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A NEW INTEGRATED TLC/MU-ATR/SERS ADVANCED APPROACH FOR THE IDENTIFICATION OF TRACE AMOUNTS OF DYES IN MIXTURES

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A new integrated TLC/MU-ATR/SERS advanced approach for the identification of trace amounts of dyes in mixtures



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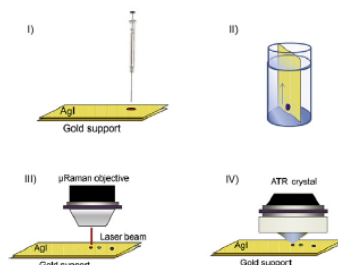
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HIGHLIGHTS

- An innovative TLC method coupled to enhanced vibrational techniques was developed.
- SERS and MU-ATR may be performed on the separated spots.
- New AgI@Au TLC plates are proposed.
- Enhanced spectra are obtained without the addition of a colloidal solution.
- The new analytical set up is promising for trace analyses.

GRAPHICAL ABSTRACT



ABSTRACT

The present research is focused on the setting up of an advanced analytical system for the detection of synthetic dyes. The system is based on the combination of an innovative thin layer chromatography (TLC) plate coupled with enhanced infrared (MU-ATR, metal underlayer attenuated total reflection) and Surface Enhanced Raman (SERS) spectroscopy. In particular, a TLC plate made of silver iodide (AgI) applied onto a gold coated glass slide (AgI@Au) is proposed as an efficient stationary phase for the separation of dyes mixtures. The separated dyes are then identified by means of both enhanced FTIR and SERS, performed directly on the same eluted spots. The use of a mid-IR transparent inorganic salt as stationary phase coupled with the underneath gold layer avoids spectral interferences, enhancing the signal obtained from ATR analyses. At the same time, SERS spectra can be recorded as the TLC plate may act as a SERS active substrate due to the photoreduction of AgI to metallic Ag caused by the exposure to the laser during the Raman analysis. Different mixtures of synthetic dyes of known composition, widely used in dyeing processes, have been tested and the method resulted to be effective in identifying trace amounts in the order of tens nanograms. Moreover, the method has been further evaluated on a real case study represented by dyes extracted from dyed wool.

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1. Introduction

Despite the remarkable progresses achieved in the last decades by analytical studies, the characterization of organic dyes still represents a challenging task. Due to their high tinting strength,

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dyes are present in very low concentrations and are usually embedded into multicomponent matrices (such as: paints, textiles, or inks). Nevertheless, their unambiguous and sensitive identification is of outmost importance in forensic studies, food quality controls as well as provenance, dating and authentication studies of art samples [1,2].

When dyes mixtures have to be analyzed, high performance liquid chromatography (HPLC) is probably the analytical technique that provides more information [3,4]. Recently, the sample amount needed for analysis has been largely reduced thanks to the development of advanced methods based on the use of ultra performance liquid chromatography systems coupled with mass-mass (MS/MS) detection [5] or to LC/LC set ups [6].

Nevertheless, the analysis of dyes by means of spectroscopic techniques may complement the above mentioned analyses, as they are versatile in identifying both the organic and the inorganic materials constituting multicomponent samples and are widely available in many conservation/restoration laboratories.

Surface Enhanced Raman Scattering (SERS) microscopy has become increasingly popular and it is, nowadays, a powerful and well established technique for the sensitive molecular detection and identification of dyes on very limited amount of samples (0.1–0.5 mg) [7–9] as well as by means of in-situ set ups [10–12]. On the other hand, infrared microscopy (FTIR) has been sporadically applied to the identification of dyes on dyed samples. In fact, interferences arising from the sample matrices, which may totally hinder the absorption bands of the colorant [13] represent a great analytical limitation. The use of enhanced FTIR methods [13,14], allowing the detection of dyes in micro-extracts, have been proposed in order to overcome this limitation. In particular, Metal Underlayer ATR spectroscopy (MU-ATR) has been proposed for the analyses of few nano-grams of dyes spotted on a gold-coated glass slide [14]. In fact, it has been shown that when the analyte is applied on a gold-coated glass slide and has a thickness larger than monolayers but thinner than the wavelength (i.e. in the order of hundred nanometers), enhanced dyes' spectra can be recorded [14].

When single dyes present in a mixture have to be analyzed, the integrated use of thin layer chromatography (TLC) and SERS has been proposed. In particular, SERS analyses can be performed onto the eluted TLC spots by adding an aliquot of a colloidal solution. This method has been widely applied for instance to the environmental [15], food [16], medical [17] and conservation fields [18–20].

However, the routinely application of this method has some drawbacks due to the partial solubilization that the applied colloidal solution can cause on dye spots located in adjacent positions. In order to overcome this limitation, Ag inkjet-printed SERS papers [21] and silver nanorod arrays fabricated by oblique angle deposition on glass [22] have been proposed.

