

A combined Surface Enhanced Raman Spectroscopy (SERS)/UV–vis approach for the investigation of dye content in commercial felt tip pens inks



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ABSTRACT

The development of protocols for the protection of the large patrimony of works of art created by felt tip pen media since the 1950's requires detailed knowledge of the main dyes constituting commercial ink mixtures. In this work Surface Enhanced Raman Scattering (SERS) and UV–vis spectroscopy were used for the first time for the systematic identification of dye composition in commercial felt tip pens. A large selection of pens comprising six colors of five different brands was analyzed. Intense SERS spectra were obtained for all colors, allowing identification of main dye constituents. Ponceau 4R and Eosin dyes were found to be the main constituents of red and pink colors; Rhodamine and Tartrazine were found in orange and yellow colors; Erioglaucine was found in green and blue colors. UV–vis analysis of the same inks was used to support SERS findings but also to unequivocally assign some uncertain dye identifications, especially for yellow and orange colors. The spectral data of all felt tip pens collected through this work were assembled in a database format. The data obtained through this systematic investigation constitute the basis for the assembly of larger reference databases that ultimately will support the development of conservation protocols for the long term preservation of modern art collections.

1. Introduction

Artists have always tried to test new materials and techniques to create original and innovative artistic forms. Since the 20th century, and increasingly over the last decades, ballpoint and felt-tip pens in particular, with their low cost, novelty and easy availability have attracted the interest of numerous artists. As a result, a large variety of ink-based works of art has been produced and it is currently displayed in museums or private collections around the world [1,2]. However, the preservation of such produced artworks presents significant conservation challenges, as the fast color fading of constituting inks can result in severe deterioration and changes in appearance in short timeframes [3]. The bright colors of felt tip pens are easily altered by exposure to the environment, mainly as result of high photo-instability and water solubility of some of constituent dyes. The inhibition of fading processes requires the development of tailored conservation protocols able to predict the reaction of inks to conservation treatments and their vulnerability to light exposure. This in turns requires knowledge of the dye chemical composition of each commercial pen. Unfortunately at

present, data on the chemical composition of inks constituting felt tip pens are fragmented, due to their complex and heterogeneous formulation (including solvents, stabilizers, plasticizers, surfactants and other additives), trademark protection and absence of a reference database [3]. Moreover, in the case of drawings or prints, where the pen ink is applied on paper, additional conservation challenges occur, associated to the inherent fragility of the paper matrix.

Currently, most of the research on the investigation on commercial pen inks on paper is focused in the field of forensic science, especially on the analysis of ballpoint and gel pens inks on questioned documents [4–7]. However, recently research focus has started to shift towards chemical characterization of commercial pen inks used in contemporary art as shown by Zaffino et al. [8] and Alyami et al. [9], who both developed spectroscopic methods for the identification of fountain and ballpoint pen inks. In parallel, some work has recently been carried out on the development of methods for the characterization of chemical content in felt tip pens. Izzo et al. applied a multi-analytical approach based on chromatography, X-ray fluorescence spectroscopy (XRF), fourier transform infrared spectroscopy (FTIR) and nuclear magnetic

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resonance (NMR) for the identification of dyes in felt tip pens and investigation of photo-degradation effects [1]. Germinario et al. used a combination of spectroscopic techniques and chromatographic techniques for the identification of dye and binder components in commercial felt tip pens [10]. Sodo et al. applied Raman spectroscopy to the analysis in situ of marker pen drawings, including historical drawings, comparing results from old and new pens [3].

Recently, Surface Enhanced Raman Scattering (SERS) has been proposed as valuable analytical technique when mass-limited samples, in situ applications and local identification of selective dyes are required [11,12]. SERS is a surface sensitive analytical technique that involves the amplification of Raman signal by several orders of magnitude for molecules adsorbed on metallic surfaces. The SERS effect is produced by two main mechanisms: the electromagnetic enhancement and the chemical enhancement. The combination of the two can enhance the Raman signal of about 10 orders of magnitude [13–15]. The use of SERS for heritage applications started in the late 1980's [16–18] when this spectroscopic technique was applied to the identification of dyes in a variety of artistic media. Since then, SERS has been used for investigation of lakes and dyestuffs in archeological textile fiber or test fibers [19,20], paper or woodblock prints [21], dye content in pastel colors [22], painting samples [19,23,24] and watercolors pigments [25]. However, despite the proven effectiveness of SERS as analytical tool in art conservation, no data are reported in literature on its application to pens ink analysis. Nevertheless, the high sensitivity, selectivity and fast analysis timescale, would make SERS the technique of choice to enable the design of necessary preventive measures for the preservation of modern art collections.

