NONDESTRUCTIVE Vis-NIR REFLECTANCE SPECTROSCOPY AS A FORENSIC TOOL FOR INK DISCRIMINATION: A PRELIMINARY STUDY

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UDC 543.42.062; 535.3

Visible light reflectance spectra were taken from signatures inscribed with five different inks of five different ball-point pens by a modular portable Vis-NIR spectrophotometer with PC. The ink-analysis procedure was nondestructive, consisting of visible reflectance spectra acquisition from multiple designated sampling spots of each signature, using a customized reflection probe holder and a tungsten white light source. Sampling spots were preselected to partly cover the signature ink-line on the white background (paper). The repeatable reflectance spectra (R%), recorded and plotted for each ink, which is subject of this study, appeared with typical spectral features (extrema) for each tested ink. To determine another characteristic spectral feature for ink discrimination, such as inflexion points specific to the absorption edges, a numerical derivative of the first order was calculated for the average R% spectrum of each ink. The wavelengths at which the typical features appear were used for Vis-NIR codification of each ink for discrimination purposes. A different code could be assigned for each ink, using the description of the "general feature," the extrema, and the inflexion points from the reflectance spectrum. This method can be used as a nondestructive tool for ink identification for forensic purposes.

Keywords: *Vis-NIR spectrophotometer, reflectance spectra, ink-line.*

Introduction. Owing to the complexity of the modern lifestyle, documents play a significant role in our everyday life as a part of our financial, legal, business, social, and personal affairs. Because of their significance and widespread use in everyday life, documents have always been subject to forgery. Forensic analysis of questionable documents [1] usually involves examining pen inks used in signatures. Characterization of pen inks is frequently needed for identification, comparison, and/or dating purposes in criminal cases involving suspected document fraud or forgery. Proving forgery implies the provision of scientifically based evidence of the changed authenticity of the document. Therefore, it is undoubtedly necessary to develop appropriate time-efficient and accurate analytical methods and tools for determining the facts concerning the questioned documents — their source, authorship, authenticity, age, and to identify any alteration from their original state.

Multiple types and brands of pens are commercially available on the market in each country. Also, there is a multitude of no-brand ink pens. Their distinction involves color differentiation, chemical composition, and type of tip. Ink analysis in forensic procedures includes classification and comparison of their complex chemical mixtures. Further, it confirms whether or not two different parts of the document (pages) were signed by the same writing instrument (same pen) and whether they have been written with the same ink [2]. Pen inks can mainly be classified into ball-point pens (inks) and inks for other pens (non-ballpoint inks). The inks for the different pens can be further divided into water-based inks (shower pens, roller pens, gel pens, markers) and pens with inks based on solvents (permanent markers) [3].

Various physical and physicochemical methods are known to be utilized in the forensic research of inks [4]. There are multiple publications on the destructive methods such as: liquid chromatography [3], high-performance liquid chromatography (HPLC) [4, 5], scanning electron microscopy (SEM) with elemental profiling (SEM-EDX), UV-Visible [6], Visible-infrared, and Fourier-transform infrared spectroscopy [2, 7], Raman spectroscopy [8], mass spectroscopy

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[9], secondary ion time-of-flight mass spectrometry [10], matrix-assisted laser desorption ionization mass spectrometry imaging, Rutherford back-scattering spectroscopy, proton-induced X-ray emission spectroscopy [11], X-ray fluorescence (XRF) [12], X-ray photoelectron spectroscopy [13], laser-induced breakdown spectroscopy [14], laser ablation inductively coupled plasma time-of-flight mass spectrometry [15], and nondestructive methods such as smartphone mapping and RGB analysis [16], as well as multi- and hyperspectral imaging [17], etc.

