Towards a Surface Enhanced Raman Scattering (SERS) spectra database for synthetic organic colourants in cultural heritage. The effect of using different metal substrates on the spectra

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ABSTRACT

Two different silver colloids were synthetized using the reducing agents sodium citrate (Lee-Meisel method) and hydrochloric hydroxylamine (Leopold-Lendl method). The properties of these colloids were evaluated by investigating a selection of 25 synthetic organic dyes and pigments that belong to different chemical classes and whose Raman spectra are usually poor or are overwhelmed by fluorescence. The observed changes in the SERS spectra acquired using both colloids were evaluated and interpreted by taking into account that enhancement of the Raman signal is influenced by the localised plasmon resonance on the silver nanoparticles as well as by the chemical affinity and molecule orientation on the metal substrate. The morphology and plasmon resonance of the single nanoparticles were characterised by means of UV–Vis absorption spectroscopy. The results revealed significant differences in terms of stability and reproducibility. Furthermore, the sensitivity of the colloids and the reproducibility of the different measurements were evaluated in terms of the Raman shift and signal intensity. SERS spectra of triarylcarbonium (BV 14, BG 1, AB 110, AB 83, PB 1, PG 1) and xanthene colourants without halogen substituents (BV 10, PV 1, BR 1, PR81) as well as the nitro dye AY 24 were very reproducible with both colloids; however, others, such as brominated xanthene dyes (AR 87, AR 91), thioindigo pigments (PR 88, PR 181) and anthraquinone colourants, may present different spectral features depending on the colloid used, which should be taken into account when interpreting unknown spectra. The hydroxylamine-reduced colloid, besides being a reproducible and easy-to-produce SERS substrate, gave satisfactory spectra with all the SERS-active dyes and pigments that were examined. Based on the results, we assume that the hydroxylamine-reduced substrate is the best choice for acquiring spectra for a future SERS database for cultural heritage (CH) applications.

1. Introduction

The history of dyeing can be divided into two great periods: the "pre-aniline" period extending to 1856 and the "post-aniline" period. The rather limited range of available colours were based on dye-producing animals and plants. Aniline (C_6H_5-NH_2), which became available from coal tar in the 19th century, was used in 1856 by William Henry Perkin to synthesise mauveine. The era of synthetic dyes was born and a fierce competition began among chemists to discover new colouring agents, mainly intended for the textile industry [1,2].

Parallel to the revolution of the colour market of the 19th and 20th centuries, artists were extensively experimenting with new colours because of their interest in new hues and shades. Thus, new organic dyes and pigments quickly became part of the artists' palettes, despite a lack of experience with their behaviour when admixed with other artistic materials. The progressive introduction of the various compounds into the market is mostly well documented [3–7]. In the course of the 20th century, >300 synthetic organic pigments became relevant for artists' paints. Moreover, the number of historic and modern synthetic dye-stuffs used for textile dyeing, writing, or as lithographic inks adds up to several thousand. Knowledge about the presence of synthetic organic colourants on an artwork is extremely valuable, not only to address queries about the historical context and chronology of the work as well as the studio practice of a specific artist, but also to identify non-original materials in order to reveal retouches or forgeries [8,9]. Moreover, the analysis of dyes and pigments is relevant for the long-term preservation of artworks because many colourants are unstable under prolonged light exposure or sensitive to solvent cleaning [10,11].

Due to their high tinting strength, organic colourants are usually present in very low concentrations and are mixed with other substances, which poses a substantial analytical challenge [12]. The analytical techniques commonly employed for identifying organic colourants

are high-performance liquid chromatography (HPLC) coupled with ultraviolet–visible (UV–VIS) spectroscopic detection [13,14]. Application of destructive HPLC analysis of artworks that are valuable and unique objects is limited because of the necessity to preserve their physical integrity. Although thin layer chromatography (TLC) [15], which is less sample-consuming, is suitable, it is more restricted in its separation power and reproducibility. Pyrolysis gas chromatography/mass spectrometry has also been used for synthetic organic pigments [4, 16], although it also has its restrictions concerning discrimination of individual compounds and sensitivity. X-ray diffraction (XRD) has been demonstrated to be an effective tool for the specific identification of synthetic organic pigment mixtures and fillers in acrylic- and alkyd-bound artists' paints; however, identification in oil-bound paints appears to be problematic [17]. Unfortunately, the currently available non-invasive methods, such as UV–VIS absorption or fluorescence spectroscopy that are employed to measure the electronic excitation of molecules with chromophores, exhibit a rather poor specificity and thus offer only limited analytical value for assessing the composition of the complex matrices found in many artworks.

During the last decades, great efforts have been undertaken to develop minimally invasive techniques with increased sensitivity for the analysis of synthetic organic colourants. Nowadays, vibrational spectroscopic techniques (Fourier transform infrared spectroscopy and, in particular, Raman spectroscopy) are routinely applied for this purpose in museum and forensic labs.