This work represents the first systematic analytical study of commercial felt tip pen dye chemical composition obtained by a combined SERS and UV–vis spectroscopy approach. Marker pens of different colors and brands have been applied on commercial A4 paper and analyzed. In general, SERS effectively quenched the dyes strong fluorescence interference allowing the generation of diagnostic signals, otherwise not visible by normal Raman spectroscopy. The main dye components of all examined pens were identified by spectral comparison with reference dyes. The complementary use of UV–vis spectroscopy allowed to confirm the data collected by SERS and also to clarify some of uncertain attributions, especially for yellow and orange colors. The information collected by the SERS/UV–vis combined approach was combined for the first time into a spectral database format made available in this work. This database well complements existing databases of industrial pigments used in commercial paint formulations [12,26,27] and constitutes the basis for the development of preventive conservation measures for modern art collections.

2. Experimental section

2.1. Materials

Silver nitrate, trisodium citrate, ascorbic acid and reference dyes (Amaranth, Auramine O, Basic Red 9, Blue 38, Crystal Violet, Copper Phthalocyanine, Eosin Y, Erioglaucine, Green S, Methyl Blue, Poinceau 4R, Rhodamine B, Rhodamine 6G, Tartrazine, Victoria Blue B) were purchased from Sigma-Aldrich and used without any further purification.

All glassware was cleaned with *aqua regia* and deionized water prior nanoparticle synthesis.

Felt-tip pens from Tombow, Stabilo, Giotto, Caran D'Ache and Carioca brands were purchased from art supplies in Ireland.

The complete list of all analyzed felt tip pens is shown in Table 1.

2.2. Synthesis of Ag nanoink

Silver nanoinks were synthesized following the Lee and Meisel method reported by Polavarapu et al. [28].

Table 1

List of all analyzed felt-tip pens, with details of colors, brands and pen models.

Color	Brand (Pen)	Color	Brand (Pen)
Red	Tombow (ABT 885)	Yellow	Tombow (ABT 061)
	Stabilo (68 50)		Stabilo (68 44)
	Giotto (Turbocolor)		Giotto (Turbocolor)
	Caran D'Ache Fibralo (185 070)		Caran D'Ache Fibralo (185 010)
Pink	Carioca (Doodles)	Green	Carioca (Doodles)
	Tombow (ABT 755)		Tombow (ABT 346)
	Stabilo (68 56)		Stabilo (68 53)
	Giotto (Turbocolor)		Giotto (Turbocolor)
Orange	Caran D'Ache Fibralo (185 030)	Blue	Caran D'Ache Fibralo (185 210)
	Carioca (Doodles)		Carioca (Doodles)
	Tombow (ABT 925)		Tombow (ABT 555)
	Stabilo (68 54)		Stabilo (68 32)
	Giotto (Turbocolor)		Giotto (Turbocolor)
	Caran D'Ache Fibralo (185 030)		Caran D'Ache Fibralo (185 160)
	Carioca (Doodles)		Carioca (Doodles)

2.3. UV–vis analysis

UV–vis spectra were acquired using an Agilent/HP 8453 UV–vis Spectrophotometer ($200 \text{ nm} < \lambda < 1100 \text{ nm}$). In order to obtain spectra from felt tip pens an extraction procedure was applied whereby colored paper squares (3 cm^2) were placed in two glass vials (30 min) containing 1.5 mL of H_2O and MeOH, respectively. The resulting colored solution was measured by UV–vis. For reference dyes analysis, solutions of $1 \times 10^{-4} \text{ M}$ in H_2O and MeOH were analyzed.

2.4. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy images of nanoinks deposited on SiO_2 substrates were acquired using a field emission SEM (JSM-6700F, JEOL UK Ltd) operating at beam voltages of 5 kV.

