Dyes and Pigments xxx (2016) 1–14

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Raman and SERS characterization of solvent dyes: An example of shoe polish analysis

Cyril Muehlethaler [a, c, *], Kara Ng [a], Line Gueissaz [b], Marco Leona [c], John R. Lombardi [a]

[a] Department of Chemistry, The City College of New York, Graduate Center of the City University of New York, United States
[b] School of Criminal Science, University of Lausanne, Switzerland
[c] The Metropolitan Museum of Art, New York, United States

ARTICLE INFO

Article history:
Received 16 September 2016
Received in revised form
30 October 2016
Accepted 30 October 2016
Available online xxx

Keywords:
Forensic science
Surface-enhanced Raman spectroscopy
Silver colloid
Extraction
Leather

ABSTRACT

Surface-Enhanced Raman Spectroscopy (SERS) has significantly contributed to the analysis and identification of dyes over the years. SERS takes advantage of the high molecular absorption of chromophores molecules in the visible to further enhance their signal by resonance mechanisms. The main categories of dyes have all been successfully described by this technique, with the exception of non-water-solubles dyes such as solvent dyes. Due to their non-polarity, solvent dyes do not mix well with aqueous silver colloids nor provide the necessary adsorption to the SERS substrate.

We show that by varying the proportions of solvent to water, we can easily and rapidly obtain very intense spectra from solvent soluble dyes, which were otherwise not possible to measure using the conventional silver colloids. We demonstrate this procedure with a preliminary collection of 13 solvent dyes which were characterized by standard Raman and SERS at 488, 633 and 785 nm. Depending on their molecular absorptions these dyes display resonant conditions with either standard Raman, SERS or both.

The second part of the paper focuses on the identification of solvent dyes in shoe polish. The use of shoe polish has already been described in a forensic context, but the identification of colorants has never been possible due to the high overlapping absorption of the waxes used in the composition. We demonstrate here that sensitive results can be obtained from amounts of shoe polish as small as a few micrograms. Positive identification of solvent dyes in four different colored shoe polish is presented.

1. Introduction

Raman spectroscopy has been an important contributor to the analysis of dyes and pigments. Since typical colorants are chromophores with a strong absorption in the visible, Raman spectroscopy allows the excitation wavelength and the molecular absorption to be matched for Resonance Raman (RR) spectroscopy. Likewise, the analysis of colorants with the concomitant use of noble metal substrates such as silver or gold further ameliorates the sensitivity and signal intensity by providing surface-enhanced Raman spectroscopy (SERS). In such situations, the enhancement in signal intensity can be as high as 10^6 to 10^8. SERS has been used for detecting colorants in both cultural heritage [1] and forensic science [2]. Dyes are particularly good SERS probes molecules because of their structures (e.g. anthraquinones, azo, …) that generally provide the necessary binding to noble metal surfaces. The main categories of dyes are respectively: Direct, Acid, Basic, Mordant, Sulfur and Vat [3]. SERS spectra of these dyes categories have been largely described in the literature [4–11]. All are water soluble to a certain extent, and hence particularly adapted to aqueous colloids such as citrate stabilized silver nanoparticles. The SERS analysis however becomes more challenging for dyes that are only slightly or not soluble at all in water. Different procedures for functionalizing the surface were proposed; in liquids by rendering it hydrophobic with capping ligands [12,13], or to use solid substrates to evaporate drops on modified or nano-patterned surfaces [14,15]. We show here that simple considerations about the solubility and miscibility between solvents allow for a rapid and sensitive detection of non-water-soluble dyes using already available aqueous colloids. We demonstrate this with solvent dyes used in the coloration of non-

