensitivity is lower than other chromatographic techniques.

TLC has been used in the study of cultural heritage for many years, examples of this are the investigations conducted by Bischoff, Nolley, and Thornton (1996) where dyes used to colored varnishes were studied. Painting binders were studied with TLC as is reported in the publication of Striegel and Hill (1996). Recent researches such as the one conducted by Xao-mei Zhang, *et al*. (Zhang, Wei, Lei, Cheng, & Zhou, 2010) and Yu-feng Yuan, *et al*. (Yuan, Tao, Wang, Li, & Liu, 2012) are examples of the utility of TLC in the study of dyes used in textiles and paintings –as lakes- in the Cultural Heritage.

Woodhead, Cosgrove, and Church (2016) used TLC for the separation of dye components extracted from four purple dresses from the 19th century. The sample treatment included a pre-scour treatment which in some cases removed part of the dye, later the extraction was done using a mixture of pyridine and water 57:43 (v/v) and a treatment with HF vapors in order to eliminate part of the metal mordant. The TLC was done using aluminium backed silica gel plates and as a mobile phase a mixture of chloroform/methanol/acetic acid (75:20:5). The investigation allowed the characterization of the purple dyes used in the dresses, the authors determine differences in the dyes employed for dyeing the warp (Methyl Violet) and weft (Mauve).

Previous researches of TLC using the AgI@Au system are reported in the thesis of Frizzera (2014), Roveri (2015), Bonacini (2015), Sakalauskaite (2016) and Kutrubis (2016). These examples will be explained later when speaking about the previous experiences with the AgI@Au system.

Fourier Transform Infrared Spectroscopy (FTIR) and Surface Enhanced Infrared Reflection Absorption (SEIRA)

The FTIR spectroscopy implies the data obtained of the chemical composition of samples due to the interaction of the Infrared radiation with the molecules. This technique is highly used for the characterization of the organic compounds and in some cases also for the identification of inorganic materials when a part of the molecule is active in the region of the electromagnetic spectrum used.

Infrared region comprehends from 14,000 to 20 cm^{-1} and is divided into three regions. Most of the molecular vibrations occur in the regions of Mid infrared (MIR) and Near infrared (NIR), which are the regions commonly used for the chemical analysis. The first one is called the fundamental since many of the vibration modes of molecules occurs by interaction with this kind of radiation. On the other hand, in the NIR region the overtones of the MIR interactions occurs (Derrick, Stulik, & Landry, 1999, p. 13).

FTIR offers information from the organic components of different art materials such as binders, lakes, dyes, etcetera. Also provides some information about the inorganic materials such as carbonatic salts, some corrosion products, and silicon compounds. Nonetheless, the matrix interference, the contamination of external materials such as embedding resins used in the sample preparation and the overlapping of some signals are the main disadvantages of this technique.

To overcome these disadvantages, the extraction of the analyte –for instance, a dye from a fiber- is important, in order to separate it from the other components present in the matrix. Since in the last decades, the development of techniques which require less amount of sample has been a main topic in the scientific research. The FTIR signal can be improved by using metal nanoparticles.

The Surface Enhanced Infrared Reflection Absorption (SEIRA) effect is produced by the combination of electromagnetic and chemical mechanisms occurring when IR radiation interacts with the analyte and the metal particles. Thus, the improvement of a system where SEIRA is combined with other techniques has show promising result for the characterization of dyes (Prati, Milosevic, Sciutto, Kazarian, & Mazzeo, 2016, p. 68).

Moreover, the metal underlayer attenuated total reflection (MU-ATR) have also shown promosing results for the dye study. This method consists of films of dye that were obtained after spotting 1 μL of a dye micro-extract on a gold coated glass slide and analyzed in ATR (Prati, Milosevic, Sciutto, Kazarian, & Mazzeo, 2016, p. 68).

The MU-ATR has been tested by studying 15 dyes from Azo and Diazo, Nitro and Triarylmethanes groups, among them BV3 and AY24[3] which are part of the present research. The MU-ATR has a sensitivity able to identified concentrations in the order of 10^{-6}, corresponding to 0.36ng approximately (Prati, Milosevic, Sciutto, Kazarian, & Mazzeo, 2016, p. 77).

Surface Enhanced Raman Scattering or Spectroscopy (SERS)

Since the present research take as one of the main techniques SERS, the basic principles of the method must be at least introduced. The Surface Enhanced Raman Spectroscopy in general terms consists in the increasing of Raman signals by means of the interaction of the radiation and metals by amplifying the laser field thanks to the so called plasmon resonance (Le Ru & Etchengoin, 2009, pp. 1-2).

As the name of the technique says, this method requires the presence of the molecules of the analyte in the surface of the metal, and the enhancement or increasing of the Raman signals thanks to the effect mentioned before. Metals can produce the enhancement effect, however, the capacity to produce it or the homogeneity of it can vary from one material to another. Silver and gold are the two most common materials used since they are able to produce plasmon resonance in the visible and near infrared region of the electromagnetic spectrum (400-1000nm) (Le Ru & Etchengoin, 2009, p. 3). In fact, both metals are involved in the method that is evaluated in the present work. This metal can

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[3] In the article the dye is referred as AY 2 Martius Yellow, however, the correct C.I. name is AY 24.

be used as colloids or, as it is in our case, planar metallic structures, which means that the metallic colloid is deposited and let dry over a plain surface. In the following chapters, the system used in our method will be explained.

The size of the metal particles have an important role in the enhancement of the signal, small dimensions, generally in the sub-wavelength range, which is less than 100nm help to obtain the enhancement effect. Moreover, the surface is also another parameter to consider since it is intimate correlated to a number of molecules that can produce the SERS effect (Le Ru & Etchengoin, 2009, p. 4).

The use of Raman for the study is related to the intrinsic Raman properties of the molecules since they possess electronic energies close to the energy of the laser used for the characterization. This is an important factor to consider however not the only one. The interaction with the metallic substrate is also important, in the case of the dyes, it can be said that they generally are in resonance with the laser radiation.

The application of the analyte into a flat surface is an aspect of major importance in the preparation of the probe since is difficult to estimate the number of molecules interact with the metallic surface and will be part of the SERS effect.

Therefore, it is important to speak about the Ag metallic substrate since is the one used in the present research. The Ag colloids, and further planar depositions are widely used in SERS since they produce a higher enhancement in the 600-650nm region of the electromagnetic spectrum (Le Ru & Etchengoin, 2009, p. 368).

The obtention of the nanoparticles generally is by reaction between an Ag salt –usually $AgNO_3$- and a reductor. The nanoparticles are formed first by nucleation and in many cases, a stabilizer is required in order to avoid the aggregation of the particles. This reaction allows the formation of a colloid. If a planar substrat is required, drying the colloid on the surface of an underlying subtrate is one of the most common methods (Le Ru & Etchengoin, 2009, p. 367-374), and it is the one used in this research.

The use of SERS in the identification of dyes have been used for many researches, the main advantage of this technique is that by increasing the signal the problem of fluorescence produce by many dyes during traditional Raman analysis, is overcome.

Moreover, the small amount of sample required to obtain information in SERS makes this method good for the identification of this kind of samples.

Studies such as the one of Whitney, van Duyne and Casadio (2006) have shown the potentiality of this technique in the study of historical samples of lakes and natural red dyestuff. The capacity to obtain information of a very small quantity of sample make this technique very useful in the field of Cultural Heritage. This technique has been adapted in order to obtain good results with the samples coming from works of art, by "dramatic fluorescence quenching and significant enhancement of the weak Raman scattering effect for the target analytes" (Casadio, Leona, Lombardi, & Van Duyne, 2010, p. 785).

Spaking specifically about the modern inks, Izzo et al. (Izzo, Vitale, Fabbro, & Van Keulen, 2015), have studied twelve different pens –manufactured in Germany, Italy, and Japan- using TLC, XRF, FTIR, NMR and Py-GC-MS techniques. The analysis of the inks allowed the identification of synthetic dyes such as AY23, AR87, and Eosine.

A similar research project was performed by Silvi Garrappa (2017), she analyzed six felt-tip pens Faber Castell® four felt-tip pens produced by the Stabilo® company in Germany. The analysis of standard dyes and pigments was also done including AB9, AY23, BV3, and BV10.

The techniques employed by Garrappa were silicon TLC and Ag nanoparticles colloid was also employed, ten different eluent solvents and mixtures were tried, been pure chloroform the most effective for the separation of the dye components of Faber-Castell® inks meanwhile, a mixture of butanol, ethanol, and ammonia gave the best results for the Stabilo ones (Garrappa, 2017).

The identification of dyes was done with a μ-Raman using 785nm YAG Laser. The Py-GC-MS was done using a pyrolyser injection system where around 50μg of sample were used. The injection of the sample was done at 280º C and MS transfer line was 260ºC with a scan range of 45-400m/z (Garrappa, 2017).

The study allowed the identification not only of the dyes but also of other pigments, additives, binders and solvents that constitute the

Previous researches on AgI@Au TLC/μ-FTIR/SERS system

The AgI@Au TLC/μ-FTIR/SERS system was developed by the M2AD laboratory at Alma Mater Studiorum – Univerisità di Bologna, the project started as part of the Cultural Heritage Advanced Research Infrastructures: Synergy for a Multidisciplinary Approach to Conservation/Restoration (CHARISMA) and continued with the Integrated Platform for the European Research Infrastructure on Cultural Heritage (Iperion CH) project. It is a system that has the main objective to reduce considerably the amount of sample and obtaining an intense signal, all combine with a separation technique without using complex instrumentation. Since then, several researches have been conducted in order to understand the behavior of the plane prove, the nanoparticles and the synthetic colorants.

The precedent of this system was the initial use of gold nanoparticles for the characterization of small quantity dye of sample. Using a system constituted by Au nanoparticles deposited over a gold coated slide, Acid Orange 7 (AO7) was studied, both as a standard and from a wool fiber dyed with the colorant. The research include three extraction methods in order to determine the best for the obtention of AO7, the use of methanol extraction at 60º C, was the most effective (Prati, *et al.*, 2014, p. 11).

The study allows determining that the sensibility of FTIR-RAS analysis consents the identification of samples with a $5x10^{-5}$ concentration. The use of the Au nanoparticles permits the identification of the AO7 dye extracted from the wool fiber even in a low concentration. Still, if the analysis of the Au nanoparticles synthesized shown small amounts of contamination, this did not interfere with the results. The data obtained from the SEIRA analysis allowed the identification of the characteristic bands of AO7 (Prati, *et al.*, 2014, p. 10).

In 2014, Silvia Frizzera (2014) presented the thesis entitled *Surface Enhanced Vibrational Techniques for the Detection of Synthetic Organic Colorants*, which was part of the first step in the development of the system. The preparation of the stationary phase for the TLC, constitute by silver iodide (AgI) nanoparticle deposited over a gold coated slide was one of the first goals of her project.

To evaluate the effectiveness of the technique Frizzera prepared a mixture of three standard synthetic dyes: Brilliant Green 1 (BG1), Rhodamine B (BV 10) and Acid Blue

9 (AB9). The mobile phase that produced a better separation of the dyes was a mixture of ethylacetate, methanol and ammonia (35:11:10 v/v) (Frizzera, 2014, p. 36).

The distribution of the AgI nanoparticles and nanoaggregates was also studied, allowing the establishment of the best method to perform the deposition over the gold coated slide. The use of isopropanol saturated chamber was the one which gave the best results even if spin-coating techniques offers also good results in less time but it requires a higher amount of salt and specific instrumentation (Frizzera, 2014, pp. 41-44).

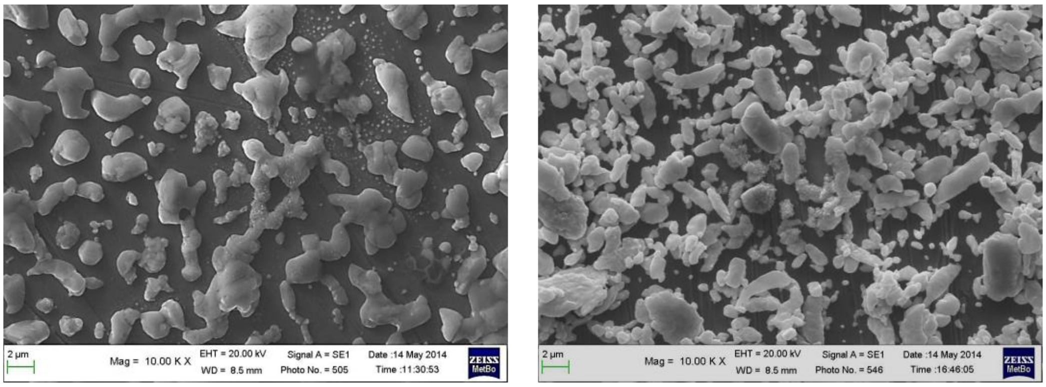

Fig. 21 SEM images showing the distribution of AgI particles over Au slide. Taken from Frizzera, 2014, p. 38.

The results of the analysis shown that the nanoparticles increase considerably the signal obtained from the samples due to the enhancement of ATR-RAIRS mechanism. In addition, the big enhancement was noticed when SERS analysis was performed. The study of the three dyes allowed the creation of a spectra library (Frizzera, 2014, pp. 45-60).

In 2015, Irene Bonacini presented the Ph.D. thesis *Development of New Analytical Procedures Aimed at the Characterization of Artistic Samples* in which the result of her investigation with Raman and FTIR spectroscopies and the use of TLC proves with AgI nanoparticles. Bonacini goes over to the investigations of Frizzera again and makes a comparison with the use of TLC nano silica analysis –denominated High-Performance Thin-Layer Chromatography (HPTLC)- using the same dye mixture constitute by BG1, BV 10 and AB9 (Bonacini, 2015, pp. 167-182).

The investigations of Bonacini let determine that the enhancement effect produced by the AgI particles over the gold coated slide was higher than the one identified using silver citrate colloid over nano silica plates. Furthermore, the reduction of AgI nanoparticle over the metallic surface occurs by using less energetic lasers and in a faster way than the procedures reported by previous researches (Bonacini, 2015, pp. 181-182).

The same year, Marco Roveri (2015) presented the thesis titled *Development of a new TLC substrates for surface-enhanced spectroscopic detection of dyes*. In his work, Roveri presents the principles of the use of AgI particles for the analysis of dyes and has pointed the main factor that helps to obtain a signal enhancement. The gaps between the particles, in an order of 2nm, can produce an enhancement close to 10^{14} for resoning molecules, as the ones of dyes.

One year later, Prati *et al.* (Prati, Milosevic, Sciutto, Kazarian, & Mazzeo, 2016) published the results of these researches, focusing on the challenging characterization of small amount of samples of dyes, and the used of SERS

In 2016, Jorune Sakalauskaite continued with the development and evaluation of the AgI@Au system, her project was focused in the study of natural dyes and lakes, specifically the flavonoids, specifically the yellow ones.

The study of natural yellow dyes has a great importance in the study of cultural heritage and is conservation since have a fast degradation and its characterization is complicated because the extraction methods can produce the molecule degradation.

In the same year, Dimitra Kutrubis (2016) resume the methodology, applying it to the study of different dyes such as Crystal Violet (BV3), Luteolin, Apigenin, and Luteolin-7-O-glucoside.

3. EXPERIMENTAL PROCEDURES AND INSTRUMENTATION

3.1 Samples preparation

Different kinds of samples were analyzed in the present research. First textile samples of wool dyed and artificially aged kindly donated by the Cultural Heritage Agency of the Netherlands and aged in the Centre de Recherche et de Restauration des Musées de France.

The wool is Bluefaced Leicester from Rowan, Purelife brand; it was washed with 10% (wool weight) Marseille soap at 40°C before dyeing process.

For dyeing two methods were followed according to the dye type. In the case of basic dyes (BV1, BV3, BG1), 750 ml of demineralized water was heated to 70 °C and kept at this temperature. 100 mg of a basic dye was weighted and dissolved in the warm water. 10 g of wool bundle was soaked in the dye bath and put in oven at 70 °C for 30 minutes. The dye bath was stirred every 5 minutes to get a homogeneous color. The bundle was left to cool down in the dye bath and afterwards it was rinsed with demineralized water.

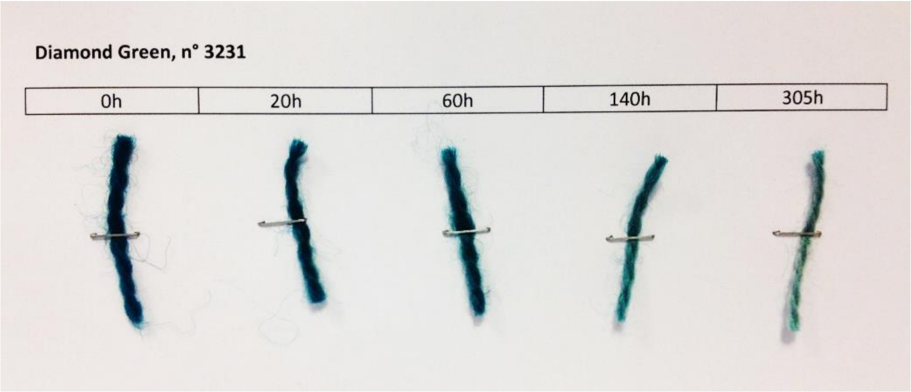

Fig. 1 Wool dyed with BG1 samples artificially aged, donated by the Centre de Recherche et de Restauration des Musées de France

For the acid dyes (AY24), 750 ml of demineralized water was heated to 70 °C and kept at this temperature during the complete dyeing process. 5 g of sodium sulphate was added and dissolved. 150 mg of the acid dye was weighted and was dissolved in the solution. 10 g of wool bundle was soaked in the dyeing solution. 200 µl of concentrate sulphuric acid was added in the beaker. The dye bath was put in oven at 70 °C for 30 minutes. The dyeing solution was stirred every 5 minutes to get a homogeneous color. The bundle was left to cool down in the dye bath and afterwards it was rinsed with demineralized water.

For the case of indigoid dyes (AB74), the procedure was different. 1.5 l of demineralized water was heated at 40°-50° C, 1 g of the dye was added to 10ml of pre heated demineralized water. 3.8g of sodium carbonate was dissolved in 10ml of demineralized water to which the solution was added to the dye dissolved and stirred. After this, a solution of 8.5g of sodium dithionite dissolved in 10ml of demineralized water was added. Once the dye solution change color to green, it was added to the 1.5 l of water. 10g of bundle wool was put into the bath for 1 min, and stirred. Then the wool was taken out and punt into cold water for 5 seconds, the squeezed and shaken in the air until the blue color was obtained. The dyed wool was rinsed with demineralized water.

The aging process was performed using a Xenon test machine, due to technical inconvenient not standard procedures were followed. The only factor consider during the ageing process was the time. In general, all the samples were treated for 20 hours, 60 hours, 140 hours and 305 hours. In the case of the yellow dye (AY24), no samples were treated for 20 hours.

The real samples also of wool were taken from a sample book by Dr. Adolf Lehne published by Verlag von Julius Springer in Berlin in 1893, entitled: *Tabellarische Uebersicht über die künstlichen organischen Farbstoffe*[1]. The samples were kindly donated by the Cultural Heritage Agency of the Netherlands.

Fuchsin. [*B.*] [*By.*] [*C.*] [*M.*] [*O*] [*P.*]
Rubin. [*A.*]
Magenta.
Anilinroth.
Roseïn.
Veraltete Bezeichnungen (theilweise unreinerFuchsinarten): Azaleïn, Solferino, Erythrobenzin, Rubianit, Harmalin, Fuchsiacin. — Unreine, Phosphine enthaltende Fuchsinsorten kommen als Marron, Grenat, Geranium [*C.*], Cerise [*B.*] [*C.*] [*P.*], Juchtenroth [*C.*] [*O.*] [*P.*] etc. in den Handel. (Schultz.)

Anwendung: Zum Färben von Wolle (V. 1), Seide (V. 7), Baumwolle oder Leinen (V. 11), Jute (V. 15). Halbwolle wird zunächst mit Tannin oder Sumach gebeizt, sodann, ohne vorher zu spülen, bei 50—60° C. ausgefärbt. (Engau.) — Zum Färben von Papier in der Masse. — Zur Darstellung von Lackfarben, welche im Buch-, Stein- und Tapetendruck Verwendung finden. — Im Wolldruck (V. 19), Baumwolldruck (V. 23 A).

Lösen: In heissem Wasser. Es empfiehlt sich, den Farbstoff vorher mit Sprit anzurühren. — In Sprit leicht löslich.

Echtheit: Nach 5 tägiger Einwirkung der Witterung (Juni) bläulicher und stumpfer, nach 18 Tagen sehr stark verblasst. — Nicht chlorecht. Durch schwaches Chloren (1 Th. Chlorkalklösung von 5° Bé : 30 Th. Wasser) stark verändert. Durch schweflige Säure von 4½° Bé stark verblasst. Wollfärbungen ziemlich waschecht.

Nachweis: Conc. Schwefelsäure — Faser gelbbraun, Lösung gelb, auf Wasserzusatz Faser blass lila. — Mit Ammoniak erwärmt: Faser rosa, auf Zusatz von Essigsäure: Faser wieder roth, lebhaft bläulich rothe Lösung.

½ % Farbstoff.

Fig. 2 Detail of the book Tabellarische Uebersicht über die künstlichen organischen Farbstoffen *by Dr. Adolf Lehne, 1893. Courtesy of Prof. Marteen van Bommel*

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[1] Tabular overview of the artificial organic dyestuffs

The samples coming from felt-tip pens, three Stabilo® markers were bought: 68/22, 68/41, 68/55. The following table present the dyes studied in the present research both from fibers and from Stabilo® pens.

Table 1 Summary of dye samples studied in the present research

C. I. Number	C. I. Name	Other names	Dye Class
42090	Acid Blue 9 (AB9)	Acid Turquoise Blue AE, Acid Turquoise Blue HE, Acid Blue E-A, Acid Blue FCF, Acid Blue FG	Triarylmethane class
73015	Acid Blue 74 (AB74)	Indigo Carmine, Food Blue 1, C Blue 2, Sicovit Indigotin 85E 132, Indigotine, Brilliant Indigo4 G	Indigoid class
42040	Basic Green 1 (BG1)	Brilliant Green 1, Basic Brilliant Green 3B	Triarylmethane class
42535	Basic Violet 1 (BV1)	Methyl Violet 2B, Methyl VioletMethyl rosanilinium chloride, Hexamethyl parosanilinium chloride	Triarylmethane class
42555	Basic Violet 3 (BV3)	Crystal Violet, Basic Violet 3B, Basic Violet 5BN, Basic Violet 6BN	Triarylmethane class
42600	Basic Violet 4 (BV4)	Ethyl Violet	Triarylmethane class
10315	Acid Yellow 24 (AY24)	Martius Yellow	Nitro class

Some standard samples were analyzed in order to obtained the reference spectrums. It was used Brilliant Green 1, Fluka®, analytical standard, 98% and Brilliant Blue FCF, Acid Blue 9, Sigma-Aldrich®, analytical standard, 97% both prepared at 10^{-3} and 10^{-4} Mol concentration.

3.2 Colorimetric measurements

The colorimetric measurements where done with a Minolta® spectrometer model CM-2600d cyberchrome with 109 sensor. The data was processed with Spectramagic 3.60 and

Office Excel software. For each sample two measurements were performed and an average of the values was done.

3.3 Microscopic fiber analysis and register

In order to confirm the identification of fibers used in the real samples, a microscopic identification was done by using an Optical Microscope OLYMPUS® model DP70. The images were taken under visible light at 20x. The identification of the fibers was done by comparing the morphology of the sample and measuring their diameter.

The register of some of the TLC slides was performed using a stereo microscope Leica® MZ6 coupled to a digital camera Canon® power shot 550 with a resolution of 5.0MP with a Tungsten WB correction. The images were processed with a Zoom Browser EX software. The magnification employed were 0.63x, 1.25x and 2.5x.

3.4 AgI nanoparticles synthesis and AgI@Au slide preparation

The synthesis of silver iodide (AgI) nanoparticles was made following the same methodology employed by the research of Alma Mater Studiorum Università di Bologna and previously reported by Sakalauskaite (2016) and Kutrubis (2016). The particles are porduce by the reaction of two solutions in pure water type 2[2]; 15ml at 0.1 mol concentration each, one of silver nitrate ($AgNO_3$, Sigma-Aldrich® puriss. p.a., ACS reagent) and the other of potassium iodide (KI, Sigma-Aldrich® puriss. p.a. Reagent ISO). The solution of $AgNO_3$ and, after the synthesis, the AgI solution were kept in the dark to avoid the photodegradation. Before the reaction both solutions were storage at 4º C for 30 minutes, while after the reaction the solution of AgI was storage at the same temperature for 60 minutes and later 50 minutes at room temperature.

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[2] It is obtained with an Elix® Essential purification system. It has a resistivity value of > 5 MΩcm at 25º and TOC <30ppb.

$$AgNO_{3\,(aq)} + KI_{(aq)} \longrightarrow \left\{m[AgI]\cdot nI^{-}\cdot(n-x)K^{+}\right\}^{x-}\cdot xK^{+} + KNO_3 \quad \text{(surplus of KI)}$$

Fig. 3 Reaction equation of $AgNO_3$ and KI. After the reaction, the nucleus of AgI is formed (in yellow) and with the time, the formation of granules of AgI plus K^+ is produce due to the aggregation. KNO_3 is also formed as part of the surplus of KI.

The AgI nanoparticles were filtrated under vacuum using a filter paper with a size pore smaller than 2µm, a wash of the particles was performed using water type 2, since KI and KNO_3 are soluble in it and are eliminated from the AgI particles.

The filter paper was dried at 40º C for 15 minutes. After the drying, the particles were collected. 1gr of AgI was put into a Becker and 7ml of isopropanol were added. The particles were suspended by sonication for 30 minutes at room temperature.

To have a control of possible residues of potassium salts into the nanoparticles, a KBr pellet with the particles was done and analyzed by transmission with a Thermo Nicolet Avatar 370 FT-IR spectrometer. The spectrum showed a small amount of nitrates, despite this, the concentration of possible byproducts of the reactions are in a very low concentration and is consider that they do not interfere in the analysis. In addition, the nanoparticles synthetized were analyzed with a XRF spectrometer Bruker® ARTAX[3]; the results showed the presence only of Ag and I.

The deposition of the nanoparticles into the Au glass was done adding 1ml of the suspension over it and left they dry slowly at room temperature for 24hrs in a isopropanol saturated atmosphere in order to obtain a homogenous film deposition.