2.5. Optical microscopy

White light optical microscopy images of colored paper were acquired with an Axioskop II, Carl Zeiss Ltd. Microscope equipped with a halogen lamp and a charge-coupled detector camera (CCD; Coolsnap CF, Photometrics).

2.6. Raman and SERS analysis

Raman and SERS spectra were collected at 514 nm by a Renishaw inVia Raman system with a helium–neon laser as excitation source. The laser beam was focused onto the sample through a Leica $20\times$ objective with 0.4 N.A. The measured power at the sampling level was in a range of 0.01–2 mW. Acquisition time was 10 s. Raman spectra of felt tip pens were collected directly from drawn colored squares or lines on commercial paper. In order to obtain SERS spectra, $5 \mu\text{L}$ of Ag colloidal solution were deposited on felt tip pen colored squares on paper and left to dry overnight in the dark prior analysis. Reference dyes were analyzed as powder deposited on glass slides.

3. Results and discussion

Ag nanoinks used for SERS analysis were synthesized according to a method developed by Polavaru et al. which consisted into decreasing the volume of Ag nanoparticles obtained by the classical method of Lee and Meisel by two orders of magnitude [28,29]. The consequent large increase of nanoparticle concentration resulted in formation of viscous, ink-like solutions that could be easily drop-deposited on felt tip pen colored paper substrates without excessive spreading or smudging of the color underneath. Fig. 1a shows a SEM image of the Ag nanoinks,

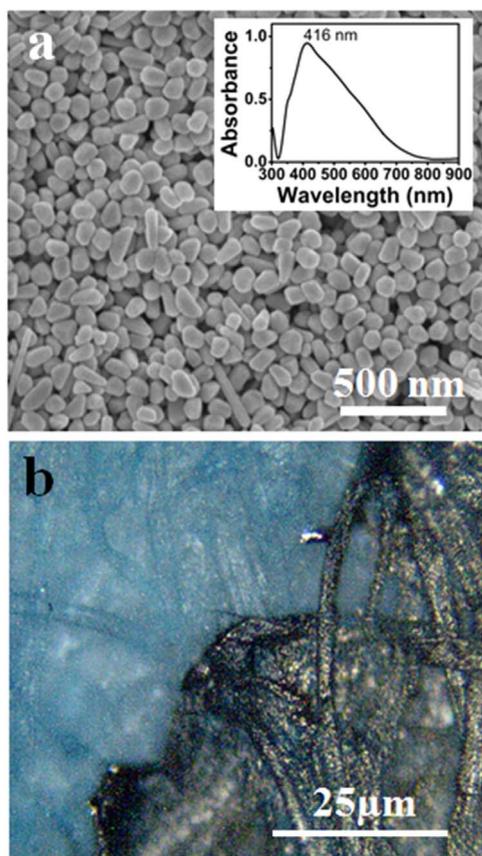


Fig. 1. (a) SEM image of silver nanoinks deposited on SiO₂ substrate. Inset: UV–vis absorbance spectrum of diluted Ag nanoink; (b) Optical microscopy image of a paper sample colored with blue felt-tip pen with deposited Ag nanoink (metallic area on the right hand side of the image). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

mostly constituted by spherical particles with an average size of 100 ± 5 nm. The nanoink solution was pale grey in color and showed a plasmonic peak centered at 416 nm (Fig. 1a inset). Fig. 1b displays a close up optical image of an Ag nanoink droplet deposited on colored paper (blue felt tip pen), showing some small heterogeneity in the distribution of ink over the paper fibers (resulting in some fibers more intensely colored than others) but also formation of well-defined SERS-active areas and concomitant preservation of the colored under-layer (grey metallic area on the right side of the optical image).

