



## ESSENTIAL CHEMISTRY AS COLORANTS OF INTEREST IN ARCHAEOLOGY

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### ABSTRACT

This paper presenting some of the chemistry behind the colour of dyes and how the target material, for example a fibre, influences the method of dyeing and the dye used. Organic Dyes in chemistry plays an important role where color is an important feature of a manufactured product. Hereby, we made an attempt to explain possible chemistry used in archaeology with research in this area.

**Keywords:** Organic Dye, Colorants, SERS, Debromination, Chromatography

### Introduction

Paintings, sculptures and several other artifacts that are part of our cultural heritage, including textiles, books, furniture, archaeological objects and the organic residues found in association with them, often contain a great variety of both natural and synthetic coloring substances<sup>1-3</sup>.

**Chemical investigation** of such materials is of great interest to art historians, restorers and art conservators. In fact, the analysis of ancient dyes can be of help in revealing what kind of substances were available in particular periods and geographical areas, providing valuable data about the historical context of a work of art, the lifestyle and the technical knowledge reached by a certain population in a given historical age, the provenance of textile materials, pigments, dyestuffs and colored artifacts, shedding light on the possible interactions between different cultures as well as the trade routes and commercial transactions which may have allowed the usage of a particular colorant far from its geographical source.

Moreover, discovering the nature and the origin of the coloring substances employed in the production of a work of art can provide precious information regarding its original color and appearance, thus offering new insights into the artist's choices and original intention, the techniques used and the dates ante quem and post quem the art object was produced, possibly leading to the uncovering of falsifications and forgeries.

Furthermore, scientific analysis applied to the study of art materials and, specifically, of pigments and dyes, may contribute to assess suitable conservation and restoration procedures to be applied to paint defects and degraded pigments in works of art of any kind; in fact, time, environmental conditions and several other circumstances unavoidably cause damage and deterioration to art objects and artifacts, which therefore require careful conservation to be safeguarded as important elements of our cultural heritage. The identification of historical dyes is currently one of the most challenging tasks in the chemical investigation of art materials, for three main reasons. First of all, colorants<sup>4-6</sup> in works of art and archaeological textiles are usually included in complex matrixes such as paint layers or cloth fibers, where they are present in mixture with other substances, e.g. binding media or mordants, and in very low concentrations due to their high tinting power. Besides, sampling of art objects is always limited to microscopic fragments, when at all allowed. An additional analytical challenge is posed by the remarkable susceptibility to deterioration of organic materials, which can undergo a number of chemical degradation processes leading to the formation of specimens with a different molecular structure in comparison to the primary organic dye.

In this regard, a few cases reported in the literature are dealing, for instance, with the detection of products such as **2,4-dihydroxybenzoic acid** and **2,4,6-trihydroxybenzoic acid** deriving from morin in samples dyed with old fustic<sup>7</sup> and from luteolin in weld and dyer's broom<sup>8</sup>; similarly, debromination upon ageing has been evidenced in indigoid components of purple<sup>9,10</sup>.

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In particular, all colorants are prone to some degree of fading caused by many **chemical oxidation processes when exposed to light**<sup>11</sup>. In this context, the recent identification of organic madder and cochineal-based purples and reds, in addition to inorganic vermilion and chrome yellow, in an important historical watercolor by the American master Winslow Homer was essential both to determine how the colorless appearance of the sky was actually the result of a fading process and to hypothesize how the painting most likely looked just after its completion<sup>12, 15</sup>. As in the case of other organic substances of archaeological interest, also the analysis of historical dyes was significantly improved thanks to the introduction of instrumental techniques, both of chromatographic and spectroscopic types. In particular, many analytical methods have been exploited thus far for the detection of organic colorants in ancient fabrics and works of art. Conventional techniques embrace, in the first place, UV-vis absorbance spectroscopy, which has allowed positive identification of several dyes including madder and indigotin on Anglo-Scandinavian textiles<sup>13</sup>; UV-vis reflectance spectroscopy was also evaluated as an alternative, sometimes leading to satisfactory results, as in the case of the detection of indigo used as a pigment or in Maya blue<sup>14,15</sup>, without the need to take a sample. Nevertheless, in the majority of cases, electronic methods are strongly affected by matrix interference and show poor specificity, typically providing broad and featureless spectra that hardly allow specific identification. In the last few years, fluorimetry has also been successfully applied to the non-destructive study of pigments and colorants from medieval illuminations, paint cross sections, millenary textiles and wall paintings<sup>16-18</sup>. However, if a sufficient amount of sample is available for analysis, chromatographic techniques are generally preferable, as they enable separation and reliable identification of individual components in dye mixtures. Among them, TLC was firstly applied to the investigation of madder lake samples from manuscripts dating to the 12th and 15th centuries in 1967<sup>19</sup> and has thenceforth found increasing application in the analysis of organic colorants<sup>20</sup>. Over the years, this separation technique has gradually been replaced by HPLC, which has become a well-established analytical tool for this sort of investigations and has to date allowed to identify the largest number of dyes in works of art and ancient textiles. Despite its great selectivity and specificity though, HPLC is a destructive tool and requires sizable sample, typically 1 mg of colorant or 5 mm of dyed fiber, which is obviously not always available from rare and priceless artifacts such as museum objects. Among the vibrational spectroscopic techniques that have been evaluated for the analysis of organic colorants, e.g. FTIR and NIR spectroscopies, Raman spectroscopy has the greatest potential for the analysis of minute amounts of dyes and has thus been used to characterize both natural and synthetic pigments. However, this technique has proven to be more suitable for the non-invasive analysis of inorganic coloring materials, as it suffers from inherently weak signals and strong molecular fluorescence from organic dyestuffs often precludes the measurement of Raman scattering; several organic colorants are in fact extremely fluorescent even when using relatively high wavelengths, namely 785 nm, for excitation, and the resulting background obscures their Raman spectrum<sup>1,5</sup>. Furthermore, because only subnanogram levels of dyes are needed to achieve intense coloration, normal Raman spectroscopy is often not sensitive enough to probe these materials, especially when they are embedded in complex matrixes such as traditional artists' paints or historical textiles. In recent years, the potential of SERS for the ultrasensitive detection of organic molecules used as artists' colorants has been widely appreciated and exploited. The introduction of this analytical tool in the field of cultural heritage investigations has significantly improved the chances of successfully identifying dyes, clearing the way for an enormous range of new possibilities of experimentation.