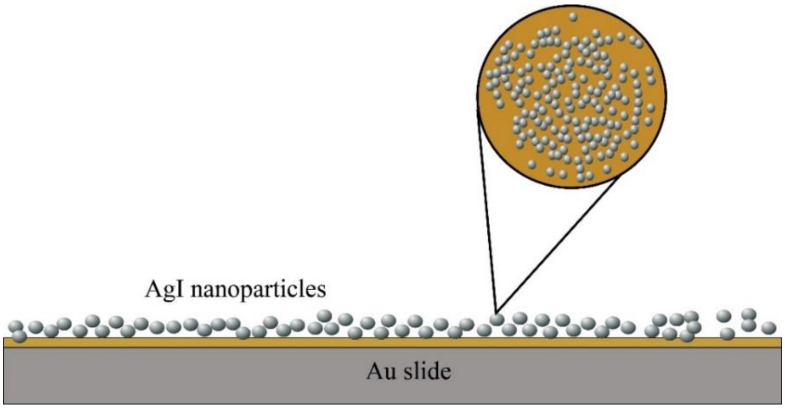

Fig. 4 Scheme of the AgI@Au system after the deposition of the AgI nanoparticles over the Au slide.

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[3] The parameters were stablish for the identification of light elements. 17kV, 1200mA, 100 seconds of time, and spot size of 0.65mm.

Since a fast reaction between the AgI particles can occur, producing a yellow association colloid, the drying, suspension and deposition of the partciles over the Au glass has to be immediately after the reaction because the colloid is unstable and aggregation begins very fast, this is reason why avoiding heating is important because a rise in temperature accelerates the random thermal moving and thus the aggregation (Ternopil State Medical University, 2016).

3.5 Dye Microextraction

The analysis requires a small amount of sample. Few fibers were taken from a piece of thread, and put into a vial with conic bottom. It was added 20μl of methanol (Sigma-Aldrich® for HPLC, 99,9%), was covered with aluminum sheet and heated in *bain-marie* at 60º C (140º F) for 10 minutes. This operation was repeated three times, adding 20μl of methanol each time. After the extraction, the fibers were dragged to the walls of the vial in order to avoid the contact with the methanol solution. It was kept in a dark dry area for 24 hours.

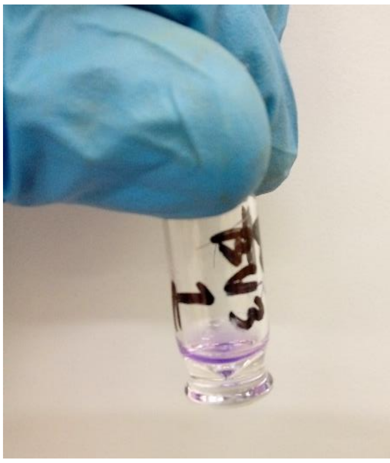


Fig. 5 Microextraction of Crystal Violet (BV3) from artificial aged sample

After the extraction, the solvent was dried in a drying chamber Binder® FED at 40º C for 15 minutes, then 10μl of water type 2 were added to the vial, in order to solubilized the colorant concentrated in the bottom of it. In the case of the BG1 the colorant was not directly soluble in water so before the addition of water, 0.5μl of methanol were added in order to dissolved the dye and the 9.5μl of water were added forming an emulsion that can be deposited over the AgI@Au slides.

In order to optimized the dye recovery, a double extraction was performed, first using pure water, both at room temperature and 60ºC for 30 minutes. Once the first extraction was performed, the fibers were transferred to a clean vial and the second extraction with methanol at 60º C for 30 minutes was done.

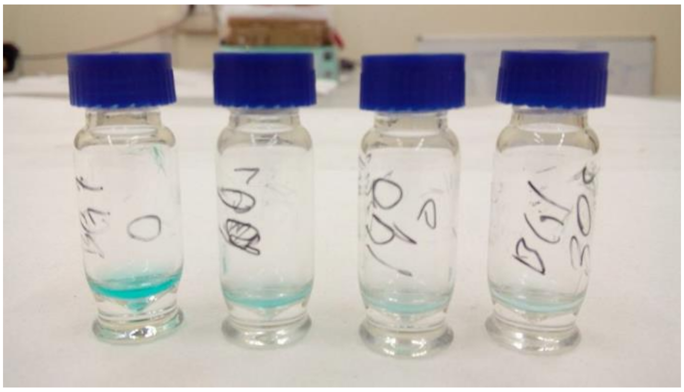


Fig. 6 BG1 extraction from artificially aged samples. From left to right: 0h, 60h, 140h and 305h.

Table 2 Summary of extraction procedures

Extraction method	Cycles	Solvent
Methanol method single extraction	3 cycles of 10µl of MeOH for 10 minutes	Methanol
Water extraction at room temperature	1 cycle of 60 µl of Pure water type 2 for 30 minutes	Pure water type 2
Water extraction at 60ºC	1 cycle of 60µl of Pure water type 2 for 30 minutes at 60º C	Pure water type 2
Double extraction	1 cycle of water extraction and the 3 cycles of Methanol extraction	Pure water type 2 and Methanol

3.6 Stabilo® pens ink extraction

Three kind of Stabilo® markers were analyzed: 68/22, 68/55 and 68/41. The extraction of the dyes was done by inserting the tip in a vial with 10µl of water type 2 for 10 seconds, since the concentration of the dyes was unknown, the solution obtained was diluted by 10 times.

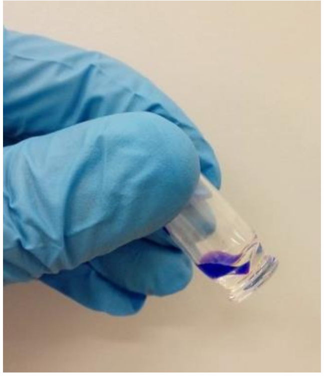


Fig. 7 Result of the extraction of Stabilo® 68/55 with water type 2.

3.7 μ-FTIR Analysis

It was used a Thermo Scientific® Nicolet iN 10MX spectrometer. 1µl of the dye extracted was deposit over an Au slide –slightly heated to accelerate the evaporation- in order to obtain the formation of the "coffee-ring". The analysis in total reflection (RAS) was performance using an aperture of 120x120μm, 64 scans and 22 seconds of analysis. In the same points, the ATR analysis was performed using a Ge crystal and aperture of 200x200μm, 64 scans, 22 seconds of analysis and 3% of pressure in the crystal. The change in the aperture is related with the reflective index of the crystal.

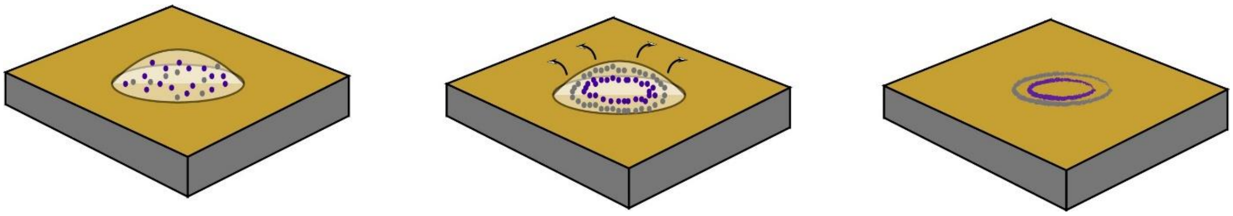


Fig. 8 Formation of "coffee-ring" after the deposition of a drop over the Au or AgI@Au slide. Adapted form Wang, W., Ying, Y., Tan, Z. & Liu, J., 2014.

In addition, another 1μl of the same sample was deposited over AgI@Au slide. In this case, the formation of a double "coffee-ring" was identified. The internal ring contained mainly the dye and the outer ring the wool extraction. The total reflection and ATR analysis were conducted in both rings. The same parameters were used for the analysis after the TLC. All the analysis were done three times in order to be sure of the reproducibility of the results.

3.8 SERS Analysis

The SERS analysis was performed using a Microscope Raman, Thermo Scientific® DXR. It was use a full range 532nm and 780nm lasers at 10x of magnification. The parameters changed according to the sample studied, however in general were 50μm of aperture, a variable laser power - from 2mW to 3mW for the 532nm laser and 10mW for the 780nm- and fluorescence correction (logarithm 6). This analysis was performed in the same samples studied before with FTIR. All the analysis were done three times in order to be sure of the reproducibility of the results.

3.9 TLC Separation


Fig. 9 TLC chamber used for the separation.

The TLC analysis was executed using different eluents; the first one tested was a solution of Ethanol (Sigma-Aldrich® 96%) and Ammonium hydroxide (Sigma-Aldrich®, 33%) in a proportion 90%-10% as a mobile phase. The second eluent was a mixture of Isopropanol (RPE Carol Erba®, ACS reagent.), Ethanol and ammonium hydroxide (33%) in a proportion of 5:2:3 (v/v/v).

The AgI@Au was put in a TLC chamber with around 3ml of the mobile phase and wait six minutes for the first eluent and ten minutes for the second. After that time the slide was put into a Petri dish, wait the evaporation of the solution for some minutes, and after it was analyzed with µ-FTIR and SERS.

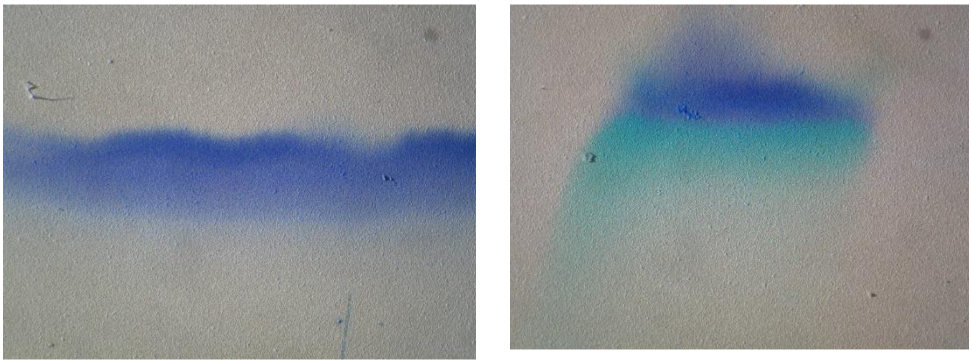


Fig. 10 Micro photo of the Post TLC result of the marker Stabilo® 68/55 (left) and 68/22 (right). 1x, exp.1/6, f 3.5, ISO 50, WB Tungsten

4. RESULTS AND DISCUSSIONS

4.1 AgI synthesis control

In order to be sure that the AgI synthesis was done correctly, a control of the product was performed. Different synthesis products were analyzed in order to have an idea of the chemical composition of the powder recovered at the end of the process. In the following table, the samples are reported.

Table 1 List of samples analyzed for the control of AgI synthesis

Synthesis	Type of analysis
1	ATR (over Au)
2	ATR (over Au)
3(a)	FTIR in transmission (KBr pellet)
3(b)	XRF powder

The FTIR analysis made with ATR over Au slide have shown a small amount of nitrates, and hydroxyl groups present, this can suggest the remain of part of potassium nitrate as byproduct of the reaction, however, since the intensity of the peaks is low it can be supposed that the concentration is negligible.

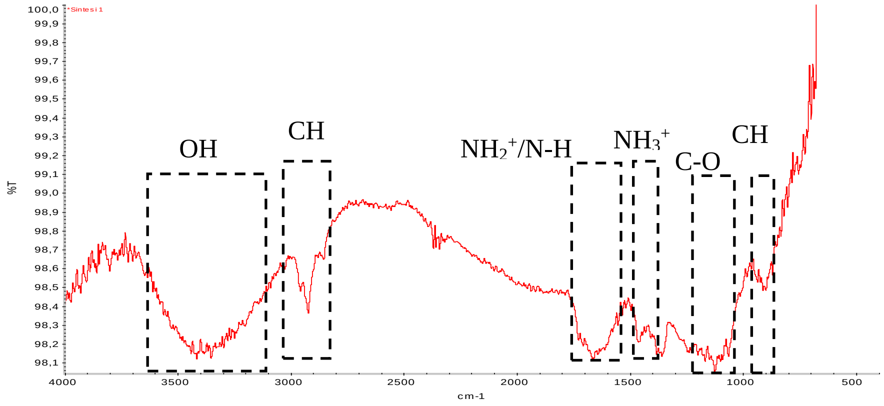


Fig. 1 FTIR spectrum of synthesis 1

When analysis the synthesis in transmission mode with a KBr pellet, the presence of nitrates still evident. As in the previous case, the concentration was low.

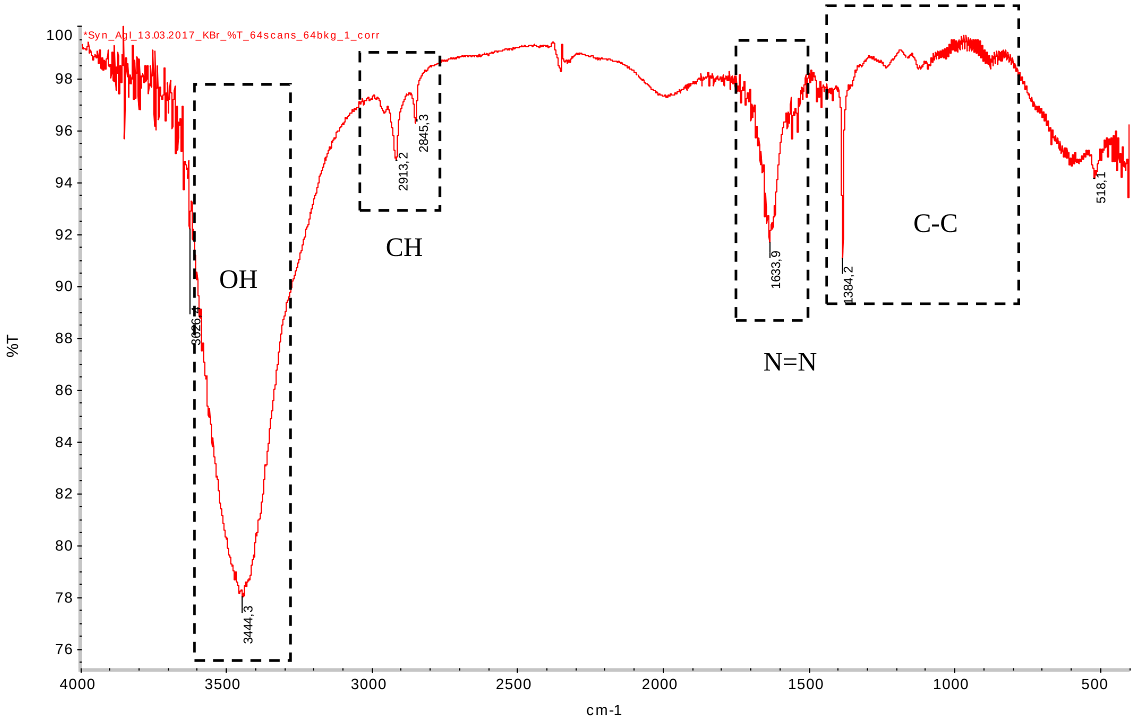


Fig. 2 FTIR Transmission mode spectra of synthesis 3

On the other hand, by analyzing the samples with XRF the spectra have shown the presence of Ag, K, and I The last one in a very low concentration, which is normal since it is part of the byproducts of the synthesis, however, the amount if potassium present in the particles is negligible.

Table 2 Element report of XRF spectrum of synthesis 3(b)

Element	Line	Energy	Net
K	Kα	3,314	**112**
Ag	Lα	2,983	2783
I	Lα	3,938	4951

4.2 Standard dye solutions

In order to have the spectra of the standard dye in order to compare with the results obtained from the samples, standard solutions of were analyzed. They were prepared in water type 2 solution with a concentration of 10^{-3} M and 10^{-4} M. Some of the data presented in this section was collected in previous researches; however, it is useful for comparing the results of the present study so it is added and interpreted.

Tri-aryl Methines class dyes

a) Acid Blue 9

The Acid Blue 9 standard was analyzed both with FTIR and SERS after de deposition of 1ml of the solution over the AgI@Au slide. The FTIR data shows peaks that correspond with the chemical composition of the dye. No contamination was found in the spectrum proving that there is no interference from the AgI particles in the result.

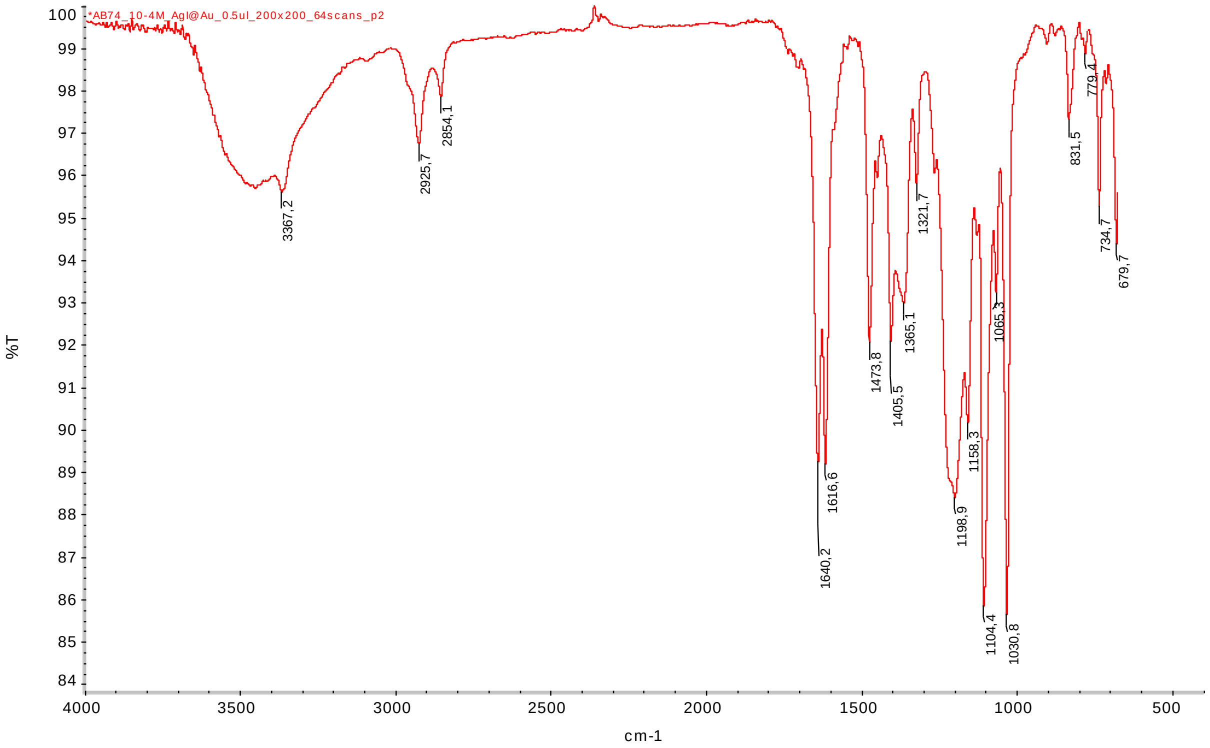


Fig. 3 FTIR spectra of AB9 standard solution 10^{-4} M

Table 3 Peak assignation of AB9 FTIR spectrum

Peaks found in solution 10^{-3} M ATR	Peaks found in solution 10^{-4} M ATR	Peak assignation (Socrates, 2001)
1618 cm^{-1}	1621 cm^{-1}	C=C in-plane deformation/ C=N
1575 cm^{-1}	1577 cm^{-1}	C=C in-plane deformation/ C=N
1405 cm^{-1}	1409 cm^{-1}	S=O Stretching from covalent sulphones
1392 cm^{-1}	1392 cm^{-1}	S=O Stretching from sulphonamides
1338 cm^{-1}	1338 cm^{-1}	C-N stretching vibration tertiary aromatic amine
1278 cm^{-1}	1284 cm^{-1}	C-H in-plane deformation and benzene ring 1:2 disubstitution
1166 cm^{-1}	1172 cm^{-1}	S=O Stretching from sulphonamides
1114 cm^{-1}	1120 cm^{-1}	C-H in-plane deformation and benzene ring 1:3 disubstitution/SO_3^{2-}
1035 cm^{-1}	1041 cm^{-1}	C-H in-plane deformation and benzene ring monosubstitution
1020 cm^{-1}	1022 cm^{-1}	C-H in-plane deformation and benzene ring 1:4 disubstitution
981 cm^{-1}	981 cm^{-1}	Not assigned
916 cm^{-1}	919 cm^{-1}	C-H Out-of-plane deformation and benzene ring 1:2 disubstitution/S=O Stretching from sulphonamides
829 cm^{-1}	833 cm^{-1}	C-H Out-of-plane deformation and benzene ring 1:2 disubstitution
792 cm^{-1}	792 cm^{-1}	C-H Out-of-plane deformation and benzene ring 1:3 disubstitution

By comparing the spectra obtained with the one reported by Izzo, *et al*. (Izzo, Vitale, Fabbro, & Van Keulen , 2015, p.6) is possible to identified the finger-print of Acid Blue 9 both at 10^{-3} M and 10^{-4} M concentrations. In the case of SERS data, the spectrum obtained shows the following bands.

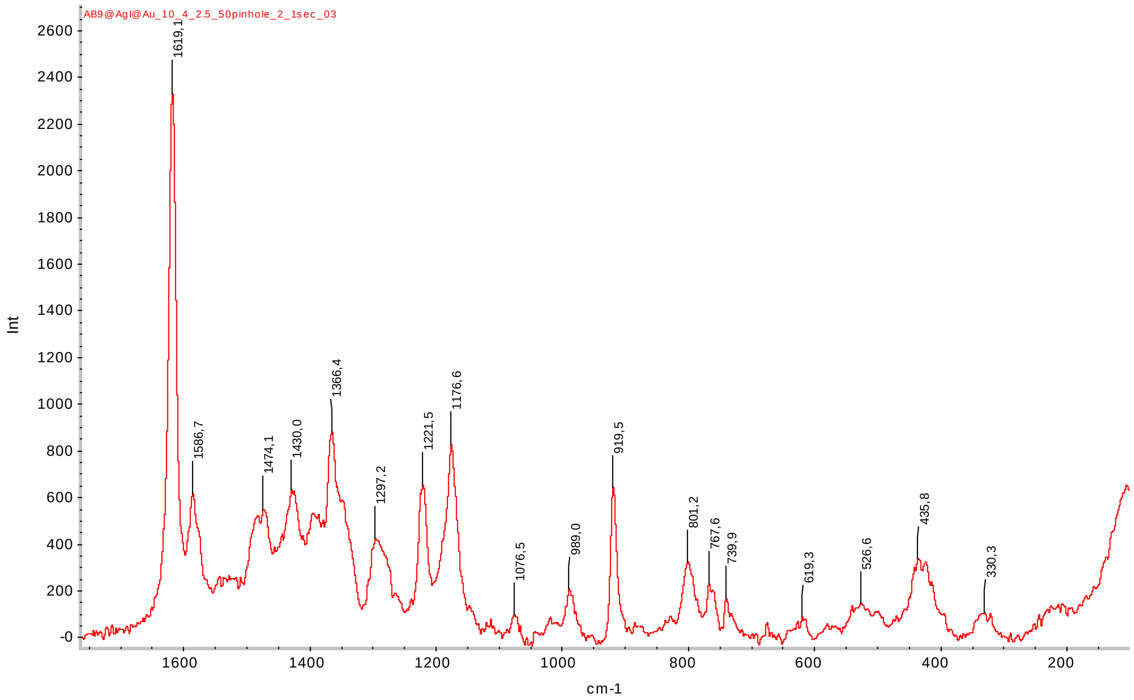


Fig. 4 SERS spectra standard solution 10^{-4} M.

Table 4 Peak assignation of SERS spectrum

Peaks found in solution 10^{-3} Raman	Peak assignation (Socrates, 2001) (HORIBA Jobin Yvon)
1618,5cm^{-1}	υ(C=N)
1586,4 cm^{-1}	υ(C=C) / u(CC) aromatic ring chain vibrations
1482,4 cm^{-1}	υ(CC) aromatic ring chain vibrations
1425,8 cm^{-1}	Aromatic ring
1365,2 cm^{-1}	Nitro
1294,4 cm^{-1}	νas(CCcenterC)/δ(CCC)ring/δ(CH)
1221,4 cm^{-1}	υ(CC) alicyclic, aliphatic chain vibrations
1177,0 cm^{-1}	Sulfonamide / νas(CCcenterC)
1074,6 cm^{-1}	Sulfone / Sulfonamide
986,6 cm^{-1}	υ(CC) aromatic ring chain vibrations
919,7 cm^{-1}	δ(CC center C)
798,9 cm^{-1}	Not assigned
767,4 cm^{-1}	C-S
741,6 cm^{-1}	Not assigned
423,0 cm^{-1}	Not assigned

b) Basic Green 1

The analysis of Basic Green 1 sample was also performed using FTIR and SERS over AgI@Au slide. The data shows the typical spectrum of the colorant without interference of the support. The FTIR data shows the following bands.

