INTERNATIONAL JOURNAL
OF
CONSERVATION SCIENCE
ISSN: 2067-533X Volume 15, Issue 3, 2024: 1407-1424 www.ijcs.ro
DOI: 10.36868/IJCS.2024.03.16

NON-INVASIVE FORENSIC EXAMINATION OF INSCRIPTIONS IN A HISTORICAL DOCUMENT AS AN ATTEMPT TO EVALUATE THE DIVERSITY OF THE COMMERCIAL OFFER OF INKS

Rafał CIEŚLA[1*]

[1]University of Wrocław, Faculty of Law, Administration and Economics, Department of Forensic Sciences
Uniwersytecka street 22-26, PL 50-145 Wrocław, Poland

Abstract

In the history of the German state, the world-wide economic crisis (1929-1939) probably also had an impact on the availability of inks. The research aimed to find out whether it is possible to discriminate between inks and determine the prevalence of ink manufacturers in a specific area, which, in statistical terms, could provide insight into the development of regional ink producers. The research covered selected inscriptions in ink written in a Diary from a small geographical area. Ink examination was carried out using non-invasive VIS-NIR and RS spectroscopic methods involving a statistical approach. The obtained results allowed effective discrimination of the inks and divided them into several groups. Research has shown that iron-gall inks from several ink manufacturers were used to prepare the entries in the Diary. It cannot be ruled out that the differences in individual inks resulted from technological changes in their production process. Additionally, the research revealed a multitude of entries made with iron-gall inks, which may testify to the development of small-scale production of iron-gall inks confined to one geographical area. This type of historical document may constitute a forgery in whole or in specific parts of the inscriptions executed to falsify significant facts, therefore it is an object of interest of forensic science. The non-invasive VIS-NIR and RS spectroscopic methods supported by statistical approach should continue to develop to become an alternative and reliable solution offering great potential in forensic examination of inks.

***Keywords**: Document examination; Forensic science; Ink research; Iron-gall ink; Non-invasive methods; Reflectance spectra; Raman spectra; Scanning microscopy; VSC8000/HS; FORAM 685-2*

Introduction

In the history of the German state, the period from 1918 to 1933 was special for many reasons. As a result of the German Empire's defeat in World War I, the Weimar Republic was established, officially called the German Reich. It was a federal, democratic state with a mixed presidential and parliamentary form of government, with its capital in Berlin. The history of the Republic from its founding can be divided into three stages. From 1919 to 1923, the Weimar Republic struggled with the immediate effects of the war, hyperinflation and attempts to overthrow the government. The second stage was the "five fat years" period, which lasted from 1924 to 1929. The republic then achieved certain political and economic stability and international recognition [1–3]. The Great Depression (1929–1939) peaked in 1930–1933 and the growing influence of National Socialism led to the agony and collapse of the Weimar Republic. The global economic crisis, which affected the German Reich to a greater extent than other European countries, had a decisive significance for the radicalization of politics. After the Wall

* Corresponding author: rafal.ciesla@uwr.edu.pl

Street crash, many short–term loans were withdrawn from the Weimar Republic and the American government began implementing a protectionist tariff policy [4, 5]. As a result, the German economy completely collapsed. In January 1928, there were approximately 1.8 million unemployed people, while at the end of the Weimar Republic, in 1933 unemployment reached 6 million. Many people lived in extreme poverty [6–8].

The economic crisis and the accompanying unfavourable events could also have impacted the availability of all types of stationery, such as writing materials and inks used to prepare documents for official and private purposes. As a result of the difficult economic situation of the Weimar Republic and the related unfavourable consequences, "home" methods of ink production were most likely frequently used, often resulting in amateur ink composition. The consequence of this situation was probably the establishment of local manufacturers and craft workshops producing writing materials and inks for customers from the local area.

A characteristic feature of liquid writing materials, including inks, regardless of their type, is their task to create a permanent colour stain of a specific shape on the surface. It follows that inks can be any substance that is able to meet the above conditions, even if its main purpose is different. Almost anything that leaves a visible or identifiable mark on paper or other surfaces can be used to write with. Over hundreds of years, very different inks of various compositions, including those responsible for colour, have appeared. For example, iron ions and various types of natural tannins, such as oak galls, were used to produce iron–tannin inks. Among many inks, iron–gall ink was the one most commonly used at the beginning of the 20th century. Its popularity resulted from its high durability, low production costs and easy access to ingredients. Iron–gall ink was used primarily to prepare documents in central and local administration offices but also for personal use to create private documents. Over time, other ingredients were used in the production of iron–gall inks, for example, plant parts rich in tannins, such as oak bark and other tree species, fruits of evergreen oak species, acorn cups, blackthorn, juniper berries and others [9]. In ancient times, it was common practice for each writer to personally prepare ink according to his own or heard recipe and often mix random ingredients in various proportions. Other additives can be found in the recipes of old iron–gall inks, such as alum, salt, honey, beer, vodka, vermouth, verdigris, urine, coloured wood extracts and many others. Many recipes recommend that the galls or bark be macerated in water or beer for one or two weeks. The obtained extract was often boiled – in this way, the substance was thickened and the tannin content was increased. Iron sulfate – green vitriol – was also added before or after cooking, depending on the recipe. It was often recommended that air be allowed free access to the ink for a few days for the latter to turn black. The advantage of the variant with the dye formation process taking place earlier was that the ink was already clearly visible when writing. The disadvantage, however, was that the black ink dye, being insoluble in water, precipitated after some time and formed a precipitate because the presence of gum Arabic did not keep it in suspension. Inks were generally stored dried in the form of powder, which was diluted with an appropriate solvent when necessary. Some recipes advise diluting the finished ink with hot wine before use. Then, the ink dye, which may already have precipitated, will reappear in the solution under the influence of the organic acids present in the wine. A good practice was to sprinkle freshly written text with fine sand to dry it, which also prevented it from blurring. In many countries, the production of iron–gall ink used to be the responsibility of a "good housewife" because to produce a relatively simple ink composition, water, galls (preferably oak), green vitriol and a bit of mineral acid were needed and according to some of the oldest recipes, only galls an iron pot and vinegar as an acid source were sufficient [10–13].

Object of research

For the purposes of researching ink entries, access was gained to private collections of various German–language documents from the late 1920s [14]. One compact document, a Diary, was selected as the object of research (Fig.1). The examined handwritten document is an element of the broadly understood written heritage. Due to the information which they convey, such documents are important for society and science, constituting the object of research, including forensic examination. Such documents need to be protected and remain unchanged as their authenticity renders them reliable sources of information [15]. This inconspicuous notebook offers interesting research potential, e.g. reference to and development of the idea indicated in the article "Forensic examination of inks used as inscription on historical documents" [16]. The material used for the ink research (journal) was also added to the collections located in the Ink and Writing Materials Library of the Department of Forensic Sciences, University of Wrocław [17–21]. The library collections have been successively expanded for many years with new inks, writing tools and various historical and contemporary documents. The library resources are used for various kinds of document examination, including that of ink. Taking into account the difficult economic situation of the Weimar Republic, especially in the late 1920s, the question arises of how the crisis affected the industry in relation to such "little things" as the production of writing products such as inks.

Purpose of research

The research aimed to find out whether it is possible to determine the commonness (multiplicity) of ink producers, which, from a statistical perspective, could provide insight into the development of the ink–producing small industry.

The following were examined (Fig. 2):

a. 14 entries from Mariensee, including 11 entries from January; 1 entry from February; 2 entries from March 1929;
b. 2 entries signed Mariensee *Ostern* (Easter)1929;
c. 3 entries from the town of Empede from February 1929;
d. 5 entries from the town of Neustadt, including 4 entries from February and 1 entry from March 1929;
e. 5 entries signed *Ostern* (Easter) 1929.

