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Cationic–anionic dye mixtures in writing inks: A straightforward multianalytical approach for minute samples

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ABSTRACT

A minimally invasive analytical protocol was developed to characterize cationic–anionic dye mixtures in minute samples from 20th/21st-century writing inks taken from literary works. While synthetic dyes in inks are well-studied, the combined identification of cationic and anionic dyes in mixtures—and their influence on light stability, both crucial in the cultural heritage field—remain largely unaddressed. Previous approaches relied on mock-ups and large samples, incompatible with cultural heritage research where samples are minute and irreplaceable. We analyzed minute ink-on-paper samples (ballpoint and fiber pens) from literary works kept in the Austrian National Library using secondary ion mass spectrometry with MeV primary ions (MeV SIMS), μ-Raman spectroscopy, and microfading testing (MFT). Without chemical sample treatment, chromatographic separation or sample consumption, even the smallest samples were preserved for further study. MeV SIMS enabled soft ionization of organic molecules, identifying cationic dyes (e.g., Basic Blue 7) and aryl guanidines—markers for anionic dyes. μ-Raman detected anionic dyes (e.g., Solvent Blue 38). MFT revealed moderate fading in most inks; fiber pen inks containing only Solvent Blue 38 faded faster than ballpoint pen inks containing mixtures of Solvent Blue 38 with Basic Violet 1 and/or 3, and aryl guanidines. Mixtures of Basic Violets and anionic dyes in inks seem to increase light stability through dye-salt formation. The results obtained, addressing molecular identification and lightfastness of real ink samples, are of high importance for libraries, archives, etc., dealing with preservation of modern literary works in terms of lighting/exposure times during exhibitions.

1. Introduction

Industrial advancements of the 20th and 21st centuries introduced modern inks to the market, offering a wide array of colors and varying degrees of permanence. Nowadays, synthetic dye-based inks dominate writing inks, being commonly found in ballpoint and fiber pens [1]. However, many ballpoint and fiber pen inks—especially black ones—contain **mixtures of cationic and anionic dyes** (e.g., blue, violet, yellow and red [2]). **Cationic dyes** (e.g., basic dyes) in ballpoint pen inks bind strongly to low-quality wood pulp and unbleached paper, which is negatively-charged because of its high lignin and acidic hemicellulose content [2]. **Anionic dyes** (e.g., acid and solvent dyes) in fiber pen inks adhere better to wood-free and bleached paper [2], as they reduce feathering (spreading on paper) and offer increased light stability [3]. Cationic and anionic dyes fade at different rates, irreversibly altering the original appearance of the written text. According to the Commission Internationale de l'Eclairage (CIE) [4], Blue Wool 1 (BW1) and Blue Wool 2 (BW2) standards are frequently used as references for fading in the preservation of ballpoint and fiber pen inks on paper, indicating that these materials are highly light-sensitive. The Blue Wool scale consists of eight wool strips dyed with colorants of different lightfastness, with Blue Wool 1 being the least and Blue Wool 8 the most stable under light exposure, and is used to assess the effects of light on paintings, documents, and textiles [5]. The proneness to fading poses challenges for curators, conservators, and art historians, especially when highly valuable manuscripts and literary works must be preserved but also displayed during exhibitions. Identifying cationic–anionic dye mixtures in writing inks from cultural heritage objects is therefore crucial for predicting their behavior under light exposure.

For investigating modern writing inks, heritage science adapts analytical protocols from forensics due to different objectives. Forensic analysis primarily focuses on authenticity and forgery detection through

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ink discrimination and commonly uses large mock-ups (e.g., 4 × 10 mm^2 [6]) enabling multiple sampling for repeated measurements. These mock-ups—self-prepared materials that mimic original objects and designed to study chemical composition, behavior, and degradation under controlled conditions—allow forensic studies to minimize intervention on original evidence while ensuring analytical robustness and providing a well-defined analytical approach for the analysis of real samples [6,7]. Heritage science likewise prioritizes the preservation of original objects, seeking to obtain **maximum information from the smallest possible sample—or even without sampling, non-invasively, directly on the objects**. As a result, some analytical approaches developed and validated using large mock-ups in forensic science may be less suitable for precious and extremely limited samples from cultural heritage objects [6,8–10]. Moreover, forensic studies have predominantly focused on cationic dyes in ballpoint pen inks, based on their assumed prevalence [8–10]. In heritage science, fiber pen inks have been more extensively studied, often using methods similar to those in forensics and mock-ups containing artists' materials [11,12], with a primary focus on anionic dyes. Therefore, in both ballpoint and fiber pen ink studies, the mixtures of opposite-charge dye types are largely overlooked. Yet in heritage science, cationic-anionic dye mixtures deserve more attention, as the interaction between these dyes may significantly influence ink (light) stability. For example, upon light exposure one dye may generate singlet oxygen, potentially accelerating the degradation of other dyes within the mixture [13].

Synthetic dyes in writing inks are mostly identified through spectroscopic techniques, favored for their non-invasive nature, and if these prove inconclusive mass spectrometry (MS)-based techniques, often preceded by chromatographic separation and sample consumption, are employed. Among spectroscopic methods, Fourier-transform infrared spectroscopy (FTIR) is widely employed but limited by overlapping bands and interference from paper substrates [14]. Chemometric analysis can aid interpretation and classification but rarely enables definitive identification [15]. Raman spectroscopy, frequently coupled with an optical microscope (μ-Raman), is widely applied in cultural heritage studies due to its high spatial resolution (~1 μm), enabling the analysis of minute samples [16]. A range of Raman techniques is applied in heritage science, including dispersive Raman spectroscopy (with or without surface enhancement, i.e. SERS) and Fourier transform Raman (FT-Raman) spectroscopy. Dispersive μ-Raman spectroscopy can identify many colorants in complex mixtures, though fluorescence from certain dye classes, like xanthenes, can obscure signals [17,18]. To suppress fluorescence, both dispersive Raman and FT-Raman configurations using near-infrared (NIR) laser excitations can be employed. SERS, which is based on colloidal metal deposition on the sample [19], offers enhanced sensitivity to detect even highly fluorescent dyes [20], but it is considered invasive and it is not allowed for valuable artworks, especially when sampling is not permitted. If results gained with spectroscopic methods remain inconclusive, dyes are generally separated using thin-layer chromatography (TLC) or high-performance TLC (HPTLC) prior to measurements and then analyzed with different MS or spectroscopic techniques. MS techniques, including secondary ion mass spectrometry (SIMS) [8], matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) and laser desorption/ionization mass spectrometry (LDI-MS) can detect molecular ions directly from chromatographically separated dyes, but also from inks on paper. SIMS and LDI-MS are less invasive, as they do not require a matrix to absorb the energy of the laser and transfer it to the sample [21], unlike MALDI-MS. SIMS has been successfully applied to blue ballpoint pen inks on paper [8], but only in positive mode and on mock-ups, detecting exclusively cationic dyes, while anionic dyes evaded detection. LDI-MS can identify both cationic and anionic dyes in blue ballpoint pens using positive- and negative-ion modes, respectively—a notable finding by Gallidabino et al. [6], as such mixtures had not been previously thoroughly studied. However, their study used large mock-ups (4 × 10 mm^2), limiting applicability to cultural heritage samples. High-performance liquid chromatography coupled with MS (HPLC-MS) is another high-sensitivity technique often used in heritage science for studying ink mock-ups, as synthetic dyes are soluble and easily ionized [22,23]. Yet HPLC-MS is less suited to real samples, as it consumes them entirely, limiting further analysis and preventing solvent system optimization when only a minute sample is available.

Secondary ion mass spectrometry with MeV primary ions (MeV SIMS) offers a promising alternative for studying real minute ink-on-paper samples. As a focused beam of primary ions bombards the sample surface, it causes the ejection (sputtering) of secondary ions that are analyzed in a mass spectrometer to obtain surface-specific chemical information from the uppermost layers (<10 nm). Unlike SIMS employing keV primary ions, dominated by nuclear stopping, MeV SIMS uses primary ions in the MeV range and operates in the electronic stopping regime, resulting in softer ionization of organic molecules, reduced fragmentation, and a higher yield of intact molecular ions in the higher mass range ($m/z > 100$). The sample can simply be placed on a conductive surface (e.g. indium) without any chemical treatment, preserving it for subsequent analyses. MeV SIMS has proven efficient in identifying colorants (e.g. synthetic organic pigments) in artists' paints and colorant mixtures [24,25], as well as the Basic Violet 3 (BV3) dye in a blue ballpoint pen ink mock-up for forensic purposes [26]. Thus, we decided to test MeV SIMS for broader identification of cationic dyes in positive-ion mode and/or anionic dyes in negative-ion mode in real ink samples of both ballpoint and fiber pen inks on paper. Since samples are not consumed during MeV SIMS analyses [27], this method can be complemented by spectroscopic techniques like μ-Raman spectroscopy to obtain additional information. Additionally, microfading provides a fast assessment of ink light stability by using a high-intensity light source focused onto very small areas (~0.5 mm) to trigger accelerated fading [28,29].

