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Changes in color and iron ions of commercial iron gall inks after artificial aging

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Abstract

Iron gall inks consist of vitriols (sulphates of certain metals), gall nut extracts; and gum Arabic: after exposure to oxygen, dark-colored compounds of the inks are formed. As the complexity of the composition of iron gall inks renders documents susceptible to environmental influences, this causes the handwriting thereon to fade. These add technical difficulties to the protection of iron gall inks. Therefore, it is particularly important to understand the changes in the inks during the aging process. For this reason, iron gall ink-stained paper specimens were subject to an intense analytical program to investigate their chemical and physical modifications after aging (temperature/humidity, temperature, and ultraviolet light aging), commercial iron gall ink was used for this experiment, making the study more applicable. The changes of iron gall inks were evaluated using color variation, color density, absorbance, and X-ray photoelectron spectroscopy (XPS). All results indicate that the temperature, humidity, and UV are harmful to the inks in both physical and chemical terms. Physical damage is mainly the aging of the ink color lightening, color density decreases, of which the color of the samples treated with damp heat for 30 days undergoes the greatest change. The chemical change is represented by the ratio of the concentration of iron ions in different valence states, the amount of Fe^{3+} in the untreated inks is much greater than that of Fe^{2+}, and the amount of Fe^{2+} exceeds that of Fe^{3+} after exposure to different methods of aging. Experiments show that UV light causes the most severe damage to handwriting. The main manifestation thereof is color-fade and the paper surface ink part of the iron ion content changes, with the increase of aging time, the Fe^{2+} content gradually increases. This experimental study of the changes produced by iron gall inks during aging can provide better technical support for the protection of the ink handwriting.

Keywords Iron gall inks, Artificial aging, Color difference, Iron ions

Introduction

Iron gall ink is an important writing and drawing ink that has been used in Europe since the Middle Ages [1] to the early twentieth century. Most important historical documents and works of art were written (or drawn) in iron gall inks [2]. The iron gall inks are used in a wide range of applications as they were easy to make, hard to remove from the surface (a valued characteristic for official record-keeping) [3]. There are several different recipes for iron gall inks that have been published over centuries [4]. These inks are composed of three main ingredients: plant extracts rich in tannins, iron (II) sulphate, and a binder that usually is gum Arabic [5]. The majority of the constituents of iron gall inks is unstable nature raw materials, such as different amounts of tannins with the galls (e.g. 50–70% in Aleppo or Turkey galls): when exposed to air, the handwriting is oxidized and easily faded, resulting in damage to the document [6] In addition, due to the large variety of historical recipes and procedures used in the production of iron gall inks, research into iron gall inks is complicated [7]. Inks with a complex composition may

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suffer many side effects that could contribute to different aspects of paper degradation, especially the presence of metal ions. Many interactions occur with surrounding components: precipitation with tannins, chelation with polysaccharides [8], etc. Studies targeting changes in iron gall inks involve analysis of the catalytic effect of metal ions present in the inks on paper, such as copper [9–11], or the effect of acid in the inks on the paper [12, 13].

Nowadays, the world's libraries, archives, and museums are faced with the problem of preserving countless documents, manuscripts and drawings, endangered by the corrosive properties of iron gall inks [14, 15]. Degradation of cellulose, the main structural component of paper, is known to depend on the pH of the macromolecular environment, iron gall inks feature low pH because of the acidity of their main components, iron (II) sulphate and tannic/gallic acid [16]. Upon formation of the iron gall ink complex, sulfuric acid is released, which is probably the most important source of acidity associated with iron gall inks. The pH of most historical paper containing iron gall inks varies considerably, ranging from 2.9 to 7.1 [17].

It is difficult to clarify the changes produced by iron tannate inks during aging, and the present work was aimed at studying the changes in color and the different valence states of iron ions before and after aging of the ink. In this experiment, physical and chemical changes of iron gall inks were studied by simulating the changes generated during storage by means of artificial aging. Chemical properties are manifest by changes in the concentration of iron ions in the handwriting, because for iron gall ink, iron ions are the main reason for its color and changes therein, so the study of changes in iron ions during the aging process is important for the protection and restoration of ink handwriting. The aging of iron gall inks has been systematically studied in fewer studies, and this experiment is a more comprehensive study of the changes produced by iron gall inks during the aging process. The iron gall inks were applied to paper and exposed to three different artificial aging processes. Chemical and physical properties of ink-paper specimens were evaluated before and after artificial aging by different instrumental techniques. The analytical study involved colorimetric analysis and observations of color variation, color density, its absorbance, and changes in iron ions of the iron gall ink handwriting.