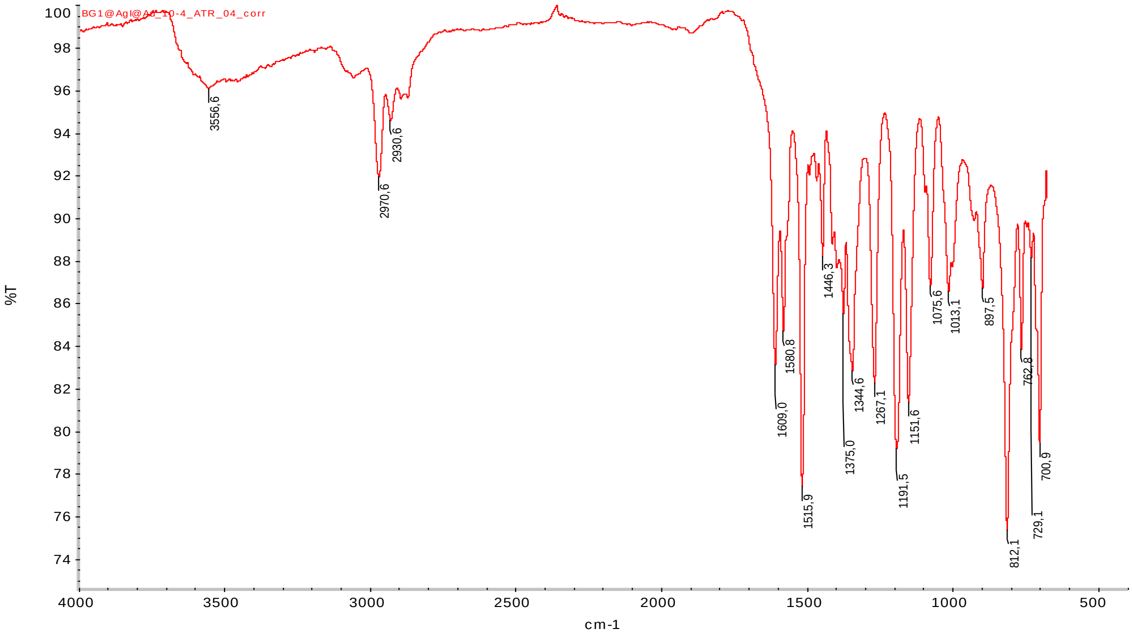


Fig. 5 FTIR spectra of BG1 standard solution 10^{-4} M

Table 5 Band assignation of BG1 standard solution FTIR spectrum

Peaks found in solution 10^{-4} M ATR	Peak assignation (Socrates, 2001)
1609 cm^{-1}	C=C in-plane deformation/ C=N
1580,8 cm^{-1}	C=C in-plane deformation/ C=N
1515,9 cm^{-1}	C=C in-plane deformation in aromatic homocyclic compounds
1446,3 cm^{-1}	Asymmetric CH_3 stretching of tertiary dimethyl amines ($-N(CH_3)_2$)
1344,6 cm^{-1}	C-N stretching vibration tertiary aromatic amine
1267,1 cm^{-1}	C-H in-plane deformation and benzene ring 1:4 disubstitution
1191,5 cm^{-1}	C-H in-plane deformation and 1:4 disubstitution benzene ring
1151,6 cm^{-1}	S-O stretching of $R.SO_2OH$
1075,6 cm^{-1}	C-H in-plane deformation and benzene ring monosubstitution
1013,1 cm^{-1}	C-H in-plane deformation and 1:4 disubstitution benzene ring
897,5 cm^{-1}	S-O stretching of $R.SO_2OH$
812,1 cm^{-1}	C-H out-of-plane deformation and benzene ring 1:4 disubstitution
762,8 cm^{-1}	C-H out-of-plane deformation and benzene ring monosubstitution
700,9 cm^{-1}	C-H out-of-plane deformation and benzene ring monosubstitution

The FTIR spectrum allow the identification of aromatic components of the molecule. The peak around 1151.6 cm^{-1}indicates the presence of the sulfur component present in the molecule. In the case of the SERS analysis, it was used the 780nm laser, since it was the one which offered the best results. In Table 4 is reported the assignation of peaks identified.

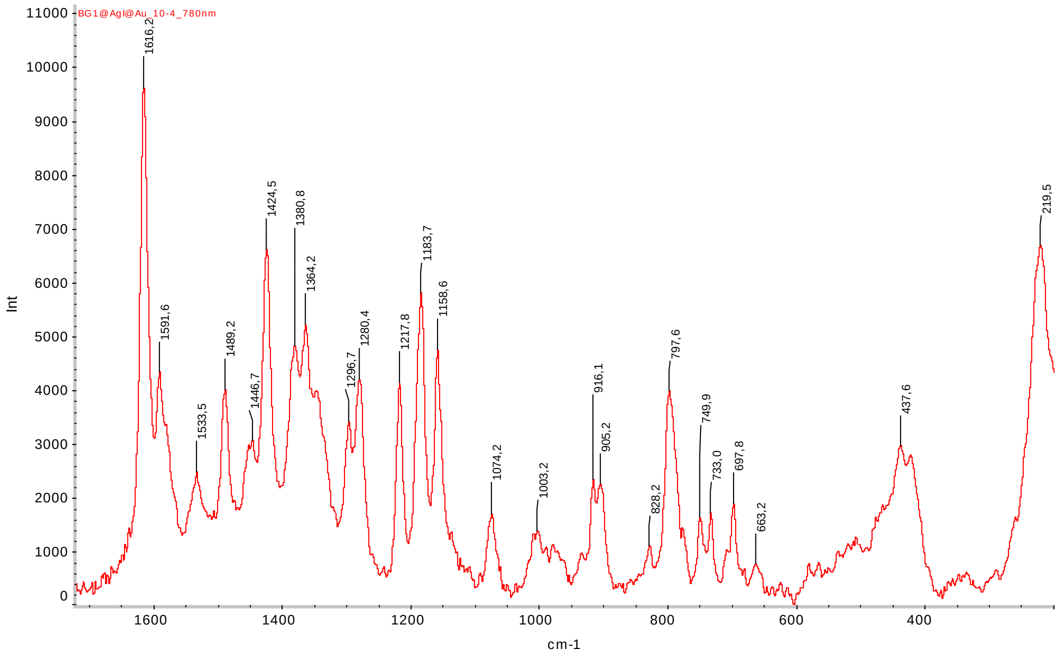


Fig. 6 Raman Spectra of BG1 standard solution

Table 6 Peak assignation of SERS BG1 spectra

Peaks found in solution 10^{-4} Raman	Peak assignation (Socrates, 2001) (HORIBA Jobin Yvon)
1614,6m^{-1}	υ(C=N)
1592,7 cm^{-1}	υ(C=C) / u(CC) aromatic ring chain vibrations
1488,8 cm^{-1}	υ(CC) aromatic ring chain vibrations
1424 cm^{-1}	Aromatic ring
1363,3 cm^{-1}	Nitro
1295,4 cm^{-1}	νas(CCcenterC)/δ(CCC)ring/δ(CH)
1279,7 cm^{-1}	Not assigned
1183,2 cm^{-1}	Sulfone (SO_2)
1157,4 cm^{-1}	Sulfone / Sulfonamide
1074 cm^{-1}	υ(CC) aromatic ring chain vibrations
904,9 cm^{-1}	δ(CC center C)
797,5 cm^{-1}	Not assigned
733,8 cm^{-1}	C-S
697,1 cm^{-1}	Not assigned
444,6 cm^{-1}	Not assigned

c) Basic Violet 1

The FTIR spectrum of Basic Violet 1 was obtained in previous studies by M2ADL, the assignation of peaks is presented in the following table.

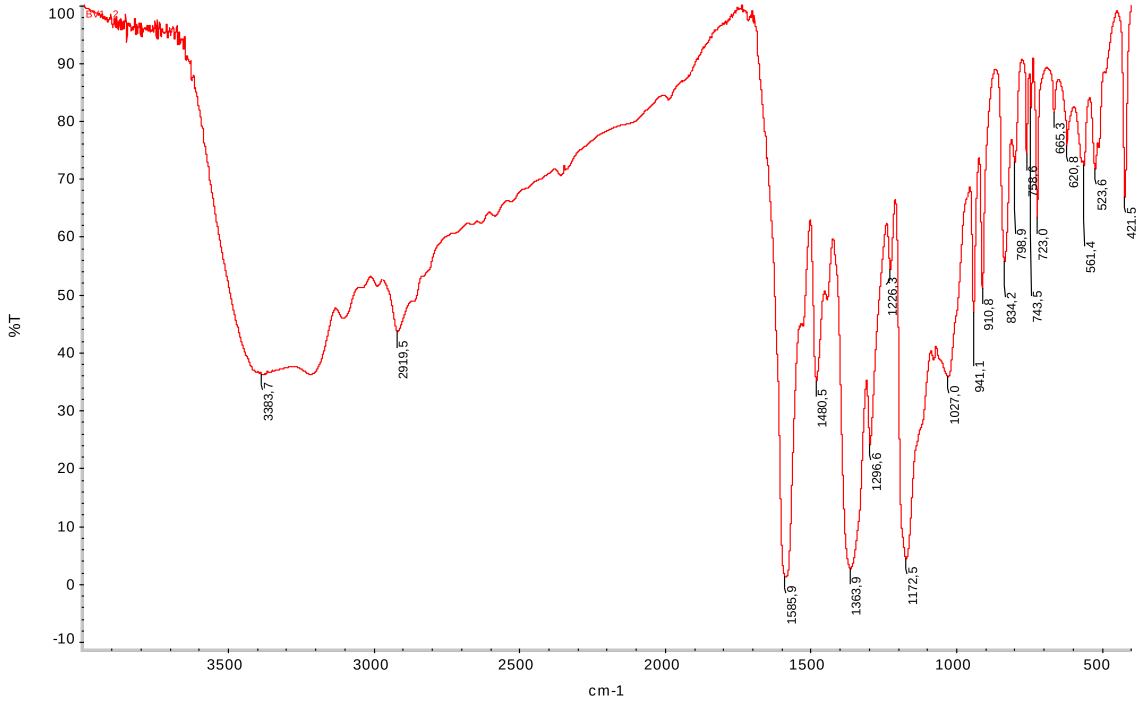


Fig. 7 FTIR spectra of BV1 standard

Table 7Peaks assignation of FTIR spectra of BV1

Peaks found in solution 10^{-4} ATR	Assignation (Socrates, 2001)
1585 cm^{-1}	C=C in-plane deformation/ C=N
1480,5 cm^{-1}	In-plane deformation of C=C of aromatic ring
1363,9 cm^{-1}	C-H symetric deformation of C-CH_3 / C-N stretching of tertiary aromatic amine
1296,6 cm^{-1}	C-H in-plane deformation 1:4 disubstitution
1172,5 cm^{-1}	C-H out-of-plane deformation 1:4 disubstitution/ Skeletal vibrations $C(CH_3)_2$
1027 cm^{-1}	C-H out-of-plane deformation 1:4 disubstitution / Skeletal vibrations $C(CH_3)_2$
941 cm^{-1}	Not assigned
910,8 cm^{-1}	Symetric streetching of Ar-$N(CH_3)_2$
834,2 cm^{-1}	C-H out-of-plane deformation 1:4 disubstitution
758,6 cm^{-1}	Not assigned
723 cm^{-1}	C-C out-of-plane bending (wagging) (ring puckering)

When analyzing with Raman there was no SERS effect so no enhancement of signal was present. However, it was possible to identify some of the characteristic peaks of the colorant. In the following table the band assignation is reported.

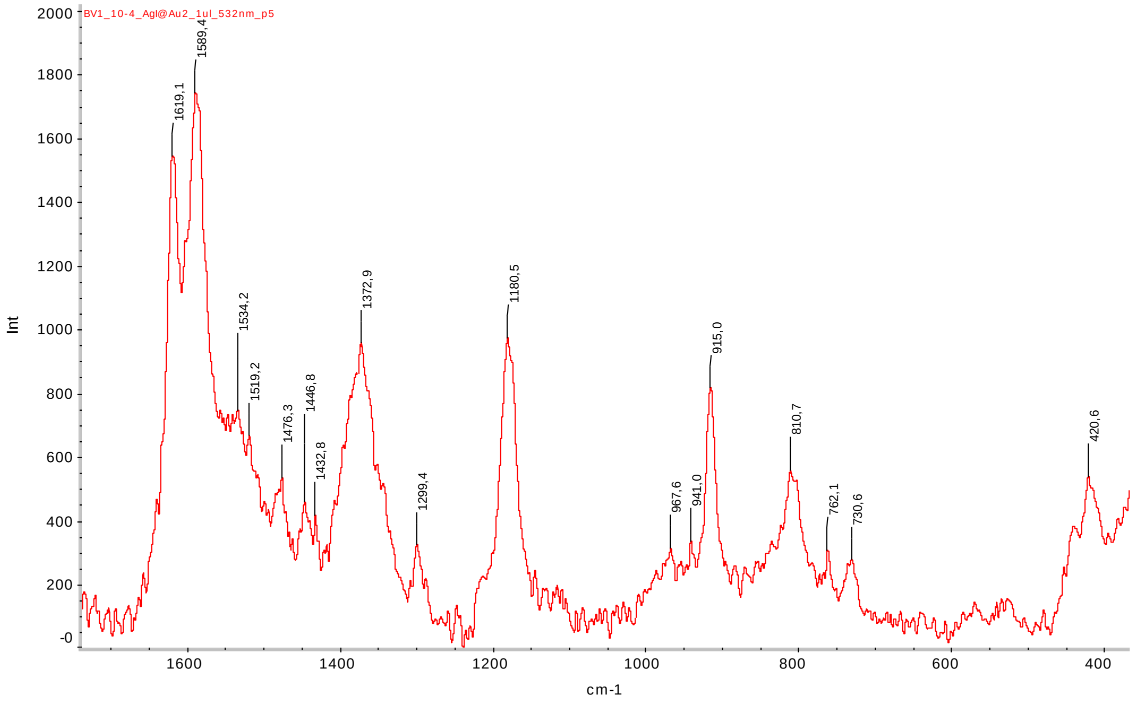


Fig. 8 Raman spectra of BV1 standard at 10^{-4} M concentration

Table 8 Peaks assignation of Raman bands present in BV1 spectra

Peaks found in solution 10^{-4} Raman	Peak assignation (Socrates, 2001) (HORIBA Jobin Yvon)
1619,2 m^{-1}	υ(C=N)
1589,5 cm^{-1}	υ(C=C) / υ(CC) aromatic ring chain vibrations
1373 cm^{-1}	Nitro
1301,3 cm^{-1}	νas(CCcenterC)/δ(CCC)ring/δ(CH)
1180,4 cm^{-1}	Not assigned
915,3 cm^{-1}	Not assigned
810,8 cm^{-1}	Not assigned
422 cm^{-1}	υ(Xmetal-O)?, Oxidation of Ag particles?

d) Basic Violet 3

The FTIR analysis of the Basic Violet 3 standard allowed the identification of the principal peaks related with the dye molecule. It is important to mention that neither the FTIR nor the SERS spectra were done during the present research but in previous experimental stages at the M2ADL. The assignation of the peaks from the FTIR spectra are reported in the following table.

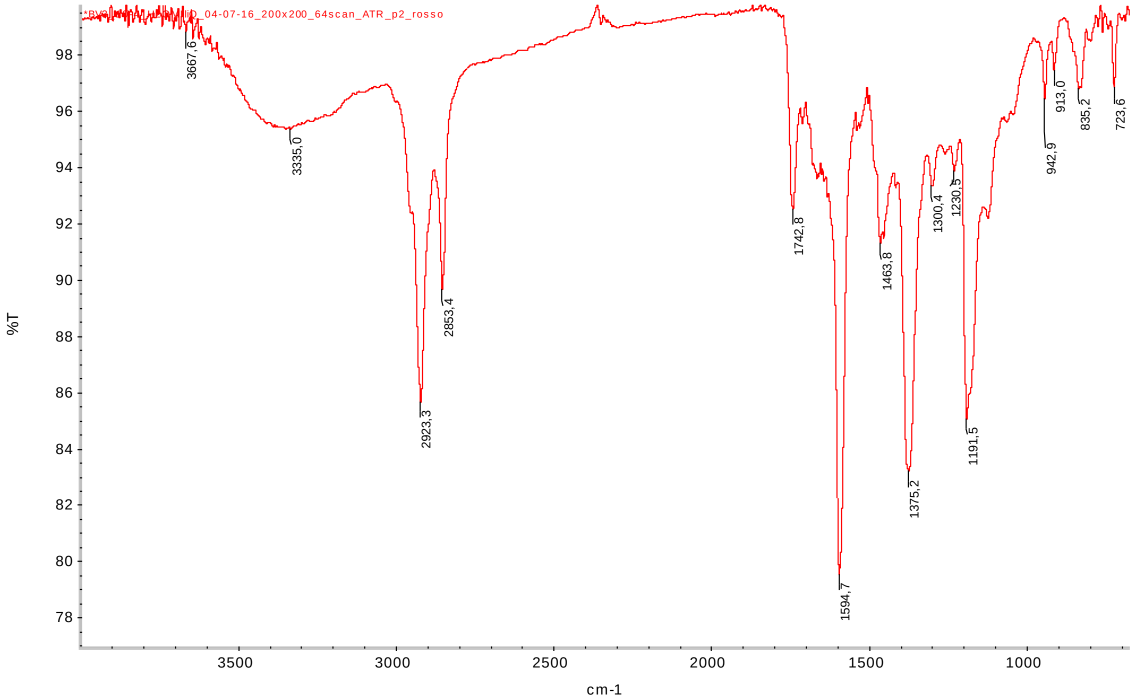


Fig. 9 Spectrum of BV3 standard solution at 10^{-4} M

Table 9 Assignation of peaks from the BV3 standard solution 10^{-4} M

Peaks found in solution 10^{-4} ATR	Assignation (Socrates, 2001)
1594 cm^{-1}	In-plane deformation of C=C of aromatic ring
1463 cm^{-1}	In-plane deformation of C=C of aromatic ring
1375 cm^{-1}	C-H symetric deformation of C-CH_3 / C-N stretching of tertiary aromatic amine
1300 cm^{-1}	C-H in-plane deformation 1:4 disubstitution
1230 cm^{-1}	Not assigned
1191 cm^{-1}	C-H in-plane deformation 1:4 disubstitution
1120 cm^{-1}	C-H in-plane deformation 1:4 disubstitution
942 cm^{-1}	Not assigned
913 cm^{-1}	Symetric streetching of Ar-$N(CH_3)_2$
835 cm^{-1}	C-H out-of-plane deformation 1:4 disubstitution
723 cm^{-1}	C-C out-of-plane bending (wagging) (ring puckering)

The SERS analysis was done using the 532nm laser; the results of analysis of standard solution at 10^{-4} M concentration are reported in the following table, as in the case of the BV1, this data was obtained in previous studies at M2ADL.

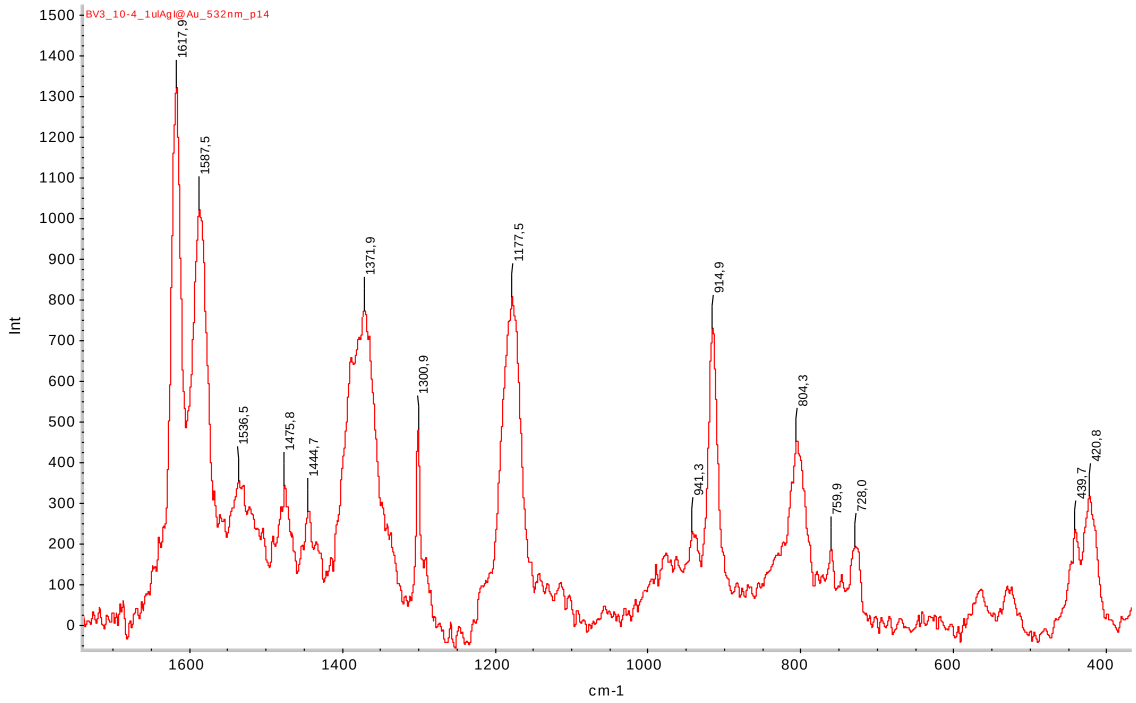


Fig. 10 Raman spectra of BV3 standard solution at 10^{-4} M concentration

Table 10 Bands assignation of BV3 Raman spectra

Peaks found in solution 10^{-4} Raman	Peak assignation (Socrates, 2001) (HORIBA Jobin Yvon)
1619,1 m^{-1}	υ(C=N)
1587,2 cm^{-1}	υ(C=C) / υ(CC) aromatic ring chain vibrations
1536,4 cm^{-1}	υ(CC) aromatic ring chain vibrations
1424 cm^{-1}	Aromatic ring
1371,9 cm^{-1}	Nitro
1301,3 cm^{-1}	νas(CCcenterC)/δ(CCC)ring/δ(CH)
1176,6 cm^{-1}	Not assigned
915,3 cm^{-1}	Not assigned
805 cm^{-1}	Not assigned
441,2 cm^{-1}	Not assigned
422 cm^{-1}	υ(Xmetal-O)?, Oxidation of Ag particles?

e) Basic Violet 4

Since no Basic Violet 4 was available for the analysis with the AgI@Au system, the reference was taken from the Spectral Database for Organic Compounds of the National Institute of Advanced Industrial Science and Technology of Japan. In the following Table are reported the principal peaks of the spectra (National Institute of Advanced Industrial Science and Technology, 2017).

Table 11 FTIR signal assignation of BV4 of spectra reported by SBDS

Standard of BV4 reported by SDBS	Assignation (Socrates, 2001)
1579 cm^{-1}	Not assigned
1524 cm^{-1}	Not assigned
1474 cm^{-1}	In-plane deformation of C=C of aromatic ring / C-H deformation of -CH_2-
1412 cm^{-1}	CH2 bending vibrations
1371 cm^{-1}	C-H symetric deformation of C-CH_3 / C-N stretching of tertiary aromatic amine
1345 cm^{-1}	CH_2 bending
1300 cm^{-1}	C-H in-plane deformation 1:4 disubstitution
1274 cm^{-1}	CH2 out-of-plane bending
1186 cm^{-1}	C-H in-plane deformation 1:4 disubstitution
1156 cm^{-1}	Skeletal vibrations (C-H) bending
1093 cm^{-1}	Not assigned
1074 cm^{-1}	C-H deformation bending
915 cm^{-1}	Symetric streetching of Ar-N$(CH_3)_2$
825 cm^{-1}	C-H out-of-plane deformation 1:4 disubstitution
793 cm^{-1}	C-H out-of-plane bending ring

For the SERS identification, the reference was taken from the Persaud & Grossman (1993), the signals and assigantion of peaks reported by them is presente in the following table.

Table 12 SERS bands assignation of BV4 according to Persaud and Grossman (1933)

Peaks (Persaud & Grossman, 1993)	Assignation (Persaud & Grossman, 1993)
1621 cm^{-1}	Ring C-C stretching
1584 cm^{-1}	Ring C-C stretching
1535 cm^{-1}	Ring C-C stretching
1492 cm^{-1}	Ring C-C stretching + ring deformation
1457 cm^{-1}	Ring C-C stretching + ring deformation
1423 cm^{-1}	N-Ph stretching + ring vibration
1371 cm^{-1}	N-Ph stretching
1284 cm^{-1} 1302 cm^{-1}	Ring C-C stretching
1162 cm^{-1} 1188 cm^{-1}	In-plane ring C-H bend
1076 cm^{-1}	In-plane C-H deformation of CH_2 CH_3 group
979 cm^{-1} 992 cm^{-1} 1010 cm^{-1}	In-plane ring C-H bend
905 cm^{-1} 917 cm^{-1}	Ring skeletal vibration of radial orientation
804 cm^{-1} 828 cm^{-1}	Out-of-plane (C-H) bend
759 cm^{-1}	Out-of-plane (C-H) bend
737 cm^{-1} 747 cm^{-1}	Out-of-plane (C-H) bend
708 cm^{-1}	Out-of-plane (C-H) bend
663 cm^{-1}	Out-of-plane (C-H) bend
620 cm^{-1}	Out-of-plane (C-H) bend
599 cm^{-1}	Ring skeletal vibration of radial orientation
567 cm^{-1}	Ring skeletal vibration of radial orientation
513 cm^{-1}529 cm^{-1}	Ring skeletal vibration of radial orientation
428 cm^{-1}442 cm^{-1} 464 cm^{-1}	Out-of-plane skeletal vibration + out-of-plane (C^+-Ph)
343 cm^{-1}	In-plane (C^+-Ph) bend
301 cm^{-1}	In-plane (C^+-Ph) bend
182 cm^{-1} 209 cm^{-1}	Breathing of central bonds

Indigoid class dye

Acid Blue 74

The AB74 FTIR spectra from a standard solution was obtained in previous experimentations at M2ADL. A solution at 10^{-4} M was analyzed over AgI@Au system. It was possible to identify the characteristic bands of the dye.

Table 13 Assignation peaks of FTIR spectra obtained from standard solutio of AB74

Peaks found in solution 10^{-4} ATR	Assignation (Socrates, 2001)
1640,2 cm^{-1}	Combination band of NH deformation and C-N stretching vibration / C=O stretching vibration of cyclopropanona
1616,6 cm^{-1}	Combination band of NH deformation and C-N stretching vibration
1473,8 cm^{-1}	NO vibration of azoxy compound? (Molecule modification, inter crosslinking?)
1405,5 cm^{-1}	CH$_2$ deformation of –CH$_2$-CO- ? (possible modification to the molecule)
1365,1 cm^{-1}	C$_R$-N stretching of tertiary amine
1321,7 cm^{-1}	C$_R$-N stretching of tertiary amine / alkyl ketone
1198,9 cm^{-1}	C-H in-plane deformation 1:4 disubstitution / S=O stretching vibration of sulphites
1158,3 cm^{-1}	C-H in-plane deformation 1:4 disubstitution S=O stretching vibration of sulphites
1104,3 cm^{-1}	C-H in-plane deformation 1:4 disubstitution
1030,8 cm^{-1}	C-H in-plane deformation 1:4 disubstitution / S=O stretching deformation
831,5 cm^{-1}	C-H out-of-plane deformation and benzene ring 1:4 disubstitution
734,7 cm^{-1}	-CH=CH- CH vibrations
679,7 cm^{-1}	Not assigned

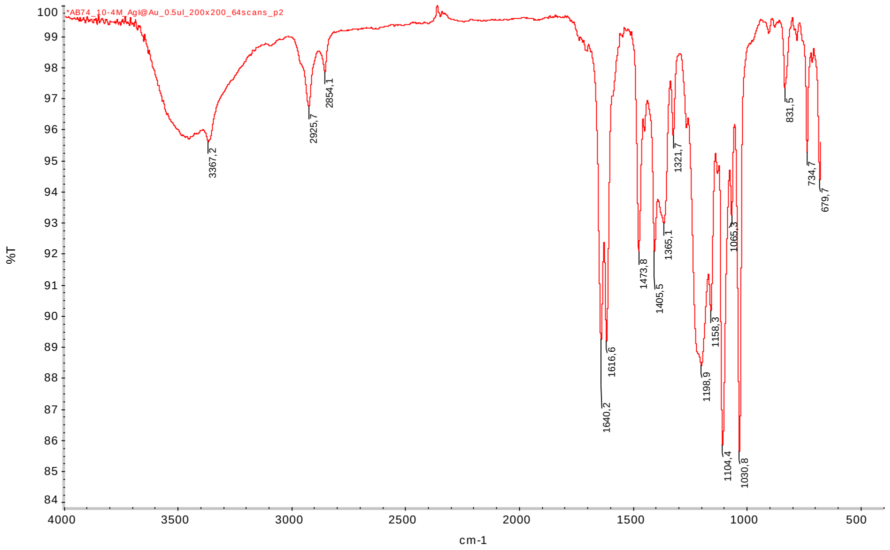


Fig. 11 AB74 standard solution FTIR spectrum. 10^{-4} M concentration.