Normal Raman (NR) and SERS identification of all ink dye constituents was carried out on small colored squares (3 cm^2) drawn on commercial paper with each of the felt tip pens listed in Table 1. Fig. 2 show representative spectra taken for each of the six analyzed colors across the five analyzed brands. In general NR spectra were featureless and displayed high fluorescence backgrounds, in some cases (pink color, Fig. 2b) leading to saturation of the measured signal. Only green Stabilo (Fig. 2,e) showed a readable low intensity NR spectrum. In contrast, SERS spectra of all colors displayed highly intense diagnostic peaks, and features enhanced compared to NR spectra even in presence of some residual fluorescence background. The complete data set showing the additional twenty-four analyzed colors is shown in Figs. S1–S6. The remaining twenty-four analyzed colors displayed featureless or extremely low intensity NR spectra except for green Caran D’Ache and blue Giotto Turbocolor. In contrast and following a similar behavior to the colors showed in shown in Fig. 2, all twenty-four remaining colors displayed highly enhanced SERS spectral responses.

The identification of the main dye components in each color was carried out by comparing the acquired SERS spectra of felt tip pen paper colored squares with bulk (from powder) NR spectra of reference dyes

measured at 514 nm. Fig. 3 show the background subtracted SERS spectra of Fig. 2 plotted against the identified reference dyes. Eosin Y [19,30], Rhodamine B [31] and Rhodamine 6G [32] were unequivocally identified as the main dye components in Red Tombow, pink Caran D’Ache and Orange Giotto Turbocolor colors, respectively (Fig. 3a–c). Rhodamine 6G and Tartrazine were identified in yellow Giotto color (Fig. 3d). Green Stabilo and Blue Carioca SERS spectra (Fig. 3e–f) showed diagnostic peaks of blue Erioglaurine dye [33] Moreover, additional peaks belonging to Rhodamine B were identified in the Carioca blue color. More details on the position of the observed signals and their spectra attributions can be found in Table S1. Overall, reliable identification was obtained for most of the remaining twenty-four colors, with some uncertain assignments, mainly for yellow inks. Poinceau 4R was found to be the main dye component of the remaining red inks, as also stated in literature (Sodo et al. [3] and Izzo et al. [1]). Rhodamine based dyes (B and 6G) and Eosin Y were found to be the main components of pink inks. Tartrazine, often with Rhodamine, was the main component of orange and yellow inks; Erioglaurine was identified in all green and blue colors (see Table S2 and Appendix in SI).

In order to carry out a more complete identification and to narrow down the number of uncertain assignments, complementary spectral analysis was carried out whereby UV–vis spectra of the ink extracted from felt tip pen colored drawings was compared to UV–vis spectra of reference dyes. As absorption maxima of reference dyes showed slight changes in H₂O and MeOH, both solvents were used for the analysis in order to obtain more accurate assignments (see Appendix).

Fig. 4 show the UV–vis spectra of three selected felt-tip pens, red Stabilo, orange Tombow and blue Giotto, for which SERS identification was uncertain or incomplete. The absorbance spectra of each pen ink highlighted that more than one dye was present in the ink mixtures. In red Stabilo 68 50 (Fig. 4a), the presence of Poinceau 4R and Rhodamine, found by SERS analysis, was confirmed and it was also possible to specify that Rhodamine B was in the formulation. In the case of orange Tombow, the SERS analysis had already suggested presence of Eosin Y (see S2) but the UV–vis analysis (Fig. 4b) allowed the complementary identification of Tartrazine. The UV–vis analysis of blue Giotto (Fig. 4c) confirmed the identification of Erioglaurine and Crystal violet found by SERS analysis but also clearly showed the presence of Rhodamine B in the pen ink formulation. Overall, UV analysis was particularly diagnostic for orange, yellow and green colors as it provided key additional information on other dyes present in the formulation, such as Tartrazine, whose SERS spectrum was often covered by other dye components. The collected UV–vis spectra for all the thirty colors analyzed are reported in the database Appendix.

Detailed identification information for the entire set of felt-tip pens is reported in Table 2, including both results from both SERS and UV–vis analyses. It should be pointed out that beside the identified dyes, others unidentified and in low concentration are likely to present in the analyzed ink formulations. In the particular case of orange pens for example, unidentified orange dyes with λ_{max} in the range of 450–500 nm were found by UV–vis (see Fig. 4b). These could be attributed to commonly used orange dyes Orange G (λ_{max} 475 nm) or Sunset Yellow (λ_{max} 482 nm) [34].