It is worth mentioning that because of the strong infrared absorption signals of both conventional TLC silica plates and SERS active substrates, FTIR analyses cannot be performed on these type of plates [23]. Therefore, TLC/FTIR set ups have been usually performed by using the transfer approach [24,25], a time consuming procedure which exposes the analytes to the risk of sample loss and contamination. In an attempt to avoid drawbacks related to the strong background absorptions in the mid-IR range (400–4000 cm^{-1}) shown by the traditional TLC stationary phases (such as silica and alumina), AgI has been recently proposed for the setup of narrowband TLC plates [26,27].

The aim of this research is to propose for the first time a new TLC plate that allows the analysis of trace amounts of dyes present in mixture by means of the integrated use of enhanced Raman (SERS) and enhanced FTIR spectroscopy (Mu-ATR), obtaining complementary results and overcoming the previous observed limitations

in terms of contamination and sensitivity. A thin layer of AgI deposited on a gold coated glass slide (AgI@Au) has been used as stationary phase. AgI has been chosen because, as previously reported [26], it allows the rinse of organic solvents by capillarity and it is transparent in the mid IR. Moreover, SERS spectra can be obtained on the same eluted spots, exploiting the AgI photo reactivity. Indeed, silver halides can absorb the incident light, generating electrons in the conduction band (CB) and holes in the valence band (VB). Then, the photo-generated electrons in the CB are captured by surface lattice Ag^+ ions to form metallic Ag^n clusters, whereas photo-generated holes in the VB oxidize lattice anions X^- to X_2 , which is released as a consequence [28]. A photo-induced self-stability mechanism has also been demonstrated for AgX compounds. Irradiated AgX nanoparticles are transformed into a stable Ag/AgX hybrid nanocomposite after early in situ formation of surface Ag^0 [29–31]. Significantly, hybrid Ag/AgX-based nanomaterials proved to be able to support localized surface plasmons upon exposure to visible light [28,32–36]. Concerning the elucidation of the enhancement mechanism, previous researches carried out on different silver halides derivatives underlined that laser irradiation produces photolytic silver particles, which play a key role in the generation of SERS effects [34,35]. On the other hand, SERS amplification is also promoted by the formation of complexes with the Ag⁺ ions formed on the silver halides nanoparticles [33].

The novel TLC based analytical protocol illustrated in this paper presents several advantages with respect to already published methods. In particular, the integrated use of two complementary enhanced techniques can be applied after the separation of mixtures of analytes, without the addition of any colloidal solution. In this way, the complementary information obtained by MU-ATR and SERS analyses may allow to better characterize the mixture's components, achieving very low detection limits thanks to the spectral enhancement.

Performances of the new TLC active plates were tested for the characterization of different mixtures of synthetic dyes and validated on a micro extract obtained on less than 0,01 mg of wool, died with a mixture of dyes. The choice of such analytes is strictly related to the important role they have been playing in industrial applications and in the forensic field [9,37]. Actually, since the half of 19th century, they have been widely used in dyeing processes.

2. Experimental section

2.1. Materials

Silver nitrate (AgNO_3), potassium iodide (KI), trisodium citrate dihydrate and all the analyzed dyes (see Table 1) were purchased from Sigma Aldrich. Gold coated glass slides (Au 200 nm thick) were acquired from Thermo Fisher Scientific. AgI particles were filtered using Whatman filter papers with a diameter of 125 mm and a particle retention <2 μm . HPTLC were performed using nanosilica plates purchased by Fluka with layer thickness of 0.2 mm and medium pore diameter of 60 Å. The citrate silver colloid paste was prepared following the standard procedure for the characterization of organic dyes in historical samples [18,38].

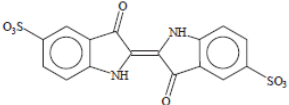
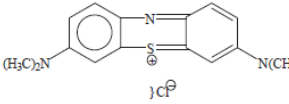
2.2. Instrumentation

FTIR ATR analyses were performed by using a Thermo Nicolet iNTM10MX microscope, fitted with an MCT detector cooled by liquid nitrogen. Spectra were recorded in the range 4000–675 cm^{-1} with an optical aperture of 200 × 200 μm , using a spectral resolution of 4 cm^{-1} and 128 scans. Raman spectra were collected with a Bruker Senterra microscope equipped with a charge coupled device (CCD) detector and using an excitation source emitting at 785 nm, with a

Table 1
Synthetic dyes submitted to the spectroscopic analysis.