The Raman analysis shows peaks that correspond to the dye and to the interaction of it with the AgI from the support. The band assignation was taken from the study if Peica and Kiefer done in 2008.

Table 14 Bands assignation of AB74 spectrum according to Peica & Kiefer, 2008

Peaks found in solution 10^{-4} Raman	Peak assignation (Peica & Kiefer, 2008)
1656,6 m^{-1}	ν_s(C9=C9'), ν(C=C), ν_s(C=O)
1575,1 cm^{-1}	ν_{as}(C=C)pr, ν(C=O), €(C=N)
1514,5 cm^{-1}	ν(ph,pr), ν_s(C=C)pr
1348,3 cm^{-1}	δ(C–H, N–H), ν(ph, pr); ν(SO_2)
1291,3 cm^{-1}	ν_s (-SO_3^-); υ (C–C), ν(N1–C2)
1165,3 cm^{-1}	ν_{sa} (SO_2); υ_{ip} (C–C)
1082,3 cm^{-1}	υ_{op} (O14–Na); υ_{ip} (C–H); υ_{ip} (C–C)
764,1 cm^{-1}	υ_{op} (C–C, C–H); pr breath.
726 cm^{-1}	ph, pr def.; υ (C–N–C)
670,1 cm^{-1}	υ_{op} (N–H, C–C)
590,9 cm^{-1}	Not assigned
572,9 cm^{-1}	υ (C C–CO–C); υ (C O, C–H, C–NH–C)
544,9 cm^{-1}	υ (C C–CO–C)
262,7 cm^{-1}	skeletal def.; υ (Ag–O)

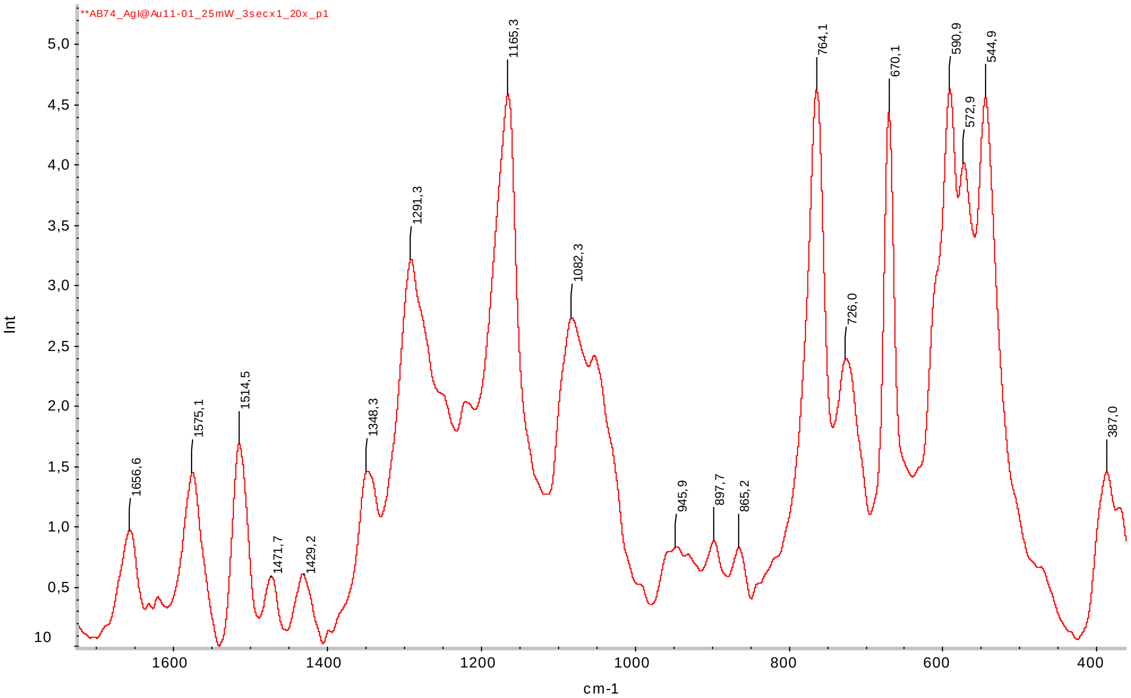


Fig. 12 Raman spectrum of AB74 standard solution at 10^{-4} M

Nitro class dye

Acid Yellow 24

As other standard spectra, the AY 24 data was obtained in previous researches conducted in M2ADL. The spectrum shows the characteristic peaks of the colorant. Since in previous researches this colorant was designed as AY 2, a comparison to other standard reported by IRUG database was done in order to confirm that the dye is AY24.

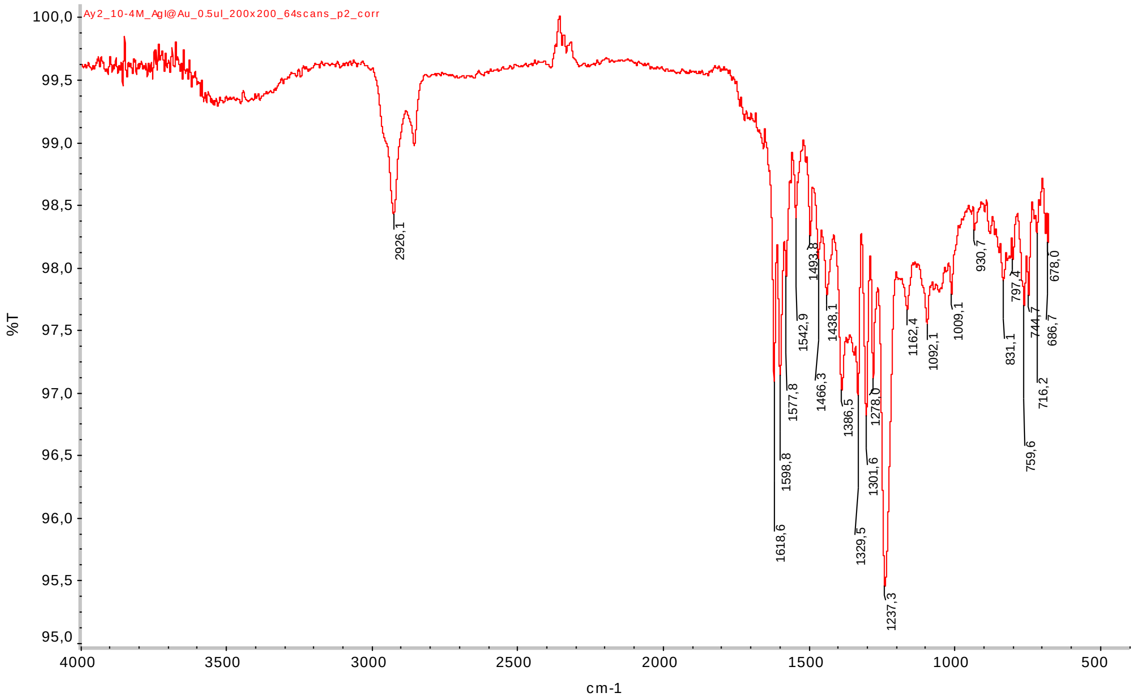


Fig. 13 AY 24 FTIR standard spectrum

Table 15 Peak assignation of AY24 standard solution spectrum

IRUG AY24 spectrum (Infrared & Raman Users Group, 1993-2017)	Peaks found in solution 10^{-4} ATR	Assignation (Socrates, 2001)
1616 cm^{-1}	1618,6 cm^{-1}	Combination band of NH deformation and C-N stretching vibration
1593 cm^{-1}	1598,8 cm^{-1}	-C=C- stretching vibration
1572 cm^{-1}	1577,8 cm^{-1}	-C=C- stretching vibration / asymmetric NO_2 stretching
1491 cm^{-1}	1493,8 cm^{-1}	-C=C- stretching vibration
1436 cm^{-1}	1438,1 cm^{-1}	-C=C- stretching vibration
1391 cm^{-1}	1386,5 cm^{-1}	Symmetric NO_2 stretching for aromatic compounds
1332 cm^{-1}	1329,5 cm^{-1}	Symmetric NO_2 stretching
1303 cm^{-1}	1301,6 cm^{-1}	Not assigned
1238 cm^{-1}	1237,3 cm^{-1}	CH_2 out-of-plane bending
1088 cm^{-1}	1092,1 cm^{-1}	C-O- asymmetric stretching
1007 cm^{-1}	1009,1 cm^{-1}	Aromatic C-O- stretching
842 cm^{-1}	831,1 cm^{-1}	1,2,4 trisubstitued benzenes out-of-plane deformation vibration
795 cm^{-1}	797,4 cm^{-1}	Aromatic nitro compounds
763 cm^{-1}	759,6 cm^{-1}	1,2,4 trisubstitued benzenes out-of-plane deformation vibration
744 cm^{-1}	716,2	1,2,4 trisubstitued benzenes out-of-plane deformation vibration

The Raman analysis gave low signal however; it was possible to identify some characteristic picks of the molecule of AY 24.

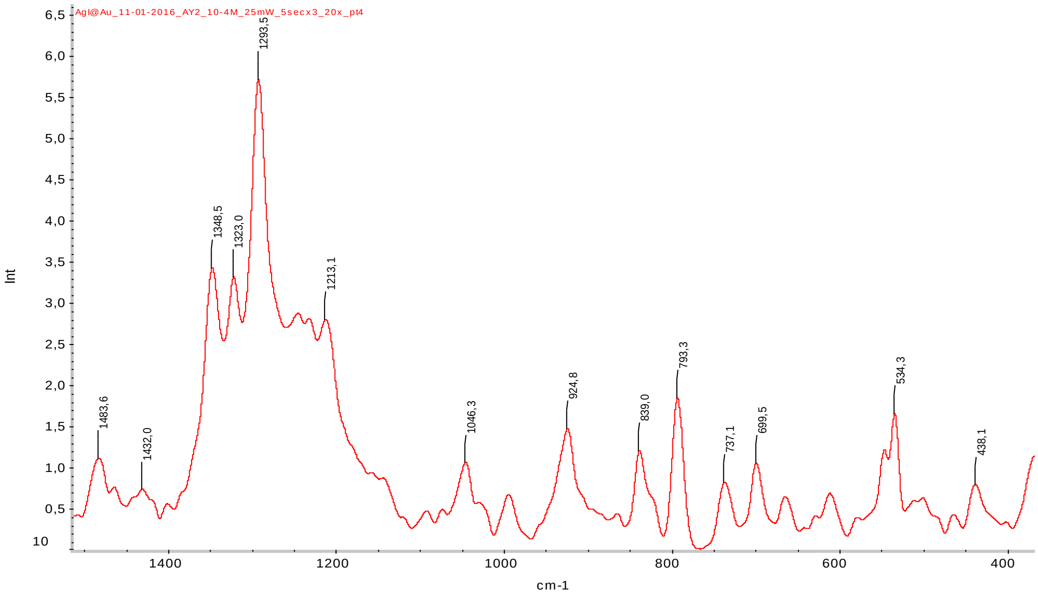


Fig. 14 Raman spectrum of AY 24 standard solution at 10^{-4} M

Table 16 Band assignation of AY 24Raman spectrum

Peaks found in solution 10^{-4} Raman	Peak assignation
1483,6 m^{-1}	Aromatic ring
1348,5 cm^{-1}	Nitro group
1323 cm^{-1}	Nitro group, symmetric NO_2 stretching.
1293,5 cm^{-1}	R-O-Ar
1213,1 cm^{-1}	Aromatic =C-H in-plane deformation of 1,2,4 trisubstituted ring
1046,3 cm^{-1}	Aromatic =C-H in-plane deformation of 1,2,4 trisubstituted ring
995,3 cm^{-1}	Not assigned
924,8 cm^{-1}	Out-of-plane deformation vibration of C-H in a trisubstituted benzene
839 cm^{-1}	Out-of-plane deformation vibration of C-H in a trisubstituted benzene
793,3 cm^{-1}	δ CO, ν C-C ar, NO_2 sb2, R2trgd
737 cm^{-1}	Aromatic nitro compounds
699,5 cm^{-1}	Out-of-plane deformation vibration of C-H in a trisubstituted benzene
665 cm^{-1}	Not assigned
611 cm^{-1}	Not assigned
534,3 cm^{-1}	Aromatic ring deformation
438 cm^{-1}	Aromatic ring deformation
367 cm^{-1}	Not assigned
339,9 cm^{-1}	ν C-C ar, ν C-N

4.3 Colorimetric measurements

Since no record of colorimetric measurements were available for the artificially aged samples, the estimation of the color change was register in terms of colorimetric information. This data allow recording changes in terms of color, even if they are not so evident under naked eye. Moreover, this information can be correlated with the chemical variations of the dyes and can be used for further researches in order to understand the damage of these synthetic dyes.

Tri-aryl Methines

a) Basic Green 1

The color modification of Basic Green 1 fibers is very evident even at naked eye. The color is almost completely lost at 305h, turning slightly yellow. The colorimetric measurements indicate that at the beginning, the dye losses part of the reflectance and then after 140h and 305h it became brighter and is shifted to the 520nm (close to yellow).

This change suggest a modification. The shifting in the reflectance values suggest that the molecule possess less chromophore groups, such as aromatic rings and conjugated π bonds, and is absorbing less radiation turning into a lighter color.

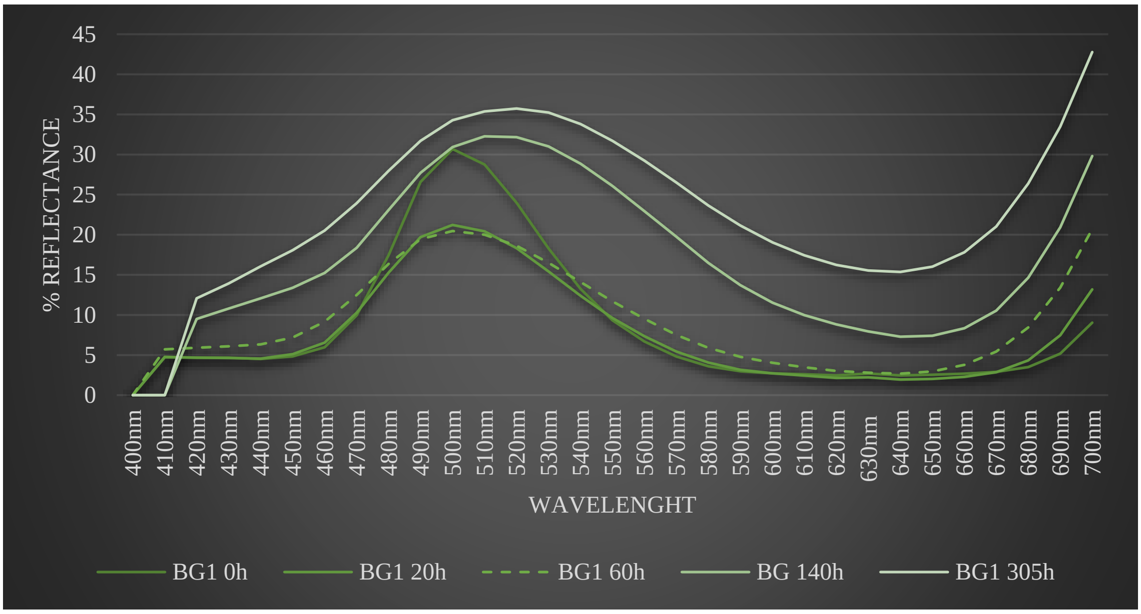


Fig. 15 Graphic of colorimetric measuremets of BG1 samples

Table 17 Values of colorimetric measurements of BG1 in CIE coordinates

Sample	L*	a*	b*	C*	h	ΔE
0 h	37.9632	-48.8699	0	-1.6475	48.8977	-
20h	35.5084	-39.735	0	-2.4169	39.8084	9.22
60h	38.006	-33.2658	0	-3.03645	33.4041	16
140h	0	51.08535	-31.2489	0	-1.99295	111.37
305h	0	57.73845	-21.48775	0	1.1876	114.54

According to the color differences, values (ΔE) calculated using the CIE76 algorithm, the biggest difference taken as reference the 0h occurs at 140h with a change in ΔE of 111.37.

This can suggest that the chemical degradation is more evident after 140h of exposition to light. The ΔE values indicates that for 20h and 60h, the color change is perceptible but still similar to the original one, but for 140h and 305h they seem to be the opposite color in comparison to the 0h.

b)Basic Violet 1

The measurements of BV1 show few changes in the color, in general the reflectance is low since the color is very dark. After 305h of artificial aging a peak around 690nm appears, with a considerable increasing in the reflectance related with red color. However, this modification is not evident under naked eye. This data suggest that probably this molecule does not suffer big modifications with the aging.

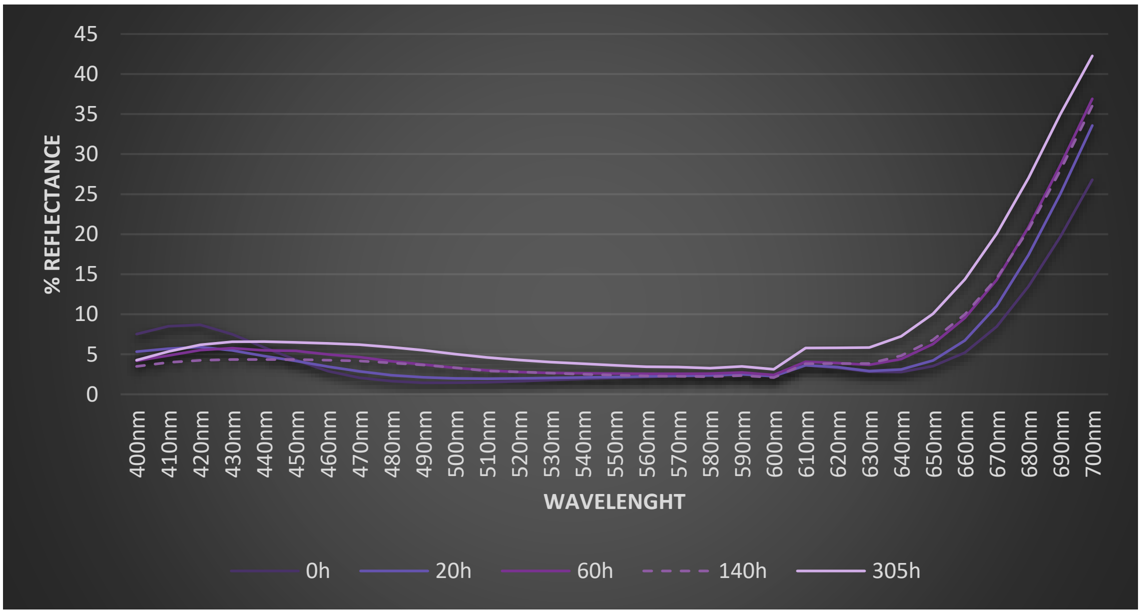


Fig. 16 Colorimentric graphic of BV1

Table 18 Values of colorimetric measurements of BV1 in CIE coordinates

Sample	L*	a*	b*	C*	h	ΔE
0 h	16.3488	14.9156	-15.1918	0	314.4745	-
20h	17.3834	10.5518	-11.0242	0	313.7455	0.8384
60h	20.1379	7.8036	-11.5774	0	303.9815	7.2867
140h	19.3863	5.8490	-8.3927	10.2298	304.8740	0.7700
305h	24.4944	6.0193	-9.5232	11.2660	302.291	4.9179

The total color difference (ΔE) between the 0h and the other samples confirm the small changes in color. Surprisingly the biggest change occurs after 20h. Is interesting to notice that after 140h and 305h there is a difference in brightness (C*), possibly result of a small loss of color, starting to turn lighter the fiber, however this is not perceptible under necked eye.

c) Basic Violet 3

The measurements of fibers dye with Basic Violet 3 show a change in the color that goes from the violet to the ultraviolet region of the spectrum. This can be perceive as a darkening modification of it that later will disappear for the human eye, since ultraviolet radiation is not perceive. The reflectance was reduced in around 50% and moved from the 450nm to the 430nm-420nm. The gradual change is evident, increasing with the exposure time to light (artificial aging). This modification shows a higher absorption of almost all the wavelengths it can indicate the increasing of conjugated π bonds. This information must be correlated to the chemical investigation.

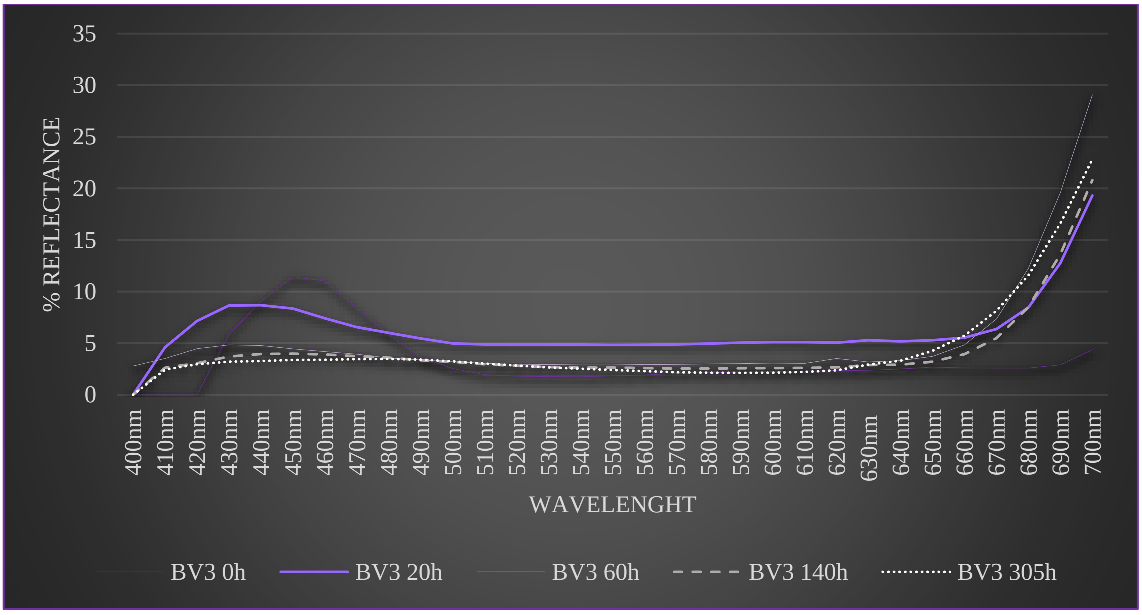


Fig. 17 Graphic of BV3 colorimetric measurements

Table 19 Values of colorimetric measurements of BV3 in CIE coordinates

Sample	L*	a*	b*	C*	h	ΔE
0 h	0	21.7041	20.2054	-26.6856	0	-
20h	0	27.079	5.9012	-8.70105	10.5134	14.86
60h	20.7029	4.7956	-6.548	8.1166	306.21695	38.19
140h	0	19.32155	4.2877	-5.81455	7.22475	16.27
305h	0	18.6378	4.69295	-4.738	6.66915	15.29

The ΔE values indicate a low change in color for the BV3 sample, it seems to be stable, whit a bigger modification at 60h however, and this can be related to problems with the sample since the other samples keep a value similar between them. The ΔE values indicates that in all cases the color change is perceptible to the human eye.

Indigoid dye

a) Acid Blue 74

As it can be expected, the highest reflectance percentage of AB74 corresponds to the blue part of the electromagnetic spectrum between 450nm to 495nm. The reflectance in this part of the spectrum increase with the artificial aging, since it turns lighter. The spectrum shifts to the 500nm which corresponds to the cyan part of the visible light. It also appears a small band in the red area, but this is not noticeable.

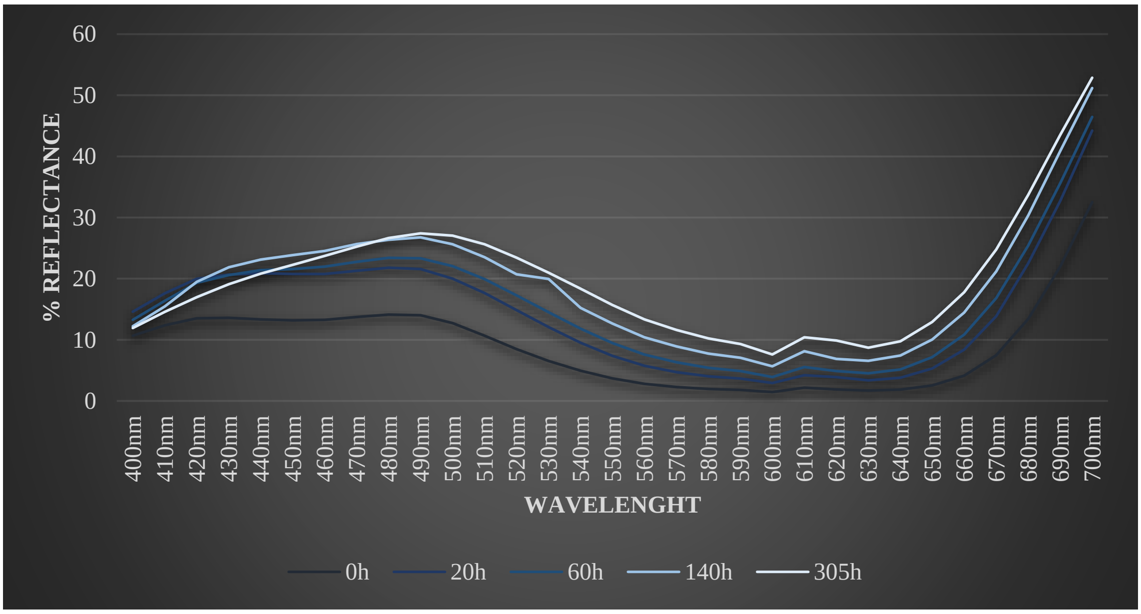


Fig. 18 Colorimetric measurements of AB74 artificially aged samples.