Experimental work

Preparation of ink-stained paper specimens

As hundreds of recipes for inks have been published over centuries, to make the effect more convincing, the most widely used, commercially available, iron gall inks (HERO232) were used in the present research (Table 1).

Table 1 The constituents of iron gall inks (HERO232)

	Ingredients	Content (g)	Ingredients	Content (g)
Iron gall ink	Tannin	24–25	Blue pigments	4–5
	Iron (II)	30	Water	1000
	Hydrochloric acid	5–6	Gum Arabic	10
	Gallic acid	7–8		

This research divided copy paper (70 g/m^2) into 12 parts (on average), and then brushed the iron-ink gently thereon, keeping the area of each ink block to about 30 cm^2. The iron gall inks were left to rest for three days at room temperature. For treatment of paper species, as sensitivity of iron gall inks to water may cause unwanted side effects, such as brown halos around ink lines and migration of iron from the ink lines, so, humidification of papers in a controlled high-humidity environment proved to be much safer and subject to fewer side effects such as color changes or migration in comparison to water treatments [18].

The resulting specimens underwent three different artificial aging processes: (i) a "temperature/humidity" procedure (T/RH aging) conducted at 80 ℃ and a relative humidity of 65% for 14 and 30 days; (ii) a "dry heat treatment" procedure (T aging) was oven-driven (using a DHG-9140A oven) for 14 and 30 days, at a constant temperature of 80 ℃, so only temperature effects were investigated. (iii) "UV" treatment (UV aging) was applied for 120 h (5 days) in a UV aging chamber (QUV) with UV irradiation at wavelengths ranging 295–365 nm at a temperature of 50 °C.

Instrumentation

The chromatic variations in the paper and inks were evaluated by determining the L^*, a^*, and b^* coordinates of the CIELAB space, and the global chromatic variations were expressed as ΔE according to the UNI EN 15886 protocol (2010) by means of a spectrophotometer. Colorimetric analyses were conducted on ink-stained paper specimens before and after aging. For each specimen, three measurements were performed on inked areas.

$$\Delta E = \left[(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2\right]^{1/2}. \quad (1)$$

Color density is an important parameter used to measure the quality of images and text on the surface of the paper: it indicates the shade of the image or text based on the ink thickness of the prints and denotes the reflectivity of the print directly. Equation (1) explains the principle of color density (D_ρ), where ρ is the reflectivity of the