The collection of UV–vis spectra for all analyzed colors also supported the data shown in Fig. 2 and helped to understand the origin of the observed differences between NR and SERS spectra among the different colors. The excitation wavelength at 514 nm was in molecular absorption resonance with all the red, pink and orange colors (absorbance maxima in the range 507–570 nm), giving rise to large fluorescence response in the NR spectra but also to an increased return SERS signal, due to a Surface Enhanced Resonance Raman Spectroscopy (SERRS) condition. Thus, while the saturated NR signals were due to fluorescence interference, the large enhancements observed in the SERS spectra of the above colors were ascribed to a combination of SERRS and electromagnetic effects (EM) arising from the use of aggregated Ag colloids in plasmonic resonance with the excitation wavelength. The

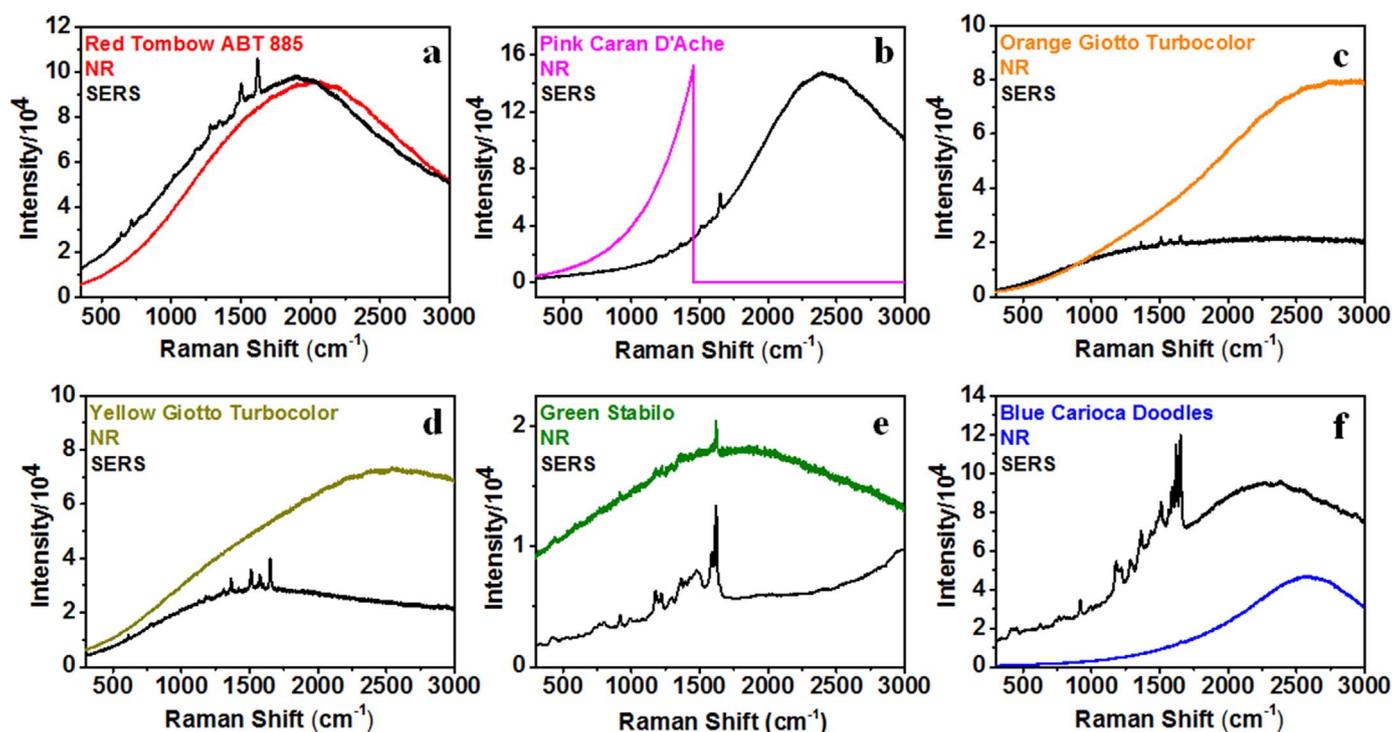


Fig. 2. Representative Normal Raman (NR) and SERS spectra collected for each color and each brand of analyzed felt tip pens; a) Red Tombow ABT 885; b) pink Caran D'Ache; c) orange Giotto Turbocolor; d) yellow Giotto Turbocolor; e) green Stabilo; f) blue Carioca Doodles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