Table 20 Values of colorimetric measurements of AB74 in CIE coordinates

Sample	L*	a*	b*	C*	h	ΔE
0 h	28.1314	-11.1640	0	-26.0884	0	-
20h	37.1809	-14.5407	0	-26.5517	0	5,6728
60h	40.2233	-16.7738	0	-22.7271	0	6,4821
140h	44.5215	-18.2653	0	-19.0642	0	9,2888
305h	47.5139	-20.5130	0	-11.6589	0	10,0335

The total color difference is clearly progressive in this case. The biggest change is registered after 305h. The fiber start to loss color and becoming lighter, however, as the values of ΔE show, the changes are not so big, so they are no so evident to the human eye.

Nitro dye

a) Acid Yellow 24

The fibers dyed with Acid Yellow 24 show a clear discoloration with the increasing time of exposure. The degradation of yellow dyes it is well known, and the light fastness is very evident in this case even at naked eyes. The colorimetric measurements show a clearly decrease in the reflectance percentage.

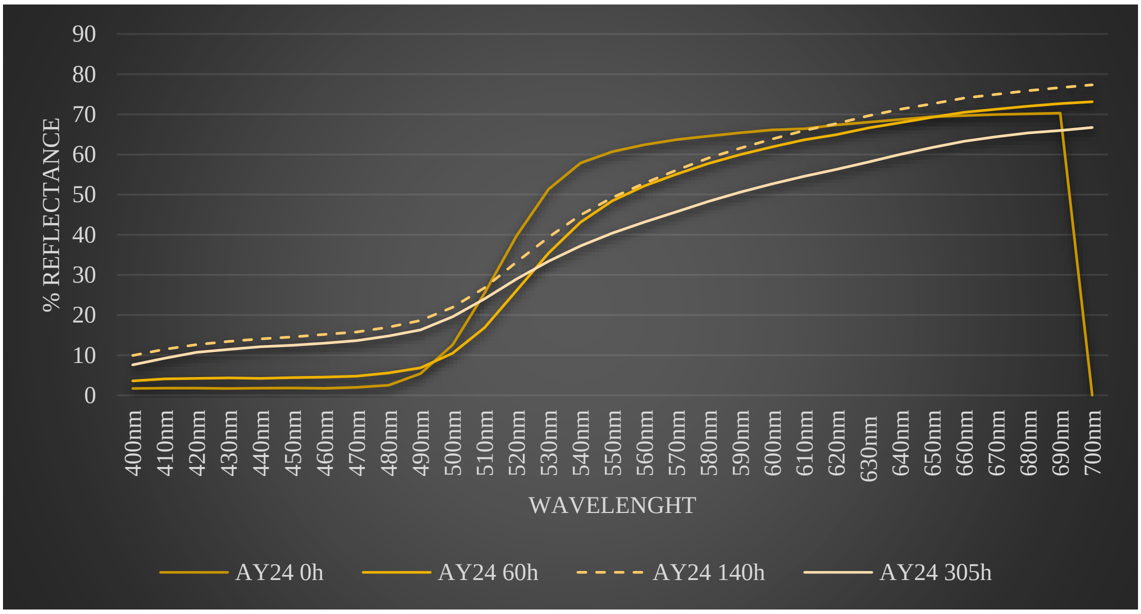


Fig. 19 Graphic of colorimetric measurements of AY24 samples

The ΔE values show a bigger change in the color of the fibers dye with AY24 after artificial ageing; this behavior is expected since the yellow colorants are the ones with more degradation problems due to light. The modifications seem to be homogenous in all the samples.

Table 21 Values of colorimetric measurements of AY24 in CIE coordinates

Sample	L*	a*	b*	C*	h	ΔE
0 h	73.2994	14.40595	97.2606	98.32165	81.5748	-
60h	0	71.0541	16.0653	76.0941	77.7715	123.04
140h	0	73.75305	13.838	48.18635	50.1339	125.76
305h	0	68.45845	12.3796	44.30305	46.1504	124.37

4.4 Set-up of the experiment procedure for the analysis of dyes extracted from textile samples

As mentioned before, some samples are textile fiber dyed with specific synthetic colorants and artificially aged. In this section, the results obtained from their analysis are discussed. The information is presented divided according to the dye class.

Extraction method

As mentioned before, two extraction procedures were performed since in many cases the interference of the wool was considerable and a small quantity of dye was extracted. In order to improve the simple extraction with methanol, a pre-wash with water was performed.

The analysis of the different extract have shown that the quantity of dye extracted with the double system is higher, mainly the one which implies a first pre extraction at 60º C with water type 2. Moreover, the initial extraction with water reduce the interference of the wool in the results after MeOH extraction. This can be attributed to the broken of the dye-fiber system, which facilitates the extraction of the dye during the second step using MeOH.

A clear example of this improvement is the data obtained from BV3 dye. In the spectra obtained is evident the elimination of the peaks related to the wool (1661cm^{-1}, 14004cm^{-1}, 1120cm^{-1}) and it is easier to identify all the peaks related to the BV3.

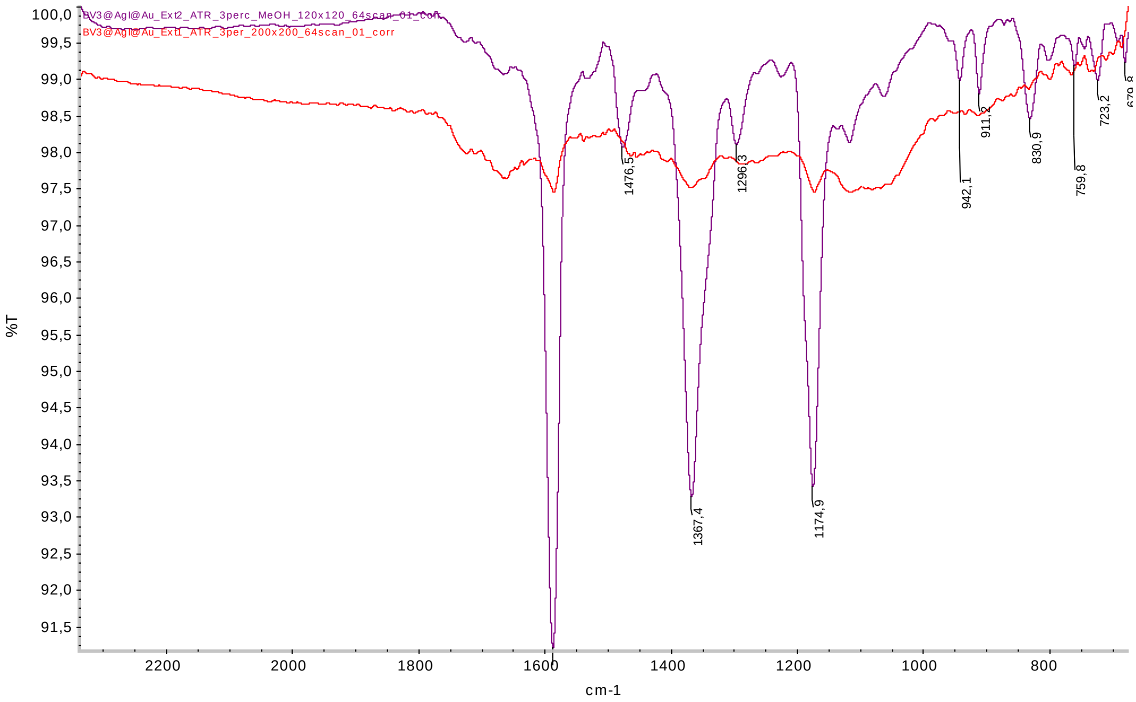


Fig. 20 Comparison between the spectra obtain from the extraction with water at room temperature and MeOH at 60ºC (red line) and extraction with water at 60ºC and MeOH at 60ºC. The spectra is shown in common scale.

Results obtained over AgI@Au versus gold coated glass slides

The comparison between the information obtained by analyzing the extracted dyes over gold coated slide and AgI@Au slides shows one of the main advantages of the system.

The analyzed samples have shown that the AgI@Au plate allowed separating different components present in the extracts even without performing a TLC separation. Indeed just applying on the support a drop of the extracted solution a double “coffee-ring” pattern is observed.

Fig. 21 Double “coffee-ring” formed over AgI@Au of a BV1 extraction

Analyses performed on both the ring allowed to verify that spectra registered in the outer ring refer mainly to wool from the one while the dye is more concentered in the inside ring, even if some signals related to wool are still present.

In all the cases this was the behavior, which indicates that this phenomena does not depends on the kind of sample but is something specific from the AgI@Au system. This reduces considerably the sample preparation. Is important to keep in mind that this is useful only for sample constituted by a single dye a not a mixture that require the separation of the component by terms of TLC.

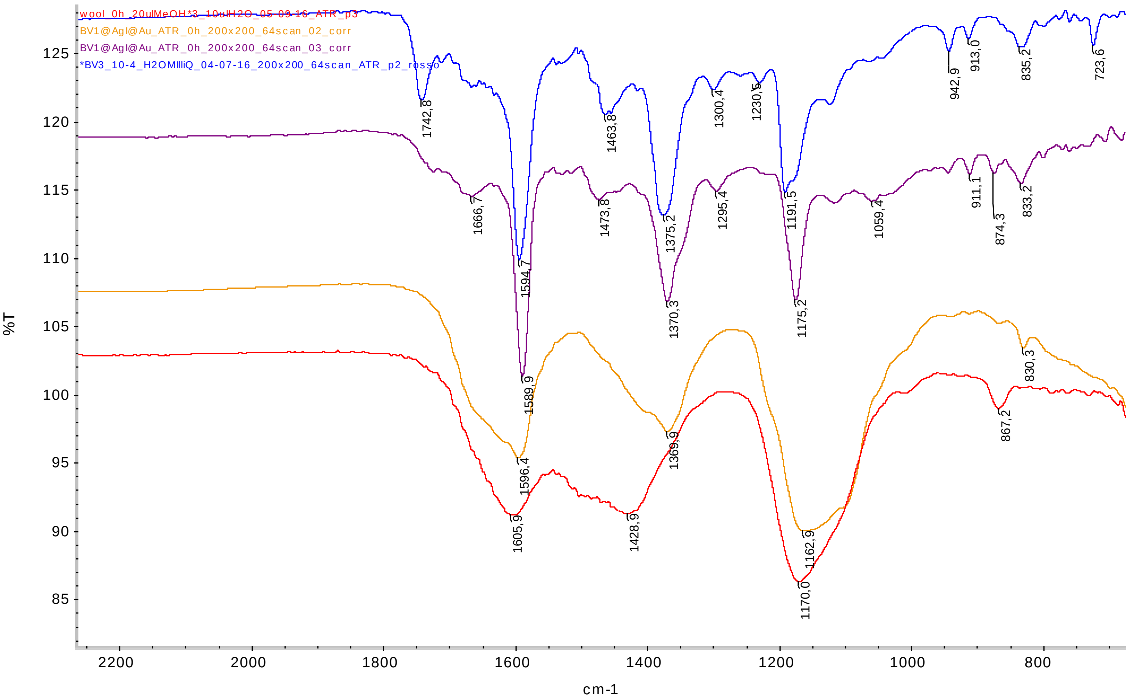


Fig. 22 Comparison between the spectra obtained from BV1 0h sample. The outer-ring (yellow line), the wool extraction (red line), inner ring (purple line) and BV1 10^{-4} M standard solution. It is evident the contribution of wool in the first and the elimination of this interference in the second one.

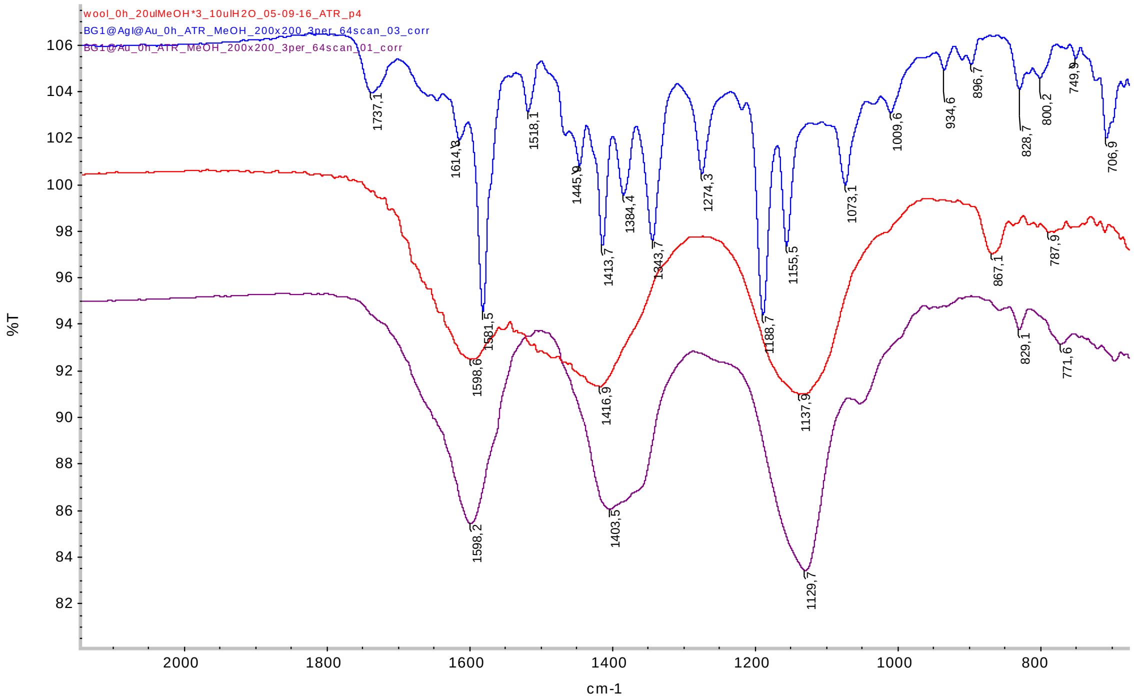


Fig. 24 Comparison between the spectra obtained from BG1 0h sample. The sample over Au slide (purple line), the wool extraction (red line), inner ring over AgI@Au (blue line). It is evident the contribution of wool in the first and the elimination of this interference in the second one.

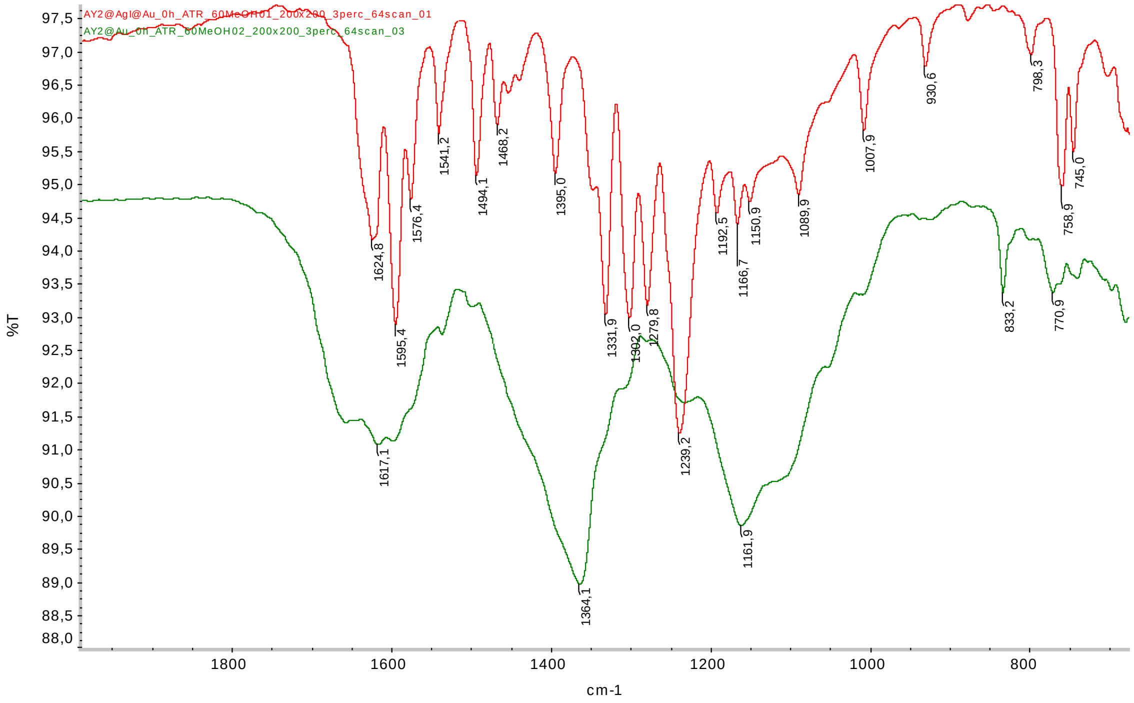


Fig. 23 FTIR spectra of AY25 at 0h. Green line: over Au slide, red line: over AgI@Au

Evaluation of ageing effects

In this section, the results of the study of the different times of artificial aged samples. The results are presented in sections organized according to the type of dye studied.

Tri-aryl Methines

a) Basic Violet 1 (BV1)

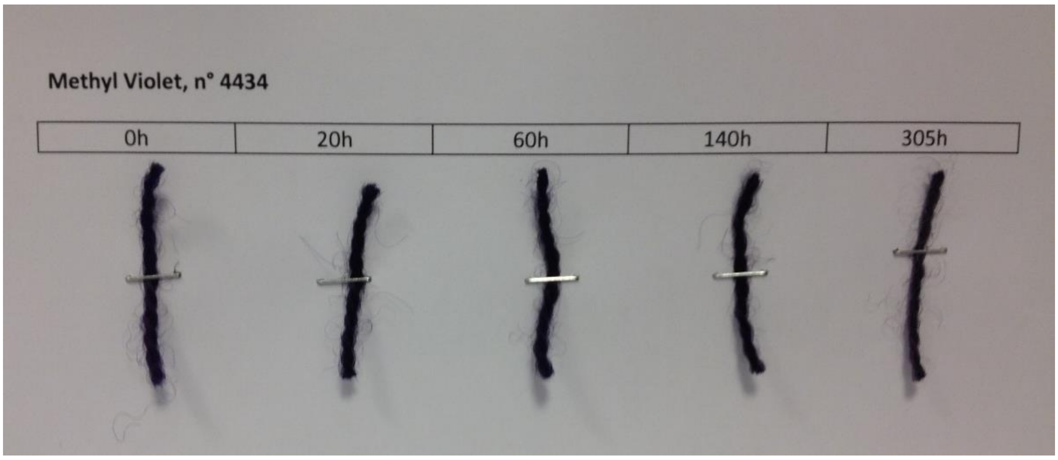


Fig. 25 Artificially aged samples dyed with Basic Violet 1

Moreover, the FTIR analysis performed have shown that the dye keeps its chemical composition almost unaltered with the ageing. The most evident change in the spectra is the increasing of the band at 1664cm-1, which has a higher relative intensity when ageing time is increasing. This probably is the result of the fiber interference.

A second hypothesis that can explain these changes in the spectra is the photooxidation of the molecule, by the loss of methyl groups and the formation of hydroxyl groups attached to the N atom, forming oximes. The presence of signals at 941cm^{-1} support this hypothesis since it is a characteristic peak of oximes (Reusch, 1999). The demethylation of this type of dyes has already reported by Confortin, Brustolon, Franco, Neevel, and van Bommel (2010) for the case of BV3 that have identified N-oxides in the photooxidation of this class of dyes (for BV3 and BG1), however further researches are required in order to prove it.

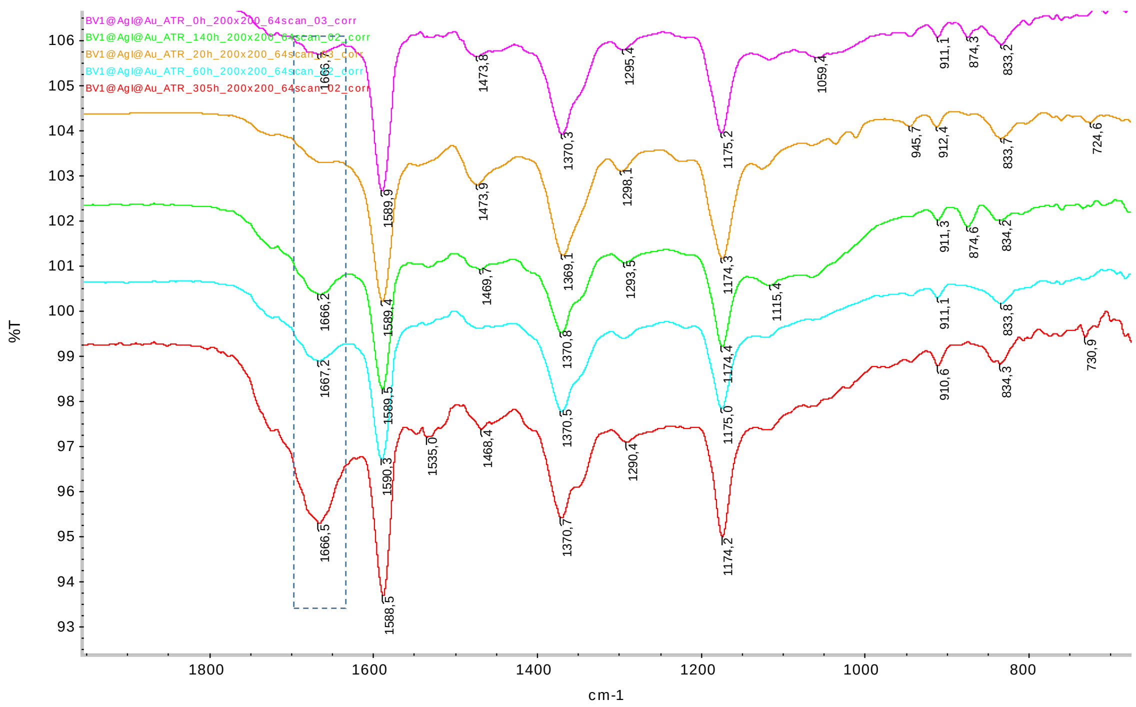


Fig. 26 FTIR spectra of BV1 samples. Pink line: 0h, yellow line: 20h, green line: 60h, blue line: 140h and red line 305h

b) Basic Violet 3 (BV3)

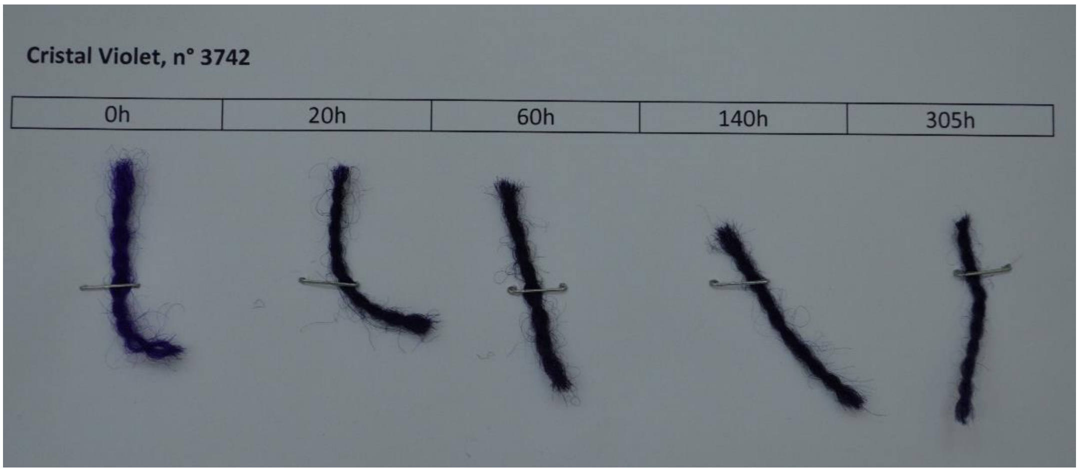


Fig. 27 Artificially aged samples dyed with Basic Violet 3.

The FTIR analysis of the extracted dyes from wool fibers allow the characterization of the characteristic bands of the peaks of Basic Violet 3. The analysis of the dyes showed an increasing with the ageing time, of the band around 1650 cm^{-1}, which can be related with both the ageing of the dye by photooxidation and by the contribution of aged wool.

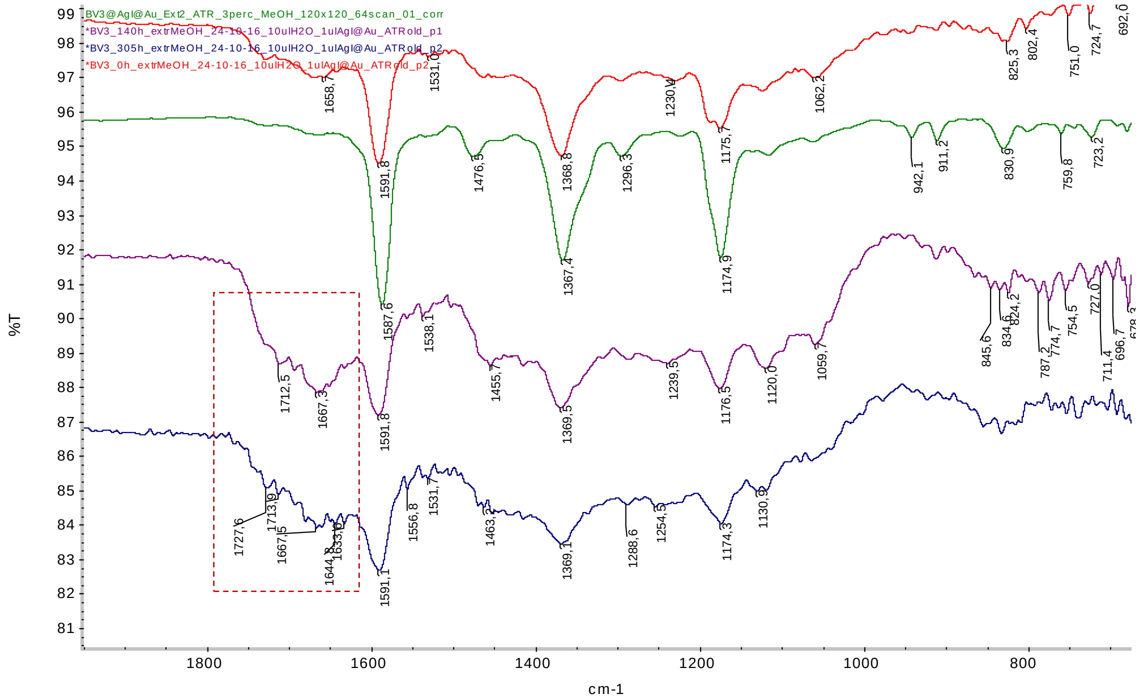
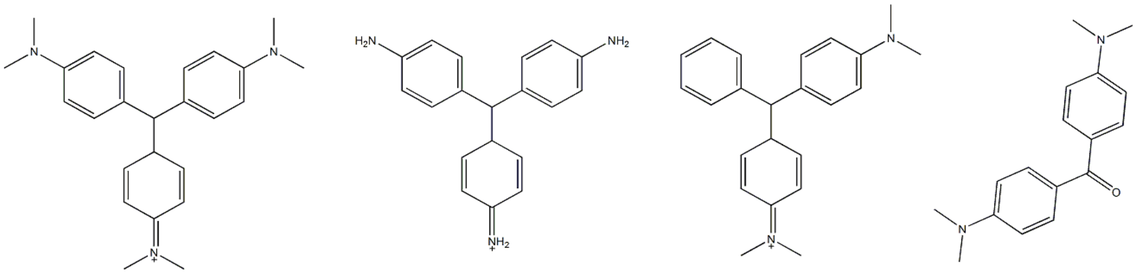


Fig. 28 Spectra obtain from the FTIR analysis of the different ageing times. Red line: 0h, green line: 60h, purple line: 140h and blue line: 305h. The red dashed line indicates the 1712-1721cm^{-1} band that might be related to the ageing of BV3.

