Chemical composition of felt-tip pen inks

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Abstract

Inks are frequently used by modern artists for the realization of sketches, drawings, architectural projects and other technical designs. The formulations of these inks are usually rather complex and may be associated to those of modern paint materials where, next to the binding medium and pigments/dyes, solvents, fillers, emulsifiers, antioxidants, plasticizers, light stabilizers, biocides and so on, are commonly added. Felt-tip pen inks are extremely sensitive to degradation and especially exposure to light may cause chromatic changes and fading.

In this study we report on the complete chemical characterization of modern felt-tip pen inks that are commercially available and commonly used for the realization of artworks. Three brands of felt-tip pens (Faber-Castell, Edding and Stabilo) were investigated with complementary analytical techniques such as thin-layer chromatography (TLC), VIS-reflectance spectroscopy, µ-Raman spectroscopy, surface enhanced Raman spectroscopy (SERS), pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS), GC-MS, and Fourier Transform infrared (FTIR) spectroscopy. The use of TLC proved to be very powerful in the study of complex mixtures of synthetic dyes. First derivatives of the reflectance spectra acquired on the TLC spots were useful in the preliminary identification of the dye, followed by Raman spectroscopy and SERS which allowed for the unambiguous determination of the chemical composition of the pigments (phthalocyanines, dioxazine and azo) and dyes (azo, triarylmethanes, xanthenes). FTIR spectroscopy was used especially for the detection of additives, such as calcite or titanium oxide, as well as for confirming the nature of solvents and dyes/pigments. Finally, Py-GC-MS data provided information on the binders (styrene-acrylic resins, plant gums), solvents and additives, as well as on pigments and dyes.

Keywords: felt-tip pen ink, TLC, SERS, Py-GC-MS, FTIR, VIS-reflectance spectroscopy

Introduction

Over the last 50 year artists have been experimenting with new materials that are not specifically established for artistic purposes, insisting on aesthetic effects, availability and low costs with respect to durability. As a consequence, many contemporary paint materials have undergone drastic deterioration and change in appearance such as fading, discoloration and yellowing due to exposure to light [1–3], but the effects of aging are also enhanced by other factors such as humidity, microbial degradation, deposition of pollutants, etc. [4, 5]. Among these modern materials felt-tip pens are increasingly used for the realization of sketches, drawings, copies, and architectural designs and the rapid degradation of many ink drawings raised some of the most complex and yet still unresolved questions regarding the conservation of these very sensitive artworks. Indeed, the most commonly used felt-tip pen inks are based on organic dyes which are known to be extremely sensitive to light, particularly of the ultraviolet (UV) region, and, therefore, inks are classified as the most sensitive material stored in a museum. For this kind of material, the exposure parameters should not exceed 50 lux and the maximum UV radiance admitted is <0,05 µW-cm² [6]. Light exposure, especially to UV-B (315-280 nm) radiation, may cause photo-oxidation being responsible of discoloration, cracking, and other damage. Accelerated aging by irradiation is a common practice to clarify the photo-induced degradation mechanisms of materials used in works of art [7, 8].

The knowledge of the exact composition is the first and mandatory step to understand the chemical behavior over time, and hence for the development of correct conservation treatments and storage conditions in order to slow down the degradation processes.

Inks may have different formulations which are protected by patents, but they are generally colloidal systems of fine pigment/dye particles dispersed in aqueous or organic solvents. Nowadays, synthetic organic dyes and pigments dominate the colorant market and have almost completely replaced the traditional natural organic and inorganic materials obtained from plants, animal or mineral sources [9]. Several synthetic colorants were produced for only a few years and then withdrawn due to poor lightfastness or toxicity. Nonetheless, the ageing pathways of pigments and dyes are not completely understood, and until now the literature has focused mainly on the photochemical degradation of textile dyes [3, 10, 11], rather than on pigments employed in paint or ink formulations [2, 7, 8, 12, 13].

Modern inks, along with the pigment/dye, also contain additional ingredients, like resins, preservatives and wetting agents, collectively known as 'vehicle'. These include pH modifiers, humectants to retard premature drying, polymeric resins to impart binding and allied properties, defoamer/antifoaming agents to regulate foam efficiency, wetting agents such as surfactants to control surface properties, biocides to inhibit the fungal and bacterial growth, and thickeners or rheology modifiers to control ink application.

The first marker pen was patented by Lee Newman in 1910 but, it took technical advancements in dye chemistry as well as in nib and reservoir design to produce a more popularized felt-tip pen which was commercialized in 1953 by Rosenthal. The use of felt-tip markers, immediately after their introduction on the market, became commonplace for a variety of applications.

Although very few scientific works address this particular subject, some analytical studies of marker pens are devoted to the chemical characterization and degradation implications of current commercial marker pens and their up-to-date formulations [2, 14, 15]. Particularly, modern felt tip pens of four brands and two marker pen ‘historical’ drawings have been investigated using thin layer chromatography (TLC) coupled with Raman spectroscopy by Sodo *et al*. [14], while pyrolysis gas chromatography–mass spectrometry (Py-GC-MS) was employed for the characterization of the inks of several brands of permanent marker pens [15]. Recently, some water-based felt-tip pens were studied by the joint use of complementary analytical techniques, such as TLC, nuclear magnetic resonance, Fourier transformed infrared (FTIR) spectroscopy, X-ray fluorescence spectroscopy and Py-GC-MS [2, 16].

Indeed, the study of modern inks and paint materials requires the use of several analytical techniques. TLC has been used for decades to analyze and characterize writing ink formulations and is covered extensively in the published literature [17–19]. This technique can be very effective at resolving mixtures of dyes and some pigments found in complex samples and food products such as pen inks, vegetables pulps (e.g., chili sauce, curry paste), soft-alcoholic drinks, concentrated juices, cosmetics [20] as well as for quantifying dyes in complex samples [18]. TLC may be coupled with FTIR spectroscopy [21, 22], but more often it is used in combination with Raman spectroscopy [23]. This spectroscopic technique has been successfully used to investigate materials and degradation mechanisms in modern paint [14, 18, 24, 25], sometimes replaced by surface enhanced Raman spectroscopy (SERS) in order to reduce fluorescence and enhance sensitivity [26–30]. In recent years, several papers have reported on the use of SERS to identify organic, highly fluorescent dyes that are significant for artistic production [29, 31]. However, very few papers have focused on the identification of colorants in samples that contain two or more dye components. Whitney *et al*. described a proof of concept experiment which showed promising results as to the ability of SERS to identify components in solutions containing two dye components [32].

Numerous papers report on the application of FTIR spectroscopy to the characterization of modern paint materials. This technique is widely used to identify binders [2, 8, 33], pigments/dyes [34] and additives [35, 36].

However, as to the identification of organic binders and additives used in the field of cultural heritage, GC-MS is among the best suited techniques [37, 38]. In particular, the use of pyrolysis in combination with GC-MS proved to be a very powerful method for the characterization of synthetic paint binders [33, 39–42], antioxidants [43], plasticizers [44], organic pigments and dyes [33, 45–49].

Here, a thorough study of modern felt-tip pen inks that are commercially available and are commonly used for the realization of artworks was carried out with the purpose to define the optimal conservation treatment and/or storage conditions. A selection of modern felt-tip pen inks of three brands (Faber-Castell, Edding and Stabilo) was investigated. Particularly, the selected Faber-Castell felt-tip pens are used by a contemporary French artist, Anne Flore Cabanis.

In order to perform the identification of all ink components, a multi-analytical approach was used. First analytical TLC was performed in order to get an overview of the complexity of the colorants mixtures and to resolve the dyes and pigments. Reflectance spectra in the visible region were acquired on the ink film as well as on the TLC spots in order to discriminate different dyes. Notably, the application of VIS-reflectance spectroscopy in studying inks is not yet widely explored [16, 50].

Pigments and dyes present could then be identified with µ-Raman spectroscopy and SERS, directly on the silica plate, allowing to obtain good quality spectra from each dye or pigment present in the formulation.

Py-GC-MS was also employed thanks to of its high potential in analyzing complex mixtures, including synthetic materials, and to the very easy sample pretreatment, reducing time-consuming procedures into a single step [37, 47, 49]. In addition, GC-MS was used for the analysis of monosaccharides. FTIR spectroscopy was essential for the detection of inorganic additives as well for confirming the identification of solvents and dyes/pigments.

Since the identification of modern synthetic dyes may be difficult and reference literature is not always available, several standard dyes were also tested and analyzed with TLC, Py-GC-MS, SERS, FTIR spectroscopy and VIS-reflectance spectroscopy.

Experimental

Materials

Felt-tip pens and standard dyes--pigments

A selection of six PITT artist pens (Faber-Castell), nine felt-tip pens of the "68 series" (Stabilo) and three 1200 super color quality (Edding) inks was investigated (Table 1), covering a wide range of colors. The following standard pigments and dyes were also analyzed: Rhodamine G, BV1 (C.I. 42535), purchased from Lambda Physik (Goettingen, Germany), Acid Blue 9, AB9 (C.I. 42090), Acid Yellow 23, AY23 (C.I. 19140) purchased from Sigma-Aldrich (Milan, Italy) as well as the blue phthalocyanines (PB15:3, PB15:1, PB15:6) obtained from Kremer Pigmente GmbH & Co (Aichstetten, Germany).

Reagents

The following solvents were used for TLC: n-butanol (≥99.9%), ethanol (≥99.9%), ammonia (≥99.95%), chloroform (≥99.9%). Silver nitrate (99.9%), ascorbic acid (99.5%) and sodium chloride (≥99.9%) were used for the preparation and activation of nano-silver colloid. All were purchased from Sigma-Aldrich (Milan, Italy).

Other reagents and reference solutions were used for the GC-MS analysis of carbohydrates. D-(+)-galactose, l-(−)-fucose, l-(+)-arabinose, l-(−)-rhamnose, l-(−)-mannose, D-(+)-xylose, D-(+)-glucose, D-(+)-fructose, D-glucuronic acid, D-galacturonic acid monohydrate, mannitol (internal standard), all with purity 99%, sodium azide (NaN_3) (99.5%) and N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) were obtained from Sigma–Aldrich (Milan, Italy). Trifluoroacetic acid (99%), O-methoxylamine hydrochloride (98%) and anhydrous pyridine (99%) were purchased from Fluka (Milan, Italy). Two standard solutions of monosaccharides with concentrations of about 100 ppm were prepared in ultrapure water (18 MΩ x cm) and 1% sodium azide was added to prevent microbial growth. The first solution (MONO1) contained D-(+)-xylose, l-(−)-rhamnose, D-galacturonic acid monohydrate, D-(+)-glucose and D-(+)- fructose; the second one (MONO2) D-(+)-galactose, l-(−)-fucose, l-(+)-arabinose, l-(−)-mannose and D-glucuronic acid. The solutions were stored at 4°C. Arabic and tragacanth gums were purchased from Kremer Pigmente GmbH & Co (Aichstetten, Germany); cherry gum was collected directly from a cherry tree.