Name	C.I. index	Code	Dye class	Chemical Structure
Diamond Green	42040	BG1	Triarylmethane	
Methyl violet	42535	BV1	Triarylmethane	
Crystal violet	42555	BV3	Triarylmethane	
Rhodamine B	45170	BV10	Xanthene	
Rhodamine 6G	45160	BR1	Xanthene	
Eosin A	45380	AR87	Xanthene	
Martius yellow	10315	AY2	Nitro	
Cochineal red A	16255	AR18	Azo	
Fast red AV	15620	AR88	Azo	

Table 1 (continued)

Name	C.I. index	Code	Dye class	Chemical Structure
Indigo carmine,	73015	AB74	Indigoid	
Methylene blue	52015	BB9	Thiazine	

power of about 10 mW. All the spectra were acquired with a single integration time of 3 s, focusing on the dyes dried spots with an Olympus 20× microscope objective. The scanning electron microscopy (SEM) images were obtained with a Quanta Inspect S FEI instrument operating at 25 keV with a tungsten filament current 100 μ A for the acquisition of the secondary electrons (SE) images. The instrument was equipped with an Edax Phillips New XL30 spectrometer. Energy dispersive XRay microanalysis was performed at 25 keV with 100 s of lifetime, within an area of 25 \times 25 μ m. Xray powder diffraction patterns were recorded on a PanAnalytical X'Pert Pro equipped with an X'Celetorator detector powder diffractometer using Cu K α radiation generated at 40 kV and 40 mA. The diffraction patterns were collected within the 2 θ range from 20° to 60° with a step size (Δ 2 θ) of 0.05° and a counting time of 150 s.

AFM images were obtained on the AgI layer applied on gold, by using a Digital NanoScope IIIa Multimode (Veeco, USA) operating in tapping mode with (n) doped Si probes (spring constant, 20–80 Nm⁻¹; resonance frequency, 200–400 kHz; nominal tip radius, < 10 nm).

2.3. AgI synthesis and deposition method

0.1 M aqueous solution of AgNO₃ and KI were cooled at 4 °C for 30 min. Then AgNO₃ solution was added to the KI solution and the mixture was kept at 4 °C for 1 h. Subsequently the obtained yellowish solution was maintained at room temperature for 50 min. The filtration was performed under vacuum created by a water pump and the precipitate was rinsed with ultrapure water to remove precursor reagents. The powder was subsequently dried in an oven at 40 °C for 15 min. Afterwards, 0.100 gr of AgI was suspended in 7 ml of isopropanol and sonicated for 30 min in an ultrasonic bath. Then, 1 ml of the obtained supernatant suspension was applied on a gold slide by drop casting deposition and dried in an isopropanol saturated chamber for 24 h. All the preparation steps as well as the experiments were carried out in the dark.

2.4. TLC analysis

Dyes solutions and mixtures (0.5 μ L at the concentration of 10⁻⁴ M) were spotted on the AgI@Au TLC plates near to the edge of the substrate by using a Hamilton syringe. Chromatographic separation was performed using as eluent a mixture of ethanol and ammonia 9:1 v/v.

2.5. Wool dyeing and extraction method

An historical recipe reported in the sample book developed by Adolf Lehne in 1893 [39] was followed for the dyeing process. Briefly, 1 mg of raw clean wool was immersed for 30 min in the dyeing bath prepared with 5 ml solution of BG1, BB9 and BV10 in ultrapure

water (with a final concentration of 10⁻⁴ M each) and warmed up to 70 °C. Then, after a slow cooling down at room temperature, dyed fibers were rinsed with ultrapure water to remove any unbound dye component and dried in oven at 40 °C for 20 min.

The extraction procedure was performed with methanol on less than 0.01 mg of the dyed wool (corresponding to few mm in length of a single fiber) following an ad hoc developed procedure for analysis of synthetic dyes [13]. Subsequently, 0.5 μ L of the extracted solution was applied on AgI@Au TLC plate for the chromatographic analysis.

3. Results and discussion

3.1. Characterization of the AgI@Au TLC plates

Synthesis and deposition of the AgI were set up in an attempt to optimise the film homogeneity, the chromatographic separation and the signal enhancement. Moreover, the synthesis was performed without the addition of stabilizers [40], which could be responsible of spurious signals in the IR and Raman spectra.

The crystalline properties of the synthesized AgI powder were characterized by XRD analyses (Fig. SI 1). Results showed the presence of γ AgI cubic crystal phase (JCPDS Card No: 090399) characterized by the presence of Bragg diffraction peaks centered at 2 θ = 23.7, 39.1 and 46.3 that corresponded to (111), (220) and (311) planes, respectively. Moreover, diffraction peaks at 2 θ = 22.3 and 25.3, ascribable to the β AgI hexagonal phase and corresponding to (100) and (101) planes (JCPDS Card No: 01-078-1614) were also identified. All these features are consistent with scientific literature [41,42].

UV/Vis spectra of AgI suspensions collected from the synthesized powder showed characteristic features in the visible and near UV spectral region. The absorption edge is extended to about 450 nm (Fig. SI 2), which is consistent with what is reported in literature [43] and corresponds to the direct band gap excitation (W1,2), responsible for the yellow color of the material.

The deposition of AgI on gold coated glass slides was performed by drop casting, after prolonged sonication of an AgI suspension in isopropanol. Afterwards, the AgI@Au system was kept in an isopropanol saturated chamber for 24 h, to assure a slow and uniform evaporation of the solvent. Morphology and microstructure of AgI thin films were investigated by SEM and AFM. Secondary electron (SE) images showed that irregular spheroidal aggregates of AgI were present with different sizes (Fig. 1a) ranging from 100 to 900 nm. Statistically, the most frequent AgI aggregates size is centered between 200 and 300 nm (Fig. 1b).

