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FORENSIC EXAMINATION OF INKS USED AS INSCRIPTION ON HISTORICAL DOCUMENTS

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Abstract

Being carriers of information, historical documents have an important role in the modern world. Unfortunately, they are also the object of criminal activity. For centuries, various types of ink have been used to produce documents. Although inks are not the only writing material in use, from a forensic point of view, the problem consists in distinguishing one type of ink from another, and more specifically, the compatibility or incompatibility of the components of two or more inks found on one document or multiple documents. Samples of ink writing dating back to 1889–1950 were examined with the aim of researching by non-invasive spectroscopic methods whether, over the years, any changes in the production technology of iron-gall inks have resulted in significant changes in their reflectance and Raman spectra. The research showed that the production technology of iron-gall inks has not changed significantly, and, in addition, contemporary methods do not differ significantly from those used in the Middle Ages. The spectroscopic methods used in the research gave positive results because they made it possible to distinguish inks by dividing them into groups. The diversity of the distinguished groups of inks was caused by the addition of different synthetic dyes during production. The research on iron-gall inks showed the need for further continuation involving a much larger reference group and the need to look for differences in ink from one place, one geographic location, and made at similar times.

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

Introduction

Among all writing materials, for centuries, ink has played one of the greatest roles in creating and communicating human thought. It is difficult to determine precisely when and where ink was first used. It is very likely that ink was used in very distant times in the countries of old cultures, such as China and Egypt. Available sources indicate that in 2697 B.C.E., the inventor of Chinese inks was Tien-Lcheu [1, 2]. The inks of the time were black lacquers, which were applied to silk with a bamboo tube. Chinese inks were made from deciduous wood soot and deer antler animal glue, then mixed with camphor and musk to give them the right colour [3]. In Egypt, on the other hand, rolls of papyrus written with ink were found, the main colouring component of which was also soot [4, 5]. The first information about iron-containing inks, harbingers of modern iron-tannic inks, dates back to the 2nd century BC. From that time, the recipe of Philo of Byzantium for the preparation of writing is known, which could be obtained by writing with a tincture of galls, which is a colourless liquid, and after drying, the written place was moistened with a solution of copper salt containing iron. The writing was then

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black. In antiquity, coloured inks were also used, occurring in red and gold [6]. Inorganic pigments were used, such as cinnabar and lead red, as well as organic dyes of plant and animal origin. Both in antiquity and in the Middle Ages, silver and gold inks were also used [7]. It is assumed that the oldest inks, or rather, ink-like products, were in the form of a solid or a more or less dense suspension. They differed in the technique of preparation, the selection of the binder, and the substances used for combustion. Most often, sticks, balls, or cakes were made of soot and binder, which, after drying in the sun, were well suited for storage. If necessary, they were dissolved in water or another liquid immediately before writing. These inks had many advantages; they were insensitive to sunlight and did not lose their colour even after a very long period of storage. The disadvantage was the lack of water resistance, which made the text easily blurred [8–10]. Inks, as old writing fluids, are divided into carbon black inks and iron gall inks. However, such a dichotomous division is not unambiguous. There are known recipes in which, next to coal products, gum arabic, and egg white, gall cakes appear. In order to improve moisture resistance, iron compounds were often added to carbon black inks, which, over time, oxidised in the air and turned into iron oxides, which formed a kind of brown coating on the surface of the letters, making it difficult for moisture to penetrate into the dried ink. The ink then acquired an unusual appearance, and the writing became brown, with spots of soot often visible. It was noticed that only the extract of galls and iron compounds was enough to make the ink black. The presence of soot was becoming redundant. This led to the creation of iron-gall inks, which over time displaced other black writing fluids [11].

Vitriol was the most frequently mentioned source of iron in iron-gall inks. Today, it is known as iron sulphate. Iron-gall inks were created from galls formed on the leaves, twigs, or fruits of various types of oaks after the gall wasp laid eggs. The growth constitutes a hiding place for the larvae, where they remain for several months. Depending on whether the galls were harvested before or after they were left by the insects, black galls rich in tannins and white galls were distinguished. By long-term heating of galls with water, a tannin-rich extract was obtained, which was used to prepare the ink. Depending on the tannin and iron content, the original colour of the ink could change over time, even to the extent that iron oxides were formed by the oxidative action of oxygen in the air, giving the ink its characteristic yellow-brown appearance. Iron-gall ink had a major advantage over carbon black ink because it was easier to prepare. In the Middle Ages, there was an increase in interest in iron-gall ink, mainly due to the development of the administration in need of a cheap and easy-to-prepare writing medium. Other ingredients were also used to make iron-gall inks. Instead of galls, tannin-rich parts of other plants were used. In addition to vitriol, rusty iron or pieces of horseshoes were used as sources of iron ions. The ink was most often prepared individually according to one's own or heard recipe, often mixing random ingredients in a random way. The inks were usually stored in a dried state in the form of powder, which, if necessary, was mixed with a suitable solvent [12-16].