In this study, we developed and applied a minimally invasive analytical protocol combining MeV SIMS, μ-Raman spectroscopy, and microfading testing (MFT) to characterize cationic−anionic dye mixtures in minute samples from literary works containing ballpoint and fiber pen inks. SERS was not considered, as it requires chemicals in its analytical protocol. Our research focused on eleven literary works—poems, novels, and authors' notes—written between the 1960s and 2012 by renowned authors born in Austria and kept at the Literary Archive at the Austrian National Library. These works are of high cultural and historical value and representative of everyday writing inks used in the 20th/21st-century. In this work, we show that the combined analytical approach used herein is highly applicable for identifying colorant mixtures in minute real ink samples, also providing results about their photostability without compromising sample integrity. As discussed later, our findings suggest the formation of complexes between cationic and anionic dyes if used as mixtures in ballpoint inks, possibly stabilized by the detected aryl guanidines. These may improve light stability of certain dyes in the inks beyond what current conservation standards assume from the values measured for standalone dyes. These important results are crucial for conservators making decisions regarding display and long-term preservation.

2. Experimental section

2.1. Synthetic organic colorants used as references

To support the interpretation of the acquired MeV SIMS and Raman spectra, a selection of reference synthetic dyes and pigments—presumed to be present in the ink samples based on preliminary spectral evaluation and literature sources [1,2]—was analyzed. These reference colorants, listed in Table 1, were taken from the INTK institute's internal 19th/20th-century Materials Collection. They were produced by various dye/pigment manufacturers, who typically disclose just the main colorant(s) present and not the full composition of their products, which may also contain additives or mixtures of various colorants. The

Table 1
Reference synthetic dyes and pigments analyzed by MeV SIMS and μ-Raman spectroscopy, selected based on the preliminary spectral evaluation of the ink samples. An “x” indicates that the colorant was analyzed using the corresponding technique, while a “-” denotes that the analysis was deemed unnecessary—for example, when the employed MeV SIMS setup could not detect anionic dyes in negative-ion mode (e.g., AR73, SB37, and SB38), or when Raman spectra were already available in the literature for certain synthetic organic pigments (e.g. PR83 [30]). BV14 was not analyzed by MeV SIMS, as preliminary evaluation of the ink spectra did not indicate its presence. The color index names of the colorants are taken from [31].

INTK Inv. No. = *i*.n.	Bottle name	Chemical class	Colorant class	Color index name	Manufacturer/Supplier	MeV SIMS	μ-Raman
552	Magenta DP.150 Powder fine	Triarylmethane dye	Basic dye	BV14	ICI	-	X
630	Methylviolett	Triarylmethane dye	Basic dye	BV1	Unknown	X	X
671	Brill. Croceine 3BA CF	Disazo dye	Acid dye	AR73	General Dyestuff Corp.	-	X
681	Kristallviolett ext. Plv. Typ 8200 neu P	Triarylmethane dye	Basic dye	BV3	BASF	X	X
1110	Krapplack	Dihydroxyanthraquinone pigment	Synthetic organic pigment	PR83	Inst. Der Hochschule für Welthandel	X	-
1327	Luxol Fast Blue ARN	Azo dye	Solvent dye	SB37	Du Pont de Nemours & Company	-	X
1329	Luxol Fast Blue MBS	Copper phthalocyanine dye	Solvent dye	SB38	Du Pont de Nemours & Company	-	X

resulting Raman and MeV SIMS spectra of the colorants will also enlarge INTK’s materials database (currently under development).

2.2. *Historical samples*

Minute ink-on-paper samples (as shown in Fig. 1) were taken under the microscope with a scalpel from eleven literary works in the Literary Archive at the Austrian National Library (Table 2). These literary works, written by famous 20th-century authors born in Austria: **Elazar Benyoëtz** (1937–), **Friederike Mayröcker** (1924–2021), **Ingeborg Bachmann** (1926–1973), **Manes Sperber** (1905–1984), **Peter Handke** (1942-), **Thomas Bernhard** (1931–1989), and **Vera Ferra-Mikura** (1923–1997)—contain several authors’ notes added with ballpoint and/or fiber pens from which the samples were collected. However, as some of these works are unnamed, they are differentiated in Table 2 based on their inventory numbers (inv. no.).

2.3. *Secondary ion mass spectrometry with MeV primary ions (MeV SIMS)*

Ink samples were pressed into indium drops (≥99.9 %, Sigma-Aldrich, USA) using an aluminum plate to produce a flat surface for the measurements.

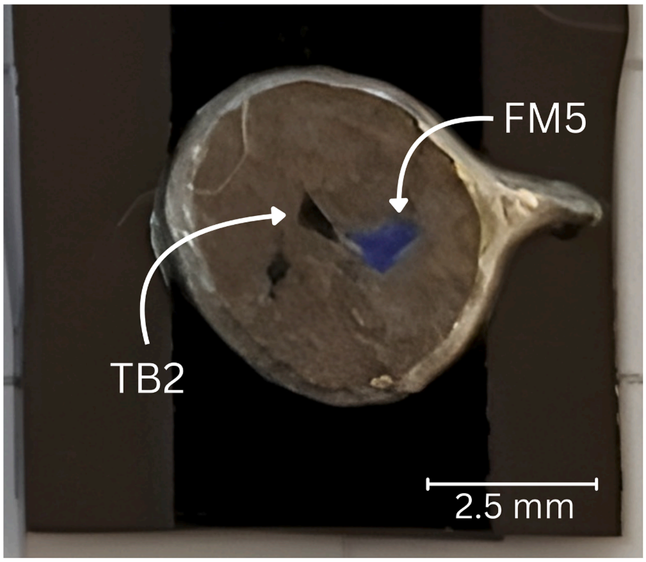

Fig. 1. Fiber pen ink-on-paper samples TB2 (black ink–two samples), and FM5 (blue ink), listed in Table 2, and pressed into indium for Raman and MeV SIMS analyses.

Table 2
Analyzed ink samples from eleven literary works at the Literary Archive at the Austrian National Library including pen type, ink color, source object/inventory number (inv. no.), and the year or decade in which they were written.

Type of ink	Ink sample	Color	Ink sample taken from	Year/ Period
Ballpoint pen	**EB1**	black	Written notes on inv.no. 378/11, NT 9/2, **Elazar Benyoëtz**	1970s
	FM3	deep-blue	Written note on inv. no. FM K32/5, **Friederike Mayröcker**	1960s
	FM4	deep-blue	Written note on inv. no. FM W115, **Friederike Mayröcker**	1970s
	IB1	dark-blue	Handwritten corrections on Typescript Malina, inv. no. 423/14, **Ingeborg Bachmann**	1960s
	TB1	dark-blue	Handwritten corrections on Typescript inv. no. 563/56/2, page 39, **Thomas Bernhard**	-
	VFM1	deep-blue	Written note on inv. no. 573/23, **Vera Ferra-Mikura**	1980s
Fiber pen	**FM1**	deep-blue	Written note on inv. no. FM 493/19, **Friederike Mayröcker**	-
	FM2	turquoise	Written note on inv. no. FM K19/7, **Friederike Mayröcker**	2000s
	FM5	deep-blue	Written notes in the Calendar of **Friederike Mayröcker**, page 24.5	2012
	MS1	red	Handwritten corrections on Typescript inv. no. 2/88/W21/2, page 151, **Manes Sperber**	1970s
	PH1	black	Written note on inv. no. 326/07/W41, **Peter Handke**	2004
	TB2	black	Handwritten corrections on Typescript inv. no. 563/56/2, page 39, **Thomas Bernhard**	-

MeV SIMS analyses were performed with the linear time-of-flight mass spectrometer installed at the heavy ion microprobe at the Ruđer Bošković Institute (RBI), Zagreb, Croatia [32]. An 8 MeV Si^{4+} primary ion beam, generated by the 6.0 MV EN Tandem Van de Graaff accelerator, was focused to a 10 × 10 μm^2 spot size and scanned over a maximum surface area of 450 × 450 μm^2, depending on the sample size area covered with ink. Measurements were carried out under high vacuum conditions (10^{-6} to 10^{-7} mbar) in positive and negative ion modes, with a target potential kept at +5 kV and –4 kV respectively. Beam fluence was kept below the SIMS static limit of 10^{12} ions/cm^2, so any surface damage could be considered negligible [27,33]. Ink samples that showed no molecular ions, protonated molecules or significant fragment ions related to colorants in positive-ion mode were also measured in negative-ion mode, with a target potential of –4 kV.

In-house SPECTOR software package [34] (version 2.3.35) was used to set measuring parameters, acquire data and perform mass calibration. Each MeV SIMS spectrum was calibrated using the monoisotopic masses of selected ions to account for differences in sample geometry that are known to affect the arrival time of secondary ions [35]. The ions selected for mass calibration and employed across all spectra were H^+, H_2^+, Na^+, $C_2H_3^+$, $C_2H_5^+$, $C_3H_5^+$, and $C_3H_7^+$. For ballpoint pen inks, the protonated molecule of ditolylguanidine ($C_{15}H_{18}N_3^+$) and the molecular ion of the main dye present were also used, whereas for fiber pen inks K^+ and Na_2OH^+ were employed. Other protonated molecules or molecular ions of dyes present in the inks were used where possible.