By means of AFM it has been possible to observe an average particle diameter ranging from 6.5 nm to 24 nm (Fig. 1c). In addition, AFM analyses allowed also estimating the thickness of the AgI layer, which resulted to have an average value of 2 μ m.

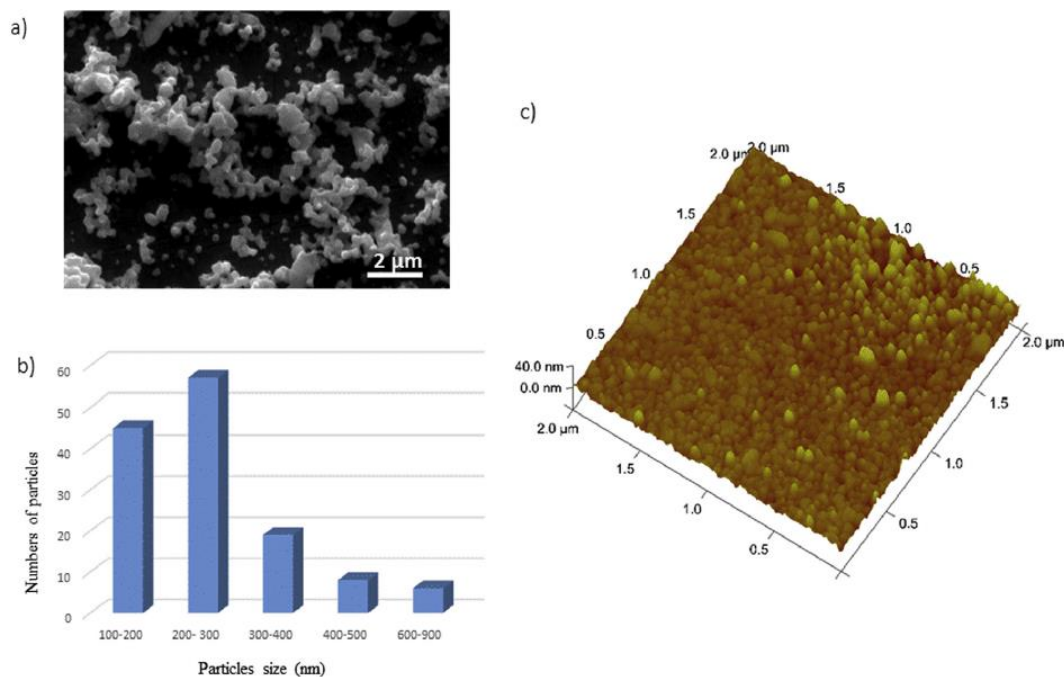


Fig. 1. a) SE image of AgI particles deposited on an Au substrate; b) Particles size distribution histogram; c) AFM image of AgI particles deposited on an Au substrate.

3.2. Enhanced FTIR and Raman analyses on AgI@Au

A preliminary study was performed to evaluate the possibility to use AgI@Au as a MU-ATR and SERS active substrate on a selection of 11 basic and acid dyes.

In an attempt to verify the possible influence of AgI on intensity, shape and position of the absorption bands, analyses were carried on both AgI coated and uncoated gold substrates. After the deposition of 0.5 μL 10⁻⁴ M of the dye solutions on the gold coated glass slides a differential evaporation rate occurs across the drop [44], which is responsible of the accumulation of the dye along the drop borders (the so called “coffee ring” effects). Such effect was less notable on the AgI@Au plates, ensuring a more homogeneous distribution of the dye (Fig. 2b). Therefore, a key role played by AgI in the water evaporation rate can be inferred.

ATR spectra recorded on both AgI@Au and Au plates present similar features, with just some slight differences in the relative intensity of the bands (see Fig. 2a BG1 spectra as example and SI Table 1, which reports a tentative assignment of absorption bands for all the investigated dyes).

In order to estimate the influence of AgI in the enhancement of the FTIR spectra, the average peak areas of some characteristic bands of BG1 have been calculated and reported in Fig. 2c. It can be noted that absorption signals are of the same order of magnitude, even if spectra recorded on AgI are slightly less intense. This evidence can be related with the distribution of the dye, which is not concentrated on the ring of the drop, but homogeneously distributed in the circular area formed after solvent evaporation. Nevertheless, the observed slight signal reduction is acceptable and it can be said that MU-ATR enhancement of spectra can be obtained also by using AgI@Au plates thanks to the transparency of AgI and the limited thickness of the deposition. In a previous paper we showed that the enhancement effect observed in MU-ATR was 20–80 times greater than that achievable with transfectance and allowed to reach a limit of dye detection of few ng [14].

It is known from scientific literature that AgI has been used as a SERS provider [36]. To verify its effectiveness, all the investigated dyes were analyzed on the AgI@Au plates (SI Table 2 reports the spectra of all the analyzed dyes as well as a tentative bands assignment).