In the Middle Ages, writing and preparing ink were mainly done by monks. Iron-tannic inks were already known and widely used at that time. In the 16^{th} and 17^{th} centuries, inks were mainly made by Italian doctors. They presented numerous features that ink should have. The basic ones included, among others, easy flow coming from water, the right consistency coming from gum arabic and gallows, blackness caused by the action of sulfuric acid, and finally the gloss, which was supposed to be obtained thanks to pomegranate shells. In the middle of the 19th century, a new ink derived from logwood extract appeared. The heated extract, together with small amounts of potassium chromate, produced an intense blue-black ink. In addition, at that time, it had an advantage over iron-containing inks because it reacted indifferently, i.e., it did not destroy the element of the writing tool, the nib [17]. At the end of the 19^{th} century, alizarin inks were created, the advantage of which was that they were not suspensions but clear, well-draining liquids. Until then, iron-tannic inks were suspensions in which highly viscous

substances held the precipitate in suspension. For this purpose, gum arabic was most often added. When writing, a dark liquid was applied with a pen to paper, to the surface of which, due to the presence of gum arabic, the dye stuck. It was assumed that it was not necessary for the ink to contain a ready-made dye, as it used to do, as it was believed that it could form on paper after writing due to the action of air. It was therefore recommended to mix an aqueous extract of galls with iron sulphate and an indigo solution. The latter addition was intended to prevent iron from combining with tannins. As a result, a clear, slightly coloured liquid was obtained, in which only after application to the paper, due to the action of air, the dye proper for the ink was formed. In order to make the writing immediately legible, small amounts of ready-made dye were added to the ink (e.g., madder root extract containing alizarin). With the development of the aniline dye industry, different dyes could be incorporated into the production of iron-tannic inks, and different colour inks could be obtained. However, after some time, the brown colour characteristic of iron-tannic inks developed in the writing, which covered the original colour [18].

The dynamically developing dye industry, on the one hand, introduced progress in the production of inks and, on the other hand, created dangerous competition as it was possible to use water solutions of certain dyes for writing without any additional preparation. It seemed that dye and logwood inks would completely displace iron-tannic inks due to their advantages. While logwood inks were discontinued quite quickly, dye-based inks, especially those based on synthetic components, have been successfully competing on the market with iron-tannic inks for several decades. Nowadays, inks are produced using raw materials of synthetic origin, which create independent inks, as well as being successfully added to iron-tannic inks and thus creating a more resistant and durable product. The basic features of inks include, apart from the chemical composition, mechanical properties related to their resistance and durability. Durability is to be understood as the degree of sensitivity to normal destructive factors that occur with the normal, intended use of the ink. These factors include the interaction of paper components, spontaneous reactions between individual components of the ink, the influence of weather conditions on the behaviour of the ink, such as the action of air (oxygen, water vapour), and light of certain intensities. Durability should be distinguished from resistance, i.e., the susceptibility of the ink to destructive factors that occur in the course of its normal use. An example may be both intentional action on the ink leading to its discoloration or complete removal from the document substrate through the action of various solvents washing the ink as well as accidental action by soaking the document in water or a solution or heating the ink at an increased temperature [19, 20].

Forensic problem

One of the more difficult and contemporary but still important challenges of forensic science is the problem of ink examination. Forensic practise often involves the problem of differentiating one ink from another, or more precisely, the compatibility or incompatibility of the components of two or more inks as inscriptions on the same document or on many documents. Research of this type is necessary in situations where there is a suspicion that the text fixed on the substrate has been falsified by an unauthorised person by adding fragments. Sometimes it is also possible to determine the correspondence between the chemical composition of the ink found on the document under examination and the ink found in the suspect. On the one hand, the current variety of ingredients facilitates ink examination but, due to mass production, deprives them of individual characteristics desirable in the ink

identification process. Therefore, in most cases, only group identification is possible, related to the affiliation of the ink to a group of inks [21, 22].