Research problem

The examined Diary contains several dozen pages of handwritten entries from 1929. The pages of the Diary with visible handwritten entries were analyzed. Inside the document, a bookbinder's stamp was revealed, stating that it was a handcrafted product (Fig. 1). Initial inspection involving the use of simple optical devices showed that every entry was made with a single type of ink. A hypothesis was adopted that iron–gall ink, the most popular at that time, was used to prepare the examined entries. The entries were written in a short period (from a few days to a few weeks). The city and villages listed on the pages of the Diary suggested the place where the entries were made – the city Neustadt am Rübenberge, village Empede, village Mariensee (Hanover Region, Lower Saxony, Germany). Determining such seemingly trivial information at the beginning of the analysis provides a solid research basis. The entries in the Diary were subjected to further examination to determine whether:

a. The inks can be differentiated?
b. Additional conclusions can be drawn by examining the mutual similarity of the inks used in the Diary entries.

The examined handwritten Diary entries came from the beginning of 1929 and specifically from the period from January to April 1929 (Figs. 1 and 2).

a b c

Fig. 1. Cover of the Diary (a); Inside the Diary – page with a stamp (b); Bookbinder's stamp (c).

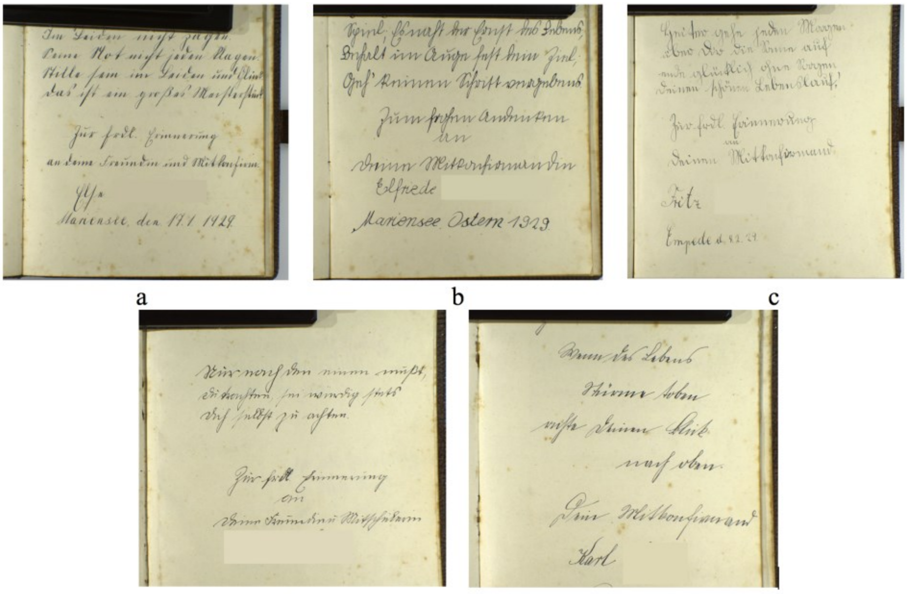


Fig. 2. Examples of examined Diary pages.

Methods

Ink analysis is based on research methods of varying degrees of complexity, from the simplest to the most complex. This is due to the historical development of available and reliable research methods as well as the historical development of the document itself, type of substrate, type of writing tool, common use of the document, state of preservation of the document, extent of its destruction, importance of the document in everyday life, type of substances used to produce ink, methods of applying ink on paper. In practice, a very large number of variables that are difficult to determine result in an impact on the ink – paper relationship and the passage of time, problems with establishing the initial conditions for document creation, difficulties in determining the conditions of storage and use of the document are just a few examples. They have influence on the selection of correct research methods, the use of appropriate research methodology, which in turn has a significant impact on the efficiency, accuracy and objectivity of ink research [22–24].

In ink examination, a general distinction can be made between non–invasive (optical) and invasive (chemical) methods. Optical methods include primarily optics, which allow determining the intensity and shade of the color of the ink as well as performing fluorescence analysis. Optical methods enable the determination of the structure and spatial properties of the substrate and ink, as well as physical properties such as light absorption/reflectance [25, 26]. Chemical methods enable the examination of the qualitative and quantitative chemical composition of the ink and its chemical properties, such as the ability to undergo specific chemical reactions. Physico–chemical methods involve examining the relationship between the composition of the ink and its physical properties. When examining documents to determine their authenticity, physico–chemical research is used, among others, to identify both the documents base and the ink (resins, dyes or solvents) used to prepare the document. The spectra obtained for the samples are compared with the spectra of standard substances to determine their composition and possible differences that could indicate forgery. Basic research employs optical methods that use information transmitted by electromagnetic waves of a specific range of length in the process of analyzing matter. The resulting optical information signal is received directly visually or preferably through devices. Non–invasive ink methods use devices that measure the light absorption or reflection coefficient [27–29]. In practice, non–invasive methods are preferable because they do not damage or destroy the research material. This makes it possible to carry out the research again in order to verify the previously obtained results by another independent researcher. Non–invasive methods enable the examination and analysis of a document without disturbing its integrity, which is crucial for maintaining the entirety of the entries in the document. The use of reliable non–invasive methods is necessary in the research of historical documents.

To protect the collector's private property, the research was carried out using only non–invasive methods. The document (Diary) was analyzed using spectroscopic methods such as (VIS–NIR) reflection spectroscopy and Raman spectroscopy (RS) [30–34]. The research also used the methods similar to those used in statistics and chemometrics to highlight possible differences between inks [35–37]. Additionally, the scanning electron microscopy (SEM) method was used for identification purposes [38, 39].

The research used advanced devices: Forensic Document Workstation VSC8000/HS (*Video Spectral Comparator* 8000 Hiper Spectra Camera), [https://fosterfreeman.com]; Raman Spectrometer for Forensic Applications: FORAM685–2 (*Raman Spectral Comparator*) with a 685nm laser excitation line making measurements in the range of 400–2000cm^{-1}, (equipped with a VIS–NIR spectrometer making measurements in the spectra range of 400–1000nm) [https://fosterfreeman.com] and SEM–EDS (*Scanning Electron Microscope–Energy Dispersive Spectroscopy*).

Reflectance spectroscopy VIS–NIR

Reflectance spectroscopy in visible and infrared light was used in the research. VIS–NIR reflectance analysis enables the determination of subtle changes in ink colour. The VIS–NIR spectrum also enables quantitative measurement of the reflectance of light by a sample in relation to the reflectance of a specific white standard [40].

Raman spectroscopy RS

Raman spectroscopy is preferable because of its high sensitivity. This method determines the content of various substances based on the analysis of inelastic light scattering on characteristic groups in the molecule of the examined substance [41, 42].

CIELab color space

CIELab has several applications and is also a useful method for the examination of inks. The CIELab colour space is defined by the "Commission Internationale de l'Éclairage (CIE)" and is used to describe all colours visible to the human eye in a three–dimensional model using L*, a* and b* as coordinates in a three–axial system for colour calculation [43–45]. The L* value indicates the brightness and corresponds to the brightness corresponding to human perception in the range of 0 (black) to 100 (white), a* and b* are colour values and represent different colour ratios, where the a* value represents the ratio of green to red and the b* value represents the ratio of yellow to blue. The L*, a*, b* values are direct output parameters of the VIS–NIR spectrophotometer. They are calculated based on the obtained spectral data in the wavelength range from 400 to 1000 nm. This allows, using the method of measuring the chromaticity of ink lines (*CIELab colour space*) based on the Euclidean distance formula, estimating the colour difference of ink entries from different dates and different places. The research checked differences in the colours of entries on the document using the ΔE* formula.