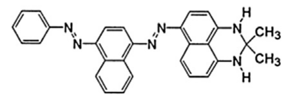
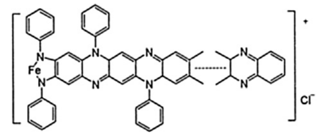
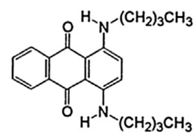
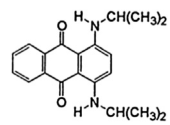
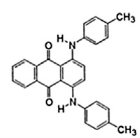
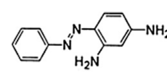
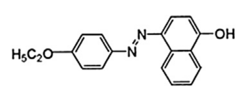
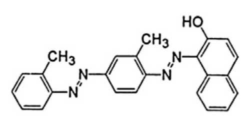
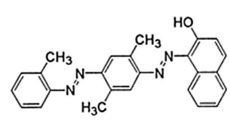
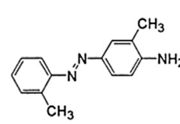
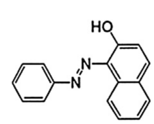
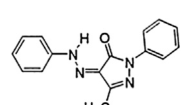
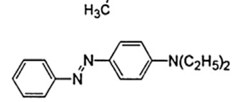
* Corresponding author. City College of New York, Department of Chemistry, 10031 New York, NY, United States.
E-mail addresses: cmuehlethaler@ccny.cuny.edu, Cyril.Muehlethaler@gmail.com (C. Muehlethaler).

http://dx.doi.org/10.1016/j.dyepig.2016.10.049
0143-7208/

polar, hydrophobic materials.

Solvent dyes are a particular type of dyes in that they are not water-soluble, but are known for their superior solubility in organic and non-polar solvents. The dying process does not occur through ionization, as with Acid Dyes or Basic Dyes, but instead takes place in solution with the dyestuff mixed with the polymers

Table 1
Summary and properties of the solvent dyes analyzed.

C.I. Name	Other names	Structure	Properties
Solvent black 3 [SBk3]	C.I. 26150, Sudan black B, Fat Black HB		Blue black Solubility acetone: >300 g/l Solubility toluene: 10 g/l Insoluble in water
Solvent black 7 [SBk7]	C.I. 50415:1, Nigrosine Base, Oil Black		Blue black Solubility acetone: <10 g/l Solubility toluene: <10 g/l Insoluble in water
Solvent blue 35 [SB35]	C.I. 61554, Oil blue B, Transparent blue R, Fat Blue B		Brilliant green blue Solubility acetone: <10 g/l Solubility toluene: 80 g/l Insoluble in water
Solvent blue 36 [SB36]	C.I. 61551, Solvent Blue AP, Transparent Blue AP, Oil Blue PB, Oil Blue 105, Oil Blue 305		Brilliant blue Solubility acetone: 30 g/l Solubility toluene: 70 g/l Insoluble in water
Solvent green 3 [SG3]	C.I. 61565, Solvent Green 5B, Oil Green 5B, Transparent Plastic Green 601		Blue light green Solubility acetone: <10 g/l Solubility toluene: >50 g/l Insoluble in water
Solvent orange 3 [SO3]	C.I. 11270:1, Chrysoidine Y, Oil Orange Y		Dark yellow orange Solubility acetone: <10 g/l Solubility toluene: 10 g/l Solubility water: trace
Solvent red 3 [SR3]	C.I. 12010, Fat Brown B, Sudan Brown B, Oil Brown B		Bordeaux Solubility acetone: 10 g/l Solubility toluene: <10 g/l Insoluble in water
Solvent red 24 [SR24]	C.I. 26105, Sudan Red BB, Oil Red BR, Transparent Red BR		Red to blue light red Solubility acetone: 10 g/l Solubility toluene: 40 g/l Insoluble in water
Solvent red 26 [SR26]	C.I. 26120, Solvent Red MXB, Transparent Red 3BR, Oil Red EGN		Dark red Solubility acetone: <10 g/l Solubility toluene: 10 g/l Insoluble in water
Solvent yellow 3 [SY3]	C.I. 11160, ABCOL Oil Yellow, Dupont Oil Soluble Yellow, Oil Yellow		Yellow light orange Solubility acetone: <10 g/l Solubility toluene: >50 g/l Insoluble in water
Solvent yellow 14 [SY14]	C.I. 12055, Solvent Yellow R, Oil Yellow E, Oil Yellow G		Red light yellow Solubility acetone: 10 g/l Solubility toluene: 80 g/l Insoluble in water
Solvent yellow 16 [SY16]	C.I. 12700, Transparent yellow 3GL, Oil yellow 3G		Brilliant green yellow Solubility acetone: 15 g/l Solubility toluene: 70 g/l Insoluble in water
Solvent yellow 56 [SY56]	C.I. 11021, Solvent Golden Yellow R, Transparent Yellow 3R, Oil Yellow 201		Red light yellow Solubility acetone: 25 g/l Solubility toluene: >300 g/l Insoluble in water