Methods

Thin layer chromatography

Analytical TLC was carried out on pre-coated aluminum foils with 0.2 mm thick silica gel (Supelco, Sigma Aldrich, Milan, Italy). The inks were directly applied on the foil. In addition, some of them, which exhibited a low separation tendency, were applied from a methanol (MeOH) solution with a capillary. Several solvent systems with different polar, non-polar, acid and basic behavior, were tested. For most inks the best results were obtained with a basic (butanol: ethanol: ammonia (2.5 M) (5:2:3 v/v)) system [2]; in some cases elution could only be obtained with pure chloroform. After elution, the Retention factor (Rf) value was calculated by measuring the location of each separation zone (dc) (distance from the origin of the plate to the center of the eluted spot) and the distance from the origin to the solvent front (ds). The Rf value is calculated from the dc/ds ratio.

μ- Raman spectroscopy

μ-Raman spectra were recorded with an Xplora (Horiba) spectrometer equipped with a YAG laser source with excitation wavelengths at 532 and 638 nm, a diode laser emitting at 785 nm, a triple grating (800 l/mm, 1200 l/mm and 1800 l/mm), an optical microscope (Olympus BX41) with four objectives (5x, 20x, 50x and 100x), and a charge-couple device detector (CCD) cooled to -65° C with a Peltier cooling system. Sample irradiation was accomplished using the 50× and 100× microscope objectives of the microscope. The exposure time, beam power and accumulations were selected to get sufficiently informative spectra. The laser spot size was adjusted between 1 and 3 μm. The wavelength scale was calibrated using a Si (111) standard (520.5 cm^{-1}). Inks were directly analyzed on a glass slide as well as on silica-gel foil after TLC separation in the spectral range of 200-1800 cm^{-1}. Identification of compounds was performed by comparison with literature data and spectral data of standard dyes/pigments.

VIS-Reflectance spectroscopy

Colorimetric measurements and reflectance spectra of the felt-tip pen inks were acquired with a Konica-Minolta CM-2600d. The Faber-Castell inks were analyzed on filter paper, (Whatman® Schleicher & Schuell, Ø 100 mm), while the Stabilo and Edding inks were analyzed both on paper and on TLC foil after elution. The experimental conditions are related to the Normal Recommendation 43/93 (“Colorimetric measurements of opaque surface”) and were as follows: spectral range 400-700 nm; lighting geometry and observation d/8; lighting source CIE C; observation angle 10°; reference system CIE L*a*b* color space; UV radiation contribution not considered; acquisition mode SCI; spot diameter 3 mm.

Surface enhanced Raman spectroscopy

Surface enhanced Raman spectroscopy (SERS) measurements were carried out utilizing silver colloids. Silver nanoparticles were prepared by a modification of the synthesis reported by Lee et al. [51]. Nanoparticles were obtained with 500 mL of a 0.018 % (m/v) solution of silver nitrate in ultrapure water (18 MΩxcm). The system was heated until the boiling point of water for an hour. Then, 100 mL of a 0.6% (m/v) solution of ascorbic acid were added to reduce Ag^+ to Ag^0. A solution of sodium chloride 0.4 M was used as activating solution. The colloid showed an absorption maximum at 435 nm and FWHM of 160 nm, as measured with a Shimadzu UV-1601 UV–Vis spectrometer (following a 1:3 dilution with ultrapure water to observe maximum absorbance within the instrumental range). SERS measurements were carried out by adding 3μL of colloid directly onto the TLC spots where spectra could be obtained between 2 and 10 min with laser excitation at 785 and 532 nm which remained constant in quality until the evaporation of the liquid. SERS spectra were recorded with an Xplora (Horiba) spectrometer (see *Raman spectroscopy*).

Pyrolysis - gas chromatography - mass spectrometry

The pyrolysis experiments were carried out with a microfurnace pyrolyser injection system Pyrojector II (SGE, USA). Small amounts (< 50 μg) of sample were inserted into a quartz tube (4 cm × 0.53 mm) which was then introduced into the microfurnace operating at a temperature (T_{Py}) of 550 °C and at a pressure of 15.0 psi. One of the ink samples (AFC129) was also analysed at T_{Py} = 700°C. The pyrolysis chamber was directly connected to the injection port (T = 280 °C) of a Perkin Elmer Clarus 680 chromatograph coupled with a Perkin Elmer Clarus SQ8T single quadrupole mass spectrometer. The MS transfer line temperature was 260 °C, and the MS ion source temperature was kept at 250 °C. The mass spectrometer was operating in the EI positive mode (70 eV) with a scan range of 45–400 *m/z*. For the gas-chromatographic separation, a 5% diphenyl–95% dimethyl polysiloxane column (Perkin Elmer Elite-5MS; 30 m × 0.25 mm i.d., 0.25 μm film thickness) was used. The injector was operated in split mode varying between 1:10 and 1:50. The column oven temperature program was 40 °C (4 min hold) to 250 °C at a heating rate of 10 °C/min (7 min hold). The carrier gas (He) was used in constant pressure mode at 10.0 psi. Data were analysed with TurboMass Ver 6.1.0 (Perkin Elmer) and AMDIS software. Identification of compounds was performed by NIST11 MS library search and comparison with literature data.

Gas chromatography - mass spectrometry

GC-MS was performed in order to characterize the carbohydrates. Therefore, standard solutions (MONO1, MONO2), and some felt-tip marker pen inks were subjected to an analytical procedure, which is a combination of two protocols in use at the Getty Conservation Institute (Los Angeles, USA) and the Department of Chemistry and Industrial Chemistry of the University of Pisa (Italy) (Lluveras, 2012).

Samples were weighed on the ultramicrobalance in a conical reaction vial and a solution of mannitol as internal standard was added to give a final concentration of 20 ppm in the injection volume. An aliquot of 100 µl of 1.2 M trifluoroacetic acid (TFA) (99%) was added, oxygen was evacuated under a stream of nitrogen for 30 s and hydrolysis was performed in the closed vials at 125°C for 1 h. After hydroysis the vial was left to stand until cool. Then 50 µl of a solution of O-methoxylamine hydrochloride (98%) in pyridine (99%) (100 mg/ ml) were added and the vial was heated at 70°C for 20 min. It was left to stand until cool and 50 µl of N,O-Bis(trimethylsilyl) trifluoroacetamide (BSTFA) were added and the vial was kept at 30°C for 45 min. An aliquot of 1 µl of the solution was injected (T injection port = 280 °C) and analysed with a Perkin Elmer Clarus 680 chromatograph coupled with a Perkin Elmer Clarus SQ8T single quadrupole mass spectrometer. The MS transfer line temperature was 290 °C, and the MS ion source temperature was kept at 250°C. The mass spectrometer was operating in the EI positive mode (70 eV) with a scan range of 40–650 m/z. For gas-chromatographic separation, a 5% diphenyl–95% dimethyl polysiloxane column (Perkin Elmer Elite-5MS; 30 m × 0.25 mm i.d., 0.25 µm film thickness) was used. The injector was operated in splitless mode. The column oven temperature program was 80 °C (1 min hold) to 170 °C at a heating rate of 2.5 °C/min (15 min hold), from 170°C to 280°C at a heating rate of 20°C/min (10 min hold). The carrier gas (He) was set in variable flow: 1.2 ml/min (30 min hold) to 0.8 ml/min at a rate of 0.4 ml/min (15 min hold) and to 1.2 ml/min at a rate of 0.4 ml/min until the end. The solvent delay was set at 10 min. Data were analysed with TurboMass Ver 6.1.0 (Perkin Elmer) and AMDIS software. Identification of compounds was performed with the NIST11 MS library search and comparison with standard monosaccharides.

Fourier transform infrared spectroscopy

FTIR spectroscopy was carried out with a BIORAD FTS6000 instrument, equipped with a KBr beamsplitter and DTGS detector. Ink films on aluminum foil were analyzed in variable angle reflectance (VAR) mode with a reflectance angle of 45°. Spectra were acquired in the middle infrared region (from 400 to 4000 cm-1), at a resolution of 4 cm^{-1} and by summing 64 scans.

Results and discussion

Faber-Castell felt-tip pen inks

Pigments and dyes

The reflectance spectra of the Faber-Castell inks applied on paper are reported in Fig. 1. TLC of the ink samples was attempted with various solvent systems. With most of these no elution and/or separation could be observed except for the green AFC264 and yellow AFC107 inks where elution with pure chloroform from the methanol ink solution proved to be effective. The yellow spots of the two inks exhibit very similar R_f values, pointing to the same pigment or dye. The green AFC264 ink was shown to contain a blue pigment or dye as well.

The yellow pigment was identified with Raman spectroscopy as the azo diarylide pigment PY81. The spectra of the azo pigments show some significant differences with respect to other classes of synthetic pigments, especially in the 1700-1100 cm^{-1} region. The Raman band at 1400 cm^{-1} is related to the azo N=N symmetric stretching vibrations of diazo molecules [52], whereas the absorption at 1288 cm^{-1}, characteristic of the C–C bridge between the phenyl groups [24], in combination with absorptions at 1250 and 1600 cm^{-1} related to amide III and aromatic ring vibration, are typical of diarylide pigments [53]. The absence of bands at 1334 and 264 cm^{-1} allows to distinguish PY81 from PY83 [54]

In the pyrograms of the yellow (AFC107) and green (AFC264) inks the presence of PY81 is testified by the following pyrolysis products: 3,4-dimethyl benzeneamine, 3,5-dimethylphenyl isocyanate [47] and 2,4,6-trimethyl-benzeneamine. The FTIR spectra of these two samples confirm the occurrence of PY81 [52].

The blue (AFC110 and AFC154) and green (AFC 264) inks were found to contain PB15:3, a blue copper phthalocyanine (CuPc). Its identification was possible taking care to use a constant Raman setting in order to allow for comparison with reference pigments [55]. The spectra of the PB15:3 standard and AFC110 show several characteristic bands: a very intense band at 1530 cm^{-1} allowing for the β-polymorph (PB15:3) discrimination, and others at 1338, 680 [56], and 230 cm^{-1}. The occurrence of the blue copper phthalocyanine (PB15:3) in the blue and green ink samples was confirmed by the FT-IR spectra [57]. The presence of a blue CuPc is also attested in the pyrograms which display a rather intense peak assigned to 1,2-benzenedicarbonitrile, a characteristic pyrolysis product of the phthalocyanine pigment class, and a smaller peak of benzonitrile [46, 58]. Py-GC-MS cannot be employed for the distinction between the blue CuPc polymorphs.

Although containing the same pigment, the two blue inks under examination exhibit different shades of color, which is most likely due to the presence of $CaCO_3$ in the light blue ink (AFC154). Calcite was recognized in the Raman spectrum showing a strong band at 1088 cm^{-1} and a weaker one at 282 cm^{-1} [59]. The presence of calcium carbonate is not visible in the FTIR spectrum, probably due to its low abundance.

Raman spectroscopy performed on the light purple AFC 136 ink showed the presence of the violet dioxazine pigment PV23, which was identified on the basis of three main absorption bands at 1347, 1392 and 1431 cm^{-1} as well as several peaks of medium and weak intensity (Lutzenberger et al. 2009) (Fig. 2A). Analytical pyrolysis of this ink shows the formation of various characteristic dioxazine pyrolysis products (Fig. 2C): 1,4-dichlorobenzene, deriving from the central part of the molecule, 1-ethyl-1H-indole, 5,6,7-trimethyl-1H-indole and 9-ethyl-9H-carbazole. In the FTIR spectrum (Fig. 2B), the presence of PV23 is testified by several absorption bands such as the aromatic C-C stretching vibrations (at 1600 cm^{-1}), and other characteristic absorptions at 1634, 1553, 1388, 1108, 1040, 929, 737 cm^{-1} [60].