Nondestructive reflectance spectroscopy was previously used by da Silva et al. [2]. The method was upgraded for discrimination of black ink in questionable document analysis using a VSC®6000 Visual Spectral Comparator by Foster & Freeman, using mathematical modeling by partial least squares [18]. This method involved nondestructive measurements applied directly to the written documents. Other authors have reported that visible reflectance spectroscopy could be a powerful discriminative tool. Their approach was nondestructive, using UV-2600 series, equipped with ISR-2600 plus Integrating Sphere (Shimadzu, Japan). Their method determines the differences in spectral features of inks by using principal component analysis and k-mean cluster analysis. This approach ensures that the blue ball-point pen inks are differentiated by their UV-Vis/UV-Vis/NIR spectra [19].

We present a preliminary study on the possibilities for ink discrimination using a nondestructive reflectance spectrophotometric method coupled with numerical derivation and a tentative coding system for ink matching. As this method is nondestructive, it allows the optical properties of the ink pigment to be differentiated.

Materials, Methods, and Calculations. Five brands of gel ball-point pens commercially available on the market (listed in Table 1) were used to inscribe signatures on a white sheet of paper. Vis-NIR reflectance spectra were taken by a modular portable Spectrophotometer Ocean Optics USB4000 with accessories: HL-2000 tungsten halogen light source with a wavelength range of 360–2400 nm, UV-Visible Reflection/Backscatter Probe 300–1100 nm, 45° reflectance measurement positioning probe and optical fibers (light guides) for white light, as well as a product by Ocean Optics. All measurements were taken at a wavelength resolution of 0.2 nm and controlled ambient temperature of 25°C. The tungsten light source was stabilized for 20 min before the measurements. A reflectance diffused light standard WS-1 (matte white) with reflectivity >98% within the spectral range 250 to 1500 nm was used to set the 100% reflectance. Dark reference (0%) was taken at a closed shutter of the light source. Collimating lenses on the optical fibers were used to customize the incidence and angle of collection to increase the signal in the reflectance measurements.

A reflectance probe was laid on the signed paper (Fig. 1). Then, the reflectance sampling spots were chosen by the "lab-technician" by sliding the reflectance probe across the paper document while looking through the aperture on the reflectance probe to select an appropriate inked area on the paper. A magnifying glass on top of the aperture was used to improve the spot selection process.

In this article, we present an analytical methodology procedure on a signature created with a blindly selected ink from the pen collection from Table 1 (nominated as Ink X). The reflectance spectra were acquired from the designated sampling spots (in a fashion presented in Fig. 1). The recorded spectra from the destined acquisition point were then averaged and smoothed using the moving average of the reflectance across 21 points (10 before and 10 after) and presented in Fig. 2a. An average reflectance spectrum was calculated for each signature from the spectra from Spot 1 to Spot 5 (black line in Fig. 2a). There are also inflexion points (IPs) between the consecutive minima and maxima in which the curve turns from concave to convex and vice versa. However, it seems challenging to extract the position of those points from Fig. 2a. On the other hand, the position of the IPs is mathematically defined as extrema (minimum or maximum) in the numerically calculated first derivative of the $R\%$ spectra. Here, the first derivative of the smoothed reflectance spectra (FD $R\%$) was calculated numerically from

$$\text{FD } R\% = \Delta R / \Delta W .$$

Bearing in mind that ΔW is the constant number (the step in the wavelength setup for the instrument is equal to its resolution of 0.2 nm), one can calculate the first derivative in arbitrary units (a.u.) as simply as

$$\text{FD } R\% = \Delta R .$$

Figure 2b shows the first derivatives (FD $R\%$) of the reflectance spectra taken from the signature inscribed with Ink X (the blindly selected pen of the five in Table 1). The narrow region in which the course of the spectrum curve turns from concave to convex and vice versa is defined as an inflexion point. Here, the slope of the curve increases and then decreases, or vice versa, meaning that the first derivative of the curve reaches its extremum (either maximum or minimum).