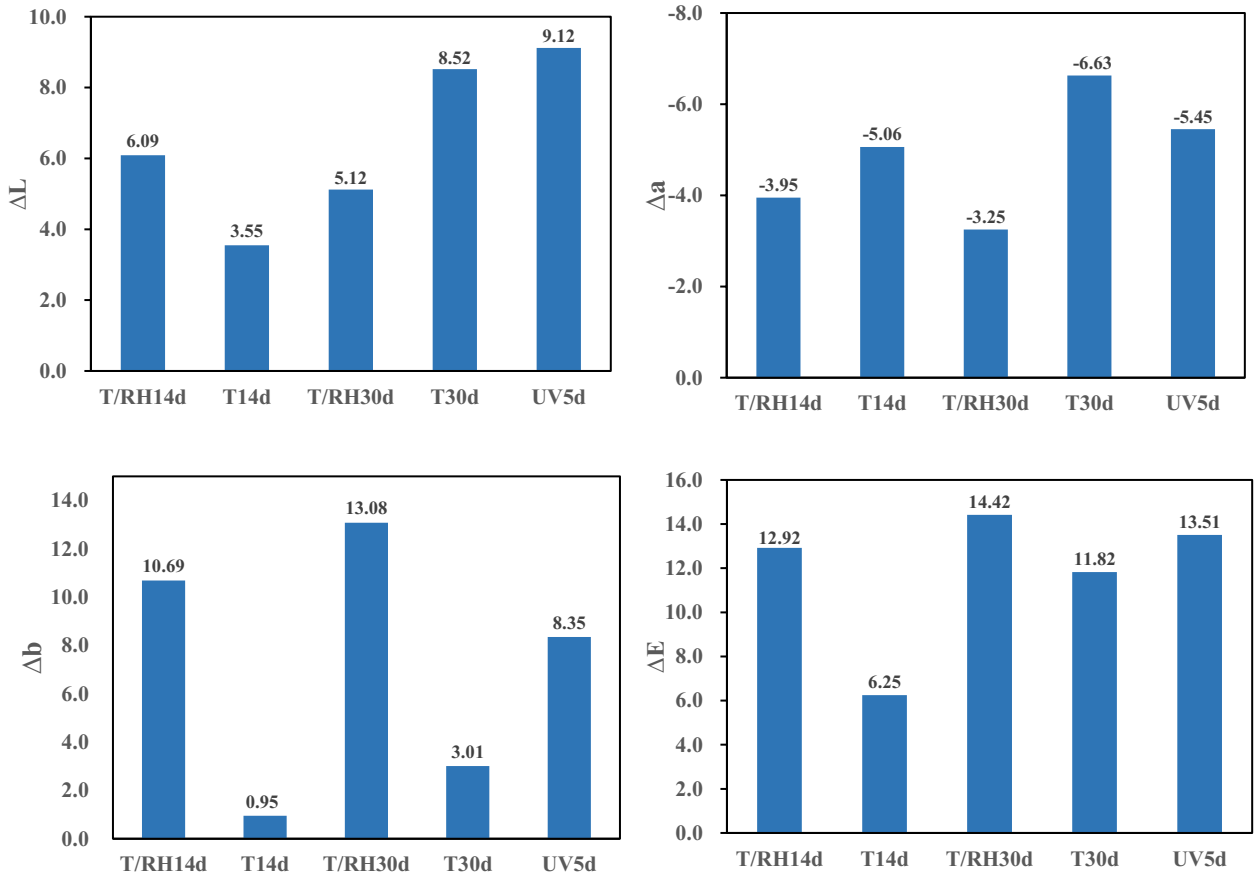

Fig. 1 Chromatic variations (average values) calculated after three different aging processes

ink sur-face. Using an X-rite530 spectrophotometer to test the color density of the ink area of the paper sample before and after aging processing, the five-point method was used to minimize error.

$$D_\rho = \log\frac{1}{\rho}. \tag{2}$$

A UV/Vis/NIR spectrophotometer (Lambda-950, Perkin Elmer, USA) was used to obtain the reflectance of visible light spectrum on the surface of paper samples. The working spectral range is from 200 to 800 nm. Each UV spectrophotometer test sample measured 4 mm × 3 mm. The more light absorbed by the surface of the object, the darker the color, the absorption data were used to examine the change in color shades of inks from an optical perspective.

XPS (Thermo Scientific K-Alpha) is one of the more effective means with which to study the chemical elemental composition and elemental valence state of the sample surface. Characterization of Fe in the ink portion of the paper surface was undertaken by use of XPS. Samples measuring 5 mm × 5 mm were prepared for testing. XPS measurements were performed at $h\nu = 1486.6$ eV, full and fine spectrum scans of the samples were acquired, followed by analysis and processing of the data.