For spectra evaluation mMass–Open Source Mass Spectrometry Tool (v.5.5.0) was used [36], and the calibrated MeV SIMS spectra were compared with reference spectra from previous experiments [24,25,37,38]. For spectra comparison, base peak normalization was employed. The chemical structures of the pigments and their fragment ions were illustrated using ChemDraw (v.18.2.0.37) and ACD/ChemSketch (Freeware, v.2023.2.4). To additionally confirm the colorants' presence, we referred to various mass spectra in the literature, especially related to basic dyes, acquired through different MS techniques, including SIMS with primary ions in keV range [8], atmospheric-pressure chemical ionization mass spectrometry (APCI-MS) [13], LDI-MS [7], MALDI-MS [39], HPLC-MS [40–42], and HPLC-MS/MS (HPLC with tandem MS) [43].

2.4. *μ-Raman spectroscopy*

Dispersive μ-Raman spectroscopy was employed on the same samples placed on indium as used for MeV SIMS analysis. Measurements were conducted using an inVia QONTOR confocal Raman microscope (Renishaw, UK). Our InVia QONTOR setup is equipped with two laser sources: a 532 nm Nd:Yag (100 mW) with a 2400 l/mm grating, and a 785 nm diode laser (300 mW) with a 1200 l/mm grating, along with a CCD detector (1024 × 256 pixels, Peltier-cooled to –70 °C). A 50x LWD (long working distance) objective was used for the analyses. Spectral acquisition and processing were performed with the Renishaw WiRE software (v.5.6). Wavenumber calibration was done before measurements using both internal and external silicon standards, with the silicon υ_1 band at 520.7 cm^{-1} ± 0.5 cm^{-1}. Acquisition parameters were optimized individually for each ink sample to maximize spectral quality. Typically, spectra were recorded with five accumulations of 15 s each. Laser power was adjusted to ensure that no sample degradation occurred: 0.1–0.5 mW for the 532 nm laser and 15–30 mW for the 785 nm laser, depending on the sample. The extended scan mode was used to cover the Raman spectral range from 100 to 1800 cm^{-1}. Three spots per sample were analyzed. Spectral processing included averaging the three spectra collected per sample, followed by baseline correction using the software's internal *intelligent polynomial* baseline method. For dye identification, processed spectra were compared with the Raman SOPRANO library [30] and the INTK's materials database. The WiRE software enabled identification of compound mixtures and provided estimates of their relative abundances, which nevertheless had to be verified by the user.

2.5. *X-ray fluorescence (XRF) spectroscopy*

As toners (basic dyes precipitated with complex heteropolyacids such as phosphotungstic acid) may be present in writing inks [44], X-ray fluorescence (XRF) analysis was performed to assess the presence of basic dyes or toners. XRF measurements were carried out using a portable XRF instrument Type ELIO (XGLab, Bruker) in a non-invasive way, directly on the ink on the original pages containing the authors' notes, listed in Table 2. The pages were analyzed in a horizontal position at a distance of 4 mm (focal point) from the detector and were placed on a 4 mm thick plexiglass (polymethyl methacrylate – PMMA) plate during measurement. The selected XRF measuring positions were located adjacent to the areas from which ink samples were subsequently collected. The ELIO XRF device is equipped with a rhodium (Rh) X-ray tube and a silicon drift detector (SDD). The generated X-ray beam has a diameter of 1 mm. The focus of the X-ray beam on the analyzed object is controlled by two laser beams (the intersection of the lasers is the focus point) and an internal camera. The measurement parameters selected for the analyses were 40 kV, 6 μA and a spectrum acquisition time of 60 s. Spectral evaluation was performed using the internal ELIO software (v.1.6.0.57). Elements originating from the PMMA support and the paper substrate were excluded from the ink results.

2.6. *Microfading testing (MFT)*

To assess the light stability of the inks, we used a Micro Fading Tester (Instytut Fotonowy, Poland) at the State Collections of Lower Austria. The device is equipped with a 2733 K LED light source, emitting up to 4 mW at the focal point, simulating indoor exhibition lighting (as opposed to natural daylight at ~5500 K). Measurements were taken using two current settings—50 mA ("half-light" option) and 700 mA ("full-light" option)—with a vertical step size of 50 μm and a 0.56 mm spotlight diameter at the focal point. Before analysis, a reference reflectance measurement was performed using a $BaSO_4$ white standard (Instytut Fotonowy, Poland).

Blue Wool 2 and 3 standards (Blue Scale, Long Life for Art, Germany) were analyzed to establish reference microfading curves, as most pen inks typically fade within their range [28,29]. Specifically, the standards we used—Blue Wool 2 and 3—are dyed with Acid Blue 109, and Acid Blue 83, respectively [5].

MFT measurements were performed directly on the objects, always in the ink area adjacent to where an ink sample had previously been taken. Color differences were measured during continuous exposure to increasing doses of LED light at a rate of 0.002 Mlux·hr/s up to a total dose of 1.1 Mlux·hr. To reflect human visual perception, color differences were expressed in terms of ΔE_{00}, which is based on the CIELAB color space, with values greater than 2 considered perceptible to the naked eye and indicating significant fading [45]. The CIELAB values (L*a*b*) were recorded using the internal software of the Micro Fading Tester (v.2.1–662), and the ΔE_{00} values were calculated directly from the real-time changes in the recorded CIELAB values. As discussed, and agreed upon with the curator, only one microfading measurement was performed per ink.

3. Results & discussion

3.1. *Dye identification*

3.1.1. *Ballpoint pen inks*

Positive-ion mode MeV SIMS spectra revealed that the analyzed ballpoint pen inks predominantly contain basic (cationic) dyes (mass spectra shown in Fig. 2a and the molecular structures of dyes in Fig. 3). Their corresponding molecular ions $[M]^+$ were accompanied by demethylated species. Regardless of their color (blue or black), mixtures of Basic Violet 3 (**BV3**) with $[M]^+$ at *m/z* 372 and of Basic Violet 1 (**BV1**) with $[M]^+$at *m/z* 358 were present across all ballpoint inks. This is in accordance with the literature indicating that **BV1** and **BV3** are fundamental dyes used in ballpoint pen inks and typically co-occur [46]. Their molecular structures are nearly identical (Fig. 3), differing only by an additional methyl group ($-CH_3$) in **BV3**.

To further investigate whether BV1 could be distinguished from BV3 by MeV SIMS, and to assess the behavior of these two dyes in an alcohol solvent—as such solvents are commonly used in ballpoint pen inks—MeV SIMS reference spectra of **BV1** and **BV3** (listed in Table 1) were obtained from powders and ethanol (99.9 %, AustrAlco, Austria) solutions of 0.008 g of each dye in 100 μL, including a 1:1 mixture, applied onto Japanese paper (Fig. 4a–c). Japanese paper (Nebel KG., Austria) was chosen as substrate as it contained no fillers that could interfere