Moreover, some peaks appear close to 1712-1727cm^{-1} which can be related to the presence of C=O group. This can be related to what have been mentioned before about the BV3 degradation. The loss of methyl groups are the first step of degradation however with the time the formation of Micheler's ketone (Confortin, Brustolon, Franco, Neevel, & van Bommel, 2010) is one of the degradation products identified in the advance degrade dye samples. The loss of intensity in the peaks related to the benzene rings in the area of 900-800cm^{-1} can be also related to the loss of them and the formation of the ketone. As in other cases, it is necessary to compare this data with other techniques in order to confirm this hypothesis.



A **B** **C** **D**

Fig. 29 A: Crystal Violet, B: p-rosalniline, C: diamond Green (basic green 4), D: Michler's ketone. (Confortin, Brustolon, Franco, Neevel, & van Bommel, 2010)

c) Brilliant Green 1 (BG1)

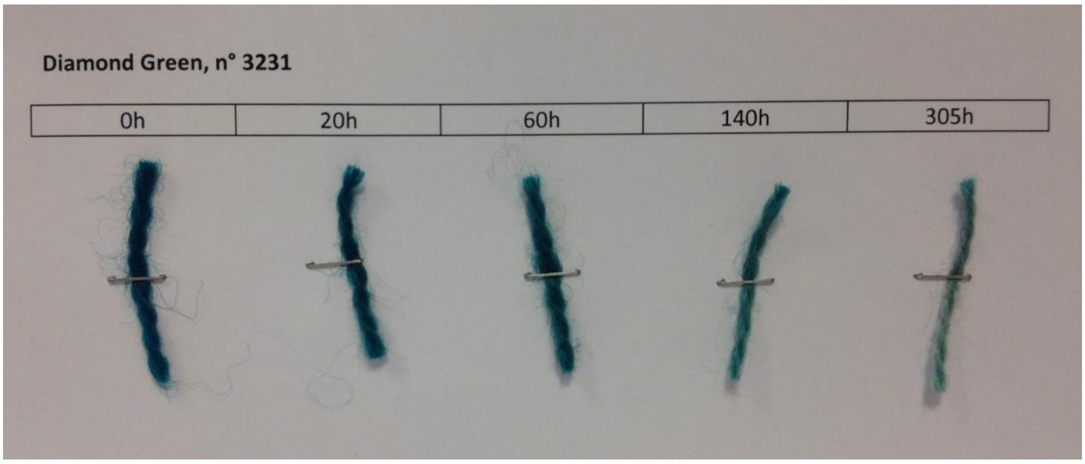


Fig. 31 Wool samples dyed with BG1 and aged artificially

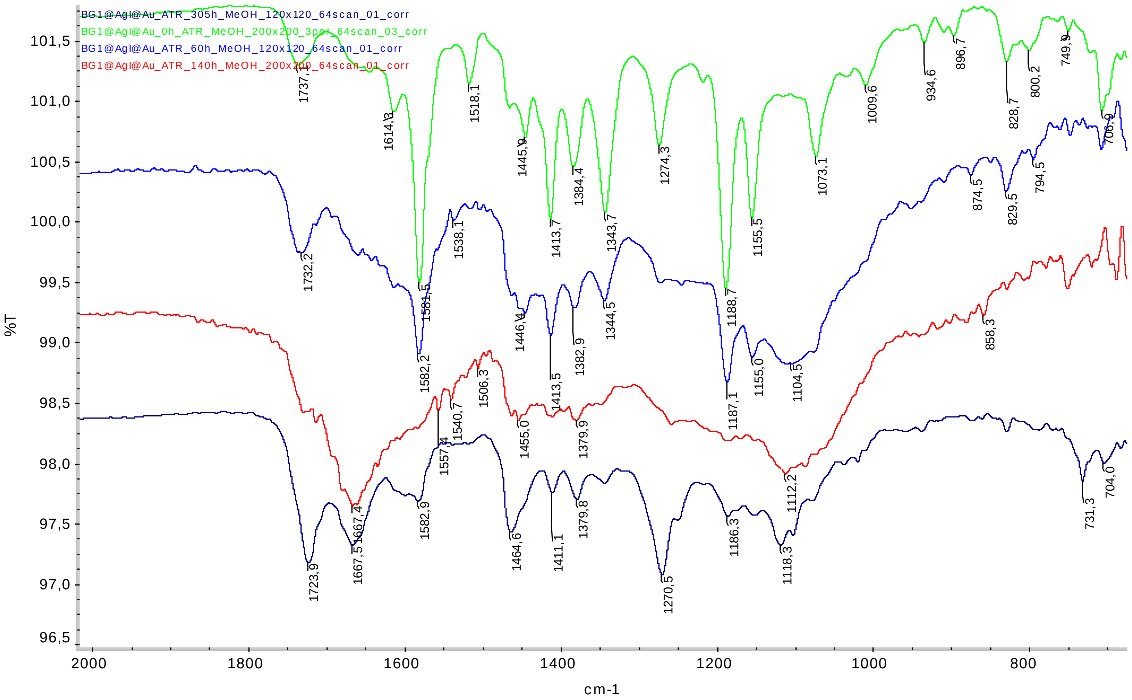


Fig. 30 Spectra obtained from BG1 samples. Pink line: 0h, purple line: 60h, red line: 140h, yellow line: 305h

The analysis of the different samples show the characteristic peaks of BG1. The sample at 140h seem to have problems since it is complicate to identify clearly the signals of the colorant. Is interesting to notice that according to the colorimetric measurements at 140h is when is registered a clear modification in the color, making broader the graph. It could be related to the chemical change of the molecule, however more analysis are required to confirm this hypothesis.

The different samples allow identifying some peaks that can be consider as indicators of the degradation of the dye. Two peaks appear after 60h and continue to be present at 140h and 305h but are more evident in the last one. They are 1120cm^{-1} and 1106cm^{-1}. By comparing the spectra with the wool spectrum at 305h, it is clear that these signals are not a contribution of the fiber since they are not present in the extraction of the wool degraded for the same exposition time.

Secondly, the decreasing in intensity indicates a modification in the benzene ring since it correspond to the =C-H in –plane deformation vibration of 1,4 disubstituite benzene. The two bands identified can be related probably with a change in the position of the substitutions in the benzene ring, to 1:3 or 1:2.

A peak at 1247cm^{-1} appears slightly at 60h but it becomes more clear as a shoulder of the band at 1272cm^{-1}, which is one of the characteristics bands of BG1 and appears in all the samples. That signal can be related with the vibration of C-O close to a NH_3^+. It can be related with the loss of ethyl groups attached to the N atom in two of the three benzene rings, and probably the addition of oxygen atoms due to a photooxidation of the molecule.

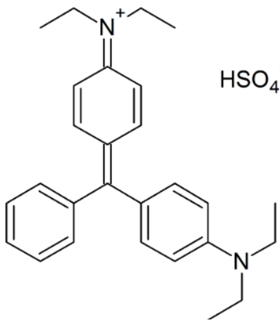


Fig. 32 BG1 molecular structure

A mechanism similar to the one mentioned before is reported by Kaur, *et al*. (2017) that have pointed in a influence of solar light in the oxidation of the molecule and the further formation of cation radicals that in combination with other groups –for instance OH coming from water molecules in the air- produce degradation products of the BG1. It has been identify that this mechanism can be catalyzed by metals and pH.

Moreover, the photooxidation of BG1 has been already study for industrial processes were the degradation of the dye is desirable since it is banned in many countries due to its toxicity (Saleh AL-Saade, Al- Saidi, & Juad, 2016).

A second hypothesis for these changes is the formation of a polyene with the Ag atom of the system since the bands at 1409cm^{-1}, which is present in all the samples, 1247cm^{-1} and 1008cm^{-1} that decrease with the ageing almost disappearing in at 305h, correspond to CH_2 deformation, CH rocking and CH out-of-plane vibration of polyenes (Socrates, 2001, p. 76).

Furthermore, the peak at 1517cm^{-1} disappears at 60h. This signal is related with -C=C- ring C=C stretching vibrations, which could indicate a possible breaking in one of the three rings that the molecule possess.

Metal ions, for instance Fe, Ti and Bi, have been used, in combination with UV and visible light, as catalyst for the degradation of BG1, this has to be consider when doing the analysis and planning experiments since the time that the molecule is in contact with the AgI@Au system can accelerated its degradation (Umabala, Suresh, & Prasada Rao, 2016). It is not recommended to store for a long time the sample after deposited over AgIAu system but analyzed immediately to avoid degradation.

According to Elsousy (2012), BG1 is the dye with the third faster rate of degradation by catalytic oxidation, between all the dyes that he has tested, indicating a quick reaction of this dye in presence of metal ions. As said before, these hypotheses are simple approximations to the possible chemical changes to the BG1 molecule. In order to understand better the chemical modifications of this molecule more analysis are required.

Indigoid dye

a) Acid Blue 74 (AB74)

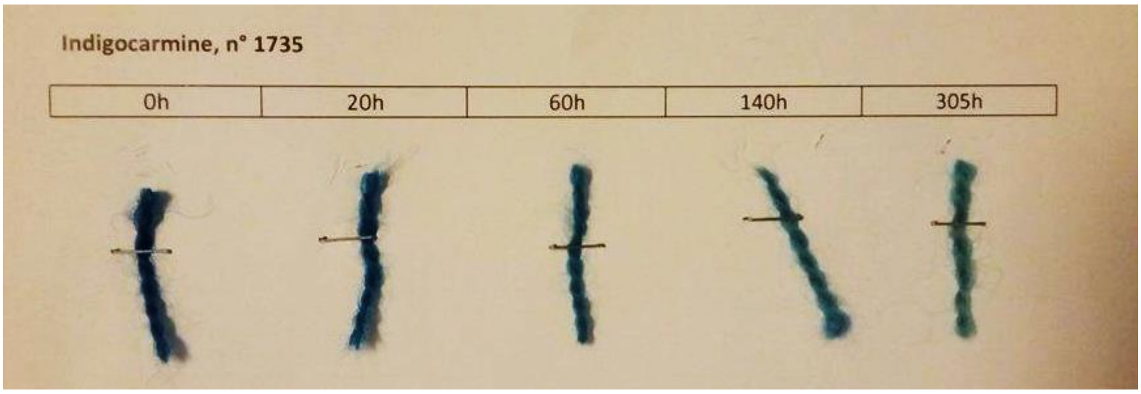


Fig. 33 Fibers artificially aged dyed with AB74

A small sample of the fiber dyed with AB74 was analyzed using µ-FTIR. The results does not correspond exactly with the spectrum of the standard sample however it has the principal bands of the dye. This suggest that the molecule is modified due to both the dyeing process and degradation even before artificial ageing.

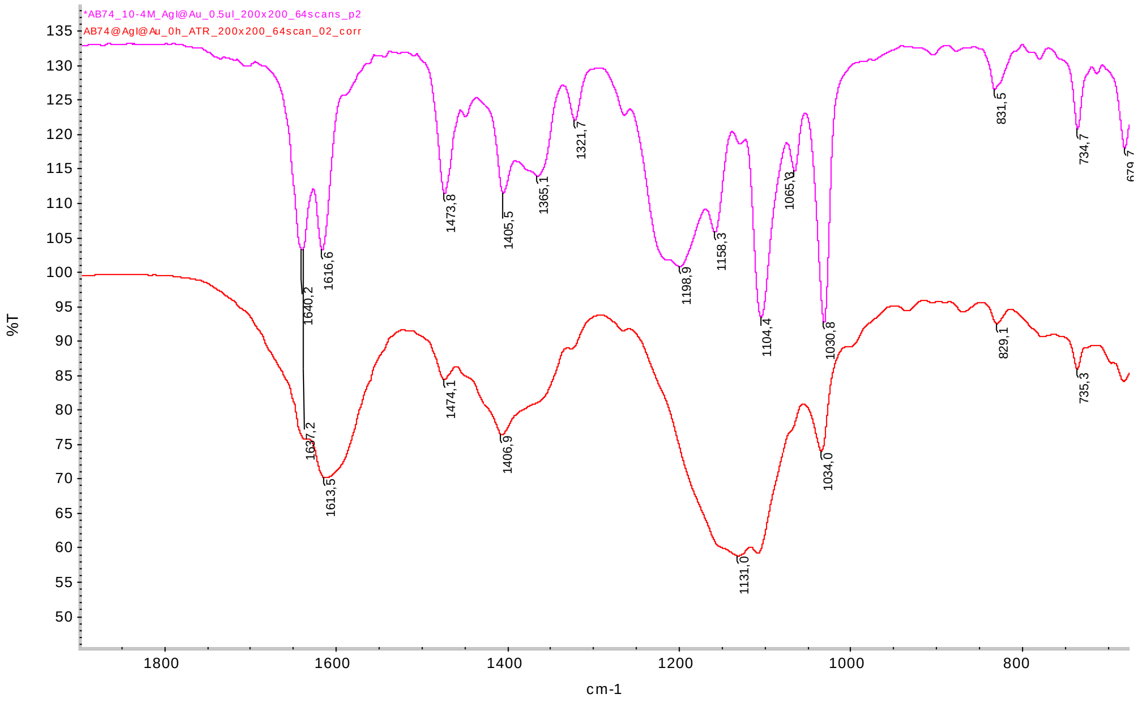


Fig. 34 AB74 standard spectrum (pink line) and AB74 sample at 0h (red line)

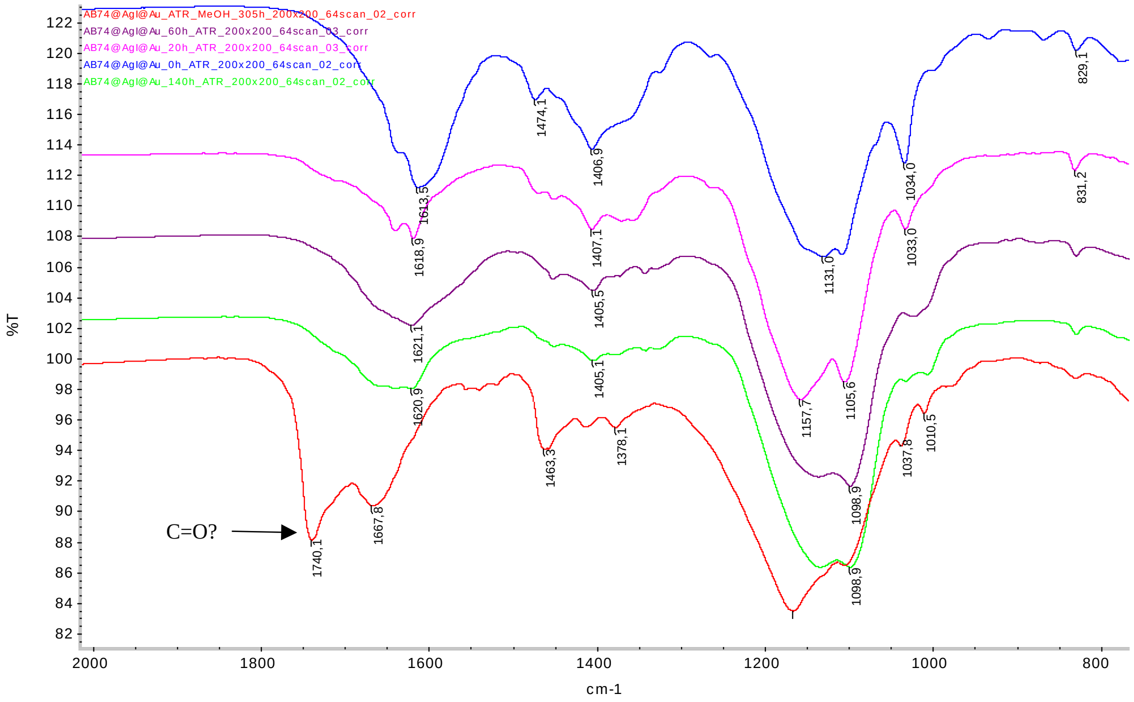


Fig. 35 Comparison of AB74 artificially aged AB74 samples. 0h (purple line), 20h (red line), 60h (blue line), 140h (yellow line) and 305h (green line).

It was noticed that the extraction of AB74 from the fiber is not completely efficient using only methanol, a trial with an acid solution was tested; however, the small amount of sample was dissolved in the solution so this method was abandoned and the extraction with only with methanol was used. More tests should be done in further researches in order to improve the extraction of AB74.

Comparing the different aged samples it can be noted that the strong band present in the 1130cm^{-1} and 1033cm^{-1} region are related to the sulphonic ions, characteristic from the AB74 molecule, this are present in all the spectra with slight shifting. The biggest change is present in the 1600cm^{-1} region in the sample artificially aged for 305h.

The degradation of AB 74 is similar to other previously reported, where light and OH radicals present induce the oxidation of the molecule. According to Galindo, Jacques, and Kalt (2001) the first product of the degradations is isatinsulfonic acid that is a modification to the rings, this is followed by the break of C=C bond, mainly in presence of OH radicals. Then the substitution of sulfonated groups by OH can also occur, in the samples studied in this experiment, the sulfonated groups still present even at 305h.

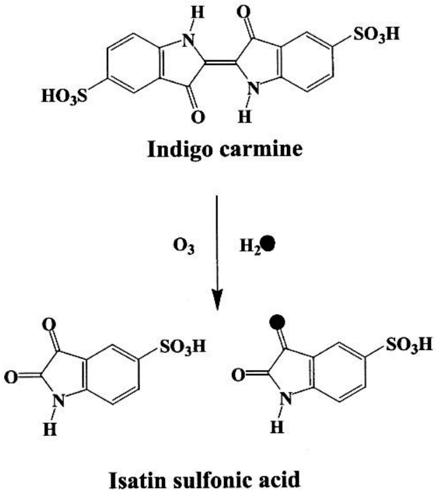


Fig. 36 Taken from (Kettle, Clark, & Winterbourn, 2004)

They have also identify a change in color, first to a yellow hue and furthermore when the benzene rings disappear due to degradation it loss completely the color (Galindo, Jacques, & Kalt, 2001, p. 53). It is clear that the samples analyzed in the present research have not reached this levels since they still have blue color, however is possible to identify a change in the fiber aged for 305h.

Nitro dyes

Acid Yellow 24

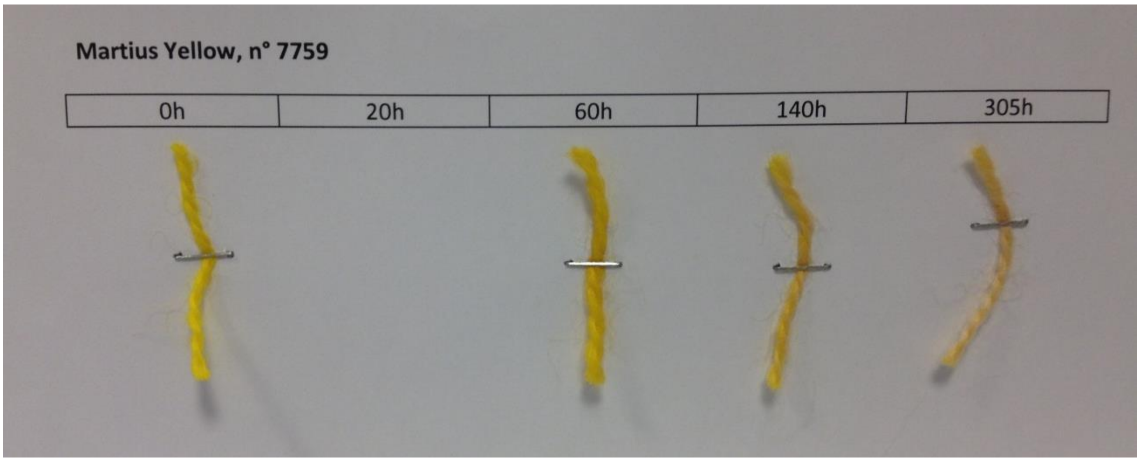


Fig. 37 Fiber dyed with AY24 samples

It is possible to identify the characteristic peaks of AY24. The analysis of the samples artificially aged shows big differences between the spectra, but stills possible to identify the peaks of the colorant.

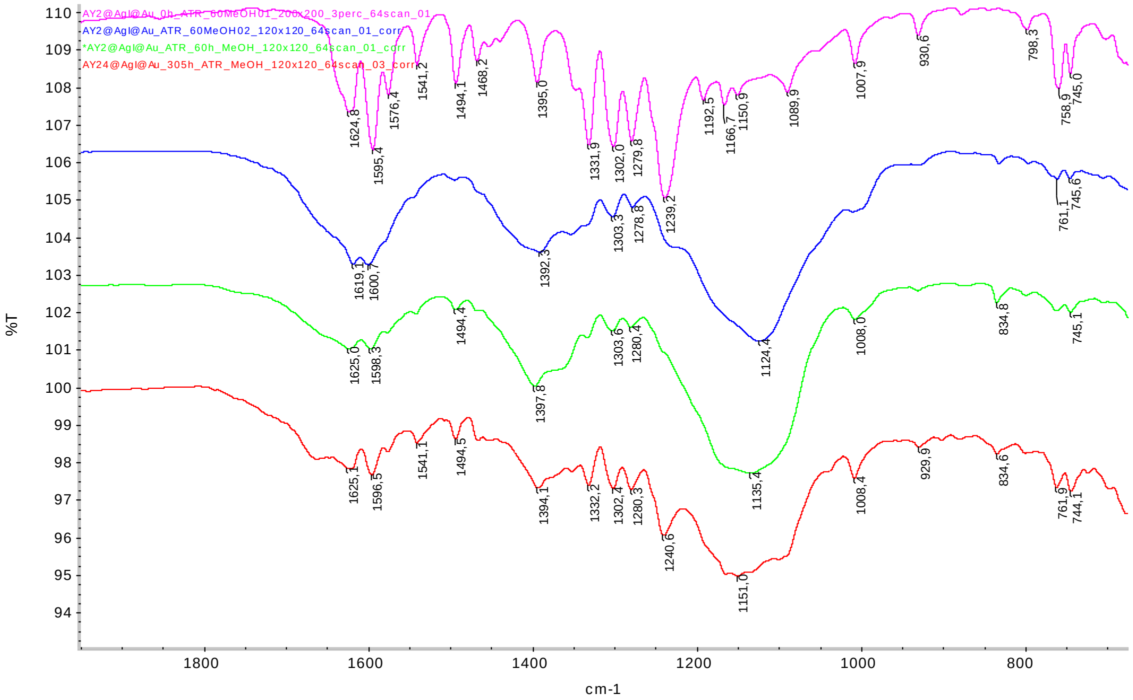


Fig. 38 FTIR spectra of AY24 samples. Pink line: 0h, blue line: 60h, green line: 140h, red line: 305h

The main change is the presence of a broad band at1135cm^{-1} after 60h, which with the time will show partially other principal peaks characteristic of the sample. The band is slightly shifted to 1120cm^{-1} at 140h. These signals can be related to the trisubstitution of the benzene ring.

4.5 Validation on real samples coming from pattern book

The sample obtained from the book *Tabellarische Uebersicht über die künstlichen organischen Farbstoffe* from 1893. Two different colors were analyzed, one violet and one green. The fibers were identified using optical microscope. They are animal hair, wool specifically; this is indicated due to the epithelial cells in the surface that are evident under the optical microscope. According to the diameter of the fibers, it can be consider as a medium wool fiber (EYTEST LIMITED, 1993).

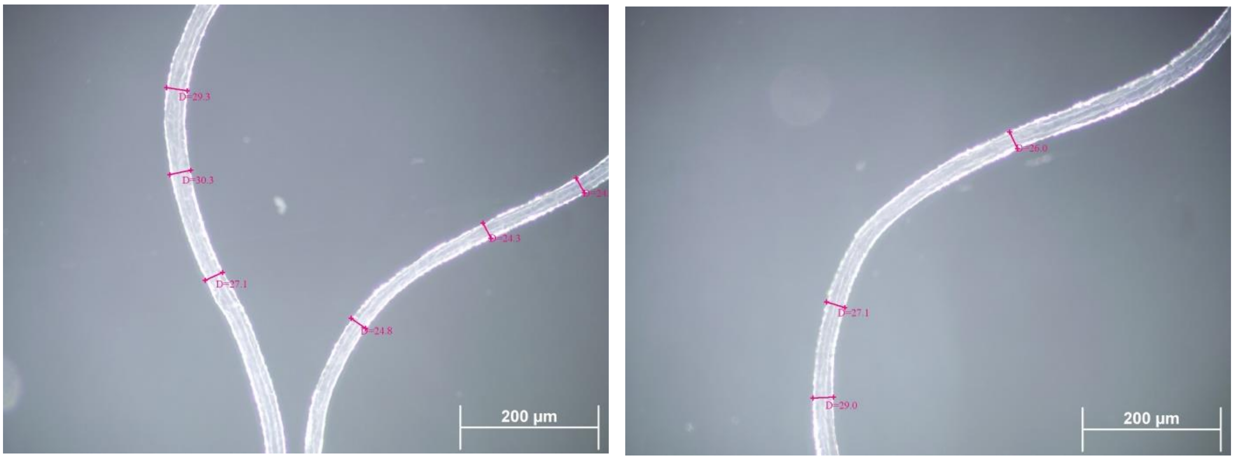


Fig. 39 Wool fibers from artificially aged samples. It is possible to see the epithelial cell in the surface of the fiber. 20x, visible light.