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad [1]$$

Scanning microscopy SEM

Scanning electron microscopy allows the analysis of faint or invisible microscopic trace evidence by imaging it, image comparison and X–ray microanalysis. The SEM microscope is a good solution due to the ease of preparing, storing and securing samples and the possibility of examining them in their natural state. It is a non–optical microscope in which a high–energy scanning electron beam moves over the sample. When the electron beam falls on a fragment of the examined object, the so–called secondary electrons, which, after being ejected from the sample, are collected, transferred to a photomultiplier and an optical amplifier and then transferred to the image. Due to the fact that the scanning electron beam is deflected so that it precisely sweeps the entire sample surface, a three–dimensional image of the analyzed preparation is obtained. SEM scanning electron microscopy combined with an EDS X–ray microanalyzer allows, for example, determining the elemental composition of ink, toner, ink and paint as well as revealing the microstructure of paper [46–50].

Research

While carefully examining the research material (Diary), several characteristic features were noticed. Very characteristic yellowish spots were found on almost all pages of the Diary when examined in white (visible) light. These spots were identified as a probable phenomenon called *foxing*, the origin of which is ambiguous. According to some scientists, these are traces of corrosion of iron particles from various sources; others claim that these are remnants of lignin breakdown and still other researchers believe that these are stains of microbiological origin [51–54].

When examined under various lighting conditions, the luminescence of the paper substrate in ultraviolet light was surprising (Figs. 3 and 4). Nowadays, UV luminescence is caused by the intentionally added presence of optical brighteners, which were introduced around the second half of the 1930s, i.e. slightly later than the creation of the document (Diary). In addition, bleach was initially used solely in the USA and only in washing powders and much later in paper production. In Europe, optical brighteners were introduced even later. A class of chemicals has been identified that can enhance bleaching through the action of fluorescence. These materials, often called colourless dyes, are known as fluorescent whitening agents or optical brighteners, i.e. a group of molecules that absorb light mainly in the ultraviolet range and emit light in the visible range, thereby brightening the substrate by emitting more than 100% of the incident visible light. These materials were first used in food packaging and X–ray film covers to prevent damage from ultraviolet light. Their bleaching properties were soon exploited and brighteners were added to many commercial materials, fostering a taste for "whiter than white" papers, textiles and non–yellowing plastics. In conservation of works of art and cultural property, the preservation and aging of optical brighteners play an important role, especially in the works from the second half of the 20th century. The technology and development of these materials and their chemical composition enhances their durability, appearance and interaction with conservation procedures [55–57].

However, at that time, a common practice in the production of higher quality paper was to use agents that compensated for the yellowish tint of cellulose pulp, such as ultramarine or Prussian blue. However, in addition to compensating for the yellowish tint, they also caused "graying" of the paper product. Then, in addition to the classic mineral fillers, ultraviolet fluorescing compounds were added, such as lithopone, zinc sulfide, gypsum (calcium sulfate), barite (barium sulfate).

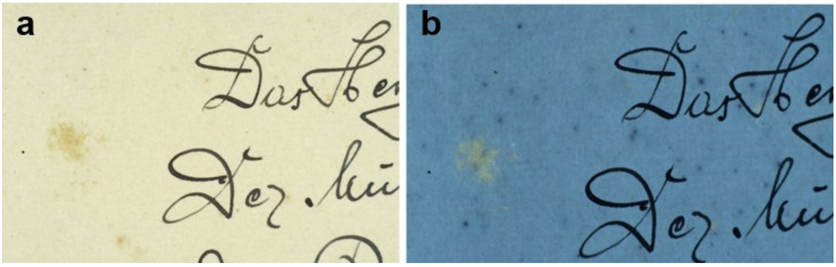


Fig. 3. View of a paper base with an entry on a random Diary page in white (visible) light (a); in ultraviolet light UV 365 nm (b).

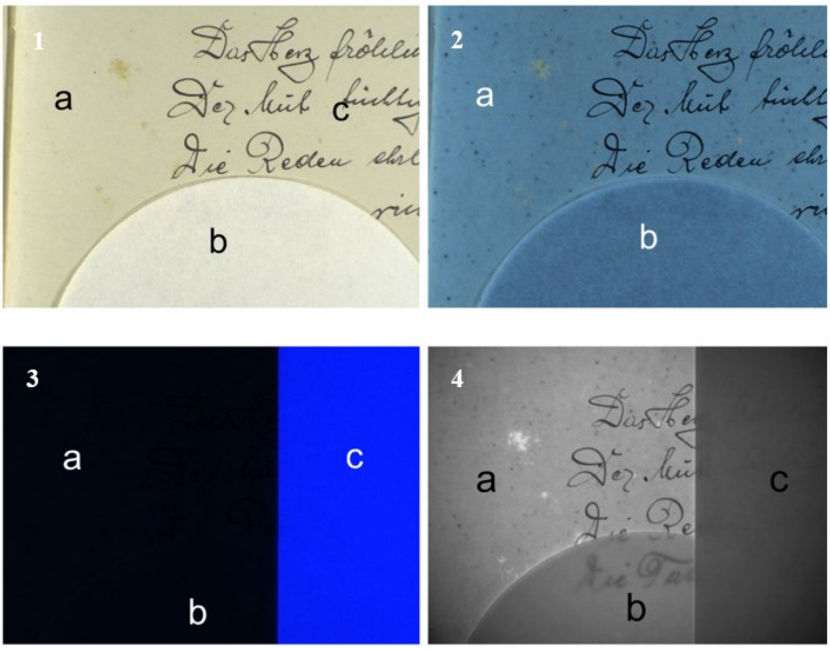


Fig. 4. Comparison of paper in various lighting conditions: white (visible) light (1), ultraviolet light UV 365nm (2 and 3), monochromatic light 490/560 nm observed through a 645nm cut-off filter (4).
a) document being examined, b) sample paper without filler and bleach (quantitative bag), c) modern printer paper.

Experimental part

In an attempt to determine what bleach was used in the case of the examined Diary, a series of spectral measurements – Raman spectra were performed (Fig. 5).

Unfortunately, the intensity of the signals coming from the paper substrate (cellulose) masked possible filler and brightener signals. Therefore, the decision was made to use the scanning electron microscopy method (Fig. 6). The SEM results showed that the probable reason for the failure of the determination attempts using Raman spectroscopy was that the filler grain size was too small to "hit" the laser beam at the image magnification offered by the Raman comparator microscope. Moreover, the colour of the filler in relation to the colour of the sheet of paper (white on white) is also important. Unfortunately, it was also impossible to examine the bleach grains, although slightly larger, using Raman spectroscopy. Additionally, it should be remembered that cellulose fibers, filler and bleach are white, so at low magnification of a Raman comparator, maximum 20 times, they are practically impossible to capture and observe.