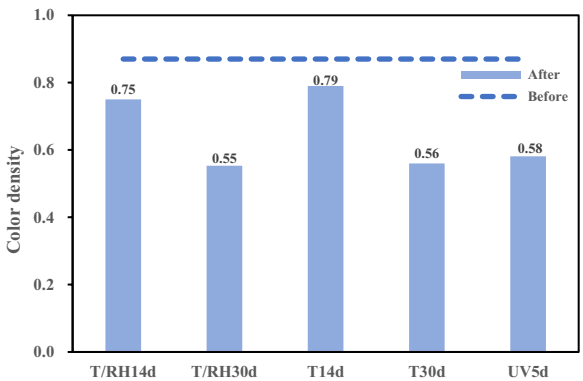

Fig. 2 Color density changes after three different aging processes

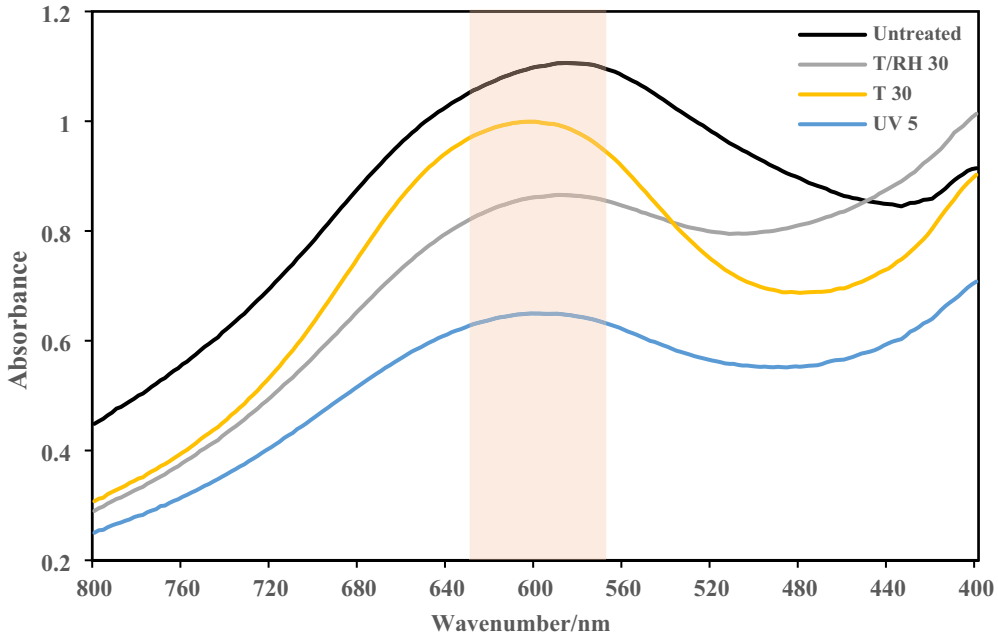

Fig. 3 Variations in absorbance of inks after three different aging processes

Results and discussion

Chromatic variations

Freshly produced iron gall inks usually have a bluish black tone, and their degradation during aging leads to the formation of brown products [19]. Reasons for color change are still not fully understood, but they are usually attributed to the degradation of iron (III) gallate complex to brown quinones, iron (III) oxides, and yellow ellagic acid [20]. For the present experiment, the ink colors were changed to some degree.

Average values of the chromatic coordinate variations determined for all specimens before and after aging are reported in Fig. 1. It can be seen that l (related to the change in brightness) and b (related to the blue/yellow change) coordinates showed strong variation. The values of Δb at 14 and 30 days of T/RH were 10.69 and 13.08. When T aging (temperature only) was applied to the samples, the value of Δb is 3.01 after 30 days, indicating that humidity has a greater effect on the b-value of the ink. ΔE represents the difference in color between treated and untreated ink, according to Eq. (1) the measured value affects it to a comparable extent. As seen in the result, the color difference is greatest after 30 days of T/RH, at a value of 14.42, followed by UV aging for five days whereupon ΔE is 13.51; the sample showing the least color change is that after 14 days of T aging, for which the color difference value is only 6.25.

Color density changes

Results of color density analyses are shown in Fig. 2: compared to the untreated samples, the color density values of the ink stains after aging were all reduced to some extent. The most significant decreases occurred after T/RH for 30 days and T aging for 30 days, with color density values decreasing from 0.87 (untreated) to 0.55 and 0.56, respectively. The color density values of samples also decreased to a large extent after five days of UV aging, from 0.87 to 0.58. Overall, the least affected ink specimens were those exposed to T aging for 14 days, with a color density value of 0.79, a reduction of only 0.08 compared to untreated specimens. When treated for 30 days, the color density decreases after T aging with only temperature effects applied compared to T/RH aging, because the inks on the paper is exposed to a high temperature (80 °C for T/RH and 105 °C for T aging) for a long time. UV light mainly affects the color of the Direct Lake Blue pigment in the ink. As the main color component of ink is colorless before oxidized, the handwriting color is light when writing on paper, not easy to identify, so added blue pigments (Direct Lake Blue) to the ink as color developer. Direct Lake Blue is reductive and the conjugated large π-bonds in the molecule are broken under the action of ultraviolet light, the molecular structure of