In the pink ink (AFC129) two red pigments were found, i.e., PR122 and PR146. The red quinacridone pigment PR122 was identified with Raman spectroscopy [56]. Py-GC-MS, however, did not show any pyrolysis products that could be related to PR122, but allowed to assess the presence of PR146, which represents an important sub-class of red azo pigments characterized by a β-naphthol ring substituted with both an aromatic azo and an aromatic amide. In particular, the two pyrolysis products 5-chloro-2,3-dimethoxyphenyl isocyanate and 4-chloro-2,5-dimethoxy benzeneamine were identified [45] (Fig. 3A). On the other hand PR146 could not be detected with Raman spectroscopy since the other red pigment (PR122) seems to prevail and TLC was not successful in separation. Since Py-GC-MS at 550°C did not provide pyrolysis products of the quinacridone PR122 it was decided to analyze this ink sample also at a higher pyrolysis temperature (T_{Py} = 700°C) (Fig. 3B). In this way several products, such as 2-aminobenzophenone, 2-methoxy-4-methyl-10H-acridine-9-one and 2-benzylquinoline, ascribable to this red pigment, could now be found. Indeed, it is known that due to the high stability of quinacridones, temperatures above 600°C are required to induce their pyrolysis [61]. In the FTIR spectrum of AFC129 both the characteristic absorptions of PR146 (at 1555, 1477, 1040 and 1341 cm^{-1}) [25] and of PR122 (3269, 3224, 3175, 1555, 1584 and 1345 cm^{-1})[33] could be detected.

Binders, solvents and additives

All pyrograms of the Faber-Castell felt-tip pen inks indicate the presence of a styrene and methylmethacrylate (MMA) binder justified by the presence of a rather intense peak assigned to methyl methacrylate, produced by the "unzipping" depolymerization mechanism, and lower peaks of styrene and α-methyl styrene, the latter being due to the styrene (ST) component [33]. Furthermore, the occurrence of cyclopentanone and ε-caprolactam suggests the addition of a polyamide (PA) binder [40]. This type of medium has been reported for permanent ink patents [62]. All FTIR spectra (see for instance the spectrum of AFC136 in Fig. 2B) show the presence of characteristic absorptions of an acrylic binder, *i.e.*, a strong doublet at 2929 and 2857 cm^{-1}, as well as a strong band at 1730 cm^{-1}. These bands, however, cannot be used for discrimination of the particular type of acrylic resin nor for a distinction from alkyd resin [33]. In addition, the presence of an acrylic polymer is related to two main absorptions in the fingerprint region between 1250-900 cm^{-1}, at 1248 cm^{-1} and at *ca*.1151 cm^{-1}, while the absorption at *ca*. 1449 cm^{-1} indicates the C-H bending of the acrylic fraction. The aromatic C-H stretching at 3024 cm^{-1} is due to the styrene of the binder as well as to the pigments bearing aryl rings, with the aromatic ring breathing in the region between 1450-1650 cm^{-1}, being extremely useful in detecting the presence of styrene [33]. In all spectra, with the exception of AFC 154, this is visible as a weak band at 1603 cm^{-1}. The N-H stretching at ca. 3290 cm^{-1} as well as the amide stretching bands, which may confirm the presence of polyamide binder, are probably hidden by the rather intense peaks of the pigments [63].

Glycerol and diethylene glycol, used as solvents, can be detected in all pyrograms, especially when the ink is analysed immediately after its application. The presence of diethylene glycol is suggested by pyrolysis products such as ethylene glycol butyl ether, diethylene glycol diethyl ether and tetraethylene glycol diethyl ether, while the use of glycerol is justified by the presence of di-glycerol.

The addition of phenolic antioxidants could be ascertained on the basis of several alkyl substituted phenols. Since the antioxidants of the hindered phenol family are relatively similar in structure, it is not easy to distinguish which specific phenol related antioxidant has been employed. However, the presence of 4-ethyl-2-methyl phenol and p-isopropenyl phenol suggests the use of the antioxidant IRGANOX 1010 [43].

The occurrence of glycerol and diethylene glycol used as solvents, and the addition of phenolic antioxidant could be confirmed by a broad band in the FTIR spectra at 3340 cm^{-1} due to the hydroxyl stretching. Di-isooctyl phthalate plasticizer was identified as well, as an intact molecule, at higher retention times [44].

Stabilo and Edding felt-tip pen inks

Pigments and dyes

The VIS-reflectance spectra of all inks applied on paper were acquired. Some of these suggest the presence of one or more components as could be successfully evidenced by deconvolution after baseline subtraction. For instance, in Fig. 4A the deconvolution of the reflectance spectrum curve of a green ink (Stabilo 68-53) clearly shows the contribution of two components. This finding was confirmed by TLC showing the presence of two spots: one yellow and one blue (Fig. 4B).

TLC separation of the Stabilo and Edding ink samples was efficiently reached with the basic solution (nBuOH: EtOH: NH_3 - 5:2:3 v/v). All inks showed the presence of two or more dyes. The Rf values were determined (Table 2) and reflectance spectra were recorded on all spots.

The similar Rf values and reflection maxima suggest that various spots are related to the same dye. It was first attempted to acquire Raman spectra directly from the TLC spots but, even with a laser emitting at λ_0 = 785 nm, only in one case satisfactory results could be obtained due to the strong fluorescence of the organic materials present in the ink formulation.

In particular, the Raman spectrum allowed, indeed, to identify the black spot of the black ink (ST68-46), which did not elute (Rf = 0.04) with the basic solvent system. The broad peaks at 1590 and at 1327 cm^{-1} are most likely due to carbon black, Pbk, (C.I.77266) [64]. In the FTIR spectrum the identification of this pigment was confirmed by the absorptions at 1575, 1475 and the shoulder at 1028 cm^{-1} [65].

Several Stabilo inks (ST68-22, ST68-36, ST68-44, ST68-53) and the blue Edding sample (ED4) contain a yellow dye showing a yellow spot with a rather low retention factor (Table 2). As can be observed in the reflectance spectra and the first order derivatives reported in Fig. 5, the maximum absorption for all spots and for the standard Acid Yellow 23 dye was found at 510 (±3) nm, with the exception of the yellow-orange spot of ST 68-46 (max at 542 nm), which showed a significantly higher TLC retention factor (0.44) than that of the others (ca. 0.34).

The weak Raman shifts of the yellow spots at 1600, 1503, 1352 , 1179, 1133 and 1013 cm^{-1} suggest the presence of tartrazine (Acid Yellow 23, AY23, C.I. 19140) (Fig. 6A). This dye, already known as E102, has been widely used in pharmaceutical drugs, foods and cosmetics. Actually it has been banned in several countries and restricted for its possible toxicity or allergenic potential [30]. However, unambiguous identification of AY23 was attained with SERS (Fig. 6B), which had shown to be successful on similar materials [27–29]. SERS consistently provided significant signal enhancement and fluorescent quenching. The best results were obtained with the 785 nm laser and no differences in the band position and relative intensities as compared with the Raman spectra were observed (see for instance Fig. 6). The SERS spectra show a strong band at 1600 cm^{-1} and a weak peak at 1682 cm^{-1} assigned to the quadrant stretching mode of the phenyl ring and the bending mode of the OH group, respectively. The bands at 1503, 1476 and 1418 cm^{-1} are attributed to the C=C pyrazole bending, the N=N bending mode and the C-H bending mode of the phenyl rings, correspondingly [30]. In addition, the medium intensity peak at 1179 cm^{-1} is attributed to the phenyl bending mode, while the band at 1352 cm^{-1} is related to the azo group stretching mode and to the symmetrical stretching mode of the carboxyl group [28]. The band at 1133 cm^{-1} corresponds to the out-of-plane C-H deformation of the phenyl rings.

The FTIR spectrum and the pyrogram of the standard Acid Yellow 23 were also acquired for comparison. In particular, the FTIR spectrum of the standard dye shows main absorptions at 3442, 1635, 1595, 1554, 1478, 1415, 1347, 1219, 1178, 1152, 1128, 1036 and 1006 cm^{-1}. The peaks around 3442 cm^{-1} due to strong bands of the OH stretching and at 1635 cm^{-1} (δ(OH) vibrations) were observed. The ring carbon–carbon stretching and the scissoring vibrations of the methylene groups (δasCH_2) appear at 1478 and 1421 cm^{-1} as well as at 1347 cm^{-1}. The deformation vibrations of the 1,4-disubstituted benzene ring were also noticed at 980 and 821 cm^{-1}[66]. The FTIR absorption at 1178 cm^{-1} can be assigned to the SO_3^- stretching in combination with the S=O stretching at 1350 cm^{-1} and with SO_3Na symmetric stretching at 1036 cm^{-1} (in common with Acid Blue 9 dye, see below). However, not all these peaks could be found in the inks due to the overlapping bands of the other dyes (Fig. 7B). In the pyrograms of the blue (ST68-22) (Fig. 7C), green (ST68-36) and yellow (ST68-44) inks the presence of pyrolysis products such as benzyl nitrile, benzothiazole, 1,2-benzenedicarbonitrile, diphenylamine, and diphenyldisulfide could be attributed to the presence of AY23 by comparison with the pyrogram of the standard dye.

The red spot of ST68-46 provided a SERS spectrum with peaks at 1595, 1577, 1518, 1486, 1462, 1444, 1366, 1304, 1244, 1168, 1155, 987, 948, 699, 585, 503 and 430 cm^{-1} which allowed for the identification of the monoazo Ponceau 4R or Acid Red 18, AR18, (C.I. 16255). The presence of this dye in Stabilo felt tip pen has been already attested by Sodo *et al.* The Acid Red 18 could be ascertained by the FTIR absorption at 1616 cm^{-1}, and in the fingerprint region at 1490, 977, 834 cm^{-1} [2]. At the same time, the pyrogram of the black ink ST 68-46 shows sulfur dioxide, and naphthalene-based compounds (naphthalene and 2-naphthalenamine) which may be ascribed to this azo-dye [2]. No other products were observed in the pyrogram probably due to the very low amount of this colorant in the mixture.

Various triarylmethane (TAM) dyes could be identified in the blue, green, violet and black inks. TAMs, derived from aniline, are the oldest synthetic dyestuffs and are composed of a triphenylmethane backbone bearing various substituents (halogen, alkyl, alkoxy, sulfonic acid and carboxylic acid groups) on the aryl rings.

The blue TLC spots with similar Rf values (ca. 0.40), eluted from the blue (ST68-22, ST68-41, ST68-57, ED3, ED10), green (ST68-36, ST68-53, ED4), and black (ST68-46) inks, showed, indeed, analogous reflectance spectra. When examining the first derivatives of all blue spots (except for St 68-46) (Fig. 8), it becomes evident that the curves are crossing zero at 457 ±3 nm (maximum absorption) and are showing a maximum in the blue range at 428 (±3) nm. These values coincide with those of the Acid Blue 9, AB9, (C.I. 42090) standard.