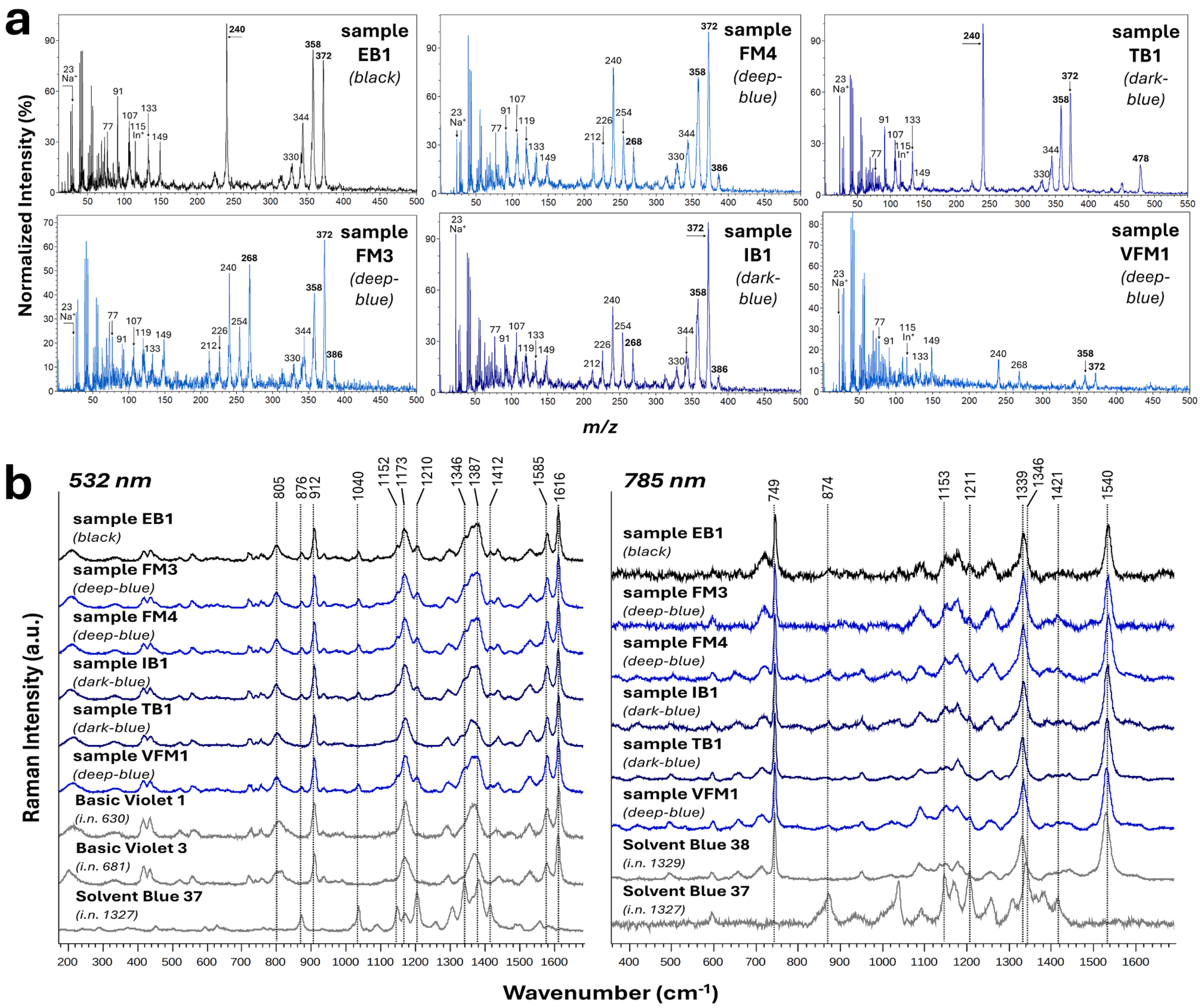

Fig. 2. MeV SIMS and μ-Raman results of ballpoint pen ink samples: (a) the positive-ion mode MeV SIMS spectra, and (b) the Raman spectra acquired with a 532 nm and a 785 nm laser, respectively, compared to the reference spectra (grey lines) of the identified dyes.

with the MeV SIMS analysis. In the BV1 dye powder, *m/z* 372 was detected, suggesting BV3 impurities from the manufacturing process. In case of BV3 dye powder, upon its dissolution in ethanol and application onto paper, and/or during the ionization process of the MeV SIMS analysis, it underwent methyl-hydrogen substitution, corroborating findings by Weyermann et al. [7], resulting in a pattern matching that of BV1. The primary distinction lies in the *m/z* 372/358 ratio, approximately 1 for BV1 in ethanol and 2 for BV3 in ethanol (Fig. 4c). This raises questions about whether demethylated products are indicative of aging as suggested by Lalli et al. [9], who associated increased *m/z* 358 intensity with older ink samples, or if they result directly from interaction with alcohol solvents.

MeV SIMS analysis of the BV1 and BV3 mixture (1:1) in ethanol on paper showed a higher intensity peak at *m/z* 358 compared to *m/z* 372. Additionally, *m/z* 330 and 344 were more pronounced in BV1 ethanol solution than in BV3 ethanol solution, suggesting their potential as markers for BV1 presence. Considering this, we calculated the relative proportions (RP_i) of characteristic ions of both dyes, namely: *m/z* 372, 358, 344, 330 in both prepared references of BV1 and BV3 and ink samples, using the formula [13]:

$$RP_i = \frac{I_i}{I_{tot}} \cdot 100\% \tag{1}$$

where I_i is the intensity of the ion at $m/z = i$, and I_{tot} is the sum of intensities of all four selected ions in the same MeV SIMS spectrum. This approach, favoring intensity over area due to broad peak widths and overlapping with characteristic fragment ions, allowed for comparative analysis (Fig. 5a and 5b). Among the samples, EB1 (black) exhibited a profile similar to the mixture of BV1 and BV3 dyes in ethanol, while samples FM3 (deep-blue), FM4 (deep-blue), and IB1 (dark-blue) aligned more closely with BV3 dye in ethanol. Dark-blue sample TB1 and deep-blue sample VFM1 resembled BV1 violet dye in ethanol. These estimations, while insightful, are tentative due to potential concentration variations of dye mixtures or presence of other additives in real samples. Notably, the ethanol mixtures used in this work mirrored the patterns observed in the samples, suggesting that the demethylated products may result primarily from solvent interactions rather than from aging. This is further supported by the determined ratio of the summed intensities of the degradation products (*m/z* 358, 344, and 330) relative to the intensity of the parent ion at *m/z* 372, (corresponding to both BV1 and BV3 dyes), as shown in Table S-1. In the ethanol reference mixtures, these values were: 1.94 for BV1, 0.97 for BV3 and 2.04 for BV1 and BV3 (which is slightly higher than the BV1 reference considering the higher BV3 content in the 1:1 mixture), and comparable to those in the ink samples (0.84 – 1.84 range). This reinforces the conclusion that the interaction with the solvent may be the main driver of degradation by

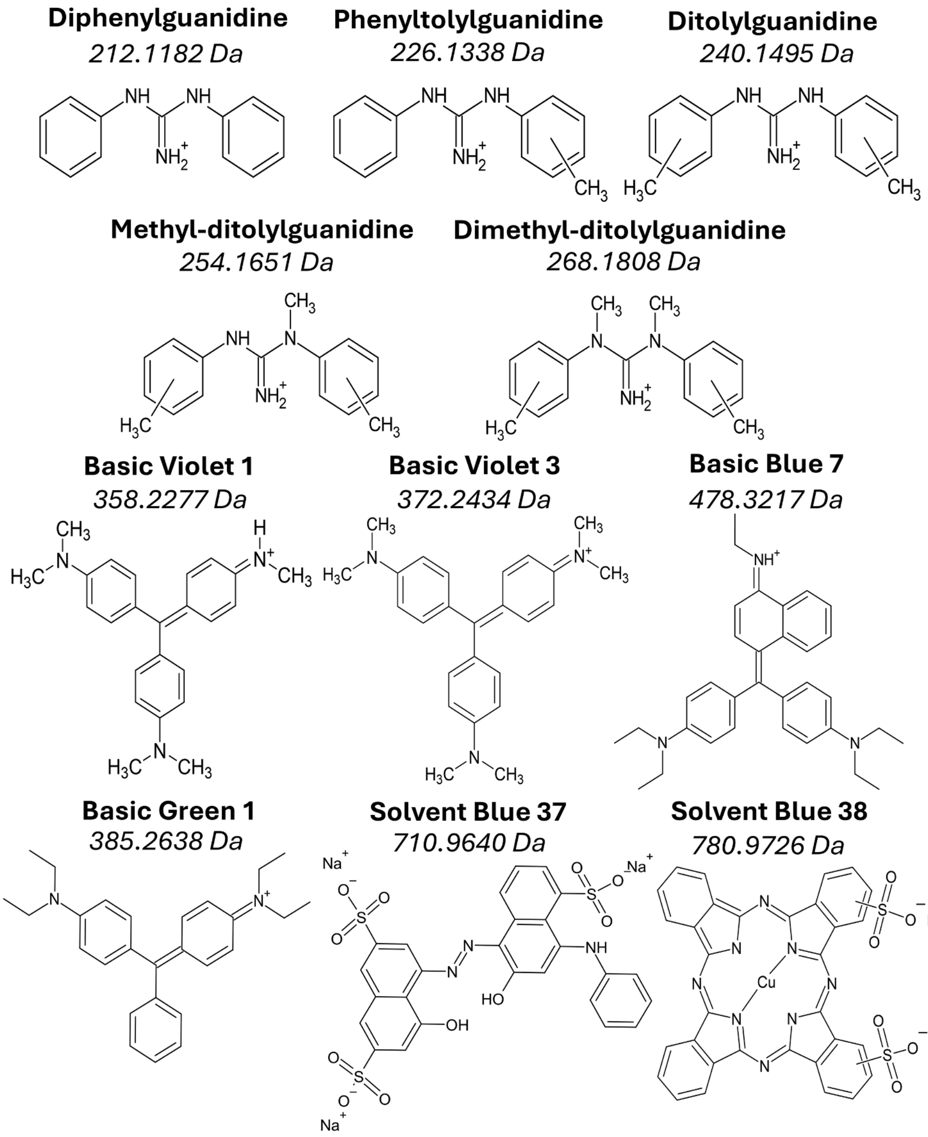

Fig. 3. Molecular structures of the cationic/anionic dyes along with the aryl guanidines identified in the minute samples by MeV SIMS and/or μ-Raman spectroscopy as shown in Fig. 2. The monoisotopic masses were calculated in ACD/ChemSketch (Freeware, v.2023.2.4).

methyl substitution, although contributions from matrix effects and ionization processes cannot be completely excluded.

Beyond violet dyes, $[M]^+$ of Basic Green 1 (**BG1**) was detected at m/z 386 in blue ink samples FM3, FM4, and IB1. In black and deep-blue samples EB1 and VFM1, respectively, mixtures of only **BV1** and **BV3** dyes were detected. The dark-blue sample TB1 contains mixtures of dyes BV1, BV3, and Basic Blue 7 (**BB7**), with $[M]^+$ at m/z 478, and its main deethylated product ion at m/z 450 (–28 Da). The detection of only violet and green dye mixtures in most blue inks suggested that at least one blue dye may have gone undetected by MeV SIMS. Moreover, none of the six ballpoint pen inks contained detectable levels of tungsten and/or molybdenum species, which was confirmed both with MeV SIMS in the negative-ion mode [25] and XRF, thereby supporting the use of basic dyes rather than toners. Toners, formed by precipitating basic dyes with heteropolyacids (e.g. phosphomolybdic/phosphotungstic acids), share the molecular structure of basic dyes but exhibit better lightfastness [47]. Thus, elemental analysis, such as XRF, supports differentiation between dyes and toners through tungsten (W) or molybdenum (Mo) detection.

