Use of Metal Nanoinks for Surface Enhanced Raman Spectroscopy (SERS) Investigation of Dyes in Felt-tip Pens

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1. Felt-tip pens in art

Felt-tip pens are increasingly used for original and creative artworks on paper.

Conservation issues:

Inks can fade, show severe deterioration and changes in appearance in a few years.

Challenging identification:



B/C. Collection of Raman spectral database of commercial dyes and identification of dyes in reference samples

A database of NR and SERS spectra of several commercial dyes was collected. The comparison between spectra from the database and SERS spectra of felt-tip pens samples helped in the identification of the dyes.

Red Tombow

Orange Giotto Turbocolor

Blue Stabilo Pen 68

Heterogeneous formulation (solvents, stabilizers, plasticizers, surfactants and others) is often protected by patent.

State of art on felt-tip pens ink identification:

Still few research works have been carried. Most include chromatographic methods (sampling) often coupled with standard spectroscopic techniques.

Oscar' ."Autoritratto con F. Fellini 1993 Fondazione Fellini © http://www.federicofellini.it

2. SERS investigation of dyes on paper

The aim of this work is to identify dyes on paper in reference felt-tip pens and some case studies by Surface Enhanced Raman Spectroscopy (SERS). The increase of Raman signal (SERS effect) is obtained by metal (silver, gold) nanoinks deposition on the colored paper samples.



2. (A) Optical Microscope image of a blue colored sample on paper with deposition of gold nanoink. (B) Schematic representation of SERS analysis on a paper sample with a layer of blue felt-tip pen ink and metal nanoink on top. (C) SEM images of (top) gold and (bottom) silver nanoink on silicon oxide. In the inset the metal nanoink liquid samples are represented. Raman spectra at 514 nm were recorded with a Renishaw inViaRaman system with a laser power range of 0.01-2 mW. The laser beam was focused onto the sample through a Leica 20X objective with 0.4 N.A



4. Selection of SERS (with silver nanoink) spectra for three colors: red, orange and blue. Each spectrum shows the comparison between the spectra of the corresponding reference dyes and the felt-tip pens ink. Spectra are shown in the range 300-1800 cm⁻¹ for a better readability, intensities scale is not shown. The list of all the results is reported in the table below. Spectra of felt-tip pens were baseline corrected.

Identification was made for most of the dyes, with some uncertain assignments, mainly for yellow inks, as shown in the table. In some cases more than a dye has been identified for a single color.

Color	Reference Brand	Identified Dye	Color	Reference Brand	Identified Dye
<u>Red</u>	Tombow	Eosin Y	<u>Yellow</u>	Tombow	Benzimidazole-based dye*
	Stabilo	Rhodamine + Poinceau 4R*		Stabilo	unknown
	Giotto	Amaranth*+ Poinceau 4R		Giotto	Tartrazine* + Rhodamine*
	Caran D'Ache	Rhodamine + Poinceau 4R*		Caran D'Ache	Indocyanine-based dye*
	Carioca	Rhodamine B		Carioca	unknown
<u>Pink</u>	Tombow	Eosin Y	<u>Green</u>	Tombow	Erioglaucine
	Stabilo	Eosin Y		Stabilo	Erioglaucine
	Giotto	Eosin Y		Giotto	Erioglaucine + unknown
	Caran D'Ache	Rhodamine		Caran D'Ache	Erioglaucine +P. Violet 23*
	Carioca	Crystal Violet*+Rhodamine*		Carioca	Erioglaucine + unknown
<u>Orange</u>	Tombow	Eosin Y	<u>Blue</u>	Tombow	Erioglaucine + Crystal Violet
	Stabilo	Rhodamine B		Stabilo	Erioglaucine + Crystal Violet
	Giotto	Rhodamine 6G		Giotto	Erioglaucine + Crystal Violet
	Caran D'Ache	unknown		Caran D'Ache	Erioglaucine + unknown

3. Outline

A. Study of SERS effect on felt-tip pens on paper.

B. Collection of a Raman spectral database of commercial dyes.

C. Identification of dyes in different brands markers of different colors. **D.** Identification of dyes in Federico Fellini's original felt-tip pens.

4. Results **A. Study Of SERS Effects**

Comparison between Normal Raman (NR) and SERS spectra showed high enhancement in intensity and reduction of fluorescence in SERS, mainly with silver ink. Selected colors are red, pink, orange, yellow, green and blue.



Carioca Erioglaucine +Rhodamine B* Carioca unknowr

5. Summary of all the obtained results. Starred results correspond to uncertain assignements.

D. Identification of dyes in a real case study: Fellini's original felt-tip markers

Traces on paper of three original felt-tip pens used by the famous director Federico Fellini were analyzed: pink, blue and green. SERS analysis allowed the identification of the dyes, respectively Eosin Y in pink, Erioglaucine and Crystal Violet in blue and green.



6. (Top) Study of SERS effect and (Bottom) identification of dyes in Fellni's original felt-tip pens on paper. (Left) Pink Tombow AB 813 (Middle) Blue Caran D'Ache (Right) Green Caran D'Ache. Spectra on the bottom were baseline corrected. In the inset, optical microscope images of the colored samples. Comparison between modern pens of the same brand where made, highlighting the same dyes.

3. Selection of SERS spectra for each color. Each spectrum shows the comparison between NR and SERS spectra with both metal nanostructures (gold and silver).

5) Conclusions

- **1.**SERS analysis allowed the identification of dyes in commercial markers of different brands and colors on paper.
- 2. The collection of the database of Raman spectra (NR and SERS) of commercial dyes helped with the identification.
- **3.**SERS analysis allowed the identification of dyes in F. Fellini's original pens. **4.**Future work: metal nanoinks on polymers as non-invasive SERS substrate.

References

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