The SERS spectra allowed, indeed, to identify Acid Blue 9. The identification was based on comparison with the spectrum of a standard. The presence of a C-S aromatic stretching at 1077 cm^{-1}, an aromatic ring vibration (C-C) at 1584 cm^{-1}, and a strong absorption band related to the C=N stretching at 1621 cm^{-1} can be observed. In Figure 7A the SERS spectra of ST68-22, including the blue spot containing AB9 (spot 2), are reported. Concerning the FTIR spectra, in addition to the absorptions in common with Acid yellow 23 due to the sulfonated groups, other peaks may be exclusively attributed to this blue dye: the C=N stretching at 1616 cm^{-1} was observed for the standard dye, but just a very weak shoulder could be found for the green sample ST68-36. In addition, the aromatic C=C stretching can be detected at 1576 cm^{-1} and 1454 cm^{-1} and the symmetric C_{Ar}-C_{Ar}-N stretching of Ar-N(CxHx)$_{2.}$

Py-GC-MS allowed to confirm the presence of various TAMs in the Stabilo and Edding inks. Aniline, N-methylaniline, diphenylmethane and acridine are in common for all TAMs [49], although aniline and acridine are also present in the pyrograms of AY23. All SO_3 — containing dyes (Acid blue 9, Acid violet 49, Acid yellow 23, Acid red 18) generate sulfonated products, such as sulfur dioxide and benzenethiol [48]. N-ethyl aniline, benzenthiol, N,N-diethyl aniline and N-butyl aniline are considered more characteristic for the Acid Blue 9 dye.

The purple spot, which was exclusively found in ST 68-55 at Rf = 0.44, shows a SERS spectrum with main absorptions due to a triarylmethane dye (1621, 1584,1533, 1379,1349,1179, 984 and 733 cm^{-1}) although comparison with the literature did not allow for a unique identification. FTIR absorptions ascribed uniquely to this dye may be at 1581 cm^{-1} and at 1192 cm^{-1}, due to the C-C stretching and to C-H bending. However, careful examination of the Py-GC-MS data hypothesized the presence of the triarylmethane Acid Violet 49, AV49, (C.I. 42640). Indeed, in addition to the common TAM products, and to N-ethylaniline and N,N-diethylaniline, which are characteristic of dyes with nitrogens bearing one or two ethyl groups (Acid Blue 9, Basic Violet 4 and Acid Violet 49), the presence of N,N-dimethylaniline is specific for dye molecules with two methyl moieties on the N atom, like Acid violet 49.

The TLC plate of the Stabilo black ink (ST68-46) showed many spots and among these an orange spot at Rf= 0.44. The SERS spectrum of this spot presents high intensity peaks at 1584, 1387, 1111 cm $^{-1}$, a doublet at 1175 and 1196 cm $^{-1}$, as well as medium and low intensity peaks at 1434, and 1624, 1471, 1278, 1140, 1073 cm^{-1}, respectively. The presence of bands at 1387 cm^{-1} (ascribed to –N=N– stretching mode) and at 1175cm^{-1} (C–N symmetric stretching) suggests an azo coloring agent. Unfortunately, neither the spectral data nor the pyrolytic products revealed to be useful for the identification of this yellow-orange dye.

Basic Violet 4, BV4, (C.I. 42600) also known as ethyl violet, could be detected in the violet spots with Rf= ca. 055 of the blue (ST68-41, ST68-22), light blue (ST68-57) and violet (ST68-55) inks by comparison with literature data [67]. The SERS spectra of these spots show peaks at *ca*. 1621, 1584, 1533, 1379, 1349, 1179, 918, 803, 763, 733, 462, 442, and 424 cm^{-1}, characteristic of TAM dyes [34]. The pyrolytic fragmentation of Basic Violet 4 produces N-ethyl aniline and N,N-diethyl aniline, in addition to the common TAM products. Its pattern appears similar to Acid Blue 9, except for the sulfonated groups.

Pink dyes are only found in the pink Stabilo ST 68-056 and in the blue Edding (ED3). The different retention factors (Rf = 0.76 and Rf = 0.50, respectively) suggest the presence of two different dyes; indeed, the SERS spectrum of the Stabilo ink indicated the presence of Rhodamine 6G or Basic Red 1, BR1, (C.I. 45160) [68]. This organic dye belongs to the family of the xanthenes, widely used in biology and chemistry. The identification of Rhodamine 6G is based on the following bands: the C-C stretching of xanthene at 1504 cm^{-1}, the C-H bending at 1311 cm^{-1} and the C-H bending in plane at 1131 cm^{-1}. Moreover, the bands at 1647 and 1362 cm^{-1} represent the stretching vibration of the xanthene ring moiety of the molecule, while the shoulder observed at 1285 cm^{-1} can be assigned to the in-plane C-H bending of the xanthene. The Raman shift at 618 cm^{-1} can be related to the stretching of the xanthene phenyl group and enhancing sensitivity [69]. The FTIR spectrum seems to confirm the presence of this dye on the basis of the absorptions at 1596, 1524, 1487, 1442, 1403 and 1307 cm^{-1} [70].

Unfortunately, due its high thermal stability, it is very difficult to detect Rhodamine 6G in the pyrogram and no characteristic products could be found.

The pink spot of the Edding ink (ED3) could be recognized as the xanthene Phloxine B or Acid Red 92, AR92, (C.I. 45410) by means of the SERS spectrum and the Py-GC-MS data. Indeed, the SERS spectrum of this polycyclic aromatic dye shows main absorptions at 1624, 1498,1439, 1340, 1298, 1278, 1179, 717 and 644 cm^{-1} [71]. Moreover, the detection of some brominated and chlorinated products (bromoethane, 4-bromo-2ethylaniline, 1-(4-bromophenyl)ethanamine and tetrachlorobenzene) in the pyrogram seems to confirm its occurrence although no literature data are available (Fig. 9).

Binders, solvents and additives

In all pyrograms of the Stabilo and Edding felt-tip pen inks triethylene, tetraethylene, and pentaethylene glycol, which are typical fragmentation products of polyethylene glycol (PEG), as well as 15-crown-5 likely due to cyclization, could be found. The use of PEG as a solvent is confirmed by the FTIR spectra where an intense and large band in the 3359-3413 cm^{-1} (-OH stretching) is observed, as well as the following spectral features: a peak in the 2870-2880 cm^{-1} region with a shoulder (or doublet) at ca. 2910 cm^{-1} (C-H stretching), peaks at ca. 1460 cm^{-1} and in the 1343-1351 cm^{-1} region (bending C-H), peaks at 1290-1280, 1000-1120 and 1065-1075 cm^{-1} (stretching C-OH) [72].

In the Edding samples another solvent was found and could be recognized as 2-phenoxyethanol (PE) as such identified in the pyrogram.

In one of the investigated Stabilo inks (ST68-056), the FTIR spectrum exhibits bands which can be most likely assigned to a poly(styrene-acrylic) binder. The aromatic C-H stretching at 3024 cm^{-1} and the aromatic ring breathing in the region between 1450- 1650 cm^{-1} are due to styrene, whereas the intense absorption band at 1730 cm^{-1}, which may be attributed to the carbonyl stretching (C=O), suggests the presence of an acrylic resin [33]. Moreover, the weak band at 1580 cm^{-1} and the C≡N stretching at 2234 cm^{-1} point to the presence of acrylonitrile.

This hypothesis was confirmed by the Py-GC-MS results. Indeed, the monomer 2-ethylhexylacrylate (2EHA) as well as 2-ethylhexyl methacrylate and 2-ethyl-1-hexanol indicate the presence of 2EHA [33]. Moreover, monomers such as 2-propene nitrile and the dimer 3-hexene-dinitrile, probably formed by thermal chain scissions along the original polymer chain, were identified. Furthermore, products like benzene propanenitrile and benzene butanenitrile may have formed by recombination of benzene radicals, produced by pyrolysis of polystyrene, with 2-

propenenitrile [73]. Polyacrylonitrile may be added for improving some physical properties of the acrylic resin such as strength, stiffness, resistance and transparency, as well as being more economical than acrylics.

In three Stabilo samples (ST 68-57, ST 68-55, ST 68-46) iso-butylmethacrylate and styrene were detected, indicating that a styrene-iso-butylmethacrylate resin was used as a binder. This resin could also be observed in the FTIR spectra where an intense peak at 1735 cm^{-1}, due to the carbonyl stretching, and other peaks assigned to the acrylic resin, at ca. 885 cm^{-1} (C-H rocking) and at ca. 940-948 cm^{-1} (C-C stretching) were found.

The pyrograms of some of the Stabilo inks (ST 68-22, ST 68-36, ST 68-44) show some typical markers of carbohydrates, which might indicate the presence of plant gum as an ink binder [74]. Indeed, traces of 1-hydroxy-2-propanone, 2-furancarboxaldehyde, 2-furanone and 5-methyl-furaldehyde were found. Since it is rather difficult to identify the type of plant gum on the basis of Py-GC-MS data, a specific GC-MS procedure for the analysis of plant gums was adopted (see Experimental section). Briefly, the samples were submitted to acidic hydrolysis with TFA followed by formation of acyclic methoximes and sililation in order to perform GC-MS of the derivatised aldoses and ketoses [75]. Xylose, arabinose, fructose, galactose, and glucose were identified and the use of a plant gum could be confirmed. However, the xylose/arabinose ratio > 1, and the lack of some characteristic monosaccharides did not allow for an unambiguous identification of the type of plant gum.

All Edding samples instead, show specific products due to the polypropylene glycol such as propanal at very low retention times, glycidol and 1-hydroxy-2-propanone [76]. In addition, triacetin was also detected together with its pyrolytic products. In particular, by following the scheme proposed by Liano 2012 *et al.* the glycidyl acetate was produced after elimination of acetic anhydride followed by the formation of glycidol via elimination of ethenone from the acetate group.

Moreover, in two of the Stabilo ink samples (ST 68-55 and ST 68-53) methyl dehydroabietate was identified, suggesting the use of colophony as an additive [2].

Two diesters of adipic acid, namely diisoctyl adipate and bis(2-ethylhexyl)adipate, could be identified in samples ST 68-57 and ST 68-46, respectively. These compounds were added to the ink formulations as plasticizers [44].

Finally, the occurrence of phenols (PH) in ST 68-22, ST68-36, ST 68-44, ST6846 and ST 68-57, indicates the use of phenolic antioxidants [43].

Conclusions

An ample selection of different types of felt-tip pens (Faber-Castell, Stabilo, Edding) in use for artistic purposes was investigated with a multi-technique approach, including spectroscopic, chromatographic and mass spectrometric methods in order to shed light on the complex formulations of these modern inks. In particular, Py-GC-MS, FTIR spectroscopy, TLC, µ-Raman spectroscopy, SERS and VIS-reflectance spectroscopy were applied.

Phthalocyanine, dioxazine and azo pigments were detected in the Faber-Castell pens, whereas the other felt-tip pens (Stabilo and Edding) contain mixtures of dyes such as triarylmethanes, xanthenes, and azo-dyes. The use of TLC in combination with the acquisition of VIS-reflectance spectra, followed by the plotting of the first derivatives, provided encouraging results to develop a simple, efficient and non-invasive method for the study of inks. SERS on the TLC spots confirmed to be a powerful tool for unambiguous identification, whereas in some cases Py-GC-MS came out to be essential for the recognition of pigments.

Next to the identification of the pigments and dyes, the multi-technique approach allowed to gather detailed information on binders, solvents and additives. In particular, styrene-acrylic resins and natural gums were detected and the use of different types of solvents, plasticizers, anti-oxidants and other additives could be evidenced.