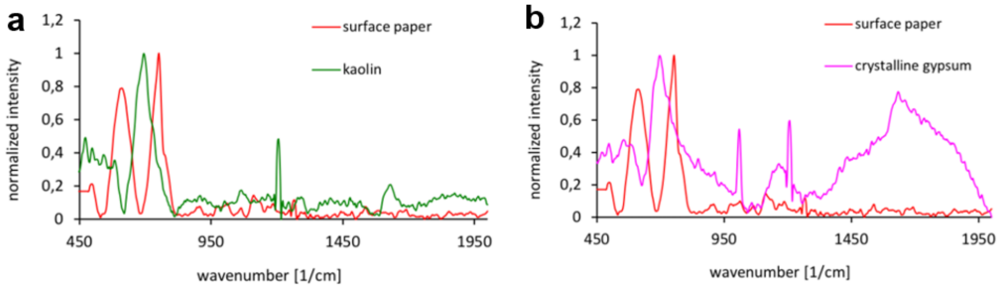
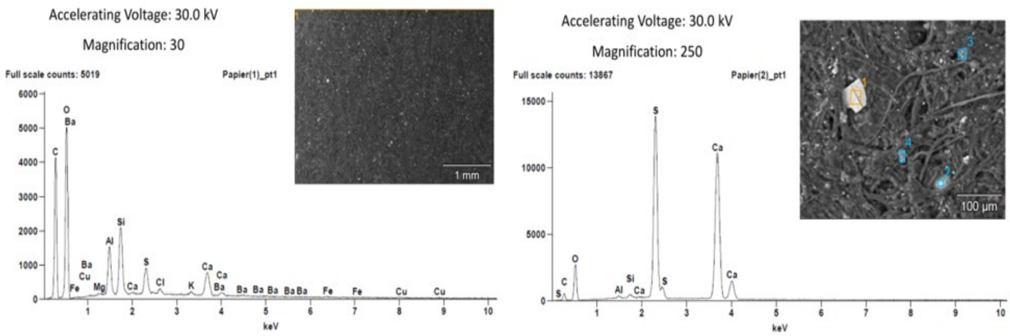


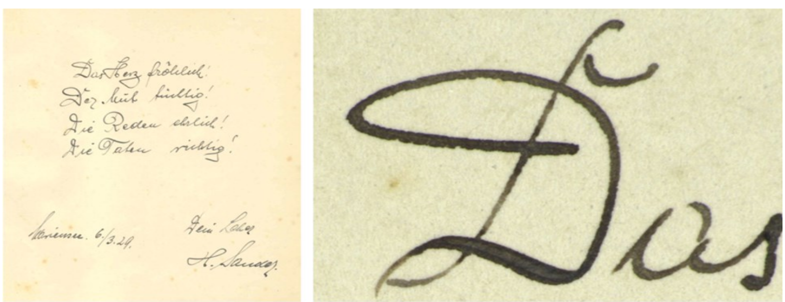
Fig. 5. Compilation of Raman spectra of a paper substrate with a possible filler - kaolin (a); bleach - crystalline calcium sulfate (gypsum) (b).



a b

Fig. 6. SEM spectrum of paper with a random Diary entry indicating that: (a). the filler is an aluminosilicate; (b). bleach is calcium sulfate

At the onset of the next part of the research, it was assumed that the ink, as a very runny medium, would evenly fill the writing line (Fig. 7).



a b

Fig. 7. General view of an example page (a); Different degrees of filling (saturation) with ink (b).

However, it turned out that there are visible differences between strongly and poorly filled places in the writing line and characteristic traces of pressure on the pen (nib) were observed in the form of a "track" effect, where the edges of the writing line are more saturated, while the centre is less so (in several cases only the "track" is visible, while its interior remains blank), which causes significant differences in the spectra (especially in the brightness value L*).

Additionally, examination of the documents in various lighting conditions (monochromatic and UV light) revealed that apart from visible *foxing spots*, there were more or less visible additional black spots (Figs. 8 and 9). To check the influence of these factors on the quality of measurements, a number of reflection (Fig. 10) and luminescence (Fig. 11) spectra were taken.

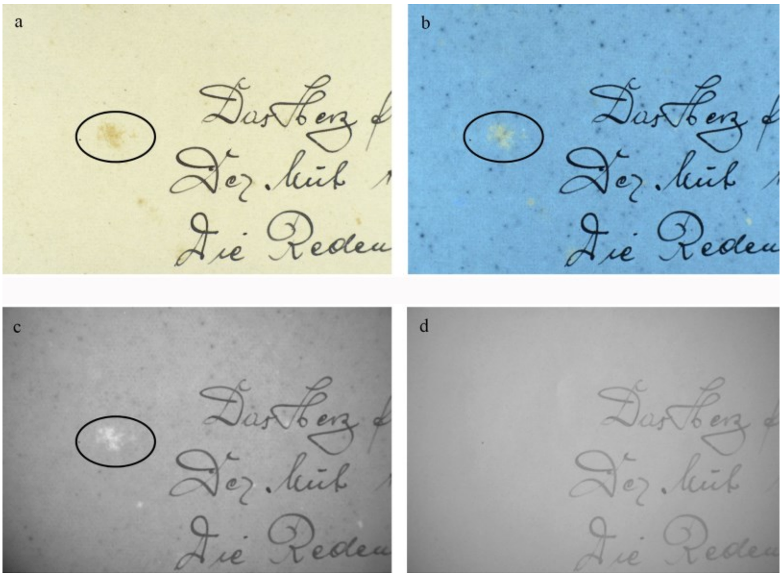
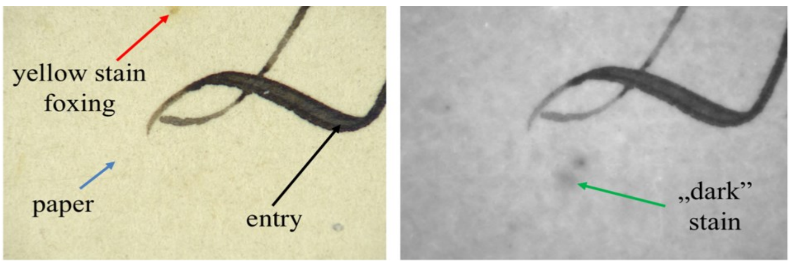


Fig. 8. Yellow spot in the paper base (so-called *foxing*) in white (visible) light (a);
365 nm ultraviolet light (b); 490/560nm cut-off filter 645nm (c); 720/800nm cut-off filter 830nm (d).



a b

Fig. 9. Fragment of the letter D. Image in white light enriched with infrared radiation (a);
Image in monochromatic 490/560nm spot light viewed through a 64 nm cut-off filter (b).

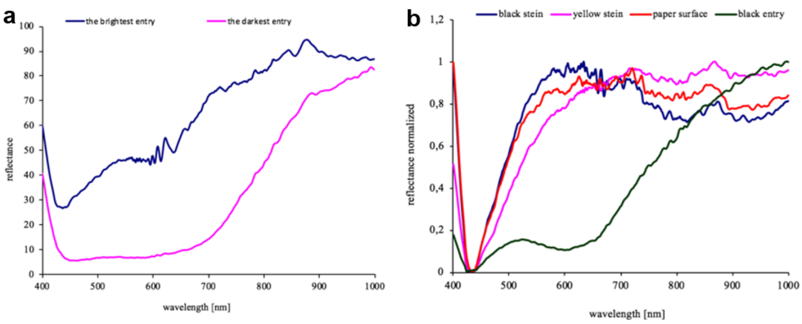


Fig. 10. Image of the maximum and minimum spectra for an example entry - here: *Mariensee 06.03.1929* (a);
summary of reflection spectra of incident white light enriched with infrared radiation after normalization (b).

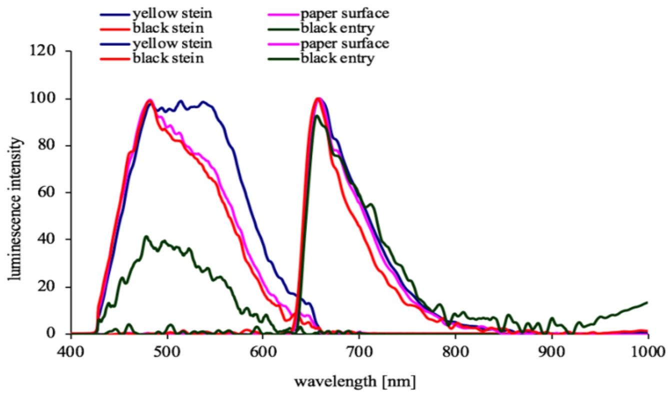


Fig. 11. Summary of spectra of luminescence induced by ultraviolet light 365 nm and luminescence induced by monochromatic light 490/560 nm, detected by a 645 nm cut-off filter.