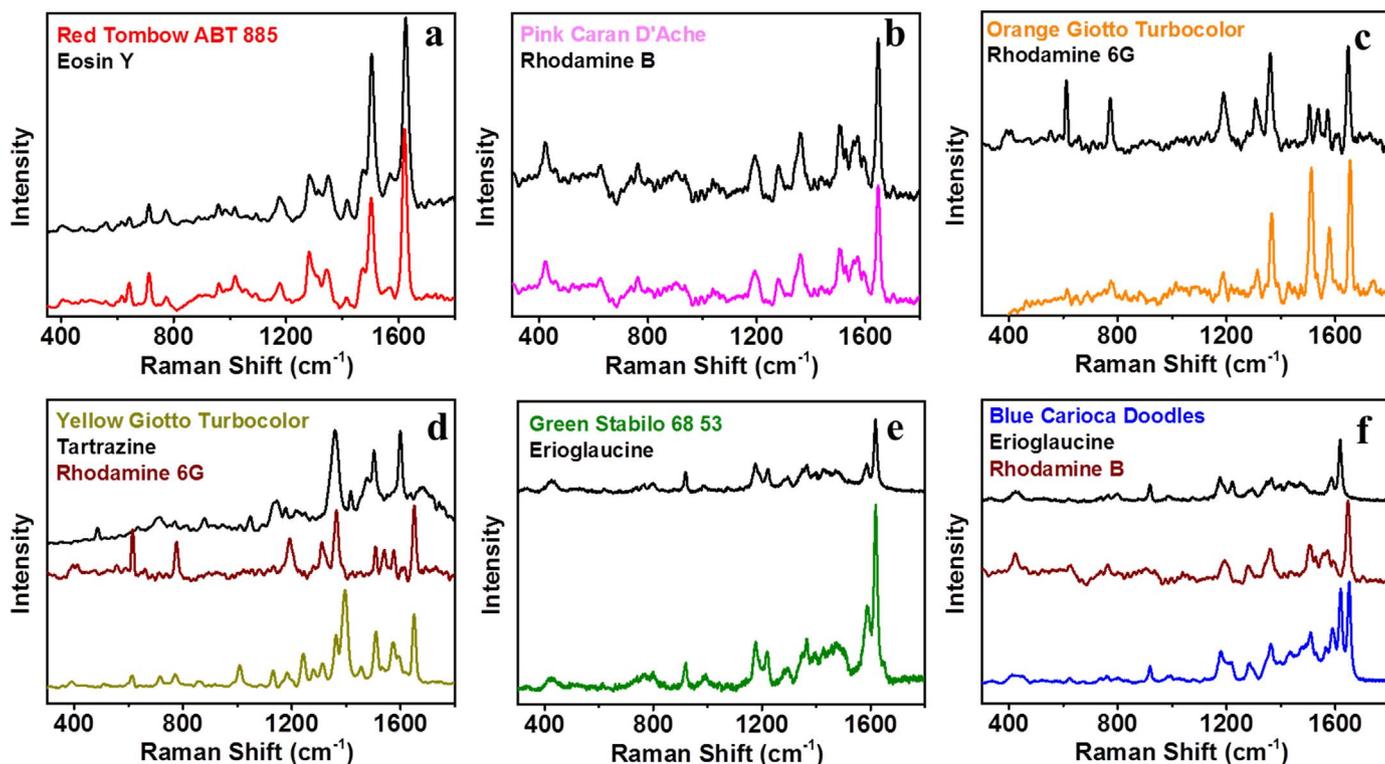


Fig. 3. Baseline corrected SERS spectra of representative felt tip pen colors and brands plotted against NR spectra of identified reference dyes; a) Red Tombow ABT 885 and Eosin Y; b) pink Caran D'Ache and Rhodamine B; c) orange Giotto Turbocolor and Rhodamine 6G; d) yellow Giotto Turbocolor, Tartrazine and Rhodamine 6G; e) green Stabilo and Erioglaurine; f) blue Carioca Doodles, Erioglaurine and Rhodamine B. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

same behavior can be extended to yellow colors, which displayed molecular resonance centered at ca. 430 nm but were characterized by broad spectra. The UV-vis spectra of green colors showed peaks at ca. 430 nm and 630 nm, associated to the presence of yellow and blue

components. At the excitation wavelength of 514 nm all the spectra displayed minimum absorption. Therefore, readable NR spectra were obtained for all pens except Carioca, as results of the low associated fluorescence emission at the excitation wavelength. The SERS spectra of