This study highlighted significant differences in chemical composition of the three types of felt-tip pens which are expected to strongly influence the stability towards aging. Indeed, the Faber-Castell inks are based on styrene-acrylic binders in combination with rather stable pigments such as phthalocyanines, red and yellow azo pigments, quinacridones and dioaxazines. The latter are all characterized by high lightfastness indices.

The Stabilo inks contain a carbohydrate binder, except for a few samples with a (styrene)- acrylic resin, whereas in the Edding samples a polypropylene glycol resin was found. The Stabilo and Edding inks show a mixture of colorants belonging to the TAMs, red and yellow azo dyes, and xanthenes. All these dyes are extremely sensitive and artworks and drawings based on these inks should therefore be stored with special care to avoid exposure to light.

Artificial aging studies have been undertaken in order better understand the degradation mechanisms of felt-tip pen inks.

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Compliance with ethical standards

Conflict of Interest: The authors declare that they have no conflict of interest.

References

1. Favaro M, Mendichi R, Ossola F, Simon S, Tomasin P, Vigato PA (2007) Evaluation of polymers for conservation treatments of outdoor exposed stone monuments. Part II: Photo-oxidative and salt-induced weathering of acrylic-silicone mixtures. Polymer Degradation and Stability 92:335–351. doi: 10.1016/j.polymdegradstab.2006.12.008
2. Izzo FC, Vitale V, Fabbro C, Van Keulen H (2016) Multi-analytical investigation on felt-tip pen inks: Formulation and preliminary photo-degradation study. Microchemical Journal 124:919–928. doi: 10.1016/j.microc.2015.09.008
3. Ghelardi E, Degano I, Colombini MP, Mazurek J, Schilling M, Khanjian H, Learner T (2015) A multi-analytical study on the photochemical degradation of synthetic organic pigments. Dyes and Pigments 123:396–403. doi: 10.1016/j.dyepig.2015.07.029
4. Papliaka ZE, Andrikopoulos KS, Varella EA (2010) Study of the stability of a series of synthetic colorants applied with styrene-acrylic copolymer, widely used in contemporary paintings, concerning the effects of accelerated ageing. Journal of Cultural Heritage 11:381–391. doi: 10.1016/j.culher.2010.02.003
5. Learner, TJS; Smithen, P; Krueger, JW; Schilling M (2007) Modern paints uncovered. Proceedings from the Modern Paints Uncovered Symposium, London May 16-19, 2006. In: Modern paints uncovered. Los Angeles: The Getty Conservation Institute, pp 227–235
6. MIBAC (Italian Ministry of Cultural Heritage) (2001) Atto di indirizzo sui criteri tecnico-scientifici e sugli standard di funzionamento e sviluppo dei musei, Ambito VI. D.Lgs. 112/1998 (art. 150, comma 6). 81–94.
7. Favaro G, Confortin D, Pastore P, Brustolon M (2012) Application of LC-MS and LC-MS-MS to the analysis of photo-decomposed crystal violet in the investigation of cultural

heritage materials aging. Journal of Mass Spectrometry 47:1660–1670. doi: 10.1002/jms.3110

8. Pintus V, Wei S, Schreiner M (2012) UV ageing studies: Evaluation of lightfastness declarations of commercial acrylic paints. Analytical and Bioanalytical Chemistry 402:1567–1584. doi: 10.1007/s00216-011-5369-5

9. Pfingstag G (1993) Colorants in inks for writing, drawing and marking. Journal of the Society of Dyers and Colourists 109:188–192. doi: 10.1111/j.1478-4408.1993.tb01556.x

10. Confortin D, Neevel H, Brustolon M, Franco L, Kettelarij AJ, Williams RM, Bommel MR van (2010) Crystal violet: Study of the photo-fading of an early synthetic dye in aqueous solution and on paper with HPLC-PDA, LC-MS and FORS. Journal of Physics: Conference Series 231:12011. doi: 10.1088/1742-6596/231/1/012011

11. Whitmore PM, Cass GR, Druzik JR (1987) The Ozone Fading of Traditional Natural Organic Colorants on Paper. Journal of the American Institute for Conservation 26:45. doi: 10.2307/3179660

12. Schutz, E. Berger F, Dirckx O, Chambaudet A (1999) Study of degradation mechanisms of a paint coating during an artificial aging test. Polymer 65:123–130.

13. Ploeger R, Scalarone D, Chiantore O (2009) Thermal analytical study of the oxidative stability of artists' alkyd paints. Polymer Degradation and Stability 94:2036–2041. doi: 10.1016/j.polymdegradstab.2009.07.018

14. Sodo A, Bicchieri M, Guiso M, Ricci MA, Ricci G (2012) Raman investigations on marker pen inks. Journal of Raman Spectroscopy 43:1781–1787. doi: 10.1002/jrs.4070

15. van der Werf ID, Germinario G, Palmisano F, Sabbatini L (2011) Characterisation of permanent markers by pyrolysis gas chromatography–mass spectrometry. Analytical and Bioanalytical Chemistry 399:3483–3490. doi: 10.1007/s00216-011-4714-z

16. Zaffino C, Passaretti A, Poldi G, Fratelli M, Tibiletti A, Bestetti R, Saccani I, Guglielmi V, Bruni S (2017) A multi-technique approach to the chemical characterization of colored inks in contemporary art: The materials of Lucio Fontana. Journal of Cultural Heritage 23:87–97. doi: 10.1016/j.culher.2016.09.006

17. Brunelle Richard L. CRK (2003) Advances in the Forensic Analysis and Dating of Writing Ink. Charles C Thomas, Sprignfield

18. Barker J, Ramotowski R, Nwokoye J (2016) The effect of solvent grade on thin layer chromatographic analysis of writing inks. Forensic Science International 266:139–147. doi: 10.1016/j.forsciint.2016.05.003

19. Sherma J (2016) Advances in the thin-layer chromatographic forensic analysis of inks.

Journal of Liquid Chromatography & Related Technologies 39:549–557. doi: 10.1080/10826076.2016.1183130

20. Houlgrave S, Laporte GM, Stephens JC (2011) The use of filtered light for the evaluation of writing inks analyzed using thin layer chromatography. Journal of Forensic Sciences 56:778–782. doi: 10.1111/j.1556-4029.2011.01733.x

21. Causin V, Casamassima R, Marega C, Maida P, Schiavone S, Marigo A, Villari A (2008) The discrimination potential of ultraviolet-visible spectrophotometry, thin layer chromatography, and Fourier transform infrared spectroscopy for the forensic analysis of black and blue ballpoint inks. Journal of Forensic Sciences 53:1468–1473. doi: 10.1111/j.1556-4029.2008.00867.x

22. Tsutsumi K, Ohga K (1998) Analysis of Writing Ink Dyestuffs by TLC and FT-IR and Its Application to Forensic Science. Analytical Sciences 14:269–274. doi: 10.2116/analsci.14.269

23. Geiman I, Leona M, Lombardi JR (2009) Application of Raman Spectroscopy and Surface-Enhanced Raman Scattering to the Analysis of Synthetic Dyes Found in Ballpoint Pen Inks. Journal of Forensic Sciences 54:947–952. doi: 10.1111/j.1556-4029.2009.01058.x

24. Vandenabeele P, Moens L, Edwards HGM, Dams R (2000) Raman spectroscopic database of azo pigments and application to modern art studies. Journal of Raman Spectroscopy 31:509–517. doi: 10.1002/1097-4555(200006)31:6<509::AID-JRS566>3.0.CO;2-0

25. Lomax SQ, Learner T (2006) A Review of the Classes, Structures, and Methods of Analysis of Synthetic Organic Pigments. Journal of the American Institute for Conservation 45:107–125. doi: 10.1179/019713606806112540

26. Cañamares M V., Reagan DA, Lombardi JR, Leona M (2014) TLC-SERS of mauve, the first synthetic dye. Journal of Raman Spectroscopy 45:1147–1152. doi: 10.1002/jrs.4508

27. Leona M, Decuzzi P, Kubic TA, Gates G, Lombardi JR (2011) Nondestructive identification of natural and synthetic organic colorants in works of art by surface enhanced raman scattering. Analytical Chemistry 83:3990–3993. doi: 10.1021/ac2007015

28. Lofrumento C, Ricci M, Platania E, Becucci M, Castellucci E (2013) SERS detection of red organic dyes in Ag-agar gel. Journal of Raman Spectroscopy 44:47–54. doi: 10.1002/jrs.4162

29. Brosseau CL, Gambardella A, Casadio F, Grzywacz CM, Wouters J, Van Duyne RP (2009) Ad-hoc surface-enhanced raman spectroscopy methodologies for the detection of artist dyestuffs: Thin layer chromatography-surface enhanced raman spectroscopy and in situ on the fiber analysis. Analytical Chemistry 81:3056–3062. doi: 10.1021/ac802761v

30. Peica N, Pavel I, Cîntă Pînzaru S, Rastogi VK, Kiefer W (2005) Vibrational characterization

of E102 food additive by Raman and surface-enhanced Raman spectroscopy and theoretical studies. Journal of Raman Spectroscopy 36:657–666. doi: 10.1002/jrs.1354

31. Leona M, Stenger J, Ferloni E (2006) Application of surface-enhanced Raman scattering techniques to the ultrasensitive identification of natural dyes in works of art. Journal of Raman Spectroscopy 37:981–992. doi: 10.1002/jrs.1582

32. Whitney, Alyson V.; Van Duyne, Richard P.; Casadio F (2006) An innovative surface-enhanced Raman spectroscopy (SERS) method for the identification of six historical red lakes and dyestuffs. Journal of Raman Spectroscopy 37:993–1002. doi: 10.1002/jrs.1576

33. Learner T (2004) Analysis of modern paints. Getty Consrervation Institute, Los Angeles

34. Doherty B, Vagnini M, Dufourmantelle K, Sgamellotti A, Brunetti B, Miliani C (2014) A vibrational spectroscopic and principal component analysis of triarylmethane dyes by comparative laboratory and portable instrumentation. Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy 121:292–305. doi: 10.1016/j.saa.2013.10.069

35. Rozenberg M, Loewenschuss A, Marcus Y (1998) IR spectra and hydration of short-chain polyethyleneglycols. Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy 54:1819–1826. doi: 10.1016/S1386-1425(98)00062-6

36. Ahmed KM, McLeod MP, Nézivar J, Giuliani AW (2010) Fourier transform infrared and near-infrared spectroscopic methods for the detection of toxic Diethylene Glycol (DEG) contaminant in glycerin based cough syrup. Spectroscopy 24:601–608. doi: 10.3233/SPE-2010-0482

37. Calvano CD, van der Werf ID, Palmisano F, Sabbatini L (2016) Revealing the composition of organic materials in polychrome works of art: the role of mass spectrometry-based techniques. Analytical and Bioanalytical Chemistry 408:6957–6981. doi: 10.1007/s00216-016-9862-8

38. Colombini M.P, Andreotti A., Bonaduce I., Modugno F. RE (2010) Analytical Strategies for Characterizing Organic Paint Media Using Gas Chromatography / Mass Spectometry. Acc Chem Res 43:715–727.