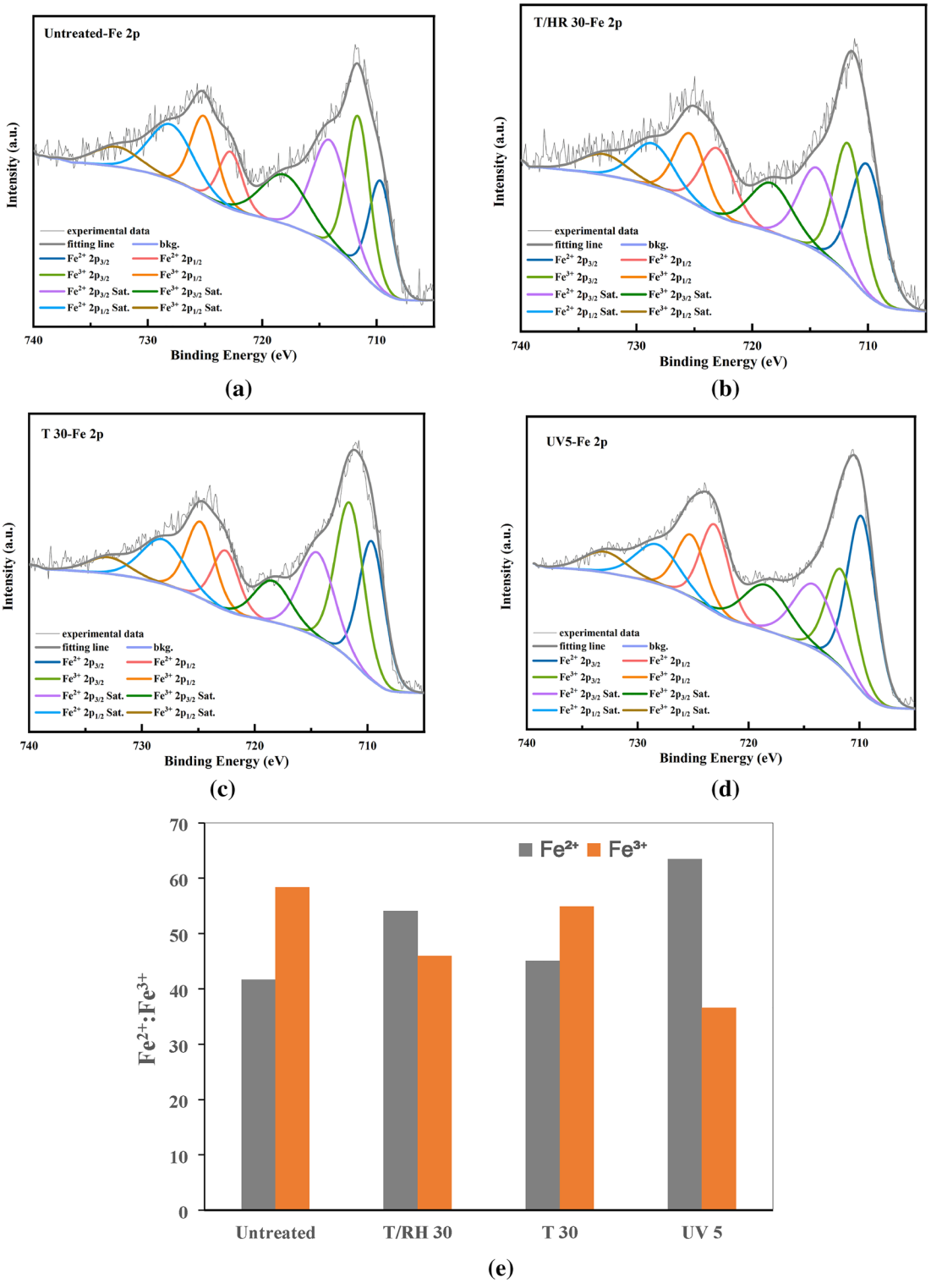

Fig. 4 Iron ions change of inks after three different aging processes

the dye was damaged, resulting in reduced light absorption and color fading, causing a large change in the ink color density index [21].