A brief outline about the historical background and development of this technique, as well as its physicochemical principles and application to the analysis of organic colorants, is given in the following paragraph. <sup>16</sup>SERS enters the scene: history, chemistry and application to dye analysis SERS is a surface-sensitive technique that allows to achieve significant enhancements of the Raman scattering intensity, as much as  $10^{10-14}$ , for substances adsorbed on nanosized metal surfaces such as properly treated electrodes, colloidal particles and thin films. Several articles, journal special issues and books are being published every year on this topic, which is currently at the center of a powerful renaissance, both in terms of a deepened fundamental understanding of the interactions between the



nanostructured noble metal substrates and model analytes, and in terms of its applications; in this regard, comprehensive studies have been recently conducted by Aroca , Lombardi and Birke.

SERS effect has been firstly observed for pyridine adsorbed on electrochemically roughened silver in 1974 by Fleischman and coworkers. The discovery of such an enormous enhancement in the Raman intensity when a molecule is in the vicinity of metal nanoparticles, coupled with the suppression of fluorescence, generated considerable excitement and suggested the possibility that SERS could provide an invaluable tool as a reliable, high-resolution detection technique for extremely minute quantities of target molecules. Fleischman and coworkers justified the intense signals obtained for pyridine simply as a matter of the number of molecules that were scattering on the surface, not recognizing the occurrence of a major enhancement effect. In 1977 two research groups independently noted that the concentration of scattering species could not account for the enhanced signal and each proposed a mechanism for the observed phenomenon: Jeanmaire and Van Duyne suggested an electromagnetic effect, while Albrecht and Creighton hypothesized a charge-transfer effect. Their theories are generally still accepted as explaining the SERS effect.

However, the exact mechanism of the enhancement effect of SERS is still a matter of debate in the literature. On the one hand, according to the electromagnetic theory, the increase in intensity of the Raman signal for adsorbates on particular surfaces is due to an enhancement in the electric field provided by the surface itself; this explanation can apply even in those cases where the specimen is only physisorbed to the surface, without chemical interactions. When incident light emitted by a laser strikes the surface, localized surface plasmons are excited, and the field enhancement is greatest when the plasmon frequency is in resonance with the radiation. In order for scattering to occur, the plasmon oscillations must be perpendicular to the surface.

Conceptual illustration of SERS mechanism are in-plane with the surface, no scattering will be observed. It is because of this requirement that roughened surfaces or arrangements of nanoparticles are typically employed in SERS experiments, as they provide an area on which these localized collective oscillations can occur. On the other hand, the chemical theory proposes charge-transfer effects between molecular orbitals of the target analyte and the conduction band of the noble metal substrate; it only applies for species which have formed a chemical bond with the surface, and as a result it does not fully explain the observed signal enhancement in all cases. As far as selection rules are concerned, the term surface-enhanced Raman spectroscopy implies that this technique provides the same information as traditional Raman spectroscopy, simply with a greatly enhanced signal.