39. Wampler TP (1996) Paints and Coatings : Pyrolysis : Gas Chromatography. Current Opinion in Cell Biology 3596–3608.

40. Tsuge S, Ohtani H, Watanabe C (2011) Pyrolysis–GC/MS Data Book of Synthetic Polymers - Pyrograms, Thermograms and MS of Pyrolyzates. Elsevier B.V

41. Peris-Vicente J, Baumer U, Stege H, Lutzenberger K, Gimeno Adelantado J V. (2009) Characterization of commercial synthetic resins by pyrolysis-gas chromatography/mass spectrometry: application to modern art and conservation. Analytical Chemistry 81:3180–

3187. doi: 10.1021/ac900149p

42. Chiantore O, Scalarone D, Learner T (2003) Characterization of Artists' Acrylic Emulsion Paints. International Journal of Polymer Analysis and Characterization 8:67–82. doi: 10.1080/10236660304884

43. Wang FC-Y (1999) Polymer additive analysis by pyrolysis – gas chromatography. Journal of Chromatography A 843:413–423. doi: 10.1016/S0021-9673(00)00647-6

44. Wang FCY (2000) Polymer additive analysis by pyrolysis-gas chromatography: I. Plasticizers. Journal of Chromatography A 883:199–210. doi: 10.1016/S0021-9673(00)00346-0

45. Sonoda N (2016) Characterization of organic azo-pigments by pyrolysis-gas chromatography. Studies in Conservation 44:195–208.

46. Germinario G, Werf ID van der, Sabbatini L (2015) Pyrolysis gas chromatography mass spectrometry of two green phthalocyanine pigments and their identification in paint systems. Journal of Analytical and Applied Pyrolysis 115:175–183. doi: 10.1016/j.jaap.2015.07.016

47. Russell J, Singer BW, Perry JJ, Bacon A (2011) The identification of synthetic organic pigments in modern paints and modern paintings using pyrolysis-gas chromatography-mass spectrometry. Analytical and Bioanalytical Chemistry 400:1473–1491. doi: 10.1007/s00216-011-4822-9

48. Rehorek A, Plum A (2007) Characterization of sulfonated azo dyes and aromatic amines by pyrolysis gas chromatography/mass spectrometry. Analytical and Bioanalytical Chemistry 388:1653–1662. doi: 10.1007/s00216-007-1390-0

49. Ghelardi E, Degano I, Colombini MP, Mazurek J, Schilling M, Learner T (2015) Py-GC/MS applied to the analysis of synthetic organic pigments: characterization and identification in paint samples. Analytical and Bioanalytical Chemistry 407:1415–1431. doi: 10.1007/s00216-014-8370-y

50. Montagner C, Bacci M, Bracci S, Freeman R, Picollo M (2011) Library of UV-Vis-NIR reflectance spectra of modern organic dyes from historic pattern-card coloured papers. Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy 79:1669–1680. doi: 10.1016/j.saa.2011.05.033

51. Lee PC, Meisel D (1982) Adsorption and surface-enhanced Raman of dyes on silver and gold sols. The Journal of Physical Chemistry 86:3391–3395. doi: 10.1021/j100214a025

52. Bouchard M, Rivenc R, Menke C, Learner T (2009) Micro-FTIRand micro-Raman study of paints by Sam Francis. e-PS 6:27–37.

53. Schulte F, Brzezinka K, Lutzenberger K, Stege H, Panne U (2008) Raman spectroscopy of

synthetic organic pigments used in 20th century works of art. 1455–1463. doi: 10.1002/jrs

54. Lutzenberger K, Stege H (2009) From Beckmann to Baselitz: towards an improved micro-identification of organic pigments in paintings of 20th century art. e-Preservation science 6:89–100.

55. Defeyt C, Van Pevenage J, Vandenabeele P, Learner T, Strivay D (2014) Distinction by Micro-Raman Spectroscopy and Chemometrical Analysis of Copper Phthalocyanine Blue Polymorphs in Oil-Based and Acrylic Paint Samples. In: Issues in Contemporary Oil Paint. Springer International Publishing, Cham, pp 105–116

56. Cucci C, Bartolozzi G, De Vita M, Marchiafava V, Picollo M, Casadio F (2016) The Colors of Keith Haring: A Spectroscopic Study on the Materials of the Mural Painting Tuttomondo and on Reference Contemporary Outdoor Paints. Applied Spectroscopy 70:186–196. doi: 10.1177/0003702815615346

57. Seoudi R, Sayed ZA El (2005) FTIR , TGA and DC electrical conductivity studies of phthalocyanine and its complexes. Journal of Molecular Structure 753:119–126. doi: 10.1016/j.molstruc.2005.06.003

58. Ghelardi E, Degano I, Colombini MP, Mazurek J, Schilling M, Khanjian H, Learner T (2015) A multi-analytical study on the photochemical degradation of synthetic organic pigments. Dyes and Pigments 123:396–403. doi: 10.1016/j.dyepig.2015.07.029

59. Bell IM, Clark RJH, Gibbs PJ (1997) Raman spectroscopic library of natural and synthetic pigments (pre- ≈ 1850 AD). Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 53:2159–2179. doi: 10.1016/S1386-1425(97)00140-6

60. Herbst,Willy; Hunger K (2006) Industrial Organic Pigments: Production, Properties, Applications. Wiley-VCH

61. Schreiver, I; Hutzler, C; Andree, S; Laux, P; Luch A (2016) Identification and hazard prediction of tattoo pigments by means of pyrolysis-gas chromatography/mass. Archives of Toxicology 90:1639–1650. doi: 10.1007/s00204-016-1739-2.

62. Cited R, City O, Data RU-A (2003) (12) United States Patent. 1:0–4. doi: 10.1016/j.(73)

63. Mahdi HA (2011) An FTIR Study of Characterization of Neat and UV Stabilized Nylon 6,6 Polymer Films. Journal For Pure And Applied Science 24:86–90.

64. Coccato A, Jehlicka J, Moens L, Vandenabeele P (2015) Raman spectroscopy for the investigation of carbon-based black pigments. Journal of Raman Spectroscopy 46:1003–1015. doi: 10.1002/jrs.4715

65. O’Reilly JM, Mosher RA (1983) Functional groups in carbon black by FTIR spectroscopy. Carbon 21:47–51. doi: 10.1016/0008-6223(83)90155-0

66. Wawrzkiewicz M, Hubicki Z (2009) Removal of tartrazine from aqueous solutions by strongly basic polystyrene anion exchange resins. Journal of Hazardous Materials 164:502–509. doi: 10.1016/j.jhazmat.2008.08.021

67. Persaud, Indira; Grossman WEL (1993) Surface-Enhanced Raman Scattering of Triphenylmethane Dyes on Colloidal Silver. Journal of Raman Spectroscopy 24:107–112.

68. Sun CH, Wang ML, Feng Q, Liu W, Xu CX (2015) Surface-enhanced Raman scattering (SERS) study on Rhodamine B adsorbed on different substrates. Russian Journal of Physical Chemistry A 89:291–296. doi: 10.1134/S0036024415020338

69. Dieringer JA, Wustholz KL, Masiello DJ, Camden JP, Kleinman SL, Schatz GC, Van Duyne RP (2009) Surface-enhanced Raman excitation spectroscopy of a single rhodamine 6G molecule. Journal of the American Chemical Society 131:849–854. doi: 10.1021/ja8080154

70. Schweppe Collection, BASF, Ludwigshafen, Germany "IOD00050, Rhodamine 6G, Basic Red 1, C.I. 45160, Infrared and Raman Users Group Spectral Database. Infrared and Raman Users Group, 2007. Web. <www.irug.org>.

71. Narayanan VA, Stokes DL, Stump NA, Begun GM, Vo-dinh T (1993) Surface-Enhanced Raman Analysis of some Polycyclic Aromatic Dyes used in the Cosmetics and Food Industries. Polycyclic Aromatic Compounds 3:137–146. doi: 10.1080/10406639308047865

72. Shameli K, Ahmad M Bin, Jazayeri SD, Sedaghat S, Shabanzadeh P, Jahangirian H, Mahdavi M, Abdollahi Y (2012) Synthesis and characterization of polyethylene glycol mediated silver nanoparticles by the green method. International Journal of Molecular Sciences 13:6639–6650. doi: 10.3390/ijms13066639

73. Sánchez-Soto PJ, Avilés MA, Del Río JC, Ginés JM, Pascual J, Pérez-Rodríguez JL (2001) Thermal study of the effect of several solvents on polymerization of acrylonitrile and their subsequent pyrolysis. Journal of Analytical and Applied Pyrolysis 58–59:155–172. doi: 10.1016/S0165-2370(00)00203-5

74. Chiantore O, Riedo C, Scalarone D (2009) Gas chromatography-mass spectrometric analysis of products from on-line pyrolysis/silylation of plant gums used as binding media. International Journal of Mass Spectrometry 284:35–41. doi: 10.1016/j.ijms.2008.07.031

75. Lluveras-Tenorio A, Mazurek J, Restivo A, Colombini MP, Bonaduce I (2012) The Development of a New Analytical Model for the Identification of Saccharide Binders in Paint Samples. PLoS ONE. doi: 10.1371/journal.pone.0049383

76. Laino T, Tuma C, Moor P, Martin E, Stolz S, Curioni A (2012) Mechanisms of propylene glycol and triacetin pyrolysis. Journal of Physical Chemistry A 116:4602–4609. doi: 10.1021/jp300997

Figure and Table captions

Fig. 1 Reflectance spectra of the Faber-Castell felt-tip pen inks applied on paper

Fig. 2 (A) Raman spectrum, (B) FTIR spectrum and (C) Py-GC-MS trace (TIC) of the Faber-Castell felt-tip pen ink AFC136

1: chloromethane; 2: 2-butanol; 3: methylmethacrylate; 4: cyclopentanone; 5: 6-chlorohexene; 6: 5-hexen-1-ol; 7: styrene; 8: ethylene glycol butyl ether; 9: phenol; 10: α-methylstyrene; 11: 1,4-dichlorobenzene; 12: diethylene glycol ethyl ether; 13: chlorohexanol; 14: 4-ethyl-2-methylphenol; 15: 2,4,6-trimethylphenol; 16: ε-caprolactam; 17; p-isopropenylphenol; 18: 1-ethyl-1H-indole; 19: tetraethylene glycol diethyl ether; 20: 2,3,4,6-tetramethylphenyl cyanide; 21: 5,6,7-trimethyl-1H-indole; 22: 9-ethyl-9H-carbazole; 23: diisoctylphthalate

Fig. 3 Py-GC-MS trace (TIC) of the Faber-Castell felt-tip pen ink AFC129 acquired at (A) T_{Py} = 550°C and (B) T_{Py} = 700°C

1: methyl acetate; 2: methylmethacrylate; 3: toluene; 4: cyclopentanone; 5: 1-hexanol; 6: 5-hexen-1-ol; 7: styrene; 8: i-butylmethacrylate; 9: diglycerol; 10: cyclohexene-1-methanol; 11: 1,6-hexandiol; 12: 3-butenyl methacrylate; 13: 2,4-dimethylphenol; 14: ethyl hexyl monovinyl ether; 15: dimethyl adipate; 16: ε-caprolactam; 17: 2-propenoic-2-methyl-cyclohexyl; 18: 5-chloro-2,4-dimethoxyphenyl isocyanate; 19: 4-chloro-2-5-dimethoxyaniline; 20: 2-aminobenzophenone; 21: 2-methoxy-4-methyl-10H-acridin-9-one; 22: 2-benzylquinoline; 23: diisoctylphthalate

Fig. 4 Reflectance spectroscopy of the Stabilo felt-tip pen ink ST68-53. (A) Deconvolution of the reflectance spectrum; (B) Reflectance spectra of the yellow and blue TLC spots