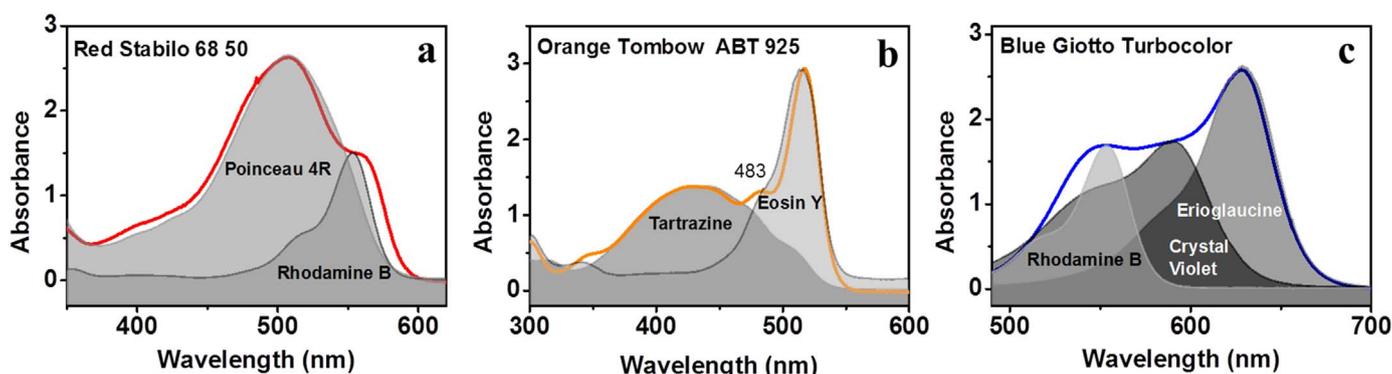


Fig. 4. UV-vis spectra of felt tip pen colored paper squares in aqueous solution plotted against spectra of reference dyes; a) red Stabilo 68 50, Poinceau 4R and Rhodamine B; b) orange Tombow ABT 925 and Eosin Y; c) blue Giotto Turbocolor, Erioglaucine, Rhodamine B and Crystal Violet. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

all green colors were enhanced due to plasmonic effects and showed substantially reduced fluorescence background compared to NR spectra. Regarding the blue colors Tombow, Giotto and Caran D'Ache showed good quality NR spectra, whereas Carioca and Stabilo showed very low intensity NR spectra, the latter associated to possible interference caused by the red Rhodamine B component. SERS spectra of all blues were highly enhanced (up to 2 orders of magnitude for Caran D'Ache). The enhancement was ascribed to a combination of electromagnetic effects associated to plasmonic resonance conditions and additional chemical effects (CE) due to possible charge transfer processes occurring between Ag nanoinks and crystal violet, which was found to be present in most of the blue colors [9].

4. Conclusions

This work presents the results of the first systematic identification of dye content in commercial felt tip pens. A total of thirty pens from six colors and five different brands were analyzed by a combined SERS/UV-vis approach. At the selected excitation wavelength of 514 nm SERS showed to be highly effective in quenching the strong fluorescence backgrounds for all examined colors, generating diagnostic spectra

otherwise not observable by NR spectroscopy. Complementary UV-vis analysis was carried out in order complement and extends the identification made by SERS. For both SERS and UV-vis analysis, identification was performed by comparing the spectral features of analyzed colors with spectra of reference dyes. The entire SERS and UV-vis spectral database of the wide assortment of felt-tip pens on paper, collected for the first time, was assembled in a database format and was made available in this work.