Fig. 3 reports the Raman spectra collected from a 0.5 μL solution of BG1 10⁻⁴ M spotted on different supports (AgI@Au, AgI@SiO₂, Au). Sensible enhancement of the vibrational features are achieved analysing the dye spotted on the AgI@Au plates (Fig. 3a). The calculation of the enhancement factor represents a challenging task when solid substrates are used as SERS providers. In an attempt to provide a tentative evaluation of the enhancement effects, the average peak areas of some specific BG1 bands have been measured and reported in Fig. 3b. The average enhancement factors (intended as ratio of the average peaks areas) are in the order of 150–300 with a preferential enhancement observed for low wavenumber spectral bands. When SERS analyses are performed, a detection limit is hard to define. Indeed the signal amplification depends on the contact between the analyte and the SERS substrate, which may even improve decreasing the analyte concentration. However, the experimental data showed that when 20 ng of BG1 are spotted on an Au support very noisy spectra are recorded while, when the same amount is spotted on AgI@Au, the dye can be easily identified. To compare the method with procedures already published, SERS spectra were recorded analysing the same amount of dye spotted on a HPTLC nano silica plate (the same plates will be used as comparison in par. 3.3.1) after the addition of a silver colloidal paste prepared as reported in Ref. [18]. Differently from what obtained on glass slides, the addition of the colloidal paste allowed identifying weak features of BG1 (Fig. 3c). However, a clear identification can be obtained when 200 ng of BG1 were analyzed at the presence of the Ag colloidal paste (Fig. 3c), but the resulting signals were weaker than what obtained on 20 ng of BG1 spotted on AgI@Au, thus confirming that the new support is promising if compared to already published systems.

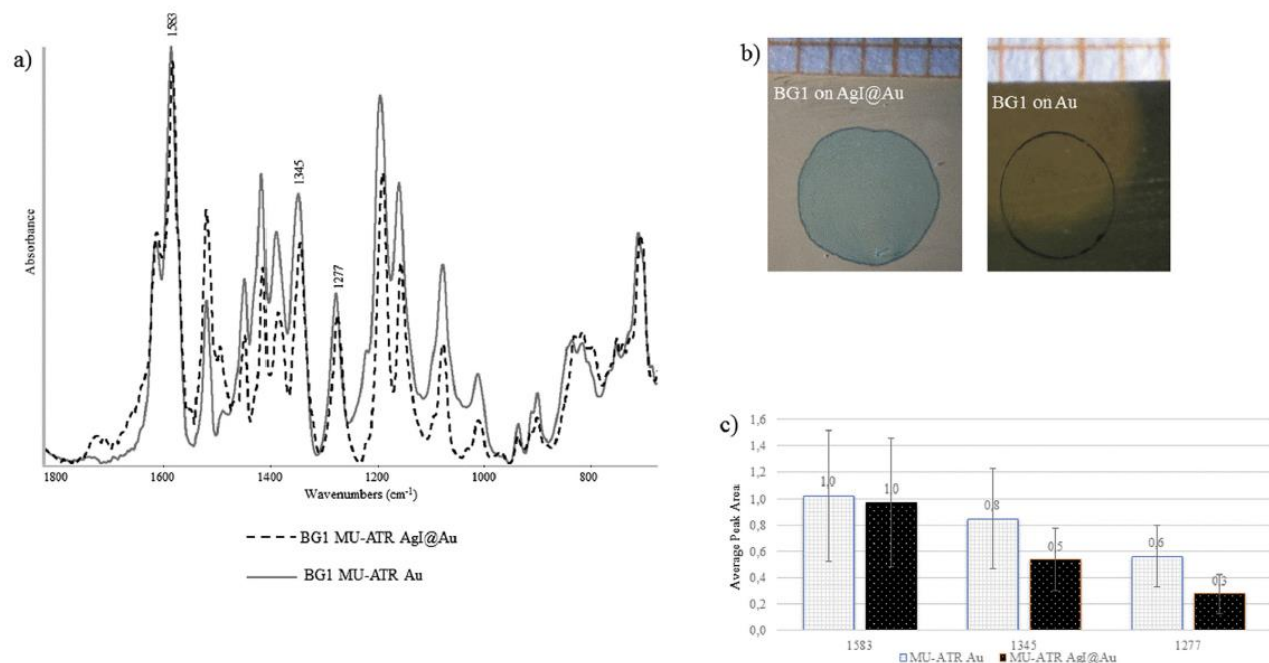


Fig. 2. a) MU-ATR spectra of BG1 10^{-4} M solution acquired on an AgI@Au plate and on a gold coated glass slide; b) BG1 applied on an AgI@Au plate and on a gold coated glass slide (Au) after solvent evaporation; c) Average peak areas of some characteristic IR bands of BG1 10^{-4} M solution acquired on an AgI@Au plate and on a gold coated glass slides.