MeV SIMS gave a hint to the type of the constituent blue colorant due to the presence of **aryl guanidine derivatives**. Manufacturers often incorporate various guanidines into ink formulations [48] to render anionic dyes water-insoluble and enhance solubility in alcohols and glycols [49–51]. Aryl guanidines form salts with sulphonated solvent or acid dyes from the azo or phthalocyanine classes, and their detection via MeV SIMS serves as a marker for the presence of anionic dyes. Aryl guanidine derivatives were detected across all ballpoint ink samples (EB1, FM3, FM4, IB, TB1, and VFM1). The fragmentation pattern of aryl guanidines was characterized by m/z 268 (protonated molecule of dimethyl-ditolylguanidine), 254 (methyl-ditolylguanidine), 240 (ditolylguanidine), 226 (phenyltolylguanidine), and 212 (diphenylguanidine). Additional smaller ions at m/z 107, 119, 133, and 149 were also present, corresponding to aniline-related species. In samples EB1 (black) and TB1 (dark-blue) only m/z 240 and 226, were detected, suggesting the sole presence of ditolylguanidine and its main degradation product. Initially, m/z 240 was considered indicative of $[M]^+$ of Pigment Red 83 (PR83); however, MeV SIMS analysis of the reference PR83 (i.n. 1110), shown in Figure S-1, did not support this, leading to its attribution to ditolylguanidine, consistent with the findings of Jones et al. [52].

Raman spectra supported the results obtained via MeV SIMS, particularly when acquired using the 532 nm laser, but also revealed the presence of solvent dyes such as Solvent Blue 37 (**SB37**) and Solvent

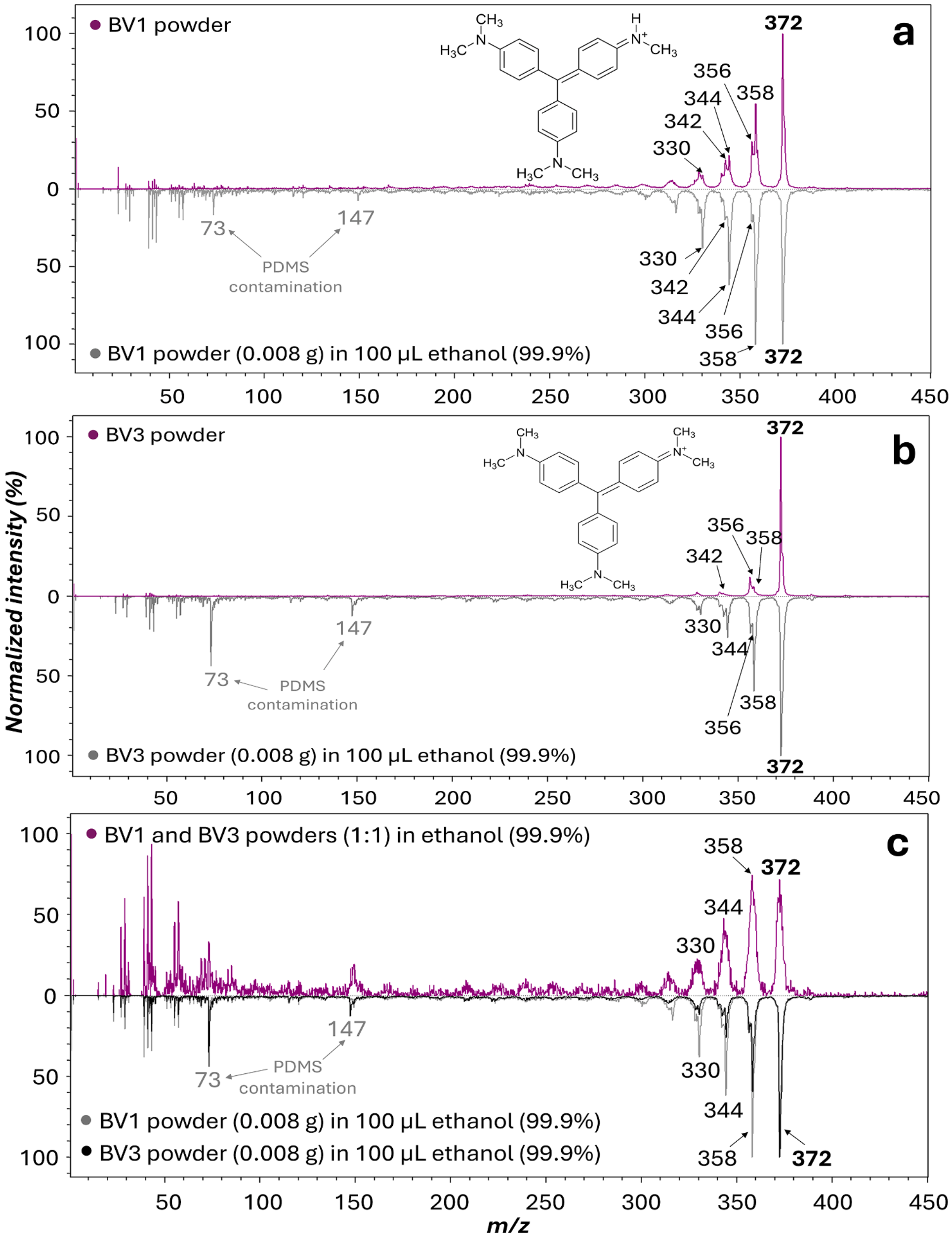

Fig. 4. Normalized positive-ion mode MeV SIMS spectra of BV1 (i.n. 630) and BV3 (i.n. 681) as pure powders and ethanol solutions: (a) BV1 powder compared to BV1 in ethanol, (b) BV3 compared to BV3 in ethanol, and (c) mixture of BV1:BV3 (1:1) in ethanol compared to BV1 and BV3 powders in ethanol.

Blue 38 (**SB38**), the latter being more pronounced with the 785 nm laser. Neither SB37 nor SB38 could be detected with MeV SIMS. BV1 and/or BV3 were the only basic dyes detected in the Raman spectra of the analyzed samples; BG1 (in blue samples FM3, FM4, and IB1) and BB7 (in dark-blue sample TB1) were not observed. As shown in Fig. 2b and suggested in the literature [53], BV1 and BV3 dyes could not be clearly distinguished in the Raman spectra taken on real ink samples, due to their similar molecular structures. Characteristic Raman bands of these dyes were found at 805, 912, 1173, 1387, 1585, and 1616 cm^{-1}, corresponding to various benzene vibrational modes [53]. Despite the known poor lightfastness of BV1 and BV3, the marker bands associated with their degradation—namely 1585 and 1616 cm^{-1}—appeared similar in intensity to those of the reference dye powders. Notably, the 1585 cm^{-1} band was less intense than 1616 cm^{-1}, which contrasts with what is typically observed in aged samples, where the 1616 cm^{-1} band usually becomes more prominent, as reported by Cesaratto et al. [53] and Saviello et al. [54]. The I_{1585}/I_{1616} ratio ranged from 0.43 to 0.60 for the six ballpoint pen inks (Table S-2), results that align with Cesaratto's unaged and slightly aged (7 days at a 0.12 Mlux·hr dose) crystal violet (BV3) samples. Consequently, the condition of the analyzed samples can be considered optimal. In the Raman spectra obtained with the 532 nm laser, SB37 was also identified in samples FM3 (deep-blue), FM4 (deep-blue), IB1 (dark-blue), and VFM1 (deep-blue), with a spectrum similar to that of reference "Luxol Fast Blue ARN" (Table 1) from the INTK's Materials Collection. As described in the literature [50,55], this dye powder consists of SB37, a sulphonated azo dye combined with mixed diarylguanidines (Fig. 3). This is consistent with the MeV SIMS results that showed the presence of mixed diarylguanidines together with basic dyes (BV1, BV3, and BG1). In the deep-blue VFM1 sample a few yellow specks of <10 µm in diameter, were found under the microscope. These yellow spots were analyzed with µ-Raman (532 nm laser), as shown in Figure S-2. In the Raman spectra, Pigment Yellow 185 (PY185), an isoindoline derivative was identified, known for its relatively good lightfastness.

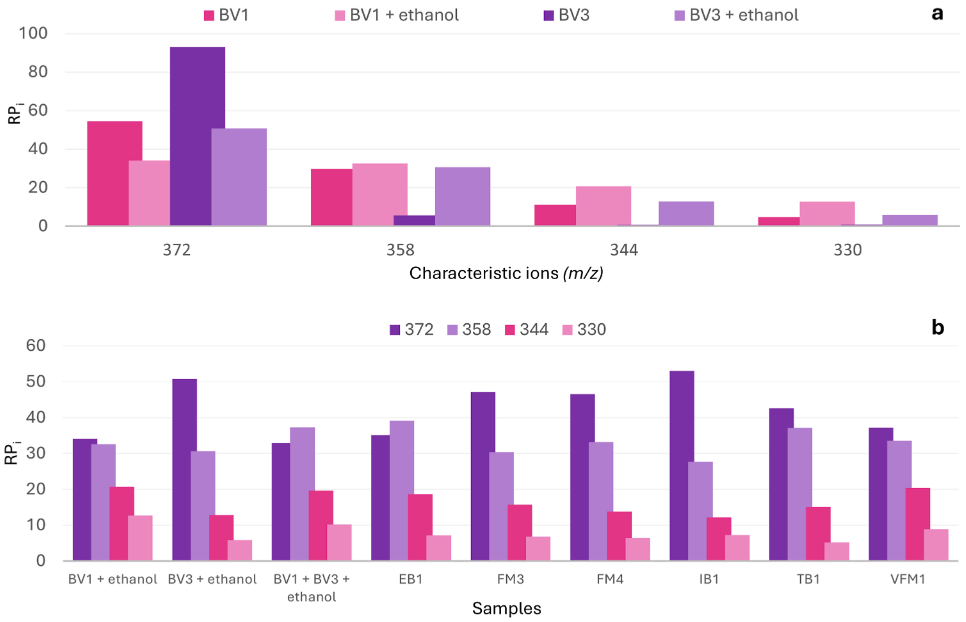

Fig. 5. Relative proportions (RP_i) of selected ions (*m/z* 372, 358, 344, 330) in BV1 and BV3 powders and their ethanol solutions, illustrating changes in peak intensities (shown in a), and comparison of RP_i values among BV1 in ethanol, BV3 in ethanol, and their 1:1 ethanol mixture against those obtained from the six ballpoint pen ink samples (shown in b).