Fig. 5 Reflectance (A) and derivative reflectance (B) spectra of the yellow TLC spots of the Stabilo and Edding felt-tip pen inks

Fig. 6 Raman e SERS spectra of the yellow TLC spot of the Stabilo felt-tip pen ink ST68-36

Fig. 7 (A) SERS spectra of the TLC spots, (B) FTIR spectrum and (C) Py-GC-MS trace (TIC) of the Stabilo felt-tip pen ink ST68-22

1: chloromethane; 2: sulfur dioxide; 3: 1-hydroxy-2-propanone; 4: furancarboxaldehyde; 5: benzenethiol; 6: 5-methyl-2-furancarboxaldehyde; 7: aniline; 8: 2-methyl-phenol; 9: tetraethylene glycol; 10: N-methyl aniline; 11: 2-methyl aniline; 12: N,N-dimethyl aniline; 13: benzyl nitrile; 14: N-ethyl aniline; 15: 2,4-dimethylaniline; 16: benzothiazole; 17: N,N-diethyl aniline; 18: pentaethylene glycol; 19: 1,2-benzenedicarbonitrile; 20: diphenylmethane; 21: 15-crown-5; 22: heptaethylene glycol; 23: diphenyldisulfide; 24: diphenylamine; 25: octaethylene glycol; 26: diisoctyl adipate

Fig. 8 Derivative reflectance spectra of the blue TLC spots of the Stabilo and Edding felt-tip pen inks

Fig. 9 Py-GC-MS trace (TIC) of the Edding felt-tip pen ink ED3

1: propanal; 2: sulfur dioxide; 3: bromoethane; 4: 1-hydroxy-2-propanone; 5: glycidol; 6: bromoacetone; 7: toluene; 8: cyclopentanone; 9: 1-acetyloxy-2-propanone; 10: styrene; 11: benzaldehyde; 12: benzenethiol; 13: aniline; 14: diethylen glycol; 15: 2-ethyl-1 hexanol; 16: N-methyl aniline; 17: glycidyl acetate; 18: N-ethyl aniline; 19: M-ethyl-N-methyl aniline; 20: 2-phenoxy ethanol; 21: tetraethylen glycol; 22: triacetin; 23: tetrachlorobenzene; 24: diphenylmethane; 25: 4-bromo-2-ethyl aniline; 26: fluorene

Table 1 Felt-tip pens investigated in this study

Table 2 Color and Rf values of the TLC spots of the Stabilo and Edding felt-tip pen inks

Table 3 Summary of the results obtained with Py-GC-MS, FT-IR spectroscopy, µ-Raman and SERS spectroscopy for all analysed felt-tip pens

Legend: CH: carbohydrates; Col: colophony; DEG: diethylene glycol; 2-EHA: 2-ethyl hexylacrylate; iBMA: iso-butyl methacrylate; MMA: methyl methacrylate; PA: polyamide; PAN: polyacrylonitrile; PEG: polyethylene glycol; PE: 2-phenoxyethanol; PH: phenols; ST: styrene; TA: triacetin; DIOAd: diisoctyl adipate; DIEP: bis(2-ethylhexyl)adipate

Faber-Castell PITT artist pen

ID	Color
AFC107	Cadmium yellow
AFC110	Phthalo blue
AFC129	Pink madder lake
AFC136	Purple violet
AFC154	Light cobalt turquoise
AFC264	Dark phthalo green

Stabilo 68 Pen

ID	Color
ST68-22	Blue
ST68-36	Green
ST68-41	Blue
ST68-44	Yellow
ST68-46	Black
ST68-53	Green
ST68-55	Violet
ST68-056	Pink
ST68-57	Turquoise

Edding 1200 super color quality

ID	Color
ED3	Blue
ED4	Green
ED10	Blue

	ST68-46	**ST68-22**	**ST68-41**	**ST68-57**	**ED3**	**ED10**	**ST68-36**	**ST68-53**	**ED4**	**ST68-056**	**ST68-55**	**ST68-44**
Color *spot /* **ink**	**black**	**blue**	**blue**	**turquoise**	**blue**	**blue**	**green**	**green**	**green**	**pink**	**violet**	**yellow**
black	0.04											
yellow		0.29					0.31	0.31	0.30			0.31
red	0.35											
blue	0.42	0.41	0.40	0.40	0.40	0.40	0.38	0.38	0.42			
purple											0.44	
orange	0.44											
pink					0.50							
violet		0.55	0.53	0.53							0.53	
pink										0.76		

	Dyes and Pigments	**Binders**	**Solvents**	**Additives**
Faber-Castell				
AFC107	PY81	MMA-STY, PA	DEG	PH, DIOPh
AFC110	PB15:3			
AFC129	PR146, PR122			
AFC136	PV23			
AFC154	PB15:3			
AFC264	PY81, PB15:3			
Stabilo				
ST68-22	AY23, AB9, BV4	CH	PEG	DIOAd, PH
ST68-36	AY23, AB9	CH	PEG	PH
ST68-41	AB9, BV4	CH	PEG	
ST68-44	AY23	CH	PEG	PH
ST68-46	PBk, AR18, AB9	ST-iBMA	PEG	DIEP, PH
ST68-53	AY23, AB9	CH	PEG	Col
ST68-55	BV4, AV49	ST-iBMA, CH	PEG	Col
ST68-056	BR1	ST-2EHA		PAN
ST68-57	BV4, AB9	iBMA	PEG	DIOAd, PH
Edding				
ED3	AB9, AR92	PG	PEG, PE	TA
ED4	AY23, AB9	PG	PEG, PE	TA
ED10	AB9	PG	PEG, PE	TA

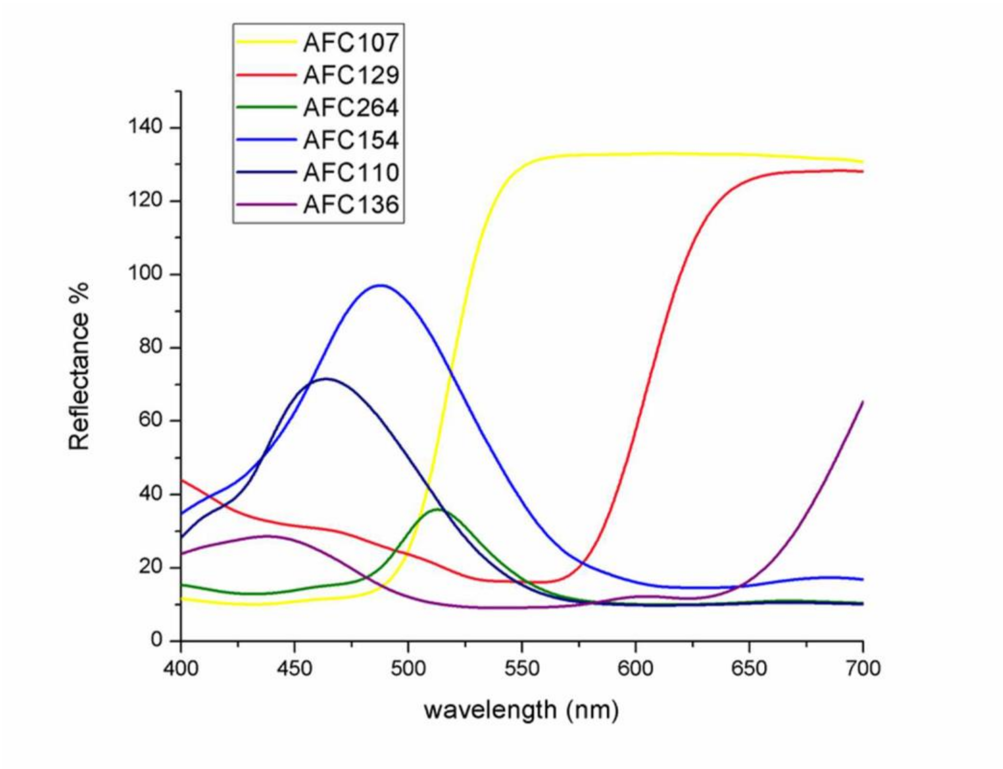
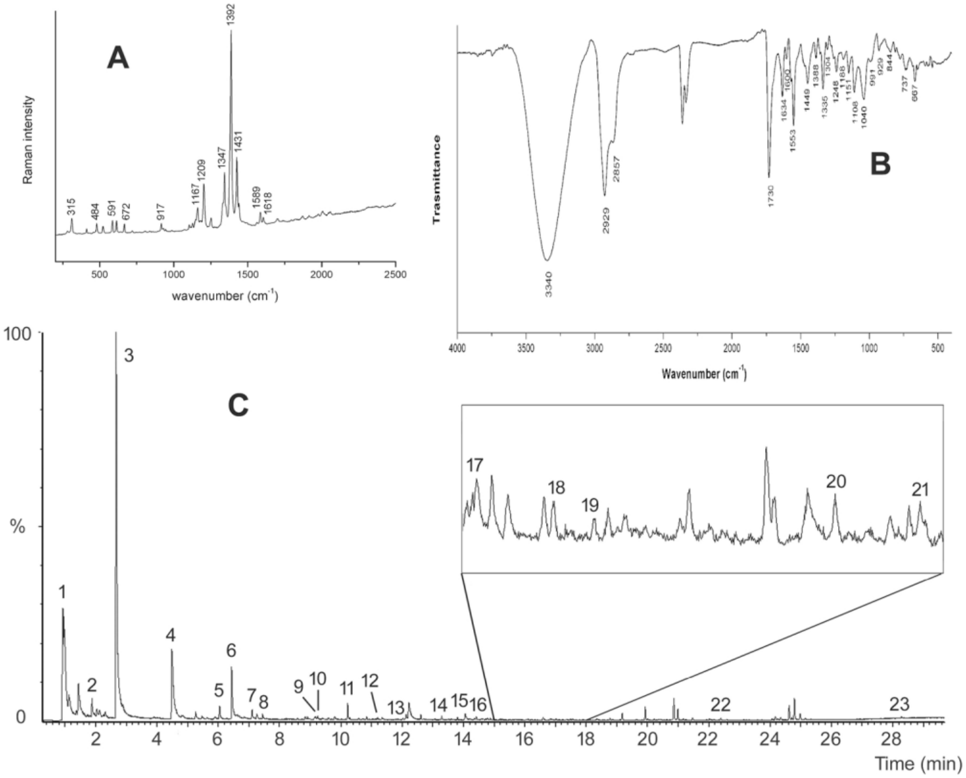


Fig. 1 Reflectance spectra of the Faber-Castell felt-tip pen inks applied on paper



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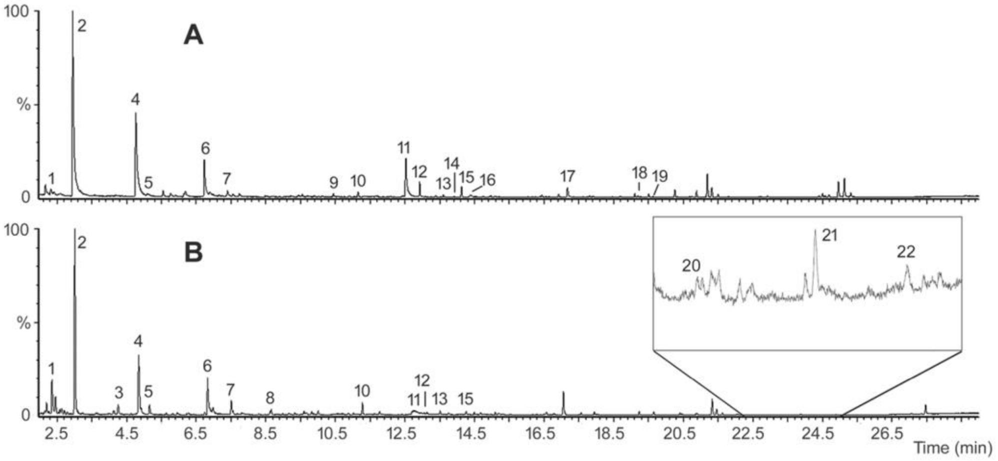