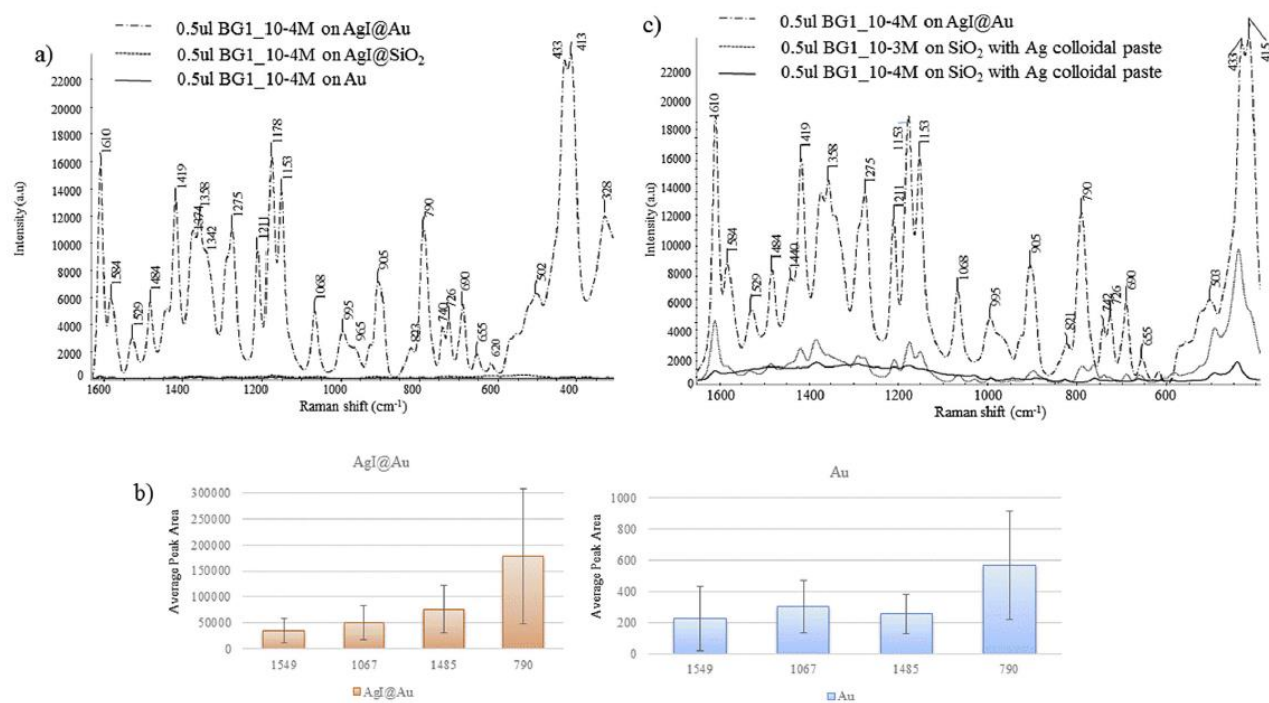


Fig. 3. a) Raman spectra of BG1 10^{-4} M solution acquired on AgI@Au, AgI@SiO₂ and Au b) Average peak areas of some characteristic Raman bands of BG1 10^{-4} M solution acquired on an AgI@Au plate and on a gold coated glass slide c) Raman spectra of BG1 10^{-4} M solution acquired on AgI@Au compared to SERS spectra of BG1 10^{-4} M and 10^{-3} M solutions acquired on HPTLC nano silica plates after the addition of a silver colloidal paste.

In order to verify if the SERS effect was a result of the local field enhancement of the photolytic silver particles (Ag⁰) produced in situ by the laser beam [33,34,45], SEM observations were

systematically carried out on the AgI@Au plates before and after the laser irradiation. Interestingly, it was evident that the laser irradiation of the AgI@Au plates converted the originally smooth surfaces

of aggregates in nano-rough substrates (Fig. 4). Moreover, the nanoparticles produced after laser irradiation had the same morphology of nanoparticles identified as silver nanoparticles (AgNPs) obtained by laser treatment of silver salts in already published papers [34,46–48].

To better elucidate the possible role played by the gold underlayer in spectral enhancement, Raman spectra of dyes were recorded on AgI film deposited directly on glass slides (AgI@SiO₂). Interestingly, in this case by applying the same experimental conditions used for the analyses on AgI@Au substrates it has not been possible to detect the same amplified signal (Fig. 3a). SEM morphological observations of AgI@SiO₂ showed that the creation of new small particles on the surface was still detectable after the laser treatment, but the amount of them and the general changes in cluster morphology appeared considerably more limited (SI Fig. 3) if compared with the effect obtained on AgI@Au substrates. These outcomes highlight the crucial role played by the gold support in the photoreduction of AgI as well as in the electromagnetic properties of the system.

3.3. TLC separation coupled to enhanced FTIR and Raman analyses on AgI@Au

3.3.1. Set up of the TLC/MU-ATR/SERS integrated analytical method on standard solutions

TLC tests have been performed on a selection of dyes. The first solution (dye mixture A), characterized by a bright violet tonality, contained three different basic dyes (BV10, BG1 and BB9). Fig. 5a reports the separation obtained from 0.5 μ L of mixture A (with a final concentration of 10⁻⁴ M for each dye) with an eluent composed by ethanol (EtOH) and ammonium hydroxyde (NH₃) 9:1 v/v. The eluent allowed the separation of the three dye components without any overlapping among them. Moreover, the short distance ran by the eluent front allowed a limited dilution and diffusion of the dyes on the TLC plate, assuring a higher intensity of the spectroscopic related signals (MU-ATR and SERS spectra are reported in SI Fig. 4).

