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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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A R T I C L E I N F O

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A B S T R A C T

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. Poinceau 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)
	Carioca (Doodles)		Carioca (Doodles)
Pink	Tombow (ABT 755)	**Green**	Tombow (ABT 346)
	Stabilo (68 56)		Stabilo (68 53)
	Giotto (Turbocolor)		Giotto (Turbocolor)
	Caran D'Ache Fibralo (185 030)		Caran D'Ache Fibralo (185 210)
	Carioca (Doodles)		Carioca (Doodles)
Orange	Tombow (ABT 925)	**Blue**	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 nm < λ < 1100 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 1×10^{-4} 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× 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 μL 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,