In the past few years, surface-enhanced Raman spectroscopy (SERS) has been demonstrated to be a very powerful tool for the ultrasensitive and highly selective detection of organic colourants in cultural heritage (CH) applications. The advantage of SERS with respect to classical Raman spectroscopy is its ability to amplify Raman scattering and quench fluorescence signals by absorbing the colourant on specially prepared metal nanostructures [18]. SERS is currently on to the way to becoming a routine method for colourant analysis in museum laboratories. It has already been successfully applied in the characterisation of different classes of organic dyes and pigments on different artistic supports, such as textiles, paper, paintings and photographs [19–28]. The available literature stresses the necessity to optimise the analytical methodologies and strategies for investigating different compounds and matrices as well as to create reliable databases. As a matter of fact, the main goal of our project is to create a reproducible searchable SERS database of the numerous available pure reference pigments and dyes in order to facilitate rapid and reliable interpretation of unknown spectra. One of the most extensive Raman databases for artistic pigments, which is available online (http://modern.kikirpa.be/), was developed at the Royal Institute for CH (KIK-IRPA, Brussels, Belgium) [29], and has lately been extended to early synthetic organic dyestuffs. It would be useful to complement those data with a SERS database that provides spectra of colourants that are difficult to detect by normal Raman. In this context, it is very important to understand whether the selection of a specific substrate may hinder the comparison and exchange of the data among institutions.

The present study investigates possible changes in the SERS spectra of a selection of dyes and pigments on metal substrates that were synthesised using two different procedures: a citrate-reduced silver colloid [30], which is the most widely used enhancing substrate for SERS in CH applications, and a hydroxylamine-reduced colloid, which has successfully been used for environmental analysis [31,32], but has not yet been subjected to exhaustive performance tests in the CH field. The use of the latter colloid in CH has been limited to alizarin-based-pigments and laccaic acid, a red dye [33,34]. These methods featured nanoparticles with very different properties in terms of size, shape and electrodynamics of the metallic surfaces [35]. The comparison and characterisation of different metal substrates has already been presented in the literature, although most of the studies considered only one dye as the probe molecule [32,36,37]. Because the enhancement of the Raman signal is influenced by the localised plasmon resonance on the

silver nanoparticles as well as by the chemical affinity and molecule orientation on the metal substrate, we used a selection of synthetic organic dyes and pigments that belong to different chemical classes and which are of historical and artistic interest to analyse the effect of the silver colloids. Since the solubility of the compounds is a major factor that may influence the affinity between colloid and colourant, we selected dyes and pigments of the same class. Moreover, to the best of our knowledge, some of the presented SERS spectra (e.g. Acid Blue 83, Acid Blue 110, Pigment Orange 1, Acid Red 112, Pigment Violet 5, Pigment Red 88, Pigment Red 181, Pigment Green 8 and Acid Green 1) have not yet been published.

2. Material and methods

2.1. Materials

$AgNO_3$ (purity > 99%, S8157), $NH_2OH \cdot HCl$ (379921) and trisodium citrate were purchased from Sigma Aldrich (Germany). The dyes and pigments are part of the collection at the Doerner Institut. A list and description of the colourants is given in Table 1.

2.2. Instrumentation

The Raman/SERS measurements were performed using a Horiba Scientific Raman Microscope XPLora equipped with three diode lasers (532 nm/25 mW; 638 nm/24 mW; 785/90 mW). In this study, only the SERS spectra recorded with the optimum laser line for each colourant are shown. The analysis was carried out with the 100× (Raman) and 50× (SERS) microscope objectives, a holographic grating with 1200 lines/mm, laser power filters between 0.1 and 10%, and an acquisition time of 10 to 60 s at 1 to 5 accumulations. The particle size distribution of each silver colloid solution (1:9 dilution with ultrapure water) was tested using a UV–Vis spectrometer (SPECORD® Plus Analytikjena).

2.3. Synthesis of the silver colloids

Two different SERS substrates were prepared according to the Lee and Meisel procedure [30] and to the Leopold and Lendl method [31].

To prepare the **Lee and Meisel** colloid (LMC), 18 mg of silver nitrate was added to 100 ml of Milli-Q water in an Erlenmeyer flask. The solution was heated to the boiling point, and then 2 ml of 1% trisodium citrate was added under vigorous magnetic stirring. The solution was held at the boiling point for 60 min with continuous stirring. The resulting colloid had a grey-milky colour. The Erlenmeyer flask was wrapped in aluminium foil, left to cool and then stored in a refrigerator at 4 °C in the dark. The procedure takes about 1 h and 30 min.

The **Leopold and Lendl** colloid (LLC) was prepared using 17 mg of silver nitrate dissolved in 10 ml of Milli-Q water. 100 ml of 11.6 mg $NH_2OH \cdot HCl$ solution containing 3.3 ml of NaOH (0.1 M) was divided into 9 ml batches in centrifuge tubes. 1 ml of silver nitrate was added rapidly to each centrifuge tube, which was then inverted to complete the mixing. The resulting colloid had a yellow-orange colour. The procedure takes 40 min or less.

A 1 ml aliquot of each colloid was centrifuged for 5 min at 5000 rpm in a Hettich EBA30 centrifuge, and then 950 μl of supernatant was removed and replaced with 150 μl of ultrapure water to concentrate the colloids and to remove excess reducing agent.

2.4. Sample pre-treatment

Before the analysis of Pigment Red 83 (alizarin lake), the powder was exposed to hydrofluoric acid (HF) vapour for 5 min in a closed micro-chamber. The pre-treatment procedure had been successfully applied by Pozzi et al. to improve the quality of the SERS spectra [38].