The above results forced the development of a methodology providing reliable colour measurements. After averaging, the difference of colours within the examined entry was close to zero. Therefore, an attempt was made to estimate the number of necessary measurements for an entry from one date that should be performed to meet the above condition. Successive spectra were taken from different entry points, then their colour parameters were determined in the CIELab system and averaged, observing a gradual reduction in the difference of colours. Research has shown that conducting reliable comparative examination of inks (by measuring the difference in their colour) requires a minimum number of approximately 100 measurements (Table 1). This should result in a maximum reduction of a possible measurement error caused by the inhomogeneity of the recording lines (Figs. 12 and 13) [58–59].

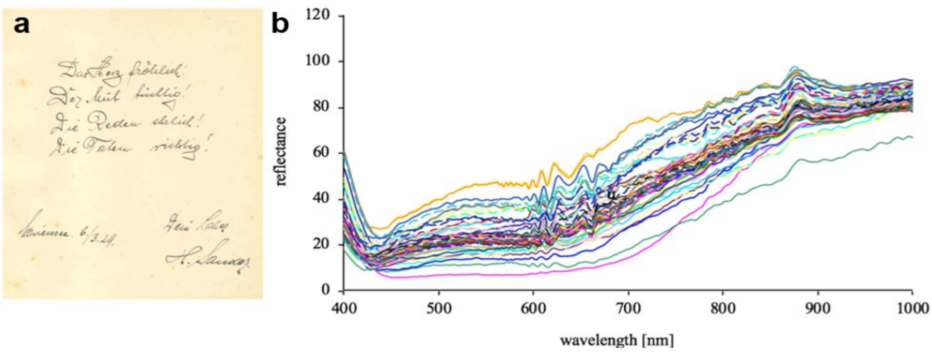


Fig. 12. Randomly selected spectrum and chromatic value extraction points for the entry: *Mariensee 06.03.1929* (a); Received image of 100 spectra for entry: *Mariensee 06.03.1929* (b).

This methodology was used in the examination of subsequent selected entries with different dates and different locations. An identical procedure was used for Raman spectra.

In order to find the range of signals originating from the ink, the Raman spectrum of the paper substrate was taken and then compared with the spectra of the entries. The reflection spectrum does not identify iron–gall ink, while the Raman spectrum hardly differentiates them at all (Fig. 14). Only expanding the spectral range for iron–gall ink allowed differences to be noticed (Fig. 15).

Table 1. Chromaticity. Euclidean distance. Averaging of measured values.

Number of spectra	L*	a*	b*
1	58.6	6.3	14.3
11	51.3	2	11.9
21	54	0.9	13.1
31	54.3	0.9	12.7
41	55.4	1.3	12.5
51	56.7	0.8	12.6
61	57.5	0.8	12.7
71	57.4	0.8	12.5
81	57.4	0.4	12.5
91	57.8	0.4	12.6
100	57.6	0.4	12.5

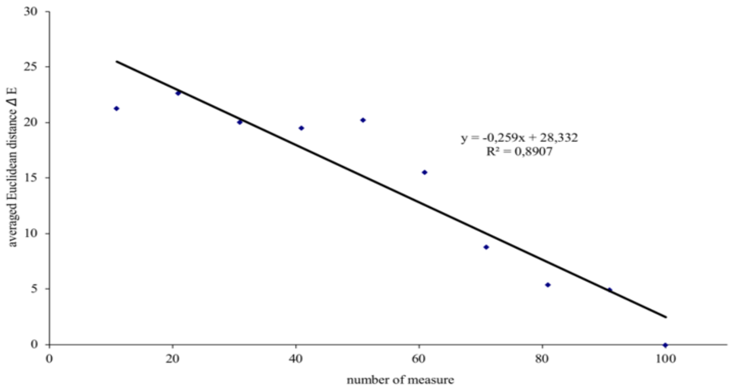
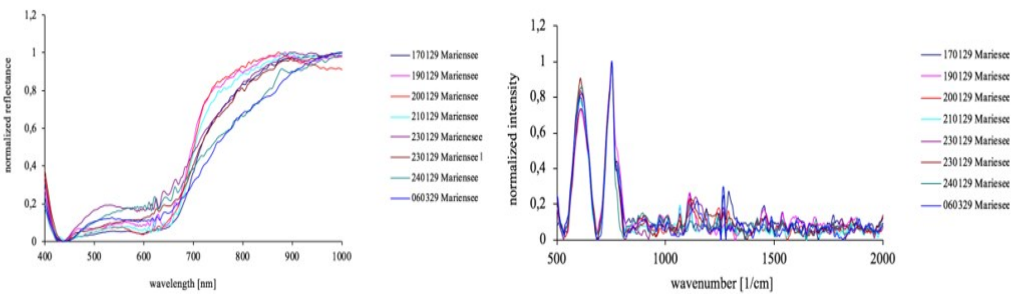


Fig. 13. Trend line of ΔE changes with an increasing number of measurements.



a b

Fig. 14. Normalized reflection spectra of white light enriched with infrared radiation of entries signed *Mariensee* (a); Normalized Raman spectra of entries signed *Mariensee* (b).

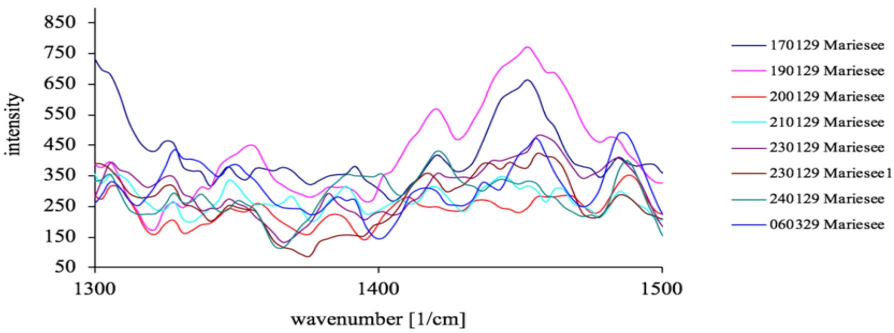


Fig. 15. The range of Raman spectra of entries marked *Mariensee* after rejection of the fragment common to the paper substrate, attributed to iron-gall peaks.

To confirm that the examined ink was an iron–gall ink, an SEM spectrum of one of the entries from the Diary was taken, which confirmed this assumption (Fig. 16).

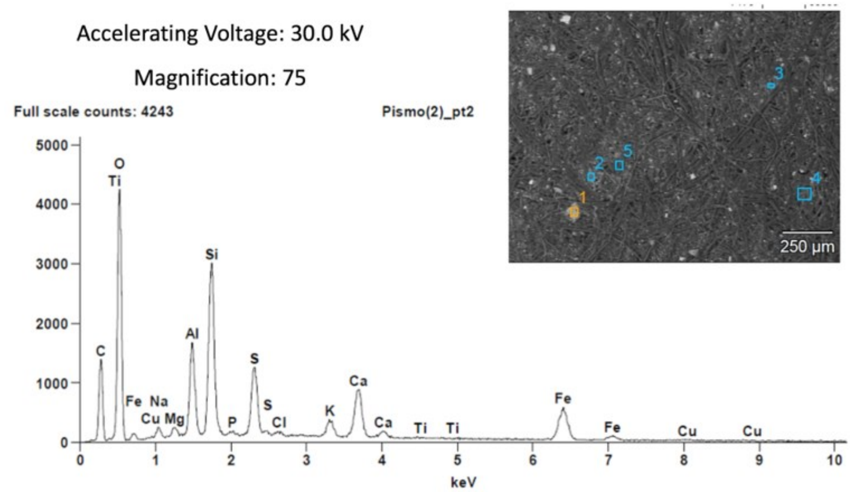


Fig. 16. SEM spectrum of a fragment of a random page from the Diary with a note indicating iron-gall ink.