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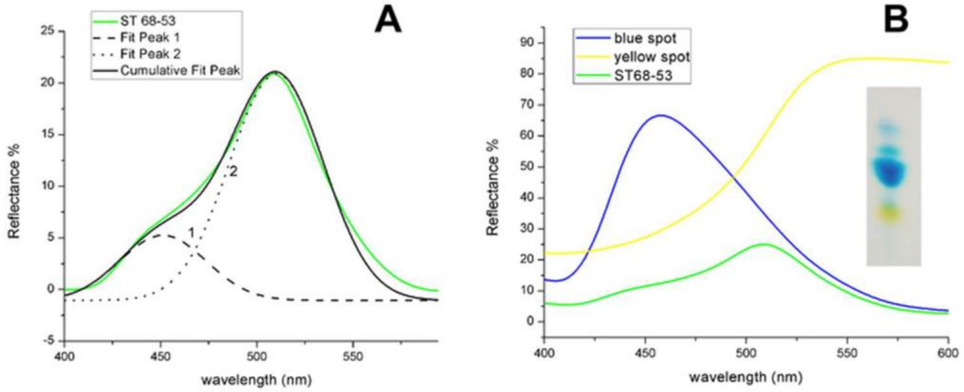


Fig. 4 Reflectance spectroscopy of the Stabilo felt-tip pen ink ST68-53. (A) Deconvolution of the reflectance spectrum; (B) Reflectance spectra of the yellow and blue TLC spots

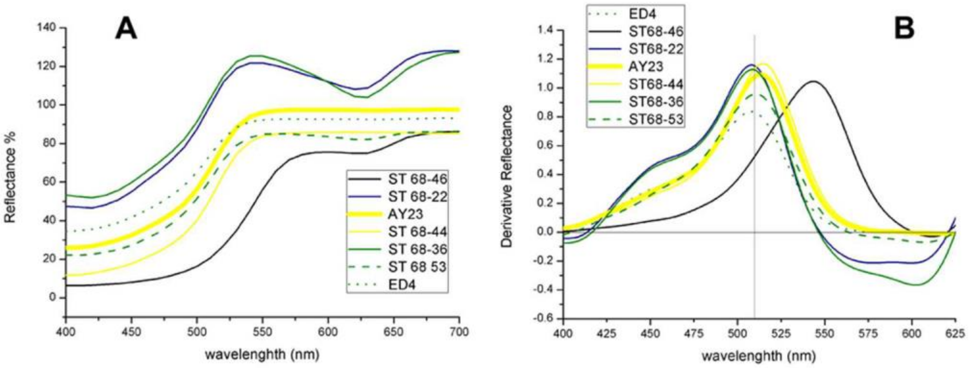


Fig. 5 Reflectance (A) and derivative reflectance (B) spectra of the yellow TLC spots of the Stabilo and Edding felt-tip pen inks

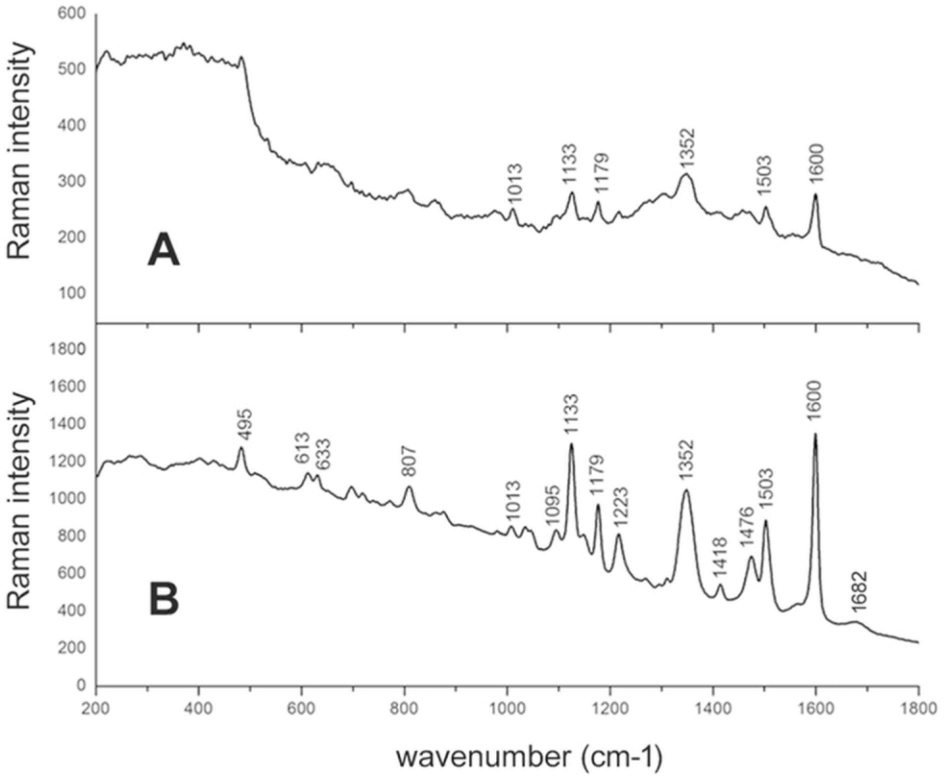
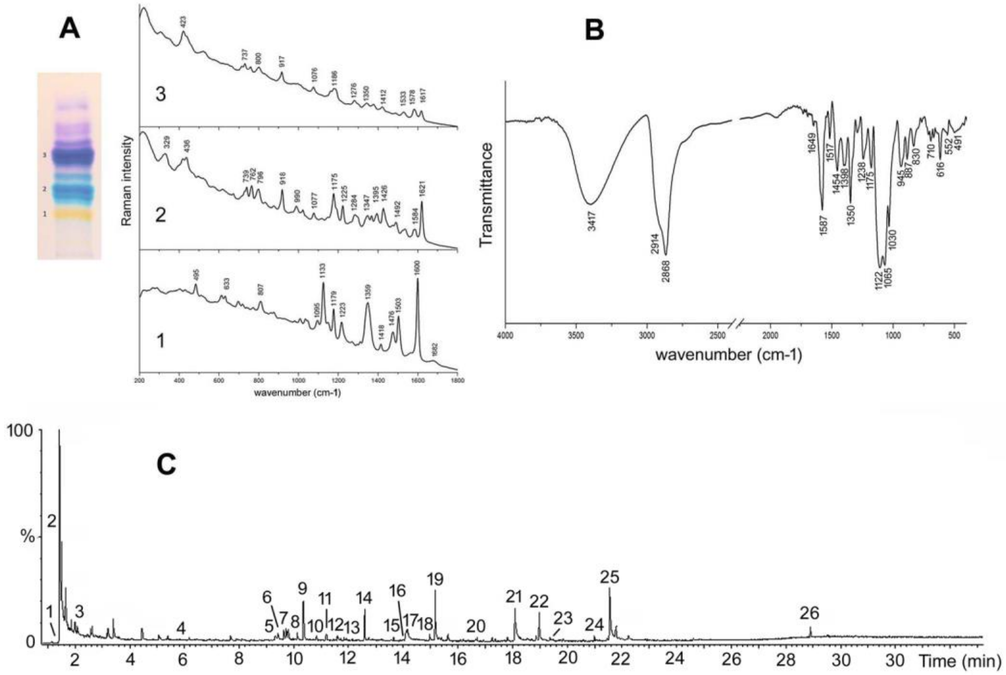


Fig. 6 (A) Raman e (B) SERS spectra of the yellow TLC spot of the Stabilo felt-tip pen ink ST68-36



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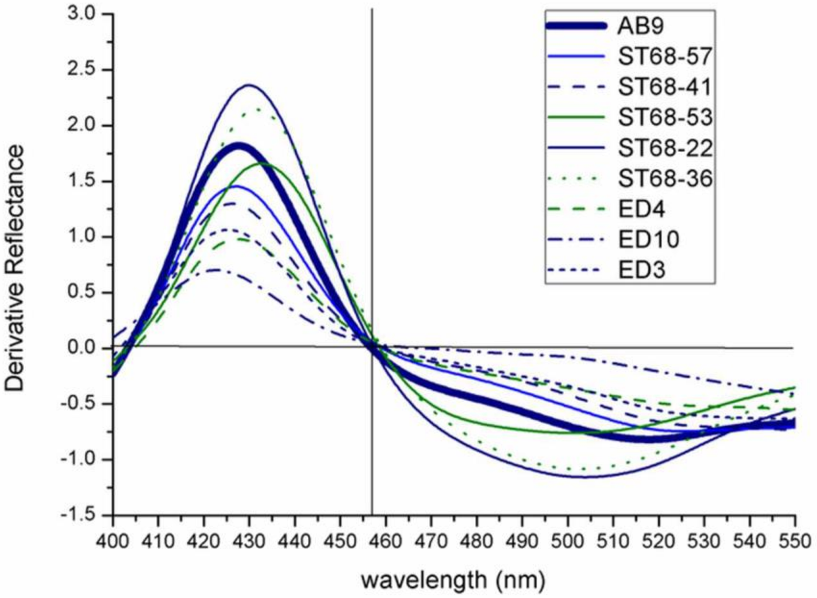

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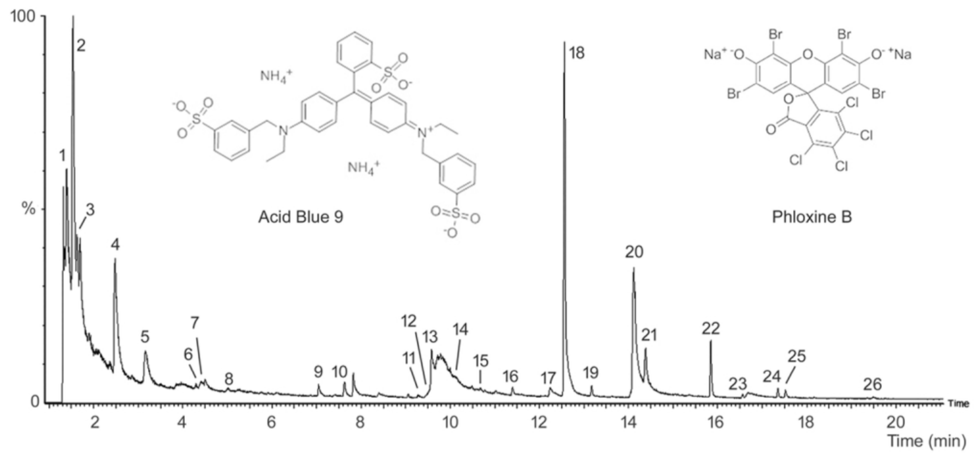

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