Changes in absorbance

Figure 3 shows the absorbance of surfaces of different ink samples in the range of 380 to 780 nm (i.e. the range of irradiation visible to the human eye). To observe more intuitively the effects of various aging processes on the absorbance of the ink, only the data pertaining to test times of 30 days were measured (under both T/RH and T aging). The curves in different colors represent absorbance values of the inked part of the paper surface after different aging processes. According to the principle of absorption and reflection of light, it is known that the darker the color the less the reflection of light, and the greater the absorption. As shown in Fig. 3, the marked area is where the maximum absorbance is located. The maximum absorbance value of the untreated ink is 1.11, that under T/RH is 0.87, and the maximum absorbances of T aging for 30-day and UV 5-day samples are 0.87 and 0.65, respectively. The overall trend of the absorbance curve shows that the biggest effect on the ink color is UV light, exhibiting the greatest decrease in absorbance compared to untreated samples.

Changes in the content of Fe^{2+} after three different aging processes

The energy spectral peaks of the Fe $2p_{3/2}$ and Fe $2p_{1/2}$ orbitals were split-fitted according to the split-peak method [22, 23], and the fitted XPS profiles are shown in Fig. 4a–d. The valence transition process of iron ions in the inks before and after aging was analyzed by calculating the peak areas of Fe^{2+} and Fe^{3+} [22], and the results are shown in Fig. 4e. As aging proceeds, the Fe^{2+} content in the treated inks tends to increase relative to that of Fe^{3+}. The order of Fe^{2+} content is: UV5 > T/RH30 > T30. When writing with iron gall ink, the Fe^{2+} meets the oxygen in the air and is converted into black Fe^{3+} precipitate, which, together with the effect of color enhancers, gives the written ink a blue-black color. The increase of Fe^{2+} content after aging compared to Fe^{3+} should be related to the presence of reducing gallic acid in the ink. It has been shown [4] that even after centuries of preservation, there is still a high share of iron (II) at the blue-black ink on paper, but it is not stated what the reducing substance is that keeps the iron (II). In addition, The paper itself may also contain certain reducing substances, such as lignin: these lignin structures contain more reducing hydroxyl functional groups, which can reduce high-valence metal ions to their low-valence counterparts [24].

Conclusion

The influences of changes in color and iron ions of iron gall inks have been evaluated after artificial aging. All results confirmed that light (UV aging) and T/RH aging exert greater effects on the color and iron ion stability of iron gall inks.

The ink samples treated by the three aging methods produced different color difference values. The largest color change occurred when the sample was treated with T/RH aging for 30 days, with a ΔE value of 14.42, which is greater than the color difference value of 11.82 produced by T aging treatment for 30 days: this shows that the greatest damage to the inks occurs when both temperature and humidity act on the ink, because when the inks are in a humid environment, water molecules keep entering the inks, resulting in severe color fading.

From the color density values before and after aging, the magnitude of the color density values of the ink samples at 30 days of T/RH and T aging treatment is not much different from the values of samples treated with UV for five days. Both show a decreasing trend compared to their untreated counterparts, indicating that, in terms of the color density of ink, the effect of UV irradiation is stronger than the effects of temperature and humidity within the same time.

The darker the ink, the thicker the ink layer, the more light that can be absorbed, the less reflected, and the darker the handwriting. The ink absorption of each sample decreases after aging, which corresponds to the lightening of the ink layer of handwriting when old books and archives are kept under natural conditions for a long time, the absorption of light decreases, which is reflected in the lightening of the color of handwriting to the human eye.

As aging proceeds, the Fe^{2+} content in the inks rises, the color-revealing components in the inks are decomposed, and the color fades.

As demonstrated, temperature, humidity and ultraviolet light affect iron gall ink handwriting, causing significant damage; iron gall ink documents in written archives need a suitable storage environment to ensure that valuable documents and information are preserved.

Abbreviations

XPS	X-ray photoelectron spectroscopy
T/RH	Temperature/humidity ageing
T	Temperature
UV	Ultraviolet light ageing

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Declarations

Competing interests
The authors declare that they have no known competing interests.

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