Figure 2a shows unique and repeatable characteristic features in the $R\%$ spectra that could be unambiguously located and quantified. Those features were chosen to be: the location of a local minimum ($I_{\min}$, counting from the IR side of
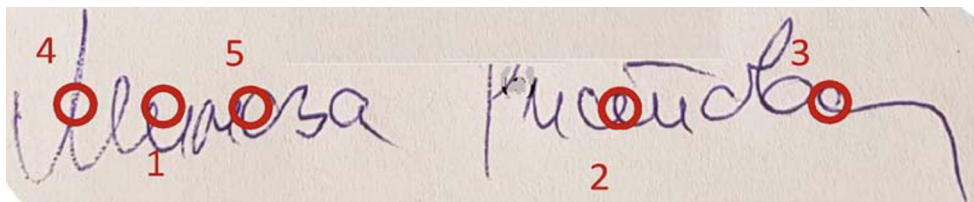
Fig. 1. A nondestructive method for signature ink analysis: reflectance ($R\%$) spectra were acquired from five sampling points/spots of the signature (ink deposited on white paper). A magnifying glass was used to focus on the chosen sampling spot.
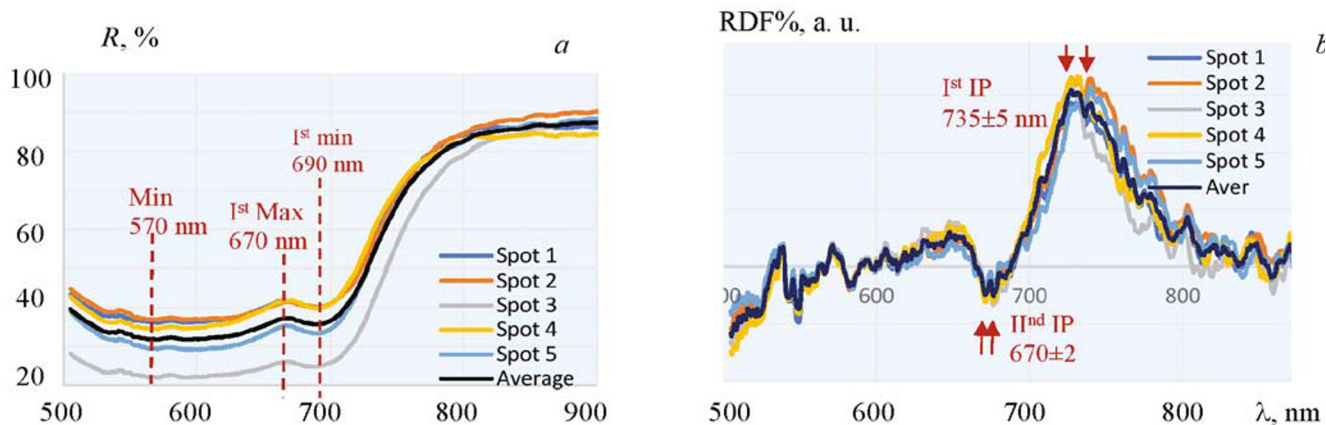

Fig. 2. (a) Repeatability of the reflectance features presented with five reflectance spectra taken from five different sampling spots of the same Ink #X and their average, and determination of overall minimum in the reflectance spectrum at 570 nm and local maximum in the reflectance well (bottom of the reflectance spectrum) at 670 nm. (b) Determination of inflexion points (extrema in the numerical first derivative of the individual $R\%$ spectra) and their average FD $R\%$.

TABLE 1. Five Gel Pens, Brands, and Colors

Ink	Product name	Ink color
Ink 1	Mitsubishi uni.ball Signo	Blue
Ink 2	Ballpoint pen Pentel Superb	Black
Ink 3	Ballpoint pen BIC	Black
Ink 4	Ballpoint pen "white label"	Blue
Ink 5	Ballpoint pen Office Cover Astro	Blue

the spectrum, located at 690 nm), followed by a local maximum (I_{max} at about 670 nm), and the overall spectral minimum (at about 570 nm). Figure 2b shows the numerically calculated first derivative of the $R\%$ spectrum for Fig. 2a. Again, the specific, repeatable features are the first maximum (inflexion point counting from the right), I IP, at about 735 nm, and the first minimum (inflexion point, counting from the right) of the II IP, located at about 670 nm.