Methods

Forensic ink examination is based on extensive scientific research methods with varying degrees of complexity, from the simplest to the most complex. This is due to the historical development of the document itself, its universality of use, importance, and significance in everyday life, as well as the type of substances used for production and the ways and methods of applying writing materials to the paper. Depending on the type of document, the technique of its preparation, and the paper used, various research methods are applied. Generally, physico-optical methods should be mentioned, which allow determining the structure and spatial properties of ink and the so-called physical properties, e.g., light absorption or electrical conductivity; chemical methods, which additionally allow studying the qualitative and quantitative chemical ink composition and its chemical properties, such as the ability of ink to specific chemical reactions; and physico-chemical methods, involving the study of the relationship between the composition of ink and its physical properties [23, 24]. As a rule, basic research uses optical methods that use information carried by electromagnetic waves of a specific length range in the process of matter analysis [25, 26]. The obtained optical information signal is received either directly visually or through devices that can amplify, process, and record this signal. Direct visual observation of the document and the entries recorded on it entails many limitations resulting from the very nature of the sense of sight; it is also a subjective assessment prone to error. Therefore, in the non-invasive methods of ink research, equipment measuring the light absorption or reflection coefficient is used [27–29]. Documents can be analysed using non-invasive spectroscopic methods, such as VIS-NIR reflection spectroscopy and Raman spectroscopy. VIS-NIR reflectance analysis allows for determining subtle changes in ink colour, while Raman spectroscopy is desirable due to its molecular specificity and high sensitivity [30-34].

Aim, scope and objects

Liquid writing materials such as inks, regardless of their type, are designed to create a permanent-coloured spot of a specific shape on the substrate. For this reason, a writing material can be any substance that is able to meet the above conditions, even if its main purpose is fundamentally different. In principle, almost anything that makes a visible or identifiable mark on the paper can be used as a writing implement. As it was mentioned above, the first liquid writing material was probably carboning ink, which was made of a suspension of soot or charcoal in water with the addition of a fixative (e.g., glue, egg, etc.). Then there were inks in which a complex compound formed from an iron ion and various types of natural tannins (e.g., from oak galls) was responsible for the colour of iron-tannin inks. Of these, iron-gall ink was the most popular and most commonly used. This type of ink also includes logwood ink. Here, tannin is an extract from logwood *(Haematoxylum campechianum)*. The aim of the research was to check whether, over the years, possible changes in ink production technology resulted in significant changes in their reflection spectra and Raman spectra. The material used for the ink research was taken from the collections stored in the Ink and Writing Materials Library at the Department of Forensic Sciences of the University of Wrocław [35-39]. Research material from

private collections was also used [40]. It was assumed that all the entries from the years 1889 - 1950 (Table 1) were made with iron-gall ink.

Table 1. List of examined documents. In the further part of this manuscript acronyms from Table 1 are used in all figure captions

No.	Document description	Acronym	Figure No.
1	A diary from the end of the 19th century from the vicinity of Biała, former Austro-Hungarian partition. The partitions of Poland 1772-1918 (currently Bielsko-Biała city, Lesser Poland Voivodeship, Poland). Written in 1889	Diary from 1889	1
2	Certificate of reporting for military service. Issued by the Kolski district, former part of the Russian partition within the Kingdom of Poland. The partitions of Poland 1772-1918 (currently Greater Poland Voivodeship, Poland). Written in 1900	Certificate from 1900	2
3	Baptism certificate in the Roman Catholic Church. Place of issue of the Wiskitki, former Russian partition. The partitions of Poland 1772-1918 (currently Masovian Voivodeship, Poland). Written in 1906	Certificate from 1906	3
4	Private letter from Nowogródek land. City Iwaniec, former Russian partition. The partitions of Poland 1772-1918 (currently territory of Belarus). Written in 1926	Letter from 1926	4
5	Payment order. Place of issue Piotrków city, former Generalgouvernment for the occupied Polish territories (currently Piotrków Trybunalski city, Łódź Voivodeship, Poland). Written in 1940	Payment order from1940	5
6	Private letter. Place of issue Warsaw city (capital of Poland). Written in 1950	Letter from 1950	6

The figures (Fig. 1) show the entries that were included in the ink research. In the examined inks, attempts were made to find and determine the features that would distinguish the inks from each other.

Fig. 1. Documents used in ink research: Diary from 1889 (1); Certificate from 1900 (2); Certificate from 1906 (3); Letter from 1926 (4); Payment order from 1940 (5); Letter from 1950 (6).

Research, experiments and results

Reflectance spectra

Non-invasive spectroscopic methods were used to test all ink entries on these documents. For this purpose, an advanced device, the VSC8000/HS* (Video Spectral Comparator), equipped with a VIS-NIR spectrometer measuring in the electromagnetic radiation range of 400nm-1000nm was used [41]. For each selected fragment of the ink writing, 26 spectral measurements were made from three different places, and then the spectra were normalised (Fig. 2).