Using the 785 nm laser, SB38 was detected in all ballpoint pen ink samples, with spectra matching that of the colorant reference "Luxol Fast Blue MBS" (Table 1), a salt of mixed diarylguanidines and a copper phthalocyanine dye (Fig. 3) [50,55]. SB38 includes between 2.5 and 2.8 sulfonic acid groups per molecule, and it is believed to form complexes with diarylguanidines via at least one of these solubility enhancing groups [55]. When diarylguanidine is present in excess, it may complex with all of them. The sole detection of SB38 in the Raman spectra with the 785 nm laser can be explained by its absorbance maximum located at ~669 nm [56], where the resonance effect is significantly enhanced for the B_{1g} and B_{2g} vibrations related to the in-plane symmetric vibrations of the phthalocyanine structure [57]. SB37, in contrast, has an absorbance maximum at ~578 nm [56], and was thus detected with both lasers, though the peaks were more intense when using the 532 nm laser.

3.1.2. *Fiber pen inks*

MeV SIMS proved effective for sample TB2 (black) (Fig. 6a), but ineffective for the other fiber pen inks (samples FM1—deep-blue, FM2—turquoise, FM5—deep-blue, MS1—red, and PH1—black). This limitation is likely due to the predominance of anionic dyes in these inks (molecular structures shown in Fig. 7), which could not be detected with the current analytical setup in negative-ion mode. The only information resulting from MeV SIMS spectra—specifically from MS1—was a peak at *m/z* 97, attributable to HSO_4^-, which is associated with sulfonated dyes in negative-ion mode [58]. In contrast, the positive-ion mode spectrum of black sample TB2 (Fig. 6a) revealed the presence of **BB7**, with its $[M]^+$ at *m/z* 478 serving as the base peak, alongside its deethylated specie at *m/z* 450 [59]. A peak at *m/z* 330 was also detected, possibly corresponding to the $[M]^+$ of Basic Green 4 (**BG4**), consistent with the results reported by Tamburini et.al. for this dye [43]. An additional information obtained by MeV SIMS was the seeming presence of benzyl alcohol in the red MS1 sample, a solvent commonly used in ballpoint pen inks and potentially present in fiber pen inks [60], according to the relatively high-intensity peak at *m/z* 109.

Anionic dyes in fiber pen inks were identified in the 532 and 785 nm Raman spectra, as shown in Fig. 6b Analysis of turquoise FM2 sample revealed the presence of Acid Blue 9 (**AB9**), an anionic triarylmethane dye (disodium sulphonated dye) [61]. The obtained Raman spectrum closely matched the one in the literature [62]. AB9 is commonly used as food colorant: Food Blue 2 or Brilliant Blue FCF. Despite a strong fluorescence background, the Raman spectrum of sample TB2 showed a good match with that of Basic Violet 14 (BV14). However, the absence of BV14 in positive-ion mode MeV SIMS spectra suggested the ink may contain its oppositely charged analogue, Acid Violet 19 (**AV19**), also known as Acid Fuchsin. AV19 differs from BV14 by the presence of three SO_3^- groups, improving its water solubility. Both dyes show an absorbance maximum at ~540 nm [56], which explains their detection with the 532 nm laser. This result is supported by the similarity of our spectral data with those reported by Longoni et al. [63] for AV19.

The 785 nm laser Raman spectra clearly highlighted additional dyes in fiber pen inks, not found with MeV SIMS. Samples FM1 (deep-blue), FM5 (deep-blue) and PH1 (black) showed spectral features consistent with SB38, akin to those observed in ballpoint pen inks. In the Raman spectra of deep-blue FM1 and FM5 samples only SB38 dye was detected, whereas black sample PH1 displayed varying bands across different measuring spots, highlighting the presence of additional colorants (as shown in Fig. 6b). As indicated by Raman bands found at 1175 cm^{-1} (probably C–N symmetric vibration), 1411 cm^{-1} (likely $N = N$ stretch), and 1585 cm^{-1} (benzene mode) these dyes might belong to the azo dye class [64]. However, no clear assignments could be made by comparing the spectra with available Raman spectral libraries. Notably, the spectra of black ink sample PH1 acquired with both 532 and 785 nm excitation were characterized by broad Raman bands in the 1000–1600 cm^{-1} range, consistent with the profile of carbon black, with the D and G bands likely present at ~1300 and 1600 cm^{-1}, respectively [65]. The red sample MS1 was found to contain Acid Red 73 (AR73), a disazo dye. Particularly, the band at 1374 cm^{-1}, specific for aromatic ring vibrations and/or N-phenyl stretching [64], appeared less intense than in the AR73 reference Raman spectrum, both measured with the 785 nm laser. This attenuation may emphasize the initial stages of N-phenyl bond cleavage, suggesting the onset of dye degradation.

3.1.3. *Short summary of the identified dyes*

A comprehensive overview of the identified colorant mixtures in the minute ink samples on paper using the combined MeV SIMS and μ-Raman spectroscopy approach is summarized in Table 3.

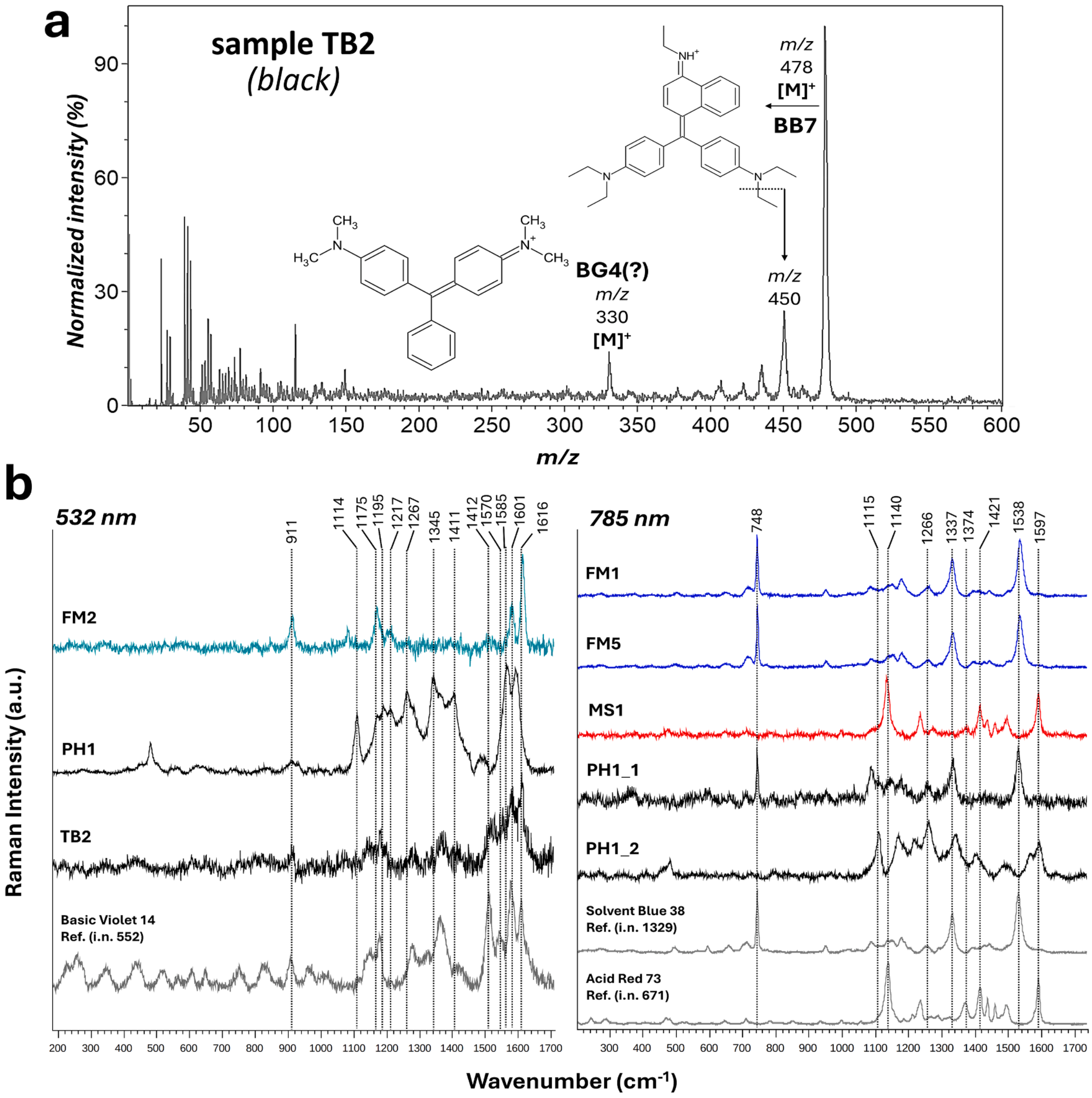

Fig. 6. MeV SIMS and μ-Raman results of fiber pen inks: (a) the normalized positive-ion mode MeV SIMS spectrum of TB2, and (b) the 532 nm and 785 nm Raman spectra, respectively, compared to the dyes reference spectra (grey lines). In comparison to ballpoint pen inks, these inks appeared to contain only anionic dyes, except for TB2 that also included basic dyes.