These unique features, appearing at defined wavelengths (as evident in Fig. 2), could be used to create a primary tool for ink discrimination. The five signatures produced by the five inks listed in Table 1 were analyzed using the same
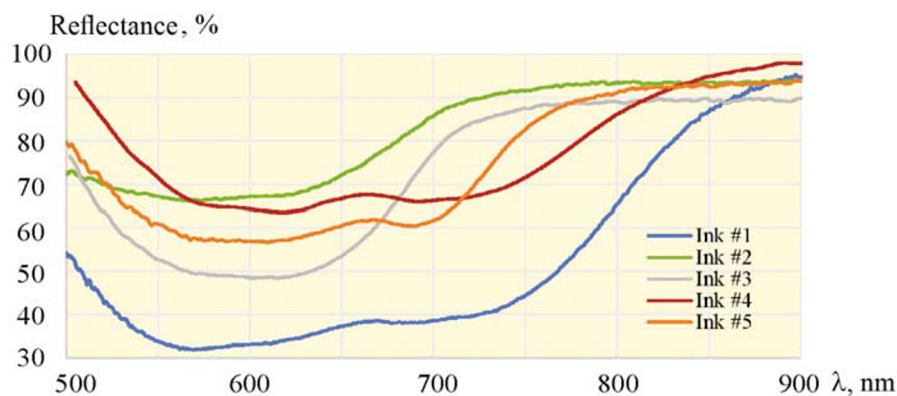
Fig. 3. Reflectance spectra of all five inks from Table 1. A general feature of the single, double, and triple well designations could be assigned to each $R\%$ spectrum.

procedure as in the case for the randomly selected Ink #X. Comparison and discrimination/identification of the Ink X was processed using the proposed simple coding system based on the general feature of the reflectance spectra and the wavelengths at which the extrema and the inflexion points appear.

Results and Discussion. Reflectance spectra of all five inks subject to this study, listed in Table 1, are presented in Fig. 3. Each recorded spectrum offers a calculated average of the spectra taken from five different sampling spots of each signature. From Fig. 3, it is evident that broad Vis-NIR $R\%$ spectra are defined with their red reflectance edges. Thus, the quantifications of those red edges were prosperous parameters for discrimination among different inks. Also, from Fig. 3, it is evident that the "bottom" of the reflectance well could be flat (as in the case with Ink 2 and Ink 3) or it could reveal one local maximum (as in the case with Ink 1 and Ink 5), or even two local maxima (as could be observed for Ink 4). Depending on the number of these local maxima inside the reflectance well, one could assign S for a single (to the $R\%$ spectrum with no local maxima), D for a double-well (the $R\%$ shows one defined local maximum), and T for a triple well, revealing two local maxima.

To further examine the possibility of quantified ink discrimination, one can consider the determination of the extrema and the local extrema in the well-like curves. Figure 4a–e on the left-hand side shows the determination of the extrema in the reflectance well-bottom of the five different inks. Figure 4f–j on the right-hand side presents the numerical first derivative of the reflectance (FD $R\%$) of the corresponding spectra shown on the left. As evident in Fig. 2b, there are extrema in the first derivative $R\%$ that correspond to the position of IPs in the $R\%$ curve from Fig. 2a. Likewise, Fig. 4 (left column) shows the position of the extrema (I maximum-local and a minimum-bottom of the well) and Fig. 4 (right column) shows the position of the apparent inflexion points (I IP, II IP).