The same eluent was tested on mixture B (Fig. 5b) containing acid and basic dyes [AR87 (xanthene dye) AR18 (azo dye) and BV1 (triarylmethane dye)]. Analogous good performances in terms of selectivity have been achieved with this chromatographic system

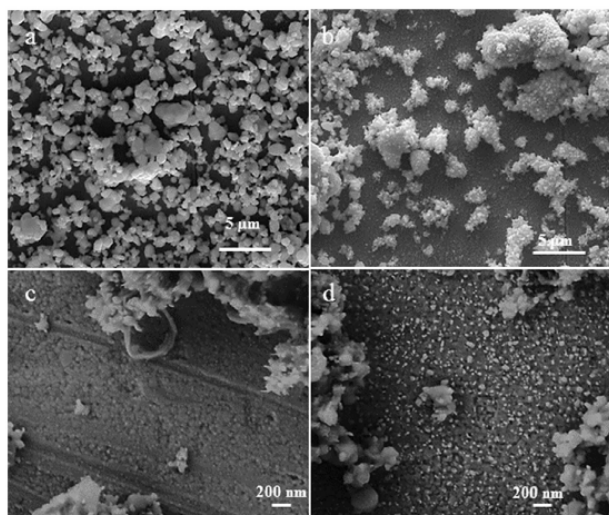


Fig. 4. SEM images of AgI@Au substrate before (a, c) and after (b, d) laser irradiation.

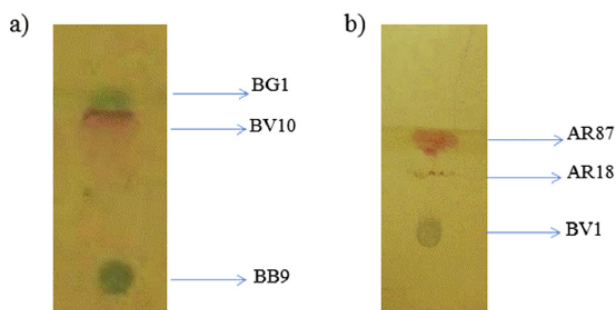


Fig. 5. a) Dye mixture A and b) Dye mixture B after TLC development on AgI@Au plates.

(Fig. 5b).

All six analytes have been identified by their spectral fingerprints, which were still well recognizable in both the enhanced Raman and FTIR spectra (SI Figure 4 and SI Table 1).

Mixture A was analyzed by SERS after the separation on HPTLC nano silica plates to compare the AgI@Au method with a TLC-SERS method already reported in literature [7]. To this purpose, few microliters of citrate reduced silver colloidal paste were applied on the eluted dye spots in order to ensure the collection of the SERS signals. Difficulties were incurred both in the identification of the proper area within the dye spot (due to the hampering effect of the colloid) as well as in the collection of data. Indeed, to assure the acquisition of an enhanced spectrum, Raman spectra should be collected before the complete drying of the colloidal paste. Moreover, the deposition of the colloidal paste on the eluted spots may lead to contamination effects as well as may affect results reproducibility. Because of all these drawbacks, only the dye BB9 (data not shown) was identified on the HPTLC plates. In addition, it has not been possible to analyse the spots eluted on nano silica HPTLC plates by means of FTIR microscopy.

3.3.2. Validation of the TLC/MU-ATR/SERS integrated analytical method on micro extracts from died wool

The validation of the advanced AgI@Au TLC substrate was performed on dyes extracted from dyed wool fibers. This methods can be of great interest when low amount of sample is available, as it occurs in forensic science and cultural heritage materials. A few fibers of wool, dyed with the mixture A, were submitted to an ad hoc mild extraction method based on the use of less than 0.01 mg of sample [13]. The extracted solution was applied on the AgI@Au TLC plate and the dyes eluted. Raman and FTIR enhanced spectroscopic measurements were then performed directly onto the three eluted spots. Both techniques succeeded in the identification of the dye mixture components as it can be seen by comparing spectra reported in Fig. 6 with the reference spectra reported in SI figure 4 and in tables SI-1 and SI-2. MU-ATR spectra acquired above the BB9 spots (Fig. SI 5) showed the typical absorption bands at 1578 and 1540 cm^{-1} of carboxylates. The presence of these compounds is justified because, before dyeing, the virgin wool was subjected to a washing treatment carried out at 40 $^{\circ}$ C by means of Marseille soap. Therefore, it can be said that the integrated use of TLC and enhanced vibrational techniques allowed both the identification of all the three dyes and additional information about the overall dyeing procedure.