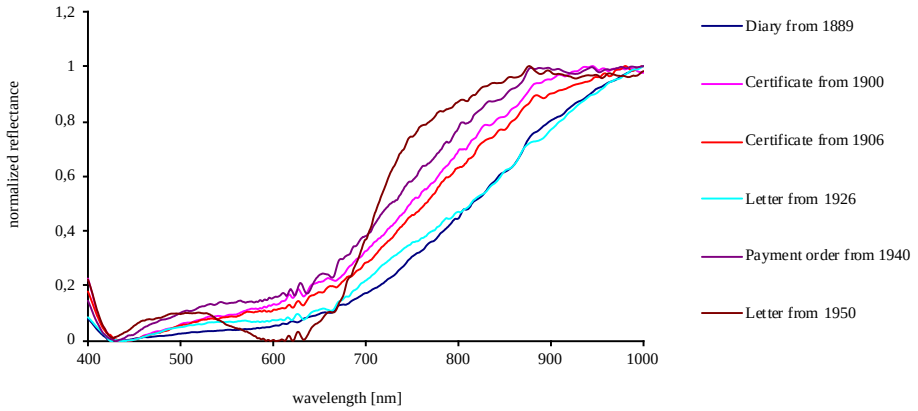


Fig. 2. Chart of normalized reflection spectra of ink entries on examined documents.

Raman spectra

Raman spectra of the inks in the mentioned entries were also taken. For this purpose, a FORAM685-2** Raman spectrometer device was used, where high levels of sensitivity can be achieved with the 685nm laser [42-44]. For each selected section of the ink writing, 16 spectral measurements were taken from three different locations, and then alignment to the baseline and normalisation of the spectra were performed (Fig. 3).

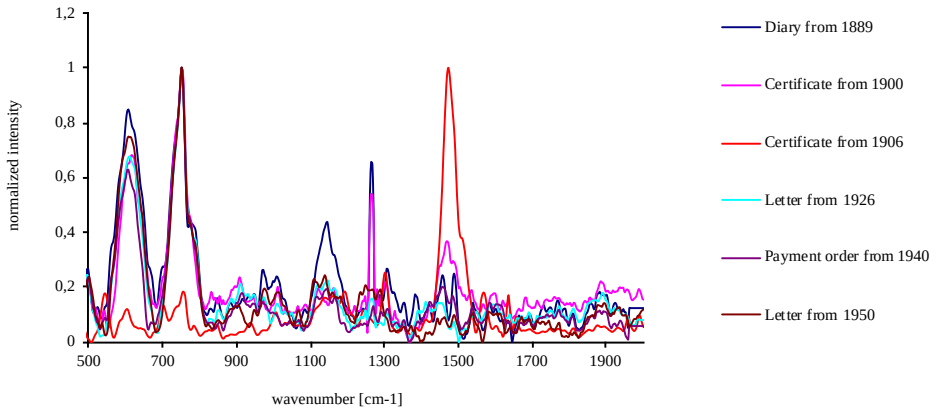


Fig. 3. Chart of normalized Raman spectra of ink entries on examined documents.

When Raman spectra were taken, yellow-brown staining of the edges was noted in the area of the oldest entry, dating back to 1889, as well as a yellow-brown stain on the writing line itself. Similar yellow-brown stains were also found on some of the other entries examined (Fig. 4).

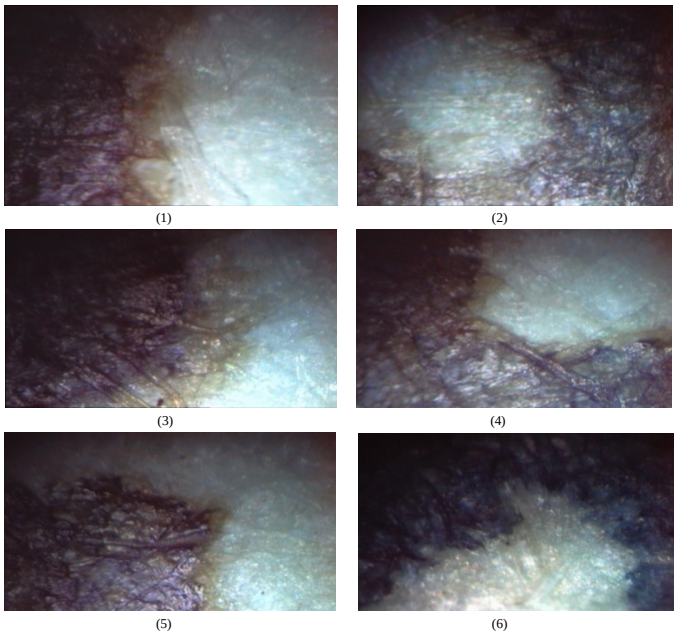


Fig. 4. Yellow-brown tints on the edges of the ink entries. Diary from 1889 (1). Certificate from 1900 (2). Certificate from 1906 (3). Letter of 1926 (4). Payment order from 1940 (5). Letter from 1950 (6).