The acquired reflection and Raman spectra provided data for further calculations that would arrange the inks into a recognizable pattern. The data used and their symbols (including their expansions) used in the calculations are presented in Table 2.

Table 2. Data preparation.

Symbol	Development
R_{min}	Reflectance at minimum [%]
λ min	Reflectance wavelength in minimum [nm]
L*	The brightness (luminance) of the entry line colour
a*	*a** component of the entry line color
b*	*b** component of the entry line color
ΔE_{place}	Colour difference between entries within one town
ΔE_{total}	Colour difference between entries from all towns
$S_{400:1000}$	The surface area under the reflectance graph in the range of 400 to 1000 nm
υ_{max}	Wave number (Raman shift) of the peak (band)
I_{max}	Peak (band) intensity in the Raman spectrum

The data obtained in various configurations were compiled and then, using statistical methods, an attempt was made to find mutual connections that would allow them to be grouped.

Discussions

After laborious calculations, the data can be presented in a more readable form of charts. They indicate that individual entries form quite distinct and characteristic groups (Fig. 17). The grouping of ink entries becomes clearer after performing another autoscaling operation (Fig. 18).

Even though all the examined inks were black, quite distinct clusters can be seen in the graphs, especially the autoscaled ones, which allow us to draw the following conclusions:

a. The inks can be discriminated and arranged into several groups.
b. There was probably more than one shop selling ink in the three places considered.
c. Various ink producers supplied shops selling ink.
d. It is quite possible that there was only one ink supplier and the differences between the inks are caused by technological changes in their production process.

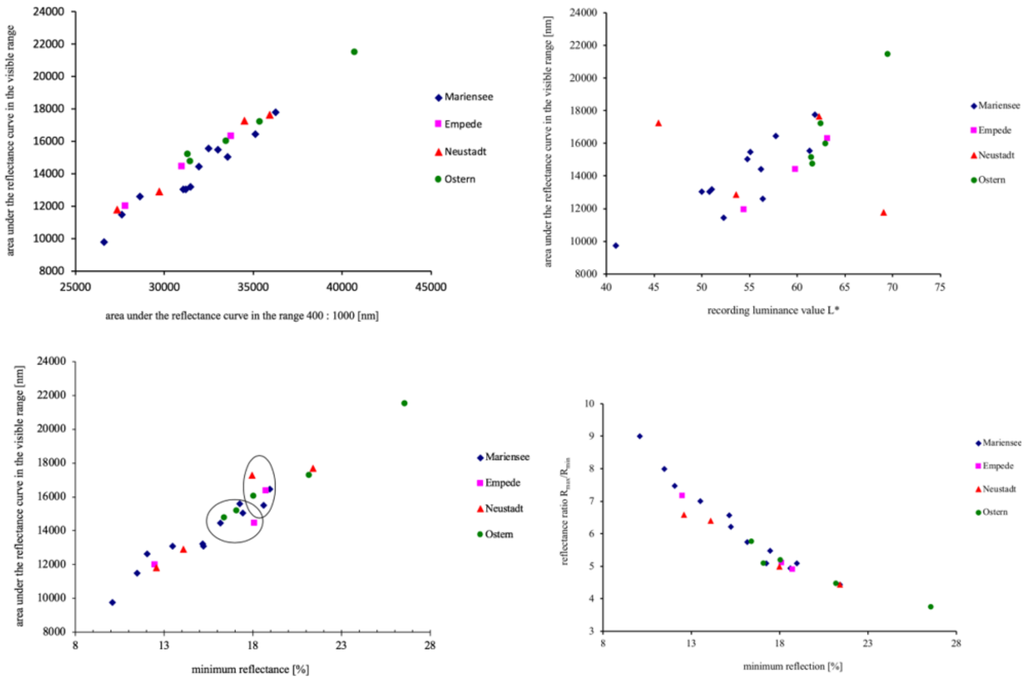


Fig. 17. Spectral relationships

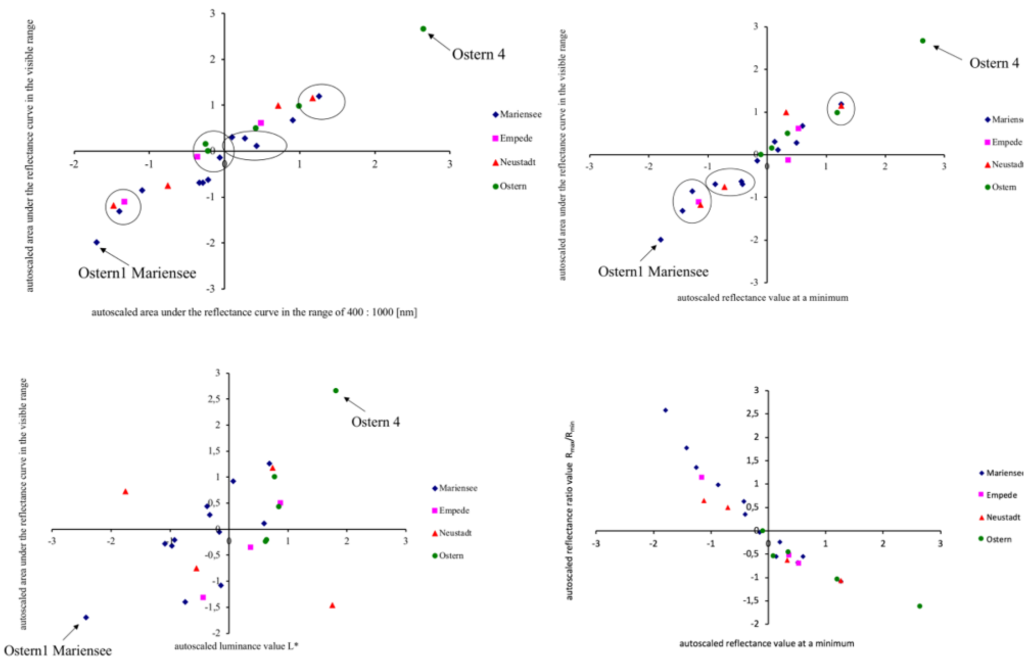


Fig. 18. Spectral relationships after autoscaling

Conclusions

The period covered by the research is the end of the 1920s. The place of origin of the samples is a relatively small geographical area. The obtained results of ink research after applying statistical analysis made it possible to discriminate inks and, additionally, to arrange them into several groups. This leads to the conclusion that inks from several manufacturers were used to prepare entries in the Diary. Although the research does not rule out the possibility of changes in the technology of producing the inks in question, the relatively short period of time during which the entries were made allows the conclusions indicated in points b. and c. to be considered correct. The multitude of different inks used also indicates the multitude of manufacturers. As a result, this suggests the development of small–scale ink production in a small area.

Historical documents such as the examined Diary may be a forgery in whole or in part carried out in order to change significant facts. False inscriptions in the document may influence findings that are inconsistent with reality and, consequently, may lead to unfavourable private or official decisions. Therefore, this type of documents is of interest in forensic examination. The non–invasive spectroscopic methods (VIS–NIR and RS) with statistical methods used and the obtained research results should be further developed and be applied in the future as an alternative approach offering great potential in the forensic examination of inks.

Acknowledgments

The author would like to thank Dr. Grzegorz Rusek for very important advice and consultations, many valuable tips, especially those concerning iron–gall inks, as well as for comments on the research of inks and paper, discussions of the obtained results, substantive criticism and comments on the statistical calculations contained in this work. I also thank him for providing access to his private collections used for this article. The author would also like to thank Dr. Wojciech Gil for his help in conducting research using the SEM method, which enabled the verification of the adopted partial hypotheses.