4. Conclusions

The present research deals with the setting up of a new

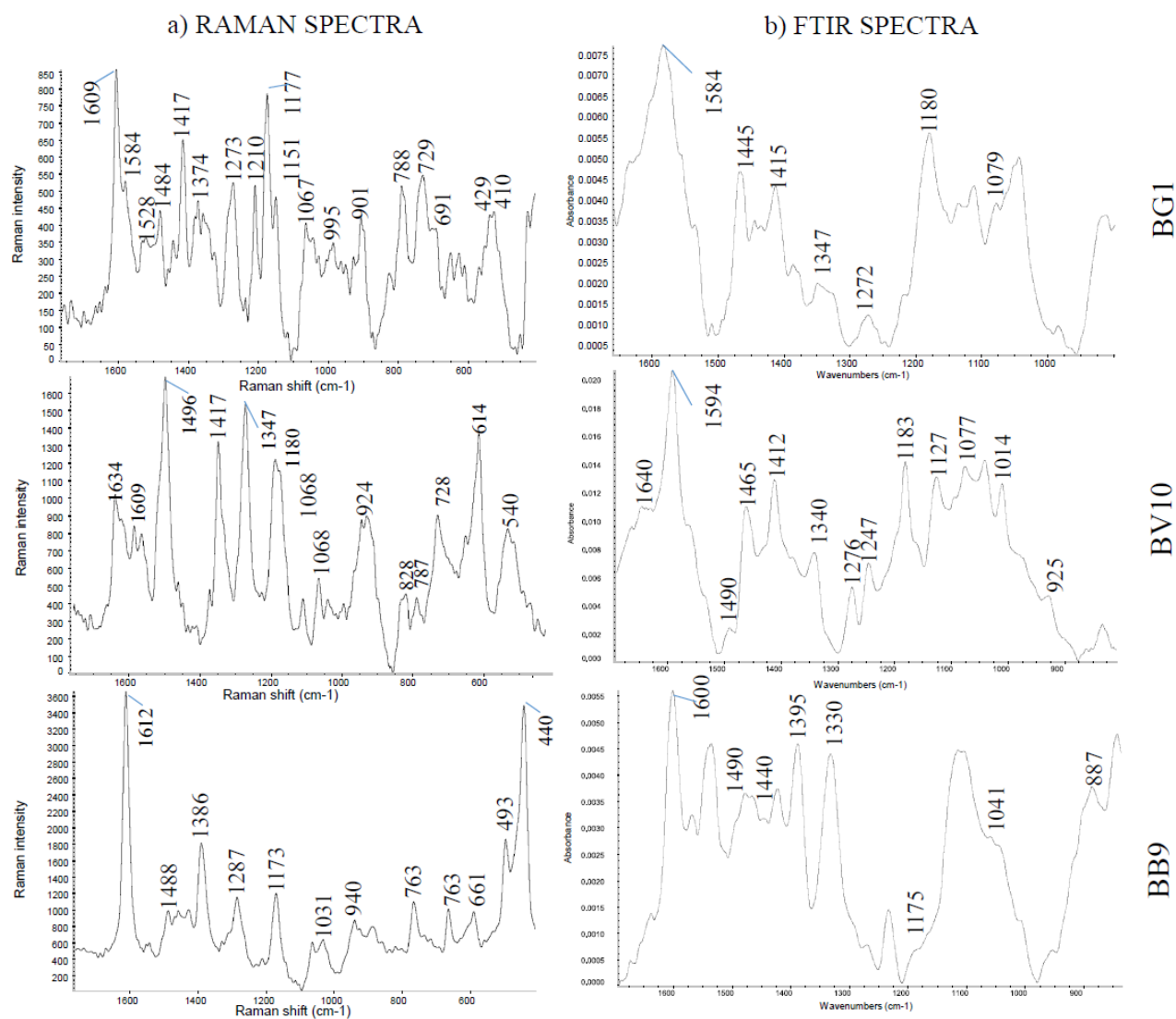


Fig. 6. a) SERS and b) MU-ATR spectra recorded on dyes spots after TLC development of the extracted sample on an AgI@Au plate.

analytical method that couples the chromatographic separation of dyes mixtures by means of a newly developed AgI@Au TLC plate and the chemical characterization of the eluted dye spots with enhanced spectroscopic techniques (MU-ATR and SERS). Trace amount of dyes can be analyzed with this method, thus exploiting the complementary information obtained from Raman and infrared enhanced spectra. In particular, MU-ATR spectra can be recorded directly on the eluted dye spots, thanks to the transparency of AgI in the mid infrared region and the presence of the reflective gold underlayer. AgI@Au plates can also be used as SERS active substrate thanks to the photoreduction properties of the silver salt, which is observed only when AgI is deposited on gold glass slides. Thus, AgI@Au plates allowed to obtain SERS spectra without the addition of a colloidal solution but just exploiting the laser exposure effect, with the advantage of avoiding contamination between the eluted spots. It is worth mentioning the fact that this new system can compete with the traditional TLC approaches coupled to the already available spectroscopic detection. Finally, this new method can find promising applications in all those scientific fields where

trace analysis of dyes is requested, such as in the forensic and conservation science fields.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.aca.2017.08.020>.

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