Violet (Basic Violet 3)

According to the book, the violet one was dyed using BV3. The analysis of it have shown the characteristic peaks of the colorant, and by comparing the spectrum with the standard, is possible to confirm the used of BV3 to give color to it.

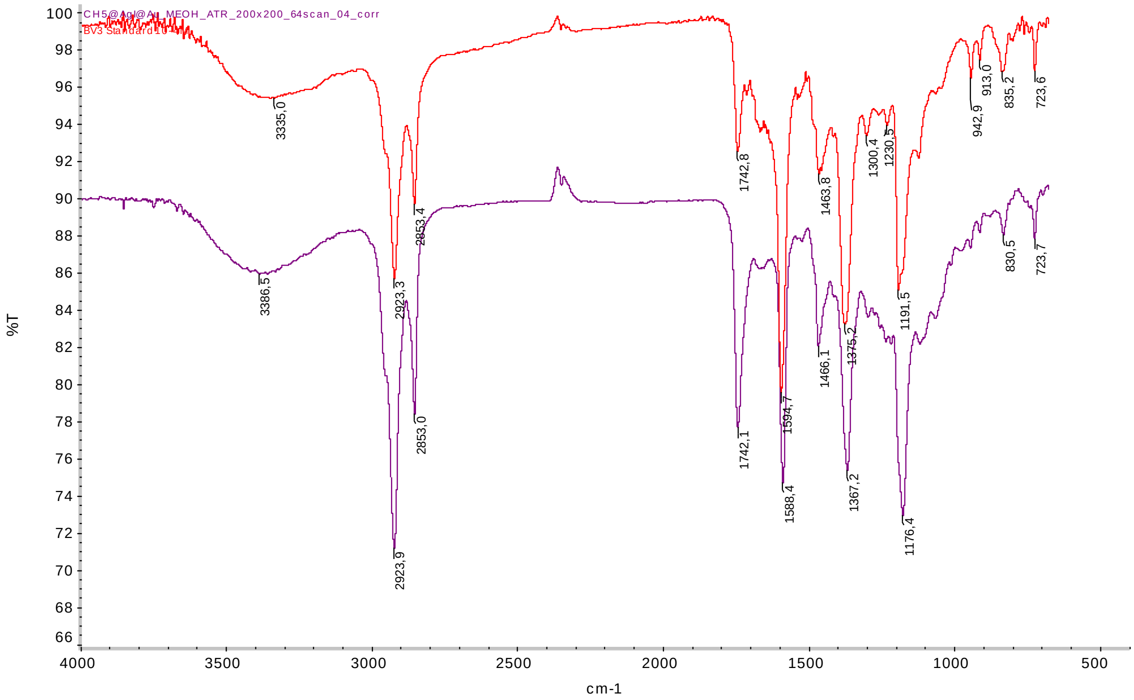


Fig. 40 Spectra comparison of real sample (purple line) and BV3 standard solution at 10^{-4}*M (Red line).*

Green (Basic Green 1)

In the pattern book is mentioned that the green sample was dyed with BG1. The FTIR spectrum obtained after the analysis of the sample indicates the presence of BG1 however it seems to be degraded since the signals are poor. By comparing with the data obtained from the artificially aged samples, the spectrum is similar to the one obtained from the BG1 at 60h of artificial aging.

This data suggest that the green colorant is less resistant that the violet one since the spectrum presents more modifications and is evident to see the chemical changes in the results meanwhile the spectrum of violet sample remains almost similar to the standard one. This must be taken into consideration when planning conservation strategies for textiles dyed with BG1. Moreover is need to continue with the study of the degradation mechanism of BG1 molecule.

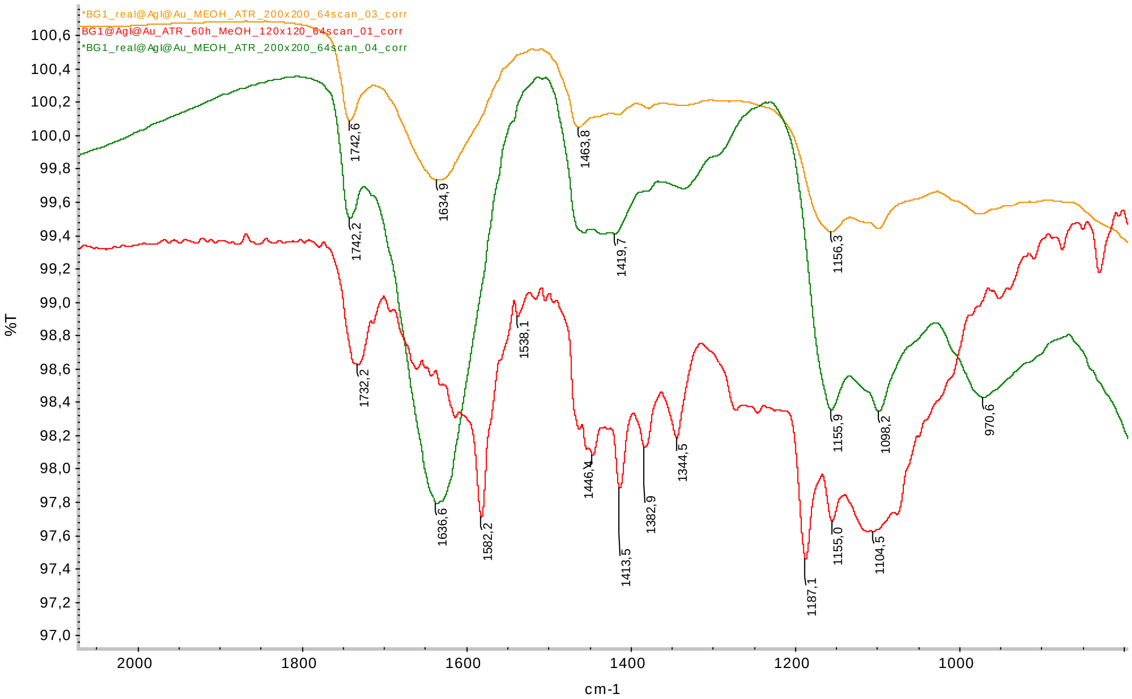


Fig. 41 Comparison between the spectra from the real sample (green and yellow lines) and the BG1 at 60h of artificial aging (red line).

4.6 Analyses of inks

Since many of the synthetic dyes are also used for the preparation of inks, the present research studied three felt-tip pens that contain some of the dyes previously analyzed. Unlike the samples coming from textile fibers, the inks are a mixture of two or more dyes, in order to obtain specific color hues. In this sense, the separation of the different components is required and those in for the study of the inks the separation with TLC was performed.

Fig. 42 Color of felt-tip pens analyzed.

All the information was compared with the data obtained by Valeria D'Ambrosio (2017) who has conducted her Bachelor’s thesis experimentation analyzing the same felt-tip pens, using different chromatografic and spectroscopic tecniques.

Set-up of the analytical procedure

The extraction of the ink from the felt-tip pens was done by putting the tip into 10μl of water type 2 for 10 seconds; the solution then was diluted by ten in order to avoid the saturation of the system by the high amount of sample.

The analysis of the inks was done by separating the components by TLC using AgI@Au supports. Two different eluents were tested as mobile phase, a mixture of EtOH:NH_3(33%) 9:1 v/v and a mixture of Isopropanol:EtOH:NH_3(33%) 5:2:3 v/v/v, the second one was the one that offered the best results. The last one is similar to the eluent used by D'Ambrosio (2017) with the difference of the use of butanol instead of isopropanol.

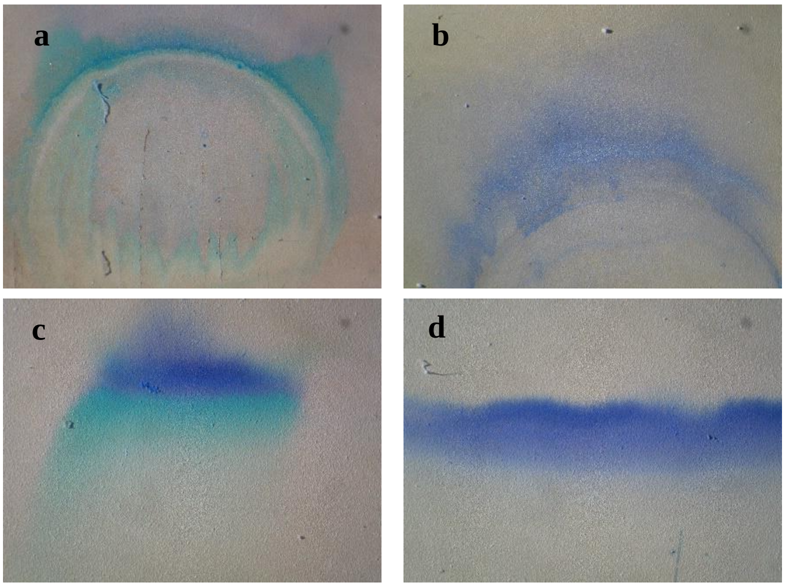


Fig. 43 Comparison between TLC results. a) Stabilo® 68/22 over a thinner deposition, b) Stabilo® 68/55 over a thinner deposition, c) Stabilo® 68/22 over a thicker deposition, d) Stabilo® 68/55 over a thicker deposition

The comparison between both eluents have shown that the one containing isopropanol act better for the separation. It was noticed, as it can be expected, that the size particle modify the TLC results, while a thinner deposition with smaller particle size will produce a bad separation, bigger particles and a thicker deposition will produce better separation of the components. Since the AgI synthesis is not completely reproducible, this is one of the main drawback for the elaboration of TLC.

Felt-tip pen analyses

Stabilo® 68/22

After the TLC separation the ink of the 68/22 pens showed two different components, one blue (R_f: 0.33) and other violet (R_f: 0.43). Comparing the results with the ones obtained by D'Ambrosio, is possible to see that the ink is also constitute by a yellow element which is not visible in the AgI@Au TLC analysis. In order to try to identify the yellow are a multispectral image analysis was perform to the TLC plate, however it was no possible to identify the yellow area.

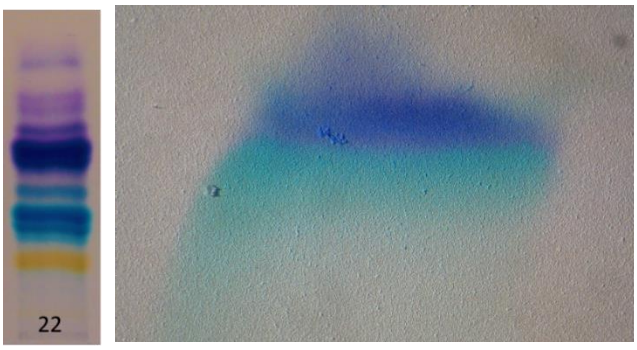


Fig. 44 TLC results of 68/22 Stabilo® ink. At left is shown the results obtained by D'Ambrosio, at right are the results using AgI@Au plates, 2.5x.

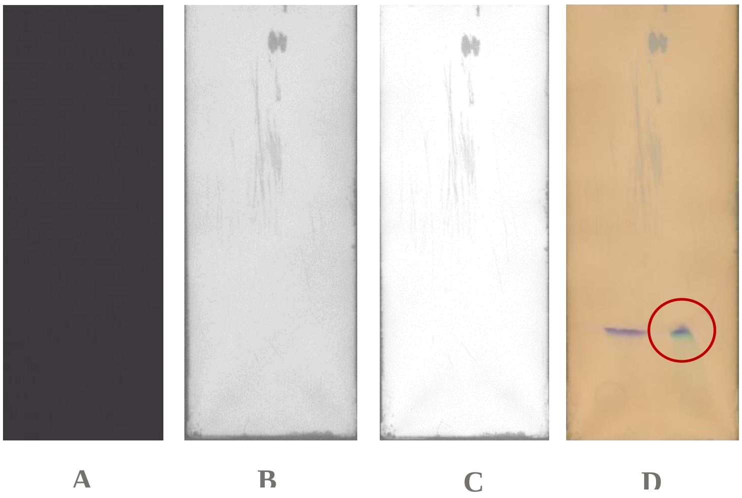


Fig. 45 Multispectral image of TLC AgI@Au plate of 68/22 ink. A: UV fluorescence, B:IR 1, C: IR 2, D: Visible light

The FTIR analysis of the blue part allow the identification of Acid Blue 9. Meanwhile Basic Violet 3 (Crystal Violet) composes the violet area. The identification of both dyes was compared with standard samples.

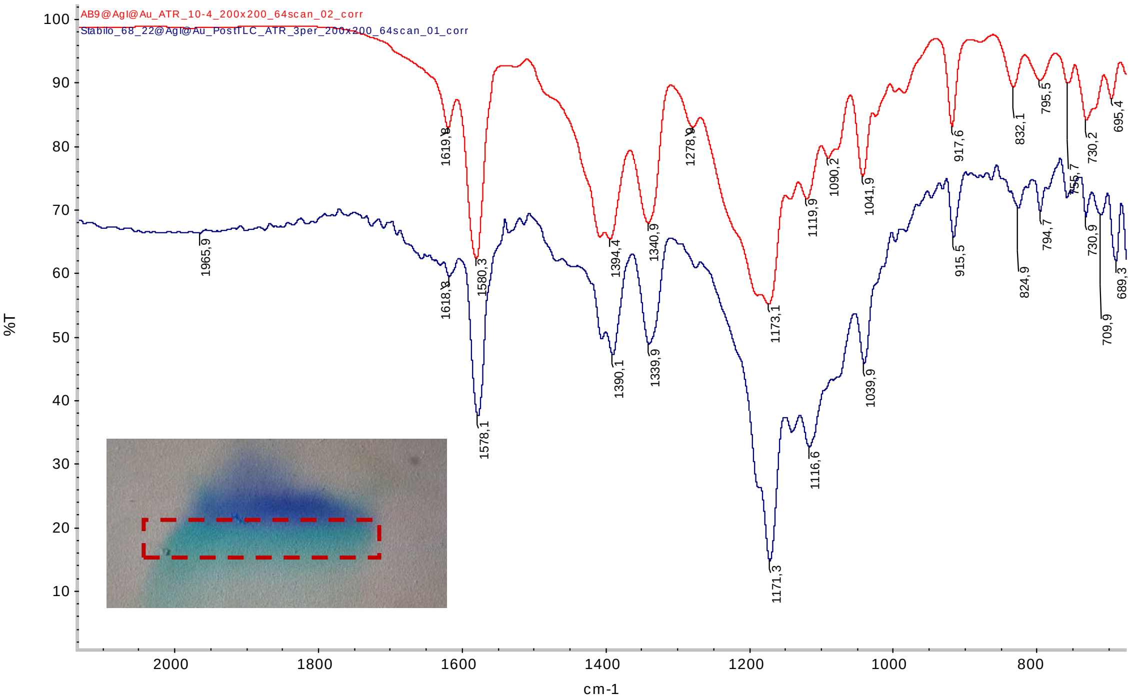


Fig. 46 FTIR Spectra obtained from the blue area. Red line: Standard AB9 10^{-4}M. Blue line: Blue area from Stabilo® 68/22 TLC

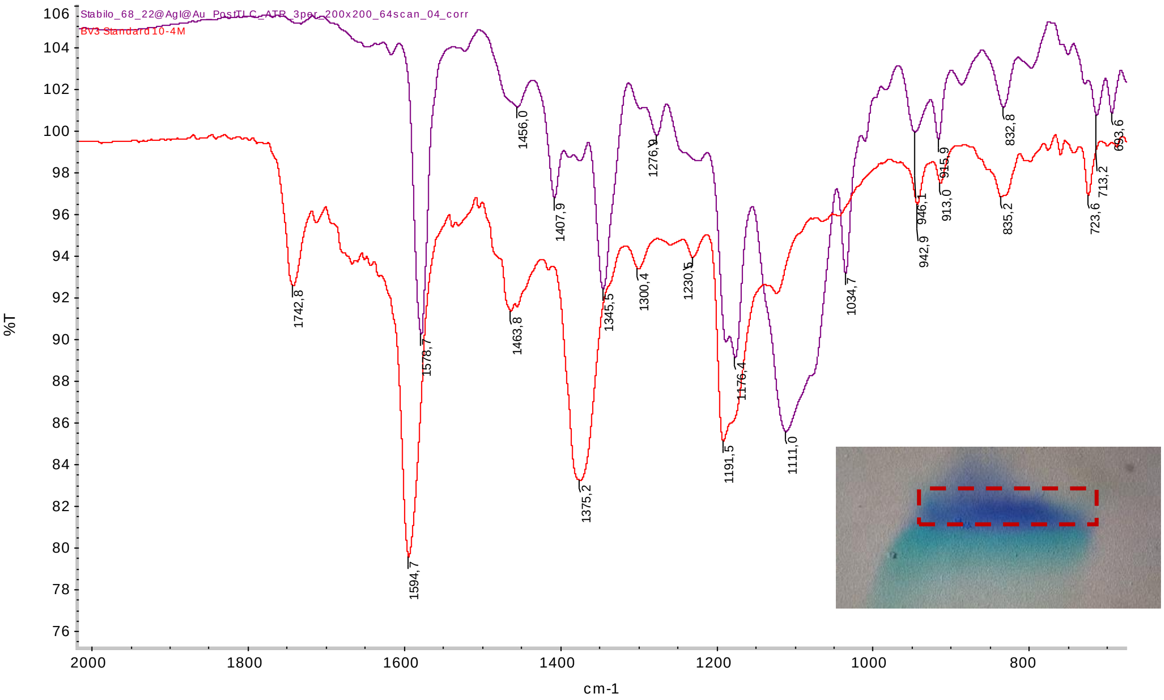


Fig. 47 FTIR Spectra obtained from the violet area. Red line: Standard BV3 10^{-4}M. Blue line: Violet area from Stabilo® 68/22 TLC

The SERS analysis of the same areas confirmed the results. The blue area is composed by AB9 meanwhile the violet area is constitute by BV3.

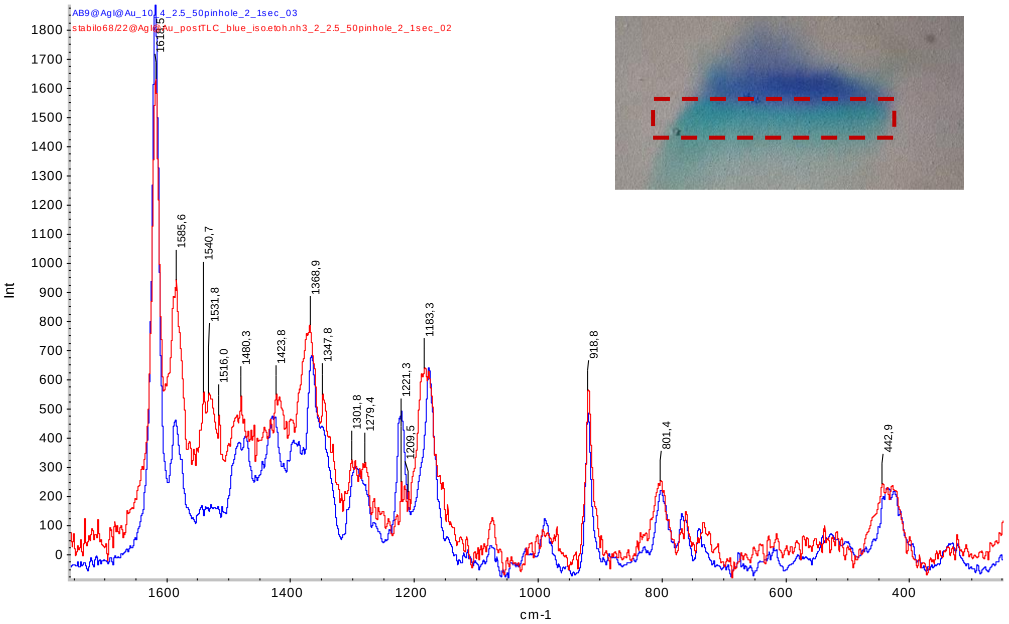


Fig. 48 SERS results of Stabilo® 68/22 ink analysis. Red lien: Blue area of TLC plate. Blue line: AB9 Standard 10^{-3}M.

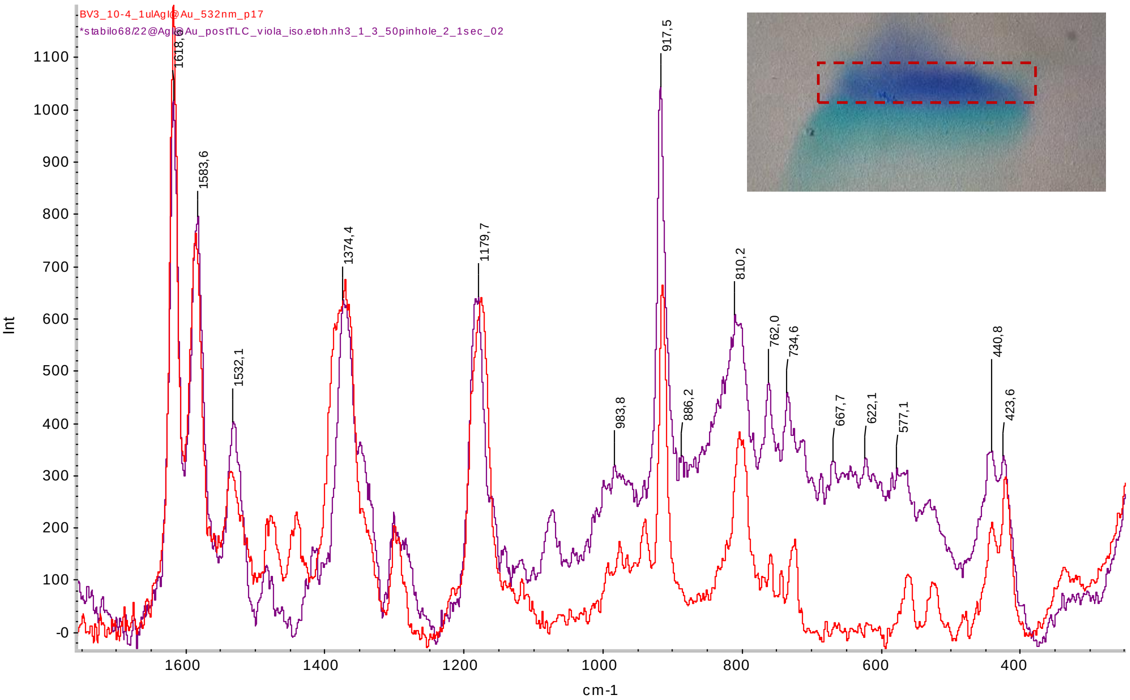


Fig. 49 SERS spectrum from the violet area. Red line: BV3 Standard 10-^{3} M. Violet line: Violet area of Stabilo® 68/22

Stabilo® 68/41

The results of the TLC show two components in this pen, one purple (R_f: 0.66) and other blue (R_f: 0.81). The same two components were identified with Si plate TLC, the main difference between the two techniques is the order of the components since they are inverted.

Fig. 50 TLC results of Stabilo® 68/41 analysis. At the left, the results obtained by D'Ambrosio using Si plates, at right the results obtained with the AgI@Au system.

The FTIR analysis allowed the identification of AB9 for the blue part, the same result is reported by D'Ambrosio (2017), the identification of the dye was done using Raman and Py-GC-MS, however, by using FTIR she was not able to identify AB9 specifically but only poly ethylene glycol and peaks characteristics of triarylmethanes but not of the specific colorant.

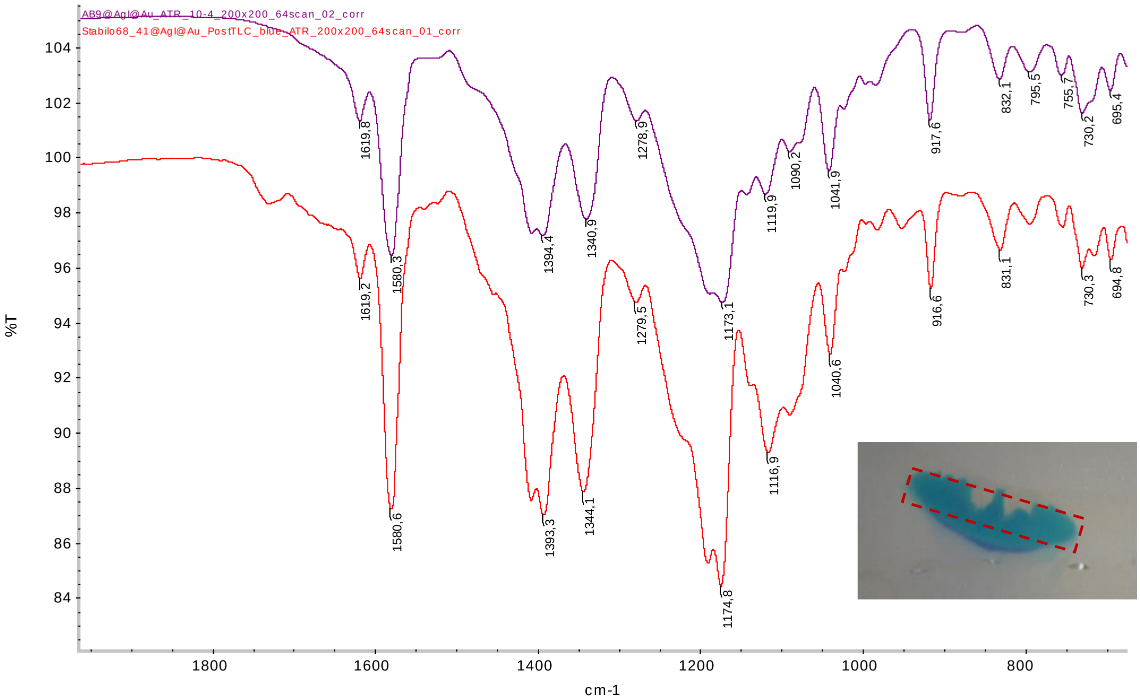


Fig. 51 FTIR Spectra obtained from the blue area. Purple line: Standard AB9 10^{-4}M. Red line: Blue area from Stabilo® 68/41 TLC

On the other hand, the SERS analysis of the blue area confirmed the presence of AB9 as one of the components of Stabilo® 68/41.