CIE Lab colour space

One way to quantify colour is the CIE Lab uniform colour scale, based on three parameters and organised in the form of a sphere. The first parameter describes lightness (L*), which is a scale of how dark or light a colour is, from black to white. The other two parameters (a* and b*) define the colour. Dimensions a and b represent the scales of the 2D colour wheel. The a* axis goes from green to red. The b* axis ranges from blue to yellow. Each colour can be divided into these three parameters and marked in space [45-46]. The differences between the two colours can then be described by calculating the Euclidean distance between these points in space, which is defined as ΔE* and computed by the formula:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \qquad (1)$$

In the research, the differences between the colours of entries on individual documents were checked using the above formula for ΔE*.

Table 2. Euclidean distance ΔE*

No.	Acronym	ΔL*	Δa*	Δb*	ΔE*
1	Diary from 1889	78,68	23,50	-57,51	19,89
2	Certificate from 1900	78,59	22,07	-45,90	9,29
3	Certificate from 1906	90,92	24,18	-57,16	20,89
4	Letter from 1926	59,14	19,19	-0,14	45,57
5	Payment order from 1940	88,12	13,47	-27,50	13,27
6	Letter from 1950	102,35	3,94	-45,57	24,69

None of the entries from the years 1889, 1900, 1906, 1926, 1940, or 1950 showed any special features when examined in different lighting conditions, i.e., in white light, infrared light, or ultraviolet light. Illuminated with a monochromatic point light and viewed through cut-off filters, they also showed no luminescence. It is known that iron-gall ink slowly degrades as it ages, releasing tannins, iron ions, and mineral acids. Iron ions slowly react with oxygen in the air, resulting in yellow-brown spots appearing on the writing line. This is a well-known and proven phenomenon, and it most often occurs in old documents created, for example, in the Middle Ages [47-48]. The mineral acid released from the colour complex causes the corrosive effect of iron-gallic inks, and the formed mineral acid affects the disintegration (hydrolysis) of paper (corrosion of the substrate-holes) [49-52]. The yellow-brown spots were assumed to be due to oxygenated iron derivatives (breakdown products of iron-gall ink) [53, 54]. Therefore, an experiment was carried out in which Raman spectra (Fig. 5) of various iron(III) oxides and iron(II) sulfate(VI) were made for comparison.

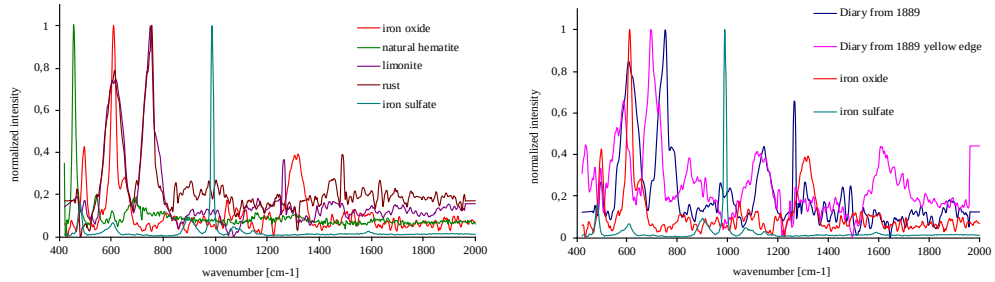


Fig. 5. Comparison of Raman spectra of various oxygenated iron derivatives (left). A summary of the Raman spectra of fragments of the entry from 1889 with iron derivatives (right).

The presence of iron(II) sulphate(VI) was not found in the tested spectra, and the spectrum of iron oxide (Fe_2O_3) suggests its presence, so the spectrum of iron(II) sulphate(VI) was removed from the list and the following image was obtained (Fig. 6).