References

[1] T. Kotłowski, **Historia Republiki Weimarskiej 1918–1933 [History of the Weimar Republic 1918–1933],** Wydawnictwo Poznańskie [Poznań Publishing House], wyd. II, Poznań 2004.

[2] E. Kolb, **The Weimar Republic, contributed by P.S. Falla, Trans.** (1st ed.), Routledge**,** 1988. https://doi.org/10.4324/9780203138007.

[3] Cz. Łuczak, **Dzieje gospodarcze Niemiec 1871–1990. Druga Rzesza i Republika Weimarska [Economic history of Germany 1871–1990. The Second Reich and the Weimar Republic],** t. 1, Wydawnictwo Naukowe Uniwersytetu im. Adama Mickiewicza w Poznaniu [Scientific Publishing House of the University of Adam Mickiewicz in Poznań], 2004.

[4] P. Temin, **Great Depression**, (Editor: G. Jones) Banking Crises, Palgrave Macmillan, London, 2016. https://doi.org/10.1057/9781137553799_16.

[5] Ch.P. Kindleberger, **The World in Depression, 1929–1939**, Berkeley and Los Angeles, University of California Press, 1973.

[6] * * * http://future.state.gov/when/timeline/1921_timeline/smoot_tariff.html [accessed on: 29.12.2023].

[7] P.D. Stachura *(ed.),* **Unemployment and the Great Depression in Weimar Germany***, Springer, 1986, pp. 29–48,* https://doi.org/10.1007/978-1-349-18355-5.

[8] D. Petzina, *The Great Depression,* **Journal of Contemporary History, 4**(4), 1969, pp. 59–74. https://www.jstor.org/stable/259836 [accessed on: 20.12.2023].
[9] W. Sobucki, *Atramenty żelazowo–galusowe [Iron–gall inks]*, **Ochrona Zabytków** [Protection of Monuments], 49(3), 1996, pp. 281–283.
[10] C.E. Mendes de Sá, F.A.O. Silveira, J.C. Santos, R.M. dos Santos Isaias, G.W. Fernandes, *Anatomical and developmental aspects of leaf galls included by Schizomyia macrocapillata Maia (Diptera: Cecidomyiidae) on Bauhinia brevipes Vogel (Fabaceae),* **Brazilian Journal of Botany, 32**(2), 2009, pp. 319–327. https://doi.org/10.1590/S010084042009000200011.
[11] M. de Pas, F. Flieder, *History and Prospects for Analysis of Black Manuscripts Inks,* **Conservation and Restoration of Pictorial Art,** London–Boston, 1976, pp. 193–201.
[12] C.E. Waters, **Inks. U.S. Department of Commerce, National Bureau of Standards***,* U.S. Government Printing Office Washington**,** 1940. https://archive.org/details/circularofbureau426wate/page/24/mode/1up.
[13] D. Cardon, **Natural Dyes: Sources, Tradition, Technology and Science,** Archetype Publications, London 2007.
[14] * * *, **The documents were made available by collector** Tadeusz Juchniewicz (Poland).
[15] D. Wilk, *Fałszerstwa dziedzictwa piśmienniczego w świetle prawa karnego i kryminalistyki [Forgeries of written heritage in the light of criminal law and forensics],* **Notes konserwatorski, 22**, 2020, pp. 33–34. https://doi.org/10.36155/NK.22.00002.
[16] R. Cieśla, *Forensic Examination of Inks Used as Inscription on Historical Documents*, **International Journal of Conservation Science**, **14**(2), 2023, pp. 481–496, DOI: 10.36868/IJCS.2023.02.07.
[17] P. Szczerbak, R. Ptak, R. Cieśla, G. Rusek, *Heterogeniczna baza danych widmowych kryjących materiałów pisarskich [Heterogeneous database of spectral writing materials*], **Współczesne wyzwania wobec badań dokumentów, [Contemporary challenges to document research]**, ed. R. Cieśla, **Wydawnictwo Uniwersytetu Wrocławskiego** [University of Wrocław Publishing House], Wrocław 2021, pp. 199–209.
[18] R. Cieśla, G. Rusek, *Biblioteki środków kryjących [Ink Libraries],* **Oblicza współczesnej kryminalistyki. Księga jubileuszowa Profesora Huberta Kołeckiego [Faces of modern forensics. Jubilee book of Professor Hubert Kołecki]**, ed. E. Gruza, **Stowarzyszenie Absolwentów Wydziału Prawa i Administracji Uniwersytetu Warszawskiego** [Association of Graduates of the Faculty of Law and Administration of the University of Warsaw Publishing House, Acta Universitatis Wratislaviensis, 4065, Warszawa 2013, pp. 55–59.
[19] * * *, *The practice of making libraries of inks for document examination is known and used by some laboratories,* **Secret Service Forensic Services Division,** United States Secret Service. https://www.secretservice.gov/investigation/forensic [accessed on: 21.12.2023].
[20] G.M. LaPorte, M.D. Arredondo, T.S. McConnell, J.C. Stephens, A.A. Cantu, D.K. Shaffer, *An Evaluation of Matching Unknown Writing Inks with the United States Internationl Ink Library,* **Journal of Forensic Sciences, 51**(3), May 2006, pp. 689–692. https://doi.org/10.1111/j.1556-4029.2006.00144.x.
[21] C. Neumann, R. Ramotowski, T. Genessay, *Forensic examination of ink by high–performance thin layer chromatography – The United States Secret Service Digital Ink Library*, **Journal of Chromatography A, 1218**(19), 2011, pp. 2793–2811, Special Issue: SI. https://doi.org/10.1016/j.chroma.2010.12.070.
[22] D. Potolinca, I.C. Negru, V. Vasilache, C. Arsene, T. Paduraru, I. Sandu, *Forensic expertise of the paper support of counterfeit documents,* **Materiale Plastice, 54**(1), 2017, pp. 41–45.

[23] D.L. Feraru, A. Meghea, N. Badea, *Forensic Discrimination of Ballpoint Pen Inks Based on Correlation of Data Obtained by Optical and Spectral Methods,* **Revista de Chimie, 64**(1), 2013, pp. 74–80.

[24] M. Owoc, Kryminalistyczna ekspertyza sfałszowanych dokumentów atramentowych [Forensic expertise of forged ink documents], **Wydawnictwo UAM** [UAM Publishing House], Poznań 1968, pp. 28–29.

[25] D. Ellen, S. Day, C. Davies, Scientific Examination of Documents: Methods and Techniques, **CRC Press**, 2018, https://doi.org/10.4324/9780429491917.

[26] J.A. Siegel, *Application of Fluorescence Spectroscopy to Forensic Science,* **Forensic Science Review, 8**(1), 1996, pp. 1–11.

[27] R.K. Shukla, N. Kapoor, A.Badiye (Eds.), **Forensic Microscopy: Truth Under the Lenses** (1st ed.), 2022, CRC Press, https://doi.org/10.4324/9781003120995.

[28] O. Hilton, **Scientific Examination of Questioned Documents,** CRC Press, 1992.

[29] R. Cieśla, M. Trzciński, K. Szwagrzyk, M. Drawc*, Interdisciplinary Examination of Documents of Historical Significance*, **International Journal of Conservation Science, 11**(3), 2020, pp. 669–678. https://ijcs.ro/public/IJCS-20-44_Ciesla.pdf.

[30] J. Zięba–Palus, R. Borusiewicz, M. Kunicki, *PRAXIS—combined μ-Raman and μ-XRF spectrometers in the examination of forensic samples,* **Forensic Science International**, **175**(1), 2008, pp. 1–10, https://doi.org/10.1016/j.forsciint.2007.04.230.