However, while spectra deriving from most SERS experiments are similar to the non-enhanced ones, several differences in the number of modes are frequently observed: in fact, additional modes not found in the traditional Raman spectrum can be present in the SERS spectrum, while other modes can disappear. The modes observed in any spectroscopic experiment are dictated by the symmetry of the molecules and are usually summarized by selection rules. When molecules are adsorbed to a surface, the symmetry of the system can change, slightly adjusting the symmetry of the molecule, which can lead to differences in mode selection. One common way in which selection rules are modified arises from the fact that many molecules that have a center of symmetry lose that feature when adsorbed to a surface. The loss of a center of symmetry eliminates the requirements of the mutual exclusion rule, which dictates that modes can only be either Raman or infrared active. Thus, modes that would normally appear only in the infrared spectrum of the free molecule can appear in the SERS spectrum. The symmetry of a molecule can be changed in different ways depending on the orientation in which the molecule is attached to the surface.

In some experiments, it is possible to determine the orientation of adsorption to the surface from the SERS spectrum, as different modes will be present depending on how the symmetry is modified. While the first



experiments were performed on electrochemically roughened silver, the most widely used methods to prepare substrates for SERS experiments are now based on wet chemistry, i.e. chemical reactions in solution. Metal colloids can be synthesized by a number of different procedures, such as chemical reduction, laser ablation and photoreduction; among these, the first one mentioned has been the most popular thus far. The reaction is usually carried out by employing a starting metal salt, which is reduced by a chemical agent to produce colloidal suspensions containing nanoparticles with variable sizes, depending on the method of production. Generally, the size regime relevant to SERS experiments is between 10 and 80 nm. The shape and size of metal nanoparticles, which strongly affect the strength of the enhancement, can be partially controlled by appropriate choice of the preparation procedure; the most important parameters in this regard are the nature of the metal, the reducing agent, the temperature, the stabilizing agents and the metal ion concentration. Different kinds of nanoparticles support different plasmon resonances, depending on the size, shape and dielectric constant of the metal; the choice of surface metal is therefore dictated by the plasmon resonance frequency. Silver and gold are typical metals for SERS experiments because their plasmon resonance frequencies fall within visible and NIR spectral ranges, i.e. radiation used to excite Raman modes, and can thus provide maximal enhancement for these wavelength ranges. The absorption spectra of copper, platinum and palladium also fall within the range acceptable for SERS experiments. Although the SERS technique has been discovered almost four decades ago, only in recent years sustained efforts have been devoted to its application to the study of cultural heritage objects. Guineau and Guichard first explored SERS to identify colorants of artistic and archaeological interest in 1987, demonstrating that significant enhancements could be obtained from the analysis of synthetic alizarin and extracts from an 8th century textile sample dyed with madder on a porous Ag electrode cooled with liquid nitrogen. However, because of the objective difficulties in achieving consistent and reproducible results with this technique, a considerable number of SERS studies started being published nearly twenty years later.

In fact, as demonstrated by recent reviews and papers, SERS has lately found increasing application for dye investigation in works of art and archaeological objects, thanks to its great potential in providing specific vibrational fingerprints even for extremely fluorescent colorants with high selectivity and sensitivity. Since it is not a separation technique, it suffers from a greatly reduced ability to resolve dye mixtures when compared to HPLC; nevertheless, it can be employed successfully with minute samples, as recent improvements have made measurements possible to be performed on a single pigment grain or a few-microns length of fiber. Silver colloids synthesized according to the Lee-Meisel method, i.e. by citrate reduction of silver nitrate, have been to date the most popular substrate for SERS investigations of colorants in artworks, thanks to their easy preparation procedure; other kinds of supports, such as silver nanoparticles produced by laser photoreduction, silver island films and silver films over nanospheres, have been also tested as an alternative, and are worth further exploration in the future.

A lot of research carried out thus far in the field of SERS applied to art and archaeology is dealing with the characterization of reference substances: for years, alizarin, purpurin and anthraquinones in general have been the subject of most works available in the scientific literature, even though a number of articles about flavonoids, indigoid dyes and a few other chromophores have been published as well. In addition to providing valuable reference spectra, these papers have also investigated aspects such as complexation geometry, influence of pH and orientation of the analyzed molecules with respect to the metal substrate. Because the orientation of the molecule with respect to the metal surface results in selective enhancement of certain signals, interpretation of the spectra can pose a real challenge, and therefore ab initio computational methods such as density functional theory (DFT) are sometimes used to assign the normal modes and interpret SERS data, even if comparison with reference spectral databases and a deeper understanding of the interactions of the dyes with various metal substrates are still required. SERS experiments on historical artifacts, which all require that samples be removed from the work of art under investigation, initially employed harsh chemical extraction in strong acids in order to isolate the organic dye from the medium, invariably resulting in degradation of the host material; in recent years, the development of milder



extraction procedures, non-extractive hydrolysis methods as well as non-hydrolysis approaches has allowed positive identification of a number of organic pigments in tapestries, carpets, paintings and other valuable art objects.

### CONCLUSION

From above study, it is clear that Opportunities for future research include the extension of spectral databases of dyes already available in the literature to reference colorants that have not been characterized so far, as well as the development of noninvasive approaches which, combined with the use of robust nanofabrication techniques, will ultimately allow SERS to become an analytical tool of general applicability in the art conservation field.

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