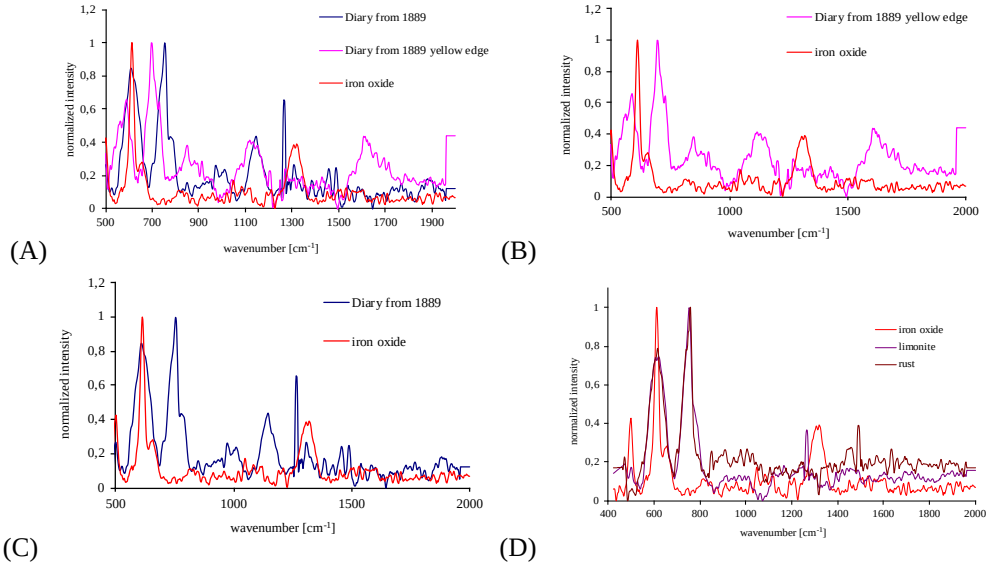


Fig. 6. Comparison of Raman spectra of fragments of the 1889 entry and iron oxide (A). Comparison of the Raman spectra of the yellow edge fragment of the 1889 entry and iron oxide (B). Comparison of Raman spectra of a fragment of the centre of the 1889 entry and iron oxide (C). Comparison of Raman spectra of various oxygenated iron derivatives (D).

It is more probable that a complex mixture of different iron oxides-neutral (e.g., iron oxide) and basic (looking like limonite or rust) are formed as decomposition products of the iron-gall ink, the Raman spectra of which differ as shown in the figure (Fig. 6D). Therefore, the spectra of yellow-brown stains were compared with the spectra of limonite (the so-called bog ore) and rust obtained from a rusty steel object.

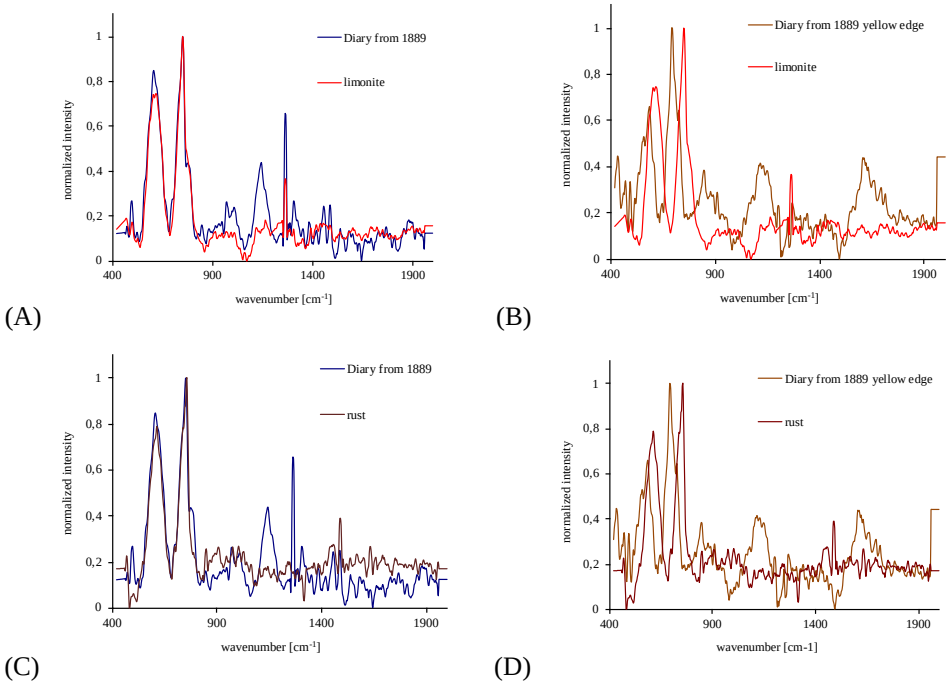
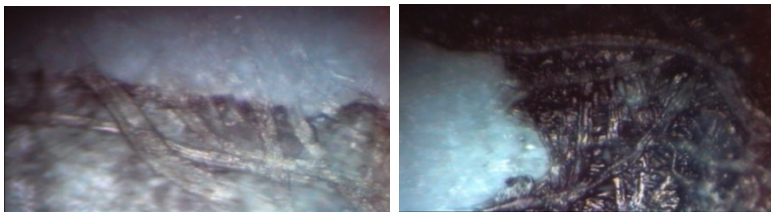


Fig. 7. Comparison of Raman spectra of a fragment of the centre of the entry from 1889 and limonite (A). Comparison of Raman spectra of a fragment of the yellow edge of the entry from 1889 and limonite (B). Comparison of Raman spectra of a fragment of the centre of the 1889 entry and rust (C). Compilation of the Raman spectra of a fragment of the yellow edge of the 1889 entry and rust (D).