Finally, the defined and repeatable local extrema from Figs. 4a–e and inflexion points apparent in Figs. 4f–j could be used for building a codification model in Vis-NIR reflectance for ink discrimination. Table 2 shows the preliminary alphanumerical coding system of the five inks that we propose for ink discrimination, based on the analysis from Fig. 4. The first letter of ten signs (one letter followed by nine numbers) signifies the general appearance of the reflectance curve (S = single well, D = double well, and T = triple well). Furthermore, the three digits following the letter signify the wavelength in nanometers of the read absorption edge – the most discriminative parameter, determined by the position of the first inflexion point (I IP — the first maximum counting from the right in the FD $R\%$ curve). The following three digits signify the bottom of the reflectance well — the wavelength of the minimum from the $R\%$-curve in nanometers. Finally, the last set of three digits indicates the II inflexion point (first minimum in the FD $R\%$ from the right).

In Table 2, we present the unique ten-sign alphanumerical code assigned to each of the five inks included in this study. To check the identification capacity of the proposed coding system, we have also given the code to Ink X (the signature inscribed by the "blind choice of the five inks"), using the wavelengths of the characteristic $R\%$ spectral features from Fig. 2. Comparing the codes of Ink X with all the previously coded inks in the list (Ink 1 to Ink 5), we could identify that Ink X is most similar to Ink 5 as it contained identical coding signs for the first eight signs. As evident, the last two characters were very close to Ink 5. To further increase the identification/discrimination capacity, one should consider adding a new set of three digits to the code, with a meaning of a wavelength at which a new feature appears.
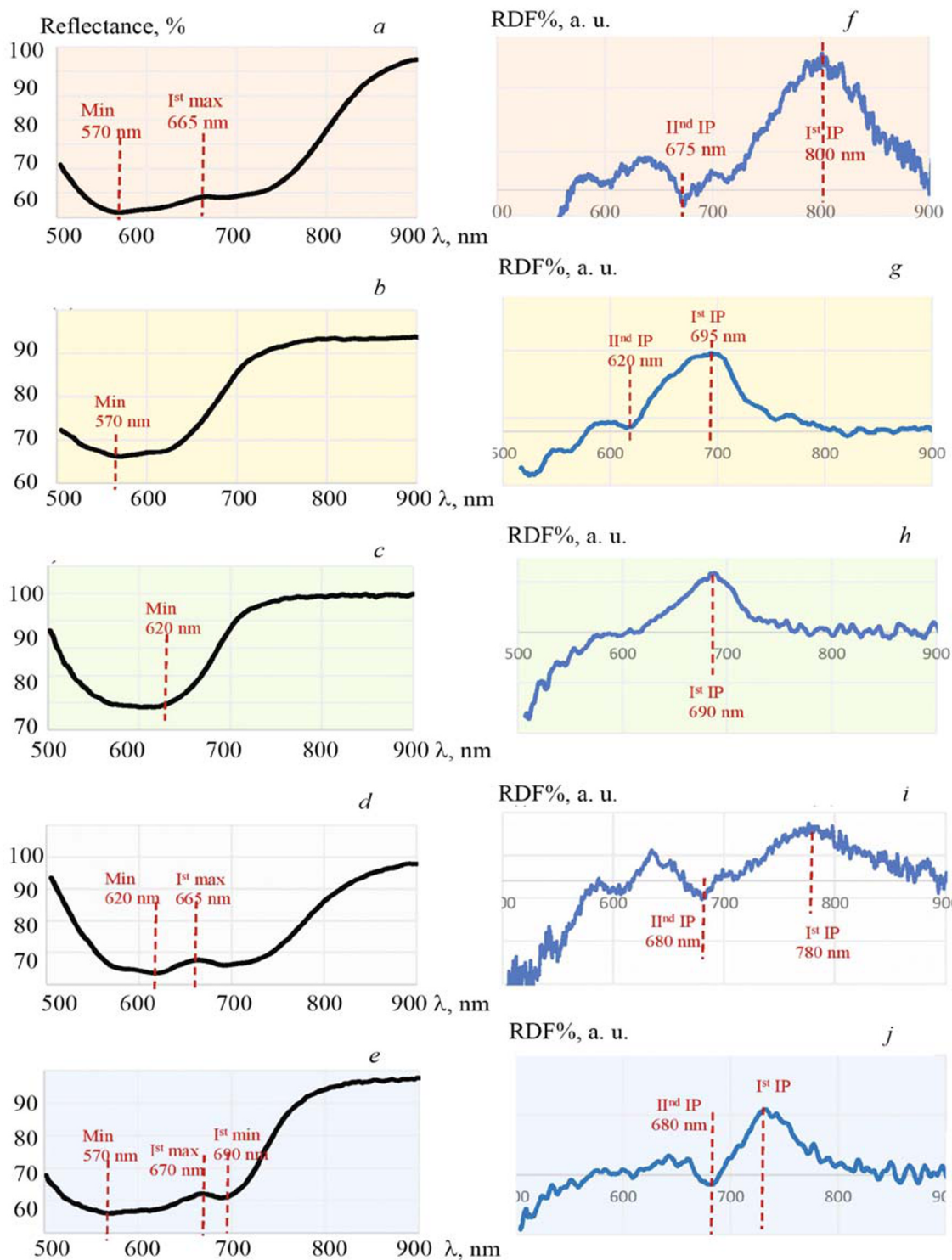
Fig. 4. (a–e) Determination of extrema (also local ones) in the reflectance $R\%$ spectra of Inks 1–5. (f–j) Determination of the well-defined inflection points (extrema in the numerically calculated first derivative of the previous $R\%$ spectra).