This work represents a substantial step beyond the state of the art in the field of modern conservation science as it presents an analytical approach suitable for the reliable and sensitive investigation of industrially produced dyes constituting the core colorant components of a large number of artwork produced since 1950's. The work further proves the effectiveness of SERS as sensitive tool for conservation science analytics and extends its applicability to the characterization of the fugitive dyes largely used in modern and contemporary artistic productions. The spectral database of analyzed colors assembled through this work will hopefully constitute a useful tool for conservators and material scientists towards the design of conservation approaches tailored to the long term preservation of modern art collections.

Table 2

Summary of all the obtained results by SERS and UV analyses. Underlined results correspond to assignments made by UV-vis analysis in water solution. Abbreviations: Unid. is unidentified, Giotto T is Giotto Turbocolor, Carioca D is Carioca Doodles, BR9 is Basic Red 9, Rhod is Rhodamine, P4R is Poinceau 4R, CV is Crystal Violet. All Tombow pens are ABT model.

Color	Brand (Pen)	Identified Dye	Color	Brand (Pen)	Identified Dye
Red	Tombow (885)	Eosin Y + <u>BR9*</u> or <u>Rhod.*</u>	Yellow	Tombow (061)	<u>Tartrazine</u> + <u>Unknown*</u>
	Stabilo (68 50)	Rhod. <u>B</u> + P4R		Stabilo (68 44)	<u>Tartrazine</u>
	Giotto T	P4R + <u>Amaranth*</u>		Giotto T	<u>Tartrazine</u> + <u>Rhod R6G*</u>
	Caran D'Ache (185 070)	Rhod <u>6G</u> + P4R		Caran D'Ache (185 010)	<u>Tartrazine</u> + <u>Auramine*</u> + <u>Unid dye (λ_{max} 410 nm)</u>
	Carioca D	Rhod (B*) + <u>P4R</u>		Carioca D	<u>Tartrazine</u>
Pink	Tombow (755)	Eosin Y + <u>Rhod B</u>	Green	Tombow (346)	Erioglaucine + <u>Tartrazine</u>
	Stabilo (68 56)	Eosin Y + <u>Rhod (6G and B)</u>		Stabilo (68 53)	Erioglaucine + <u>Tartrazine</u>
	Giotto T	Eosin Y + <u>Rhod 6G</u>		Giotto T	Erioglaucine + <u>Tartrazine</u>
	Caran D'Ache (185 030)	Rhod <u>B</u>		Caran D'Ache (185 210)	Erioglaucine + <u>Auramine*</u> + <u>Unid dye (λ_{max} 410 nm)</u>
	Carioca D	Rhod* + <u>P4R</u>		Carioca D	Erioglaucine + <u>Tartrazine</u>
Orange	Tombow (925)	Eosin Y + <u>Tartrazine</u> + <u>Unid. dye (λ_{max} 483 nm)</u> likely <u>Sunset Yellow*</u>	Blue	Tombow (555)	Erioglaucine + CV
	Stabilo (68 54)	Rhod + <u>Tartrazine</u> + <u>Eosin Y*</u> + <u>Unid dye (λ_{max} 450–470 nm)*</u>		Stabilo (68 32)	Erioglaucine* + <u>Rhod B*</u> + <u>Victoria Blue</u>
	Giotto T	Rhod 6G + <u>Tartrazine</u> + <u>Unid dye (λ_{max} 471–504 nm)</u>		Giotto T	Erioglaucine + CV + <u>Rhod B</u>
	Caran D'Ache (185 030)	<u>Tartrazine</u> + <u>Unid dye (λ_{max} 481–501 nm)</u> likely <u>Sunset Yellow*</u>		Caran D'Ache (185 160)	Erioglaucine + <u>CV*</u>
	Carioca D	<u>Tartrazine</u> + <u>Unid dye (λ_{max} 474–505 nm)*</u>		Carioca D	Erioglaucine + Rhod B

* Uncertain assignments.

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Supporting information

Normal Raman (NR) and SERS spectra of all analyzed felt tip pens.
SERS assignments of representative felt tip pens.
Table of Raman attributions for analyzed colors.
Appendix: List of felt tip pen ink SERS and UV-vis spectra.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.talanta.2018.01.049>.

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