A comparison of the Raman spectrum obtained from various places in the 19th century entry and iron oxide showed that iron oxide is a very large simplification. In fact, complex derivatives of iron oxide are formed, most often mixed derivatives of iron hydroxide and iron oxide. The analysis of the figures (Fig. 7) shows that the presence of hydroxide iron derivatives is very likely; this may indicate the progressive decomposition of the ink, which could be expected due to the age of the writing. Looking at the dissimilarity of the Raman spectrum of the entry from 1906 made in black ink, an assumption was made that the document might have been written in logwood ink. Due to the intensity of the colour, it could have been a document made with carbon ink. For the purpose of comparison, the Raman spectra of the examined entry with the ink from 1906 and the corresponding spectra of writing with logwood ink (prepared for this purpose in the laboratory) and with the spectrum of amorphous carbon (soot) as a substitute for carbon ink, as well as with the iron-gall ink prepared in the laboratory, were compared. The view of fragments of entries made with inks prepared for the purposes of the experiment (Fig. 8).

They show (Fig. 9) that the 1906 entry definitely was not made in logwood ink because the range of intensity of Raman signals in logwood ink occurs in completely different places. The same applies to the entries made with carbon ink.



(A) (B)

Fig. 8. Inscription in iron-gall ink made for the purposes of the experiment (A). Entries made in logwood ink made for the purposes of the experiment (B).

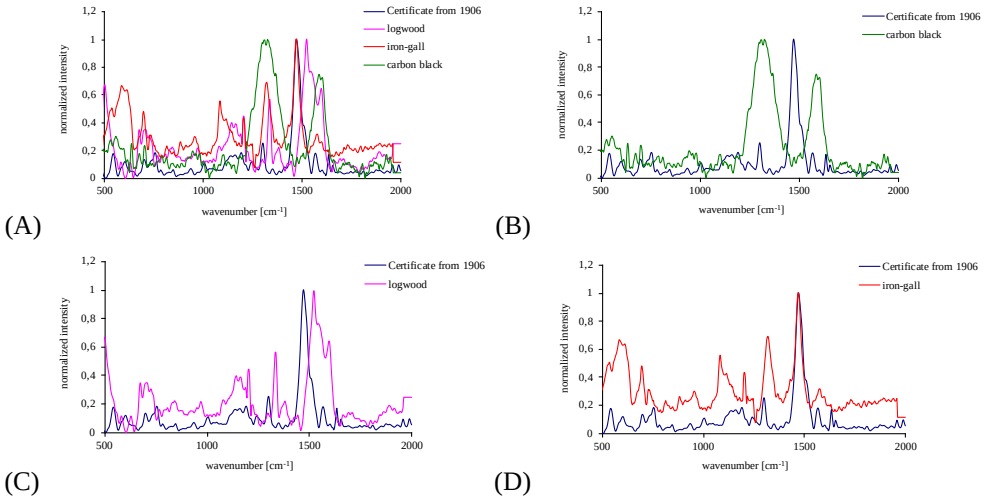


Fig. 9. Summary of normalised Raman spectra of entries made with iron-gallic and logwood inks and carbon black as a substitute for carbon ink (A). Summary of the normalised Raman spectra of the 1906 writing and soot in lieu of carbon ink (B). A comparison of the normalised Raman spectra of the writing from 1906 and the one made with logwood ink prepared for the purposes of the experiment (C). Comparison of the Raman spectra of the writing from 1906 and the one made with iron-gallic ink prepared for the purposes of the experiment (D).

The Raman spectra measured in the research allowed determining that iron-gall ink was used to make the analysed writing on the documents, which was not surprising given its widespread use at the time. However, in the case of ink from 1906, it can be stated that standard ingredients were used for its production, but the production itself was probably based on a changed (different) technology. For example, some mediaeval recipes for the production of iron-gall inks recommend leaving the prepared ink free with air access before use until it was clearly blackened [55, 56], whereas the difference in the VIS-NIR spectra of the ink from 1950 could be caused by the presence of a dye added in its production. Reflection spectra of old iron-gall inks are poorly differentiated, with the exception of an entry in modern ink (Letter from 1950, Fig. 2). Looking for a way to highlight the differences, a decision was made to use methods similar to those used in statistics and chemometrics. The results obtained are presented in the charts below. Comparing the spectra, the calculated value of the area under the

reflectance curve was referred to the value of ΔE*. The obtained image may suggest approximately three groups of spectra. Similarly, if we postpone the position of the reflectance maximum relative to the position of the maximum signal in the Raman spectrum, then this system also has three groups, but with a clearly different composition (Fig. 10A and B).