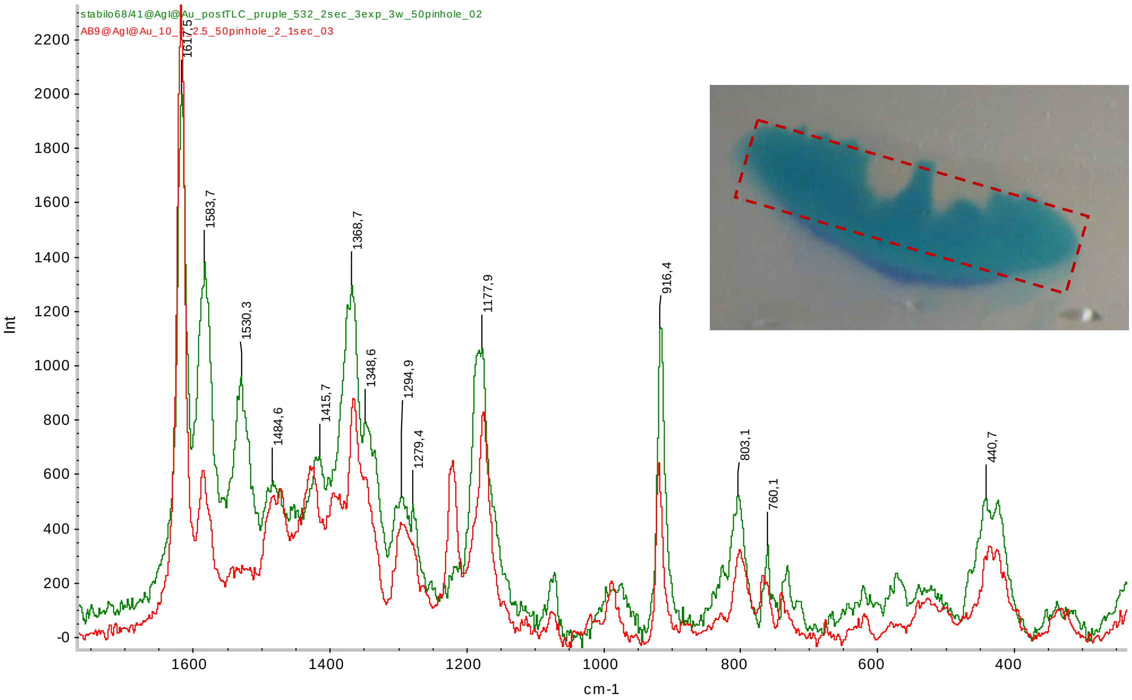


Fig. 52 SERS spectra of AB9 standard (red line) and blue area of Stabilo® 68/41 TLC over AgI@Au (green line)

In the case of the purple area, the FTIR analysis showed the presence of Basic Violet 4, since no standard solution was available for the present research a comparison with a spectrum reported by SBDS (National Institute of Advanced Industrial Science and Technology, 2017) database was used for the comparison with the data obtained from Stabilo® 68/41.

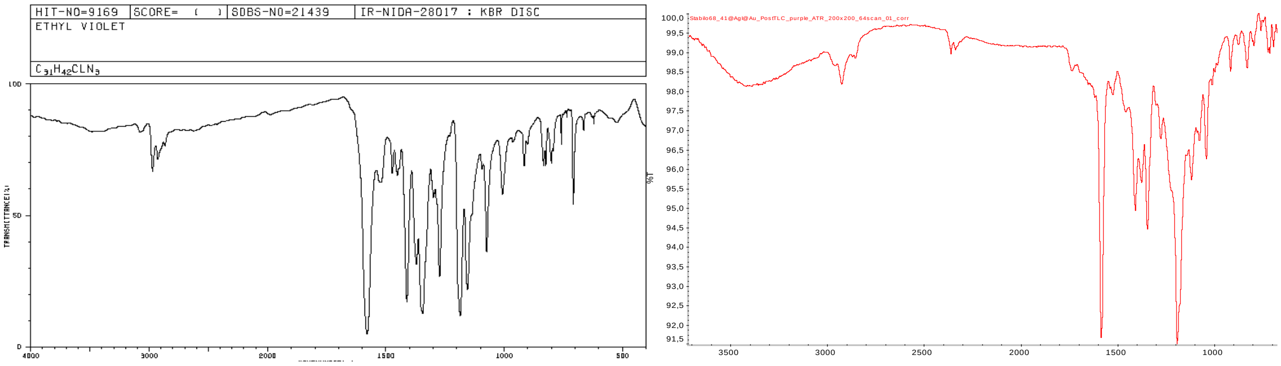


Fig. 53 Spectrum reported in SBDS (National Institute of Advanced Industrial Science and Technology, 2017) at left and spectra obtained fromStabilo® 68/41

Table 22 Comparison between peaks in SBDS spectrum and Stabilo® 68/41 spectrum obtained with AgI@Au system

Standard of BV4 reported by SDBS	ATR Post TLC 68/41	Assignation
1579 cm^{-1}	1584 cm^{-1}	Not assigned
1524 cm^{-1}	1524 cm^{-1}	Not assigned
1474 cm^{-1}	-	In-plane deformation of C=C of aromatic ring / C-H deformation of -CH_2-
1412 cm^{-1}	1408 cm^{-1}	CH_2 bending vibrations
1371 cm^{-1}	1376 cm^{-1}	C-H symetric deformation of C-CH_3 / C-N stretching of tertiary aromatic amine
1345 cm^{-1}	1345 cm^{-1}	CH_2 bending
1300 cm^{-1}	-	C-H in-plane deformation 1:4 disubstitution
1274 cm^{-1}	1276 cm^{-1}	CH_2 out-of-plane bending
1186 cm^{-1}	1191 cm^{-1}	C-H in-plane deformation 1:4 disubstitution
1156 cm^{-1}	1178 cm^{-1}	Skeletal vibrations (C-H) bending
1093 cm^{-1}	-	Not assigned
1074 cm^{-1}	1077 cm^{-1}	C-H deformation bending
915 cm^{-1}	915 cm^{-1}	Symetric streetching of Ar-N$(CH_3)_2$
825 cm^{-1}	830 cm^{-1}	C-H out-of-plane deformation 1:4 disubstitution
793 cm^{-1}	795 cm^{-1}	C-H out-of-plane bending ring

D'Ambrosio (2017) when studying the same felt-tip pen using Raman and Py-GC-MS identified the same colorant. The SERS analysis showed the presence of Basic Violet 4, since no standard solution was available; the comparison of the spectrum was done based on the signals reported by Persaud and Grossman[1] (1993, p. 110).

Table 23 Comparison of bands reported by Persaud and Grossman for BV4 and the peaks found in the Stabilo® 98/41 felt-tip pen ink analysis

Standard of BV4 reported by Persaud and Grossman (1993), p.110	SERS Post TLC 68/41, purple area	Assignation (Persaud & Grossman, 1993)
1621 cm^{-1}	1617 cm^{-1}	Ring C-C stretching
1584 cm^{-1}	1583 cm^{-1}	Ring C-C stretching
1535 cm^{-1}	1529 cm^{-1}	Ring C-C stretching
1492 cm^{-1}	1482 cm^{-1}	Ring C-C stretching + ring deformation
1423 cm^{-1}	1418 cm^{-1}	N-Ph stretching + ring vibration
1371 cm^{-1}	1369 cm^{-1}	N-Ph stretching
1284/1302 cm^{-1}	1300 cm^{-1}	Ring C-C stretching
1162/1188 cm^{-1}	1179 cm^{-1}	In-plane ring C-H bend
1076 cm^{-1}	1072 cm^{-1}	In-plane C-H deformation of CH_2 CH_3 group

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[1] We kindly want to thank Dr. Giulia Germinario from University of Bari for the contribution of this reference.

979/992/1009 cm^{-1}	982 cm^{-1}	In-plane ring C-H bend
905/ 917 cm^{-1}	916 cm^{-1}	Ring skeletal vibration of radial orientation
804/828 cm^{-1}	802 cm^{-1}	Out-of-plane (C-H) bend
759 cm^{-1}	760 cm^{-1}	Out-of-plane (C-H) bend
737/747 cm^{-1}	732 cm^{-1}	Out-of-plane (C-H) bend
663 cm^{-1}	667 cm^{-1}	Out-of-plane (C-H) bend

Stabilo 68/55

The TLC of this pen has shown only one purple component (R_f:0.36). The TLC made with Si plate shows the presence of two components, however, the identification of a second component is not clear.

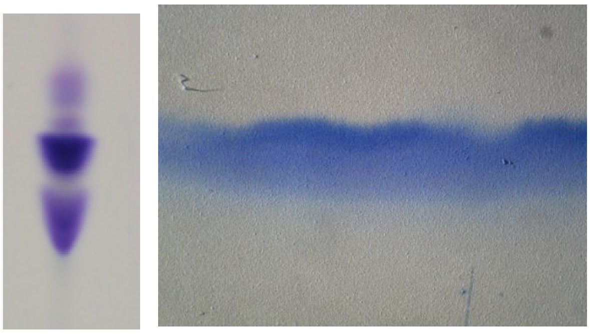

Fig. 54 Comparison between Si TLC results (left) and AgI@Au TLC results (right)

The FTIR analysis allowed identifying Basic Violet 4 (BV4), also called Ethyl violet, by comparing the spectra with a standard reported by the SBDS database. As in the previous cases, D’Ambrosio (2017) using Raman and Py-GC-MS identified the same dye. In addition, they also proposed the possible combination with Acid Violet 49, however, that result was not confirmed. By comparing the peaks reported in the spectra obtained from SBDS (National Institute of Advanced Industrial Science and Technology, 2017) it is not clear if the purple area of Stabilo® 68/55 contains both dyes, since it possess signals of both colorants (see Table 25). As in the information reported by D’Ambrosio, it our case it is not clear if there is a combination of both dyes or just due to the similar composition the spectra can be confusing.

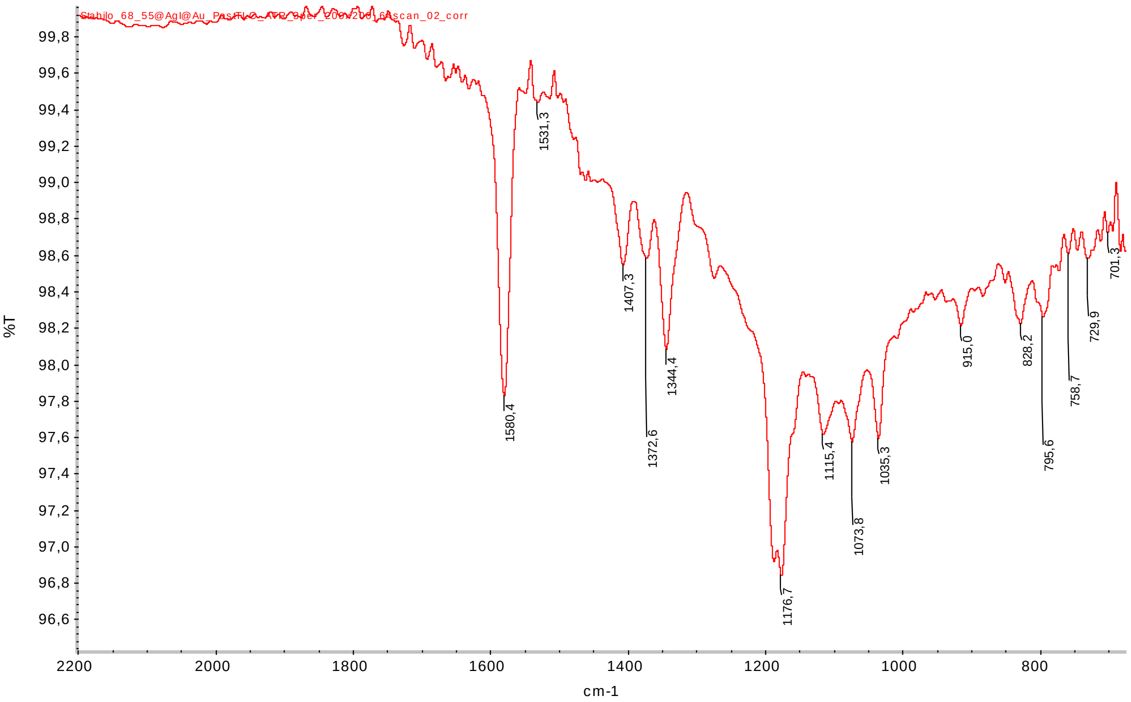

Fig. 55 Spectrum obtained from the FTIR analysis of Stabilo® 68/55 over AgI@Au TLC

Table 24 Band comparison of BV4 and AV49 dye spectra reported by SBDS and the result of the Stabilo® 68/55

Standard of BV4 reported by SDBS	ATR Post TLC 68/55	Standard of AV49 reported by SDBS
1579 cm^{-1}	**1579 cm^{-1}**	1585 cm^{-1}
1524 cm^{-1}	1533 cm^{-1}	1524 cm^{-1}
1412 cm^{-1}	**1405 cm^{-1}**	**1406 cm^{-1}**
1371 cm^{-1}	1373 cm^{-1}	1373 cm^{-1}
1345 cm^{-1}	1344 cm^{-1}	1346 cm^{-1}
1274 cm^{-1}	**1276 cm^{-1}**	1225 cm^{-1}
1186 cm^{-1}	1187 cm^{-1}	1187 cm^{-1}
1156 cm^{-1}	**1174 cm^{-1}**	**1176 cm^{-1}**
1093 cm^{-1}	**1114 cm^{-1}**	**1116 cm^{-1}**
1074 cm^{-1}	1074 cm^{-1}	1074 cm^{-1}
915 cm^{-1}	**914 cm^{-1}**	941 cm^{-1}
825 cm^{-1}	829 cm^{-1}	830 cm^{-1}
793 cm^{-1}	796 cm^{-1}	796 cm^{-1}

The SERS results allow confirming the presence of Basic Violet 4, since all the peaks match clearly with the information reported by Persaud and Grossman (1993) for it.

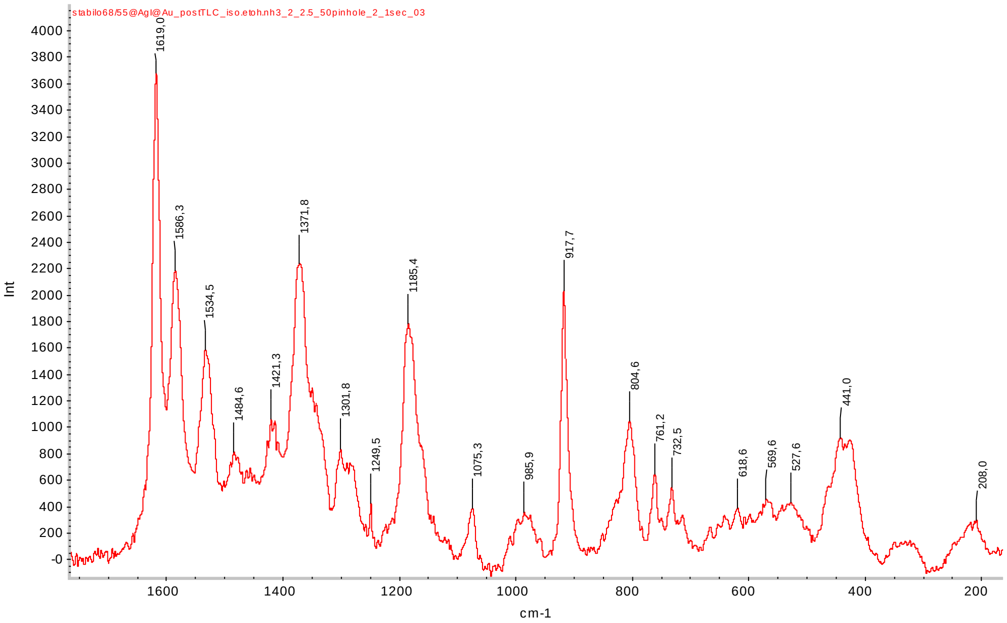

Fig. 56 SERS spectrum obtained from Stabilo® 68/55 analysis after TLC separation

Table 25 Comparison of bands found in Stabilo® 68/55 Raman spectrum and the ones reported by Persaud and Grossman.

BV4 Spectra reported by Persaud and Grossman (1993)	Sample Stabilo 68/55	Assignation (Persaud & Grossman, 1993)
1621 cm^{-1}	1622 cm^{-1}	Ring C-C stretching
1584 cm^{-1}	1587 cm^{-1}	Ring C-C stretching
1535 cm^{-1}	1533 cm^{-1}	Ring C-C stretching
1492 cm^{-1}	1482 cm^{-1}	Ring C-C stretching + ring deformation
1423 cm^{-1}	1422 cm^{-1}	N-Ph stretching + ring vibration
1371 cm^{-1}	1371 cm^{-1}	N-Ph stretching
1302 cm^{-1}	1301 cm^{-1}	Ring C-C stretching
1284 cm^{-1}	1284 cm^{-1}	Ring C-C stretching
1188 cm^{-1}	1182 cm^{-1}	In-plane ring C-H bend
1074 cm^{-1}	1076 cm^{-1}	In-plane C-H deformation of CH_2 CH_3 group
979 cm^{-1}	979 cm^{-1}	In-plane ring C-H bend
917 cm^{-1}	918 cm^{-1}	Ring skeletal vibration of radial orientation
804 cm^{-1}	804 cm^{-1}	Out-of-plane (C-H) bend
759 cm^{-1}	762 cm^{-1}	Out-of-plane (C-H) bend
737 cm^{-1}	732 cm^{-1}	Out-of-plane (C-H) bend
442 cm^{-1}	442 cm^{-1}	Out-of-plane skeletal vibration + out-of-plane (C^+-Ph)

CONCLUDING REMARKS AND FUTURE PERSPECTIVES

The present research allowed evaluating the performance of AgI@Au system for the analysis of synthetic dyes employed in Cultural Heritage. After the experiment, it is clear that the method offers many advantages for the study of these materials, however, it also possesses some drawbacks.

The capacity to perform three analytical techniques using the same system diminishes the time and cost. It also reduces the manipulation of samples, reducing the interference factor due to human errors. It represents a viable solution for institutions that do not have complex chromatographic instruments.

The analysis of artificially aged samples have shown that even without the performance of TLC separation the AgI@Au system is able to separate part of the fiber interference – in this case wool- in terms of double coffee ring formation. Reducing the time and the requirements for the analysis of a single dye sample.

The technique allowed the characterization of dyes in real samples, as the two samples from a pattern book have shown. This displays the promising capacity of it in the field of conservation science. It also allows the identification of possible degradation or changes to the chemical structure of dyes, but due to the characteristic of FTIR and Raman techniques, it is necessary to make further investigation using different techniques in order to confirm the results.

The analysis of contemporary materials such as the felt-tip pens has shown very good results, allowing the identification of almost all the dyes. The results are similar to the analysis performed with techniques more complex, such as Py-GC-MS. This can have not only an application in the study of modern and contemporary artworks but also in the industrial and forensic fields.

The quantity of sample is highly reduced since the amount of fibers is low and with one deposition it can be performed both Raman and FTIR analysis. The sample pretreatment is reduced at only the extraction of dye. In this experimentation was only used water or methanol for a “soft” extraction, however, it was noticed some problems with the extraction of colorants such as Acid Blue 74, making necessary to try other extraction methods. This can represent a problem when analyzing real samples where mordant was used and the dye-mordant-fiber system would be more difficult to break.

It is important to take into consideration that the resulting spectra will not be as similar as the standard one since the molecule would be degraded and in some cases can be modified due to the linkage with fabrics, this should be taken into consideration during the data interpretation.

The main drawback of the method is the low reproducibility of AgI synthesis since the reaction is unstable and not complete control of factors such as temperature and homogeneity of the product is conducted constantly. Even if the measurements with SEM have been done in 2014, it is necessary to control the products of the reaction each time is performed due to the clear differences between each synthesis.

Another limitation of the method is the difficulty to identify the yellow dyes after TLC separation due to the color of the AgI. Even if different radiation were employed to try identifying the possible dyes, no good results were obtained.

The small amount of sample can also complicate the identification of the different components after TLC since in many of the cases, due to the low concentration of the sample, it was diluted, the signal was reduced, and not good results were obtained.

Future perspectives

Since the AgI synthesis still not completely reproducible and it depends on many factors due to the instability of the reaction, it is proposed to establish a systematic control of the synthesis in order to understand better the mechanism and found the better conditions to obtain a homogenous reproducible product.

First, it is recommended to control the temperature of solution all the time and, when adding the reagents to produce the reaction, stir the solution continuously in order to obtain a homogenous product, as many of the bibliographic sources recommend. Many of them consider necessary to leave the solution under agitation time, 2 hours in some cases (Santo, *et al*., 2017).

Huang, Wen, and Zhu (2014, p. 37188) recommended the vigorous stirring when making reacting KI with $AgNO_3$. They also suggest different washes using water and ethanol in order to eliminate byproducts of the reaction. I suggest following these recommendations for improving the results of the synthesis.

During this evaluation is necessary to observe the particles obtained with SEM in order to obtain the size and shape of them even if Roveri in 2014 has already done it, the control of particles after each synthesis is required due to the difficulty to reproduce the exact result.

Related with the particle size and shape, I suggest performing some trials to determine which is the particle size and deposition thickness more adequate for the TLC separation of colorants, since it has been observed in the present research that the results can vary considerably from one to another synthesis due to its reproducibility problems. To have more control of this factor is necessary to obtain images with SEM from the different slides, even if it has been done before, this is important since until now the results after the deposition are not homogenous.

By considering the problems in the extraction of some dyes from the fibers, it is necessary to try other methods, considering the possibility of performed acid-pretreatments in order to break the system dye-fiber or dye-mordant-fiber when it is required. Even if the small amount of sample is lost during an acid extraction, the TLC separation can help to eliminate the interference coming from the fiber.

After the analysis of felt-tip pens, it is required to make further analysis in order to establish a methodology for the extraction of the dyes over a support, presumably paper, which can be found in artworks. After this step, the following research should be focused in the study of real cases as the portraits done by Tosi.

Moreover, the further steps for this research is to continue with the analysis of real samples. The study of textiles preserved in the Gandini Collection of Modena Museums are interesting cases to test the system.

More studies about the Basic Green 1 (BG1) dyes are requires, by using standard solutions aged artificially in order to identify in a best way the possible chemical changes and the sub-products that can be formed as result of the degradation.

Overall, from the Conservation Science point of view, the development of new methodologies for the study of Cultural Heritage, as is the case of the present research, must always be focused on reducing technical problems related to adaptation of pre-existing analytical techniques not developed specifically for those purposes or solving specific problems related to certain kind of objects.

Thus, the present research has contributed with the evaluation and better understanding of a methodology that reduces not only the sample size required but also the time and cost. It also allows obtaining useful data with not so specialized equipment.

Furthermore, the historical information offers to the non-specialized conservation scientist to learn more about the synthetic dye industry, production and historical importance, which must not be forgotten when studying Cultural Heritage.

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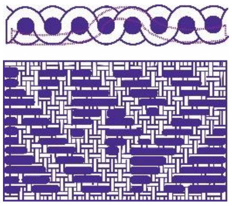
GLOSSARY

A

ATR. Attenuated total reflection

Auxochrome. A group of atoms attached to a chromophore that modifies the ability of that chromophore to absorb light. –OH, $-NH_2$.

B



Brocade. A weave fabric that gives the appearance of having been embroidered. The brocade effect is achieved by introducing additional weft threads as appropriate during the weaving process. This creates a permanent fabric design on the surface, slightly embossed. Usually, this results in thread groups at the back of the fabric, called floats.

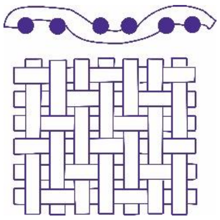
C

Chenille. Chenille fabric gets its name from the way in which the fabric is manufactured. It is made by forming a tightly wound core for the yarn. Piles, which are short lengths of yarn, are wrapped around this core, causing its edges to stand on right angles from the centre of the fabric. It is this that gives chenille fabric its unique look, softness, and change of colour dependent on how light shines on the fabric from each direction. The yarn is commonly manufactured from cotton, but can also be made using acrylic, rayon and olefin. It emerged between 1754 and 1895 in three different countries; France, Scotland and the United States (What is a Chenille Frabric?, 2013).

Chromophore. Any chemical group that produces color in a compound, as the azo group -N=N-, $-NO_2^+$, -C=C-, -C=O, -N=O, benzene ring.

D

Dye or Dyestuff. Colored organic compound –in general soluble in water- that may be used for imparting color to a substrate in a reasonably permanent way (Chatwal, 2009).



Denim. A sturdy cotton warp-faced textile in which the weft passes under two or more warp threads. This twill weaving produces a diagonal ribbing that distinguishes it from cotton duck.

F

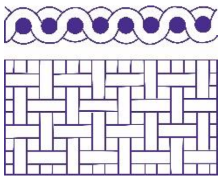
FTIR. Fourier transform infrared spectroscopy

FTIR-RAS. Fourier transform infrared reflection absorption spectroscopy

L

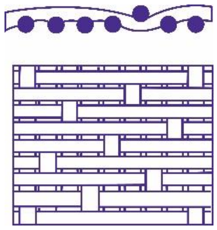
Lake. A pigment manufactured by precipitating a dye with an inert mordant usually a metallic salt. The most common is Alum.

P



Plain weave. The most common and tightest of basic weave structures in which the filling threads pass over and under successive warp threads and repeat the same pattern with alternate threads in the following row, producing a checkered surface (Dictionary.com, 2017).

S



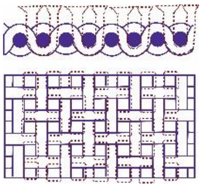
SERS. Surface-enhanced Raman spectroscopy or surface-enhanced Raman scattering

Satin. A smooth, glossy fabric, usually of silk, produced by a weave in which the threads of the warp are caught and looped by the weft only at certain intervals.

T

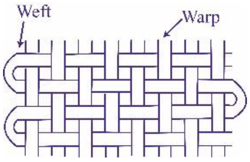
TLC. Thin Layer Chromatography

V



Velvet. A fabric appreciated for its lush, dense pile surface. Is woven as supplementary warp loops on a foundation; the loops are usually later cut, resulting in the raised surface pile, but may also remain uncut. (Phipps, 2011)

W



Warp. Threads lengthways in a fabric as woven.

Weave. A pattern of or method for interlacing yarns.

Weft. Threads widthwise in a fabric as woven.