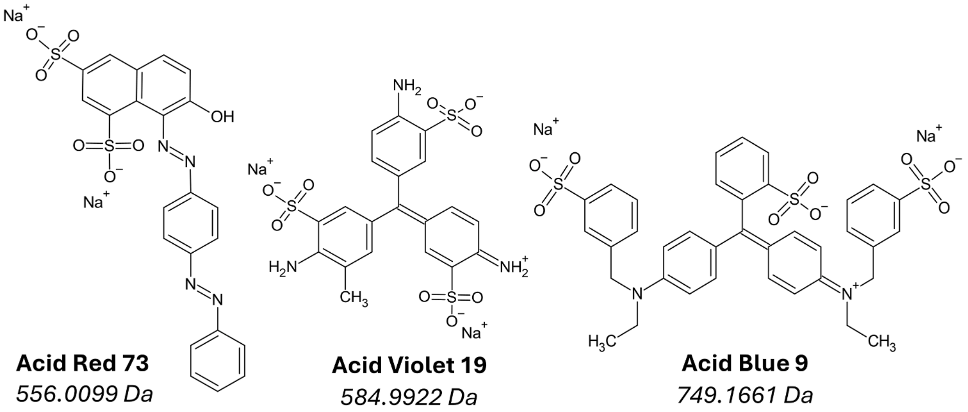

Fig. 7. Molecular structures of the anionic dyes found in fiber pen inks. Solvent Blue 38 was also identified – molecular structure already shown in Fig. 3, as it appeared in ballpoint pen inks as well.

Table 3

Summary of the positive-ion mode MeV SIMS and μ-Raman results obtained for analyzed ink samples.

Type of ink	Ink code	Color	MeV SIMS	μ-Raman	
				532 nm laser	785 nm laser
Ballpoint pen	EB1	black	**BV1** and **BV3**	**BV1** and/or **BV3**	**SB38**
	FM3	deep-blue	**BV3** and **BG1**	**BV1** and/or **BV3** and **SB37**	**SB38**
	FM4	deep-blue	**BV3** and **BG1**	**BV1** and/or **BV3** and **SB37**	**SB38**
	IB1	dark-blue	**BV3** and **BG1**	**BV1** and/or **BV3** and **SB37**	**SB38**
	TB1	dark-blue	**BV1** and **BB7**	**BV1** and/or **BV3**	**SB38**
	VFM1	deep-blue	**BV1**	**BV1** and/or **BV3** and **SB37** + specks of **PY185**	**SB38**
Fiber pen	FM1	deep-blue	-	-	**SB38**
	FM2	turquoise	-	**AB9**	-
	FM5	deep-blue	-	-	**SB38**
	MS1	red	-	-	**AR73 (SR69)**
	PH1	black	-	**carbon black**	**SB38** + additional colorant(s) and **carbon black**
	TB2	black	**BB7** and **BG4(?)**	**AV19**	-

3.2. *Lightfastness and fading behavior*

3.2.1. *Ballpoint pen inks*

As shown in Table 4 and Fig. 8a, most ballpoint pen inks presented relatively high light stability. Samples FM4 (deep-blue), IB1 (dark-blue), TB1 (dark-blue) and VFM1 (deep-blue) were slightly more light-sensitive than the Blue Wool 3 standard, with an average color difference ΔE_{00} of 0.58 at a dose of 1.11 Mlux·hr. Among these, the black sample TB1 was the least stable, displaying a ΔE_{00} of 1.18 at the same dose, ranking third in light sensitivity among all analyzed inks, following the least stable fiber pen inks. The microfading curve type of sample TB1 differs from those of the other ballpoint pen inks and aligns with type V, which implies that fading accelerates over time as dyes are present in large aggregates that are broken down into smaller particles by heat or illumination, as classified by Giles et al. [66]. This behavior might be explained by the presence of BB7 besides basic violet dyes BV1, BV3, and solvent blue dye SB38, a dye with similar molecular structure to BB26, that has been shown to promote/accelerate the degradation of BV1 and BV3 dyes [13]. It is likely that blue dye BB7 absorbs light more efficiently due to its larger conjugation system, which enhances singlet oxygen production that affects the stability of dyes like BV1 and BV3 [13]. For deep-blue VFM1 sample, the color difference at 1.11 Mlux·hr was theoretically calculated based on the observed fading rate and trend at lower doses, as measurements were not taken up to that point as decided by the curator. However, based on the initial part of the microfading curve, its behavior appears similar to that of the other ballpoint pen inks. Consequently, the presence of PY185 did not seem to significantly enhance fading resistance. The black EB1 and deep-blue FM3 pen inks showed values that suggested the highest lightfastness, with their fading curves lying below that of Blue Wool 3 standard. This outcome was unexpected, considering the poor lightfastness of basic violet dyes BV1 and/or BV3, which we identified in all the examined ballpoint pen inks. According to Hagan et al. [67], these dyes exhibit a ΔE_{00} of approximately 20 at a dose of 1.11 Mlux·hr in dyed textiles. Additionally, in ballpoint pen inks they are known to often have a light stability lower than the Blue Wool 3 standard, even approaching the values of Blue Wool 1 and 2, according to common conservation guidelines [4].

The improved light stability observed in our samples suggests that other compounds in the ink formulations, such as solvent blue dyes SB38 (in all six samples), and SB37 (in samples FM3, FM4, IB1, and VFM1), and/or aryl guanidines (in all six ballpoint ink samples)—may have positively contributed to lightfastness. It has already been shown that combining differently charged dyes—specifically alkylbenzene acid/solvent dyes (anionic) and basic dyes (cationic)—can lead to the formation of salts with strong ionic bonds [68]. These salts enhance the ink's light stability, reducing the likelihood of fading over time. Moreover, aryl guanidines are strongly basic compounds that manufacturers add directly to acid or solvent dye powders to form water-insoluble dye salts. This formulation is used e.g. in reference colorants examined here, namely Luxol Blue MBSN (SB38) and Luxol Fast Blue ARN (SB37), both of which are frequently reported in ballpoint pen inks, according to several patents [50,55]. The incorporation of aryl guanidines has been shown to improve the lightfastness of solvent dyes, although the exact mechanism remains not fully understood [69]. It is plausible that the formed salts between acid/solvent dyes and aryl guanidines dissociate in solution, and if basic dyes (e.g. BV1, BV3) are present, new water-insoluble salts form between the initial acid/solvent dyes and the basic dyes, as suggested by Fookson et al. [68]. Regarding reduced photodegradation, it might be that aryl guanidines absorb light more efficiently than the formed water-insoluble salts, potentially degrading in their place and thereby acting as sacrificial compounds. It should also be noted that dye concentration in the spots selected for microfading plays an important role in photodegradation. Higher dye concentrations reduce the likelihood of fading due to the so-called *layer effect*, as observed by Giles et al. [66]. Dye molecules tend to distribute uniformly

Table 4

Color difference (ΔE_{00}) values of the ballpoint and fiber pen inks, along with those of Blue Wool standards 2 and 3 (shown in gray), measured at the same light dose of 1.11 Mlux·hr. The ΔE_{00} value for deep-blue sample VFM1 (shown in italics) was manually calculated based on the available measured data and the observed trend, as this sample was measured up to 0.25 Mlux·hr.