In addition, the discrimination capacity of these different inks 1 to 5 was also tested with two other spectroscopy methods, one is destructive, energy dispersion X-ray spectroscopy (EDX) and one is nondestructive, XRF, with portable, modular instrumentation. Unfortunately, some differences were randomly identified in the contents of the trace elements Al, Si, S, Mg, and Cu in the EDX spectra of the inks, hence making the results of the analysis inconclusive. Furthermore, our

TABLE 2. Codification/Quantification of Spectral Features for Ink Discrimination

	S/D/T	I IP, nm			Minimum, nm			II IP, nm			Feature, nm		
Ink 1	D	8	0	0	5	7	0	6	7	5	?	?	?
Ink 2	D	6	9	5	5	7	0	6	2	0	?	?	?
Ink 3	S	6	9	0	6	2	0	0	0	0	?	?	?
Ink 4	T	7	8	0	6	2	0	6	8	0	?	?	?
Ink 5	D	7	3	5	5	7	0	6	8	0	?	?	?
Ink X	D	7	3	5	5	7	0	6	7	0	?	?	?

XRF results spectra taken from the inks on paper with portable equipment, applying a reasonable scanning time (25 min), also produced an inconclusive analysis, allowing no discrimination/identification possibilities.

Conclusions. Reflectance Vis-NIR spectra of inks from documents show unique features feasible for the preliminary discrimination of inks. Both the extrema in the $R\%$ and the inflexion points between the extrema, appearing as extrema in the numerically calculated first derivative of the $R\%$ spectrum, could be used for reflectance ink codification. Thus, codification of each ink can be suggested for discrimination between two inks. This analysis is nondestructive, involving super-fast technical procedures. A semiautomated smart method for spectrum analysis, using MATLAB, can make the procedure as quick as a few minutes. The $R\%$ extrema and the inflexion points could be defined with higher precision if the utilized Vis-NIR light source was with higher intensity, the resolution of the spectrophotometer is higher, and the spectral recording procedure is optimized. Furthermore, much more extensive research using a higher number of ink samples is needed, allowing calibration and validation procedures, as was done by other authors [2, 18, 19]. Also, spectrum recording optimization and longer spectrum integration times should be employed.

If this proposed method is compared with the other nondestructive methods based on reflectance spectroscopy [18, 19], it is promising because of its cost-effectiveness (the complete equipment should cost less than USD 5000) and easy operation (simple in situ spectroscopy procedures). Finally, this method allows high accuracy in detecting the wavelengths at which the typical spectral features are revealed, using numerical derivation. This nondestructive Vis-NIR spectroscopy procedure holds the potential to become a new paradigm for forensic ink analysis.

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