[31] A. Braz, M. López–López, C. García–Ruiz, *Raman spectroscopy for forensic analysis of inks in questioned documents,* **Forensic Science International**, 232(1–3), 2013, pp. 206–212. https://doi.org/10.1016/j.forsciint.2013.07.017.

[32] R. Cieśla, *Application of non–invasive forensic methods of document research in establishing historical truth*, **International Journal of Conservation Science, 13**(1), 2022, pp. 163–174. https://ijcs.ro/public/IJCS-22-12_Ciesla.pdf.

[33] I.C. Negru, V. Vasilache, I. Sandu, R.I. Olariu, P.O. Tanasa, D. Potolinca, I.C.A. Sandu, *Depth Profiling of Diffraction–based Security Features in Authentic and Counterfeit Banknotes*, **Materiale Plastice, 54**(2), 2017, pp. 322–325.

[34] B. Łydżba–Kopczyńska, T. Czaja, G. Rusek, R. Cieśla, *Application of chemometric methods for the determination of fading and age determination of blue ballpoint inks,* **Journal of Raman Spectroscopy, 52**(1), 2021, pp. 159–169. https://doi.org/10.1002/jrs.6037.

[35] R. Kumar, V. Sharma, *Questioned Document Examination*, **Chemometric Methods in Forensic Science**, (Editors: V. Sharma, G. Sauzier & S.W. Lewis), Royal Society of Chemistry, 2023, 346p. https://doi.org/10.1039/9781839166099.

[36] J. Mazerski, **Podstawy chemometrii [Basics of chemometrics],** Wydawnictwo Politechniki Gdańskiej [Gdańsk University of Technology Publishing House], 2000.

[37] J. Miller, J. Miller, **Statystyka i chemometria w chemii analitycznej [Statistics and chemometrics in analytical chemistry**], Wydawnictwo Naukowe PWN S.A [Scientific Publishing House PWN S.A], Warszawa, 2016.

[38] L. R. e Brito, A. R. Martins, A. Braz, A. B. Chaves, J. W. Braga, M. F. Pimentel, *Critical review and trends in forensic investigations of crossing ink lines*, **TrAC Trends in Analytical Chemistry, 94**, 2017, pp. 54–59. https://doi.org/10.1016/j.trac.2017.07.005.

[39] D. Wilk, **Nowoczesne metody fizykochemii kryminalistycznej w procesie karnym. Zagadnienia wybrane [Modern methods of forensic physicochemical in criminal proceedings. Selected issues],** Wydawnictwo JAK [JAK Publishing House], Kraków 2018, pp. 52–57.

[40] M. Ristova, M. Skenderovska, T. Jovkovski, *Nondestructive Vis–NIR Reflectance Spectroscopy as a Forensic Tool for Ink Discrimination: A Preliminary Study*, **Journal**

Applied Spectroscopy, 89, 2022, pp. 967–973. https://doi.org/10.1007/s10812-022-01455-w.

[41] J. Zięba–Palus, M. Kunicki, *Application of the micro–FTIR spectroscopy, Raman spectroscopy and XRF method examination of inks,* **Forensic Science International, 158,** 2006, Article Number:165. https://doi.org/10.1016/j.forsciint.2005.04.044.

[42] F. Cappa, B. Fruehmann, M. Schreiner, *Raman Spectroscopy for the Material Analysis of Medieval Manuscripts,* **Nanotechnologies and Nanomaterials, 2019**, pp. 127–147. https://doi.org/10.1016/B978-0-12-813910-3.00007-0.

[43] D. Rawtani, C.M. Hussain (Eds.), **Modern Forensic Tools and Devices: Trends in Criminal Investigation,** John Wiley & Sons, 2023, p. 349. https://doi.org/10.1002/9781119763406.

[44] J. Schanda, **Colorimetry: Understanding the CIE System**, Jon Wiley & Sons, 2007. https://doi.org/10.1002/9780470175637.

[45] R.T. Marcus, **The Measurement of Color,** Chapter 2, vol.1, Elsevier Masson SAS, 1998.

[46] Ch. Mignot, *Color (and 3D) for Scanning Electron Microscopy*, **Microscopy Today***,* **26**(3), pp. 12–17, https://doi.org/10.1017/S1551929518000482.

[47] A. Łasińska, *Skaningowa mikroskopia elektronowa w badaniach kryminalistycznych,* **Prokuratura i Prawo, 10**, 2013, pp. 145–166.

[48] D.K. Shaffer, *Forensic document analysis using scanning microscopy*, **Scanning Microscopy, 7378***,* 2009, pp. 398–408. SPIE, 2009. https://doi.org/10.1117/12.825186.

[49] M. Owoc, *Thermic transformations of writing materials*, **Problems of Forensic Sciences, LIII**, 2003, pp. 51–59.

[50] * * * http://home.agh.edu.pl/~graboska/doc/NTBwIM-cw5-instrukcja.pdf [accessed on: 18.12.2023].

[51] S. Choi, *Foxing on paper: a literature review*, **Journal of the American Institute for Conservation, 46**(2), 2007, pp. 137–152.

[52] G. Meynell, R. Newsam, *Foxing, a fungal infection of paper*, **Nature, 274**, 1978, pp. 466–468, https://doi.org/10.1038/274466a0.

[53] G. Pinar, H. Tafer, K. Sterflinger, F. Pinzari, *Amid the possible causes of a very famous foxing: molecular and microscopic insight into Leonardo da Vinci's self–portrait,* **Environmental Microbiology Reports, 7**(6), 2025, pp. 849–859. https://doi.org/10.1111/1758-2229.12313.

[54] A. Koochakzaei, G.S. Alizadeh, *Paper Foxing Stains on a Historic Manuscript from the Early Qajar Era: Abiotic or Biotic Foxing?* **Heritage, 4**, **2021**, pp. 1366–1374. https://doi.org/10.3390/heritage4030074.

[55] R.A. Mustalish, *Optical brighteners: history and technology*, **Studies in Conservation, 45**(Sup1), 2000, Supplement–1.133, pp. 133–136. https://doi.org/10.1179/sic.2000.45.

[56] R. Higginbotham, F. Thomas, *Fluorescent Whitening Agents,* **Nature**, **181**, 1958, pp. 1437–1439. https://doi.org/10.1038/1811437a0.

[57] P. Bajpai, *Additives for Papermaking*, Chapter 4, (Ed.) P. Bajpai, **Biermann's Handbook of Pulp and Paper,** (Third Edition), Elsevier, 2018, pp. 77–94. https://doi.org/10.1016/B978-0-12-814238-7.00004-0.

[58] G. Rusek, R. Cieśla, *Zmiany właściwości spektroskopowych jako efekt fotodegradacji barwników [Changes in spectroscopic properties as a result of photodegradation of dyes],* **Dokumenty a prawo : prawne oraz praktyczne aspekty korzystania z dokumentów i e–dokumentów [Documents and law: legal and practical aspects of using documents and e–documents],** editors Magdalena Tomaszewska–Michalak, Tadeusz Tomaszewski, **Stowarzyszenie Absolwentów Wydziału Prawa i Administracji Uniwersytetu**

Warszawskiego [Alumni Association of the Faculty of Law and Administration of the University of Warsaw], Warszawa 2015, pp. 21–34.

[59] G. Rusek, R. Cieśla, *Badania wieku dokumentów historycznych wykonanych atramentem [Research of the age of historical documents written by ink]*, **Dokumenty we współczesnym prawie, [Documents in the Contemporary Law]**, editor E. Gruza, **Stowarzyszenie Absolwentów Wydziału Prawa i Administracji Uniwersytetu Warszawskiego** [Alumni Association of the Faculty of Law and Administration of the University of Warsaw], Warszawa 2009, pp. 11–21.

Received: February 20, 2024
Accepted: August 30, 2024