	Color difference (ΔE_{00}) at 1.11 Mlux·hr					
Ballpoint pen inks	EB1	FM3	FM4	IB1	TB1	*VFM1*
	0.4	0.37	0.51	0.52	1.18	*0.14*
Fiber pen inks	FM1	FM2	FM5	MS1	PH1	TB2
	1.06	4.66	1.11	1.42	0.93	0.82
Blue Wool standards	BW2	BW3				
	5.82	0.73				

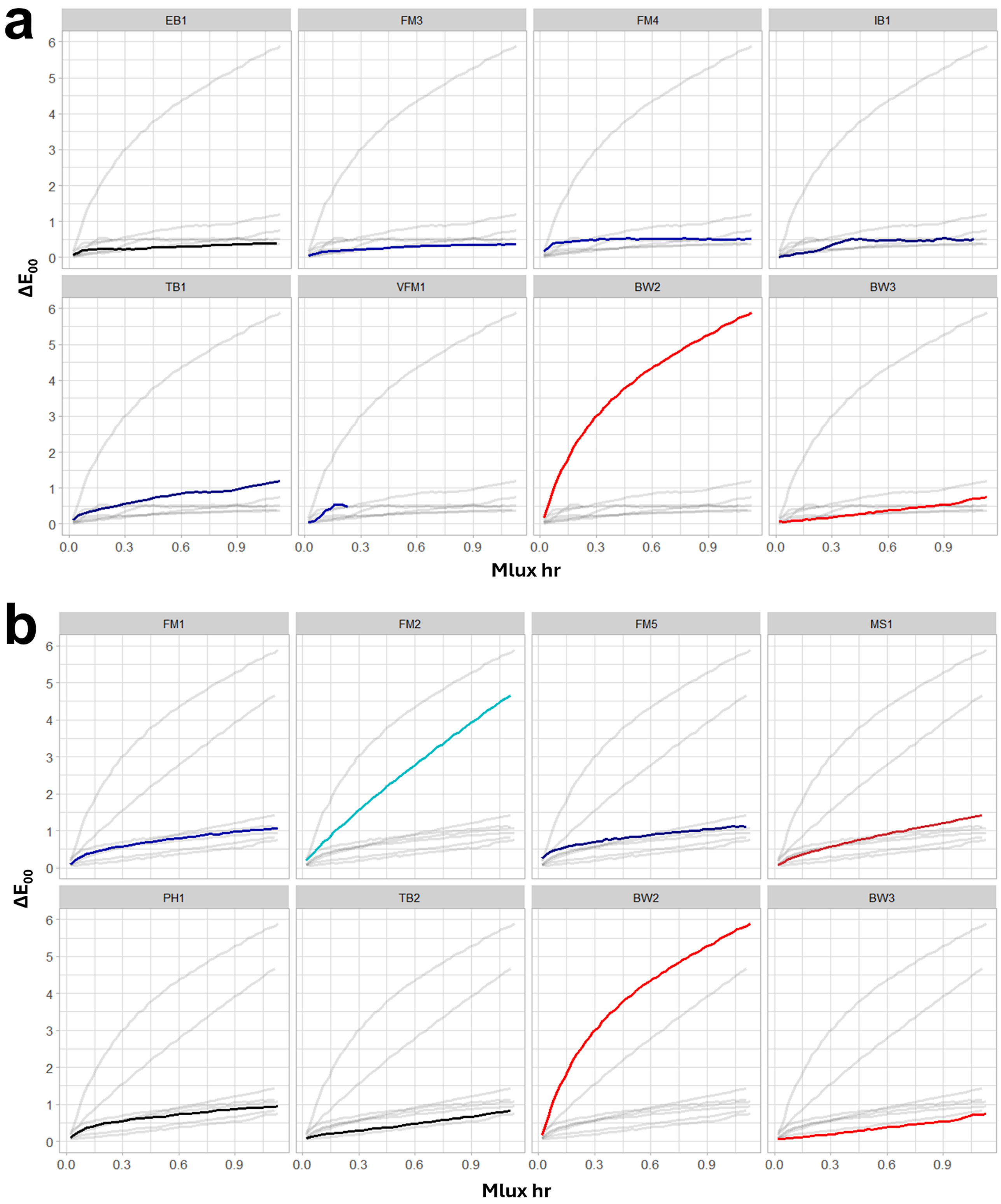

Fig. 8. Microfading curves of (a) ballpoint pen inks and (b) fiber pen inks. In both (a) and (b) the microfading curves corresponding to the Blue Wool 2 (BW2) and Blue Wool 3 (BW3) standards are also shown in bright red. The colors of the highlighted microfading curves correspond to the colors of the analyzed inks. The grey lines represent all the microfading curves that have been acquired.

in layers within a substrate such as cellulose fibers. As a result, higher concentration forms more layers, and dye molecules in deeper layers fade more slowly than those closer to the surface. However, other external factors—such as temperature, humidity, pH, type of substrate, and type of solvent—are also known to influence photodegradation, as emphasized by Groeneveld et al. [70]. Therefore, we also measured the light stability of the paper substrates of the eleven examined objects (Figure S-3), which appeared to have minimal influence on the microfading curves of the inks.

3.2.2. *Fiber pen inks*

As depicted in Table 4 and Fig. 8b, most fiber pen inks presented lower light stability compared to ballpoint pen inks, with the exception of black sample TB2, which outperformed one of the ballpoint pen inks, namely dark-blue sample TB1. The higher stability of TB2 might be explained by the presence of AV19 violet dye, which, according to Hagan et al. [67], shows a ΔE_{00} value of 3.5 in dyed textiles. This performance is substantially better than that of BV1 and BV3 that exhibit a ΔE_{00} of ~20 at a dose of 1.11 Mlux·hr [67]. However, it might be possible that another, more stable dye is present in the ink that we could not detect. Deep-blue FM1 and FM5, and black PH1 samples displayed similar ΔE_{00} at an average of 1.03 at 1.11 Mlux·hr. Among the fiber pen inks, the turquoise sample FM2 was the least stable, with a ΔE_{00} of 4.66 at 1.11 Mlux·hr, followed by MS1, which had a ΔE_{00} of 1.42 at the same dose.

As mentioned before, the fiber pen inks deep blue samples FM1 and FM5, and black sample PH1 all contain solvent blue dye SB38. However, their lightfastness was lower than that of ballpoint pen inks including SB38 in combination with aryl guanidines and basic dyes, which seems to have had a positive effect in preventing their photodegradation. This suggests that while SB38 is considered highly lightfast, its effectiveness is augmented when it forms stable salts with other compounds. The absence of aryl guanidines in these fiber pen inks is intentional, as their inclusion could render the inks water-insoluble, contrary to the water-soluble nature desired for fiber pen applications. Although the black sample PH1 contained additional dyes, their presence did not significantly alter its fading behavior, which closely resembled that of FM1 and FM5. FM2 (turquoise) was the only fiber pen ink with a type V fading curve [66], indicating accelerated fading. While such behavior has been previously attributed to thermal effects from illumination-induced heating [66], recent studies suggest that autocatalytic effects may also play a role in this degradation process [29]. Fiber pen ink MS1 also demonstrated considerable light sensitivity, likely due to the presence of acid red dye AR73, with an OH group in the ortho position to the azo group, which has been shown to be prone to photodegradation [71]. Ortho substituents in monoazo dyes are particularly sensitive to light due to increased electron donation generated by their proximity to the chromophore ($-N=N-$). This position may also enhance intramolecular interaction or electron delocalization, which can weaken the chromophore and make it more light-sensitive, especially when it is the sole dye present [72].

4. Conclusions

This study presents a minimally invasive analytical protocol for characterizing cationic–anionic dye mixtures in real minute ink-on-paper samples from literary works containing ballpoint and fiber pen inks. The combination of MeV SIMS, μ-Raman, and microfading testing (MFT) led to complementary results, detecting dye mixtures in inks without chemical sample preparation and chromatographic separation. Thus, the use of the same sample during the presented analytical approach was ensured and sample consumption of irreplaceable samples was avoided. Furthermore, light stability was generally higher than expected, often exceeding the range of Blue Wool 1 and 2 standards—frequently used as reference in the preservation of ballpoint and fiber pen inks on paper [4]—and in some cases even surpassing Blue Wool 3.

In ballpoint pen inks, MeV SIMS identified cationic dyes and aryl guanidines, the latter suggesting the presence of anionic dyes detected by μ-Raman. Microfading curves suggested cationic-anionic dye mixtures enhance light stability in ballpoint pen inks. In fiber pen inks, positive-ion mode MeV SIMS detected cationic dyes, aiding the interpretation of Raman spectra of dyes with nearly identical molecular structures, but that were oppositely charged. Fiber pen inks containing only the typically stable Solvent Blue 38 (SB38) dye exhibit lower lightfastness than ballpoint pen inks that contain mixtures of SB38, the light-sensitive Basic Violet 1 and 3 (BV1 and BV3) dyes, and aryl guanidines. This indicates that the addition of basic dyes, despite their inherently fugitive nature, together with aryl guanidines may improve the overall photostability of the inks. However, further studies are required to evaluate whether matrix effects also contribute to the differences in lightfastness between ballpoint and fiber pen inks.

The analytical protocol used in this work led to dye characterization within non-destructive sample analysis and yielded crucial results concerning cationic–anionic dye mixtures in writing inks that have not been previously reported. We also clearly showed that degradation of basic dyes arises also from solvent-dye interactions within ink formulations, and not simply through natural aging. These results are very important for conservators for making precise decisions regarding display and storage of literary works for future generations.

Data availability

The data that support the findings of this study are available on request.

CRediT authorship contribution statement

Teodora Raicu: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Matea Krmpotić:** Writing – review & editing, Validation, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Zdravko Siketić:** Writing – review & editing, Resources, Methodology. **Iva Bogdanović Radović:** Writing – review & editing, Resources, Methodology. **Katja Sterflinger:** Writing – review & editing, Supervision, Resources. **Dubravka Jembrih-Simbürger:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Dubravka Jembrih-Simbuerger reports financial support was provided by BMBWF (Federal Ministry of Education, Science and Research Austria) and the Ministry of Science, Education and Youth of the Republic of Croatia. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.talo.2026.100632.

Data availability

The data that support the findings of this study are available on request.

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