By checking the differences that may result from the use of different units, the autoscaling operation was performed. The autoscaling of colour differences (ΔE*) in relation to the autoscaled surface area clearly confirmed the division into three groups. Autoscaling carried out for reflectance at minimum and reflectance at maximum also showed three groups of inks. The division into three groups appears in many different autoscaling configurations and combinations of different methods. Also, for these signals, the autoscaling of their values indicated three groups of spectra, determining the differences in the research of ink samples (Fig. 10C and D).

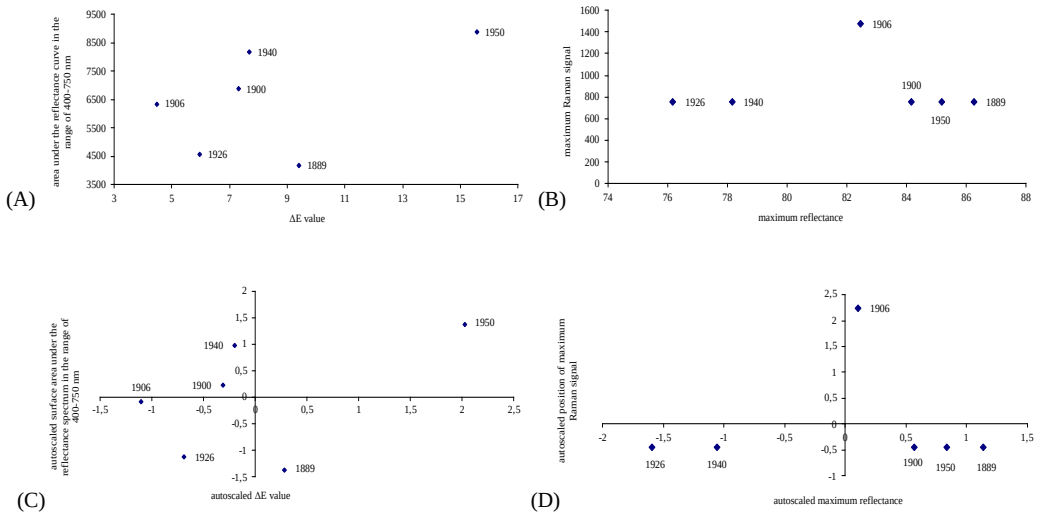


Fig.10. Comparison of the value of the area under the reflectance curve versus the ΔE value (A). Comparison of the value of the maximum signal in the Raman spectrum versus the reflectance value of the reflection spectrum (B). Comparison of the value of the area under the reflectance curve versus the ΔE value after autoscaling (C). Comparison of the value of the maximum signal in the Raman spectrum versus the reflectance value in the maximum of the reflection spectrum after autoscaling (D).

Discussion

Reflection spectra in the examination of inks from the years 1889, 1900, 1906, 1926, 1940, and 1950 showed their weak dissimilarity. The discrepancy in the results of measuring the Euclidean ink colour distances suggests greater differences between them. A failure to find clear differences in the spectra could be due to too few measurements taken to average. The measurements made for the ballpoint pen ink showed that in order to obtain the correct result for averaging, about 100 spectra should be taken from one fragment of the ink entry [57-60]. Unfortunately, making such a large number of spectra is a very time-consuming activity. In the case under study, it was assumed that the entries were made with iron-gall ink. The uniform opacity of the writing line was assumed, resulting from the nature of the ink (significant fluidity),

which also implied that a much smaller number of spectral measurements is sufficient for averaging (in this case, 26 VIS-NIR measurements were made). The results of comparisons of the Raman spectra confirmed the assumption that all entries were made with iron-gall ink. However, the spectra are also poorly differentiated (Fig. 3). The high peak intensity of some entries (Certificate from 1906, Figs. 3 and 9) may result from a different ink production technology. Some production regulations recommend that freshly made ink should be left for several days with free access to air until a clear black colour is formed. Due to the poor visibility of a fresh writing line made with iron-gall ink, the regulations also recommended the addition of any dye (e.g., coal in the Middle Ages) to improve readability. Thus, the different appearance of the reflection spectrum of the ink entry from a private letter from 1950 may be caused by the addition of dye to the ink. Research has shown that the technology of production of iron-gall inks for which research has been carried out over the years has not changed significantly and additionally does not differ from the methods used in the Middle Ages. Only recently has a synthetic dye been massively added to shorten the time of "maturation" of the ink. The term "maturation" means a certain amount of time for the ink to become black ("matured"). Possibly the spectral appearance of the reflective ink on the letter from 1950 (Fig. 2) is the effect of such an addition.

Conclusions

The spectroscopic methods used in the examination gave promising results because they allowed distinguishing the inks by dividing them into groups. However, the research requires further continuation so that it can be carried out on a much larger reference group in the future. In addition, an attempt should be made to find differences in ink records from one place (one geographical location) and made at a similar time.

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