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Short communication

Some parameters affecting the diffusion of SO_4^{2-} used in iron gall ink: Preliminary findings

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ABSTRACT

A systematic evaluation of the effect of components of the ink, types of the paper, temperature and humidity of environment and the direction of the paper fibers on the diffusion percentage of SO_4^{2-} was made. The results showed that the diffusion percentage of SO_4^{2-} was associated with all factors mentioned above. The general rule is that the higher the humidity and temperature, the greater the diffusion percentage; the smaller the basis weight of paper, the greater the diffusion percentage of SO_4^{2-}; diffusion percentages of SO_4^{2-} in strokes perpendicular to the paper's fiber is more bigger than ones of strokes parallel to the paper fibers.

In order to estimate the age of iron gall ink entries, it is necessary to select a suitable sample, which used for comparison should be the same as those of the document in question.

1. Introduction

During the forensic examination of documents, dating of ink entries can be of considerable importance, but remains very challenging for forensic examiner. There are two approaches to the dating of inks: relative dating and absolute dating. There has been extensive literature regarding these efforts for many years [1–5]. When a questioned document is produced, it might be possible to figure out its maximum age based on the first commercial introduction of the writing or printing ink. Verification with the manufacturer is necessary to make a conclusive finding that the document was not produced on the purported date. In some cases, this type of information may not be adequate if the ink was produced after the purported date of the document.

Iron gall ink, as the material of great importance in almost all questioned documents, has been an object of study from the earliest days in the field. An important task for forensic document examiners was to identify whether two or more ink entries in one or more documents are written with the same ink type. To this end, information on the relative ages of ink entries would also be useful, e.g., to determine whether entries in some questioned documents involved in some cases were written on the specified date or later. Determining the age of written ink entries is of great importance and one of the biggest challenges currently facing document examiners.

Many different methods have been employed to analyze pen ink entries [6–12]. The diffusion degree of sulfate ion proposed by Mitchell and Hess is one of effective methods, which has been used by document examiners all over the world to estimate the writing age of iron gall ink entries [7,8]. The theoretical basis of this method is that sulfate ions diffuse continually beyond the boundaries of the entries written on the surface of paper; the longer the age of entries, the greater the degree of diffusion. The image of strokes treated by chemical reagents was shown in Fig. 1.

The diffusion of sulfate ion has not been studied more for dating purpose because that iron gall inks are still used in China, but not much in other parts of the world. In china, document examiners adjusted the order of chemical reagents used to handle entries according to the type and proportion of components in iron gall inks made in china, and received good results [13]. From this work, we concluded that many factors could influence the diffusion of sulfate ion, such as components of the ink, types of the paper, temperature and humidity of environment where entries were stored, the direction of the paper fibers, etc.

This paper addresses the influence of some factors on the diffusion results of SO_4^{2-} used in iron gall ink.

2. Materials and methods

2.1. Inks

Five different brands of iron gall inks made in five factories in China, including Ostrich brand, Boss brand, Dr. brand, Hero brand and People's brand, were obtained and used to make sample ink entries.

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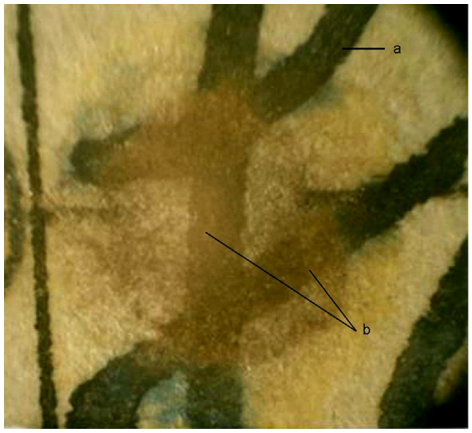

Fig. 1. The image of stroke treated by chemical reagents. (a) The image of stroke untreated by five chemical reagents; (b) the image of stroke treated by five chemical reagents.

2.2. Papers

Five types of paper (made in China), including single-side glossy paper (basis weight: 40 g/m^2), single-side glossy paper (basis weight: 56 g/m^2), single-side glossy paper (basis weight: 58 g/m^2), double-side glossy paper (basis weight: 68 g/m^2), and double-side glossy paper (basis weight: 80 g/m^2), were used as carriers for the iron gall ink entries.

2.3. Chemical reagents

The chemical reagents used in the tests are the following: 5% $Pb(NO_3)_2$ solution, mixture of 4% $KMNO_4$, 0.5% HNO_3 and 5% $Pb(NO_3)_2$ (this mixture is 2:1:2 in percent by volume), 4% NH_2NH_2·HCl (hydrazine hydrochloride) solution, 20% Na_2SO_4 solution, and 4% Na_2S solution.

2.4. Apparatus

The following instrumentation was used: a JC-10 reading microscope (made in China), a DL302 temperature and humidity controlling box (made in China). JC-10 reading microscope was chosen for performing the measure of diffusion degree of SO_4^{2-}, and DL302 temperature and humidity controlling box was employed to heat the samples.

2.5. The experimental procedure

The ink entries were written on five types of paper using five different brands of iron gall inks. All specimens were written by the same person with similar and normal pressure under no other specific requirements.

To conduct the required tests, measuring points of entries were selected, and the width of the entries was measured using JC-10 reading microscope. To reduce error and ensure accurate results, ten measuring points of each entry were selected and measured. The average value of ten widths was obtained. In accordance with the above practice, another two width values of entries were obtained according to the measuring results of the other two entries. The average value of three values, which regarded as the original width of entry was obtained. And then, all specimens were heated in controlling box. Temperature and humidity were constant when the same sample was heated, however, the temperature and humidity could be changed when different samples to be heated. After that, chemical reagents were dipped respectively with different cotton swabs and dripped in turn onto the ink entry. The order of chemical reagents dripped onto the entries was in the follows: 5% $Pb(NO_3)_2$ solution, mixture of 4% $KMNO_4$, 0.5% HNO_3 and 5% $Pb(NO_3)_2$, 4% NH_2NH_2·HCl solution, 20% Na_2SO_4 solution, and 4% Na_2S solution. 5% $Pb(NO_3)_2$ solution was used to precipitate sulfate ion, mixture of 4% $KMNO_4$, 0.5% HNO_3 and 5% $Pb(NO_3)_2$ was used to implement stroke oxidation fade and suppress the lead sulfate solution, 4% NH_2NH_2·HCl solution was used to eliminate the color of the potassium permanganate and the reaction product, 20% Na_2SO_4 solution was used to improve the background of the image, and 4%Na_2S solution was used to realize image conversion. The equations are the following:

$$Pb^{2+} + SO_4^{2-} = PbSO_4 \downarrow$$

$$S^{2-} + PbSO_4 = SO_4^{2-} + PbS \downarrow$$

Table 1
Data showing the diffusion percentage of SO_4^{2-} used in Ostrich brand of iron gall ink.[a]

Aging time (min)	Relative humidity (%rh)			
	70	75	85	90
	Diffusion percentage (%)			
3			5.32	7.08
4.5				9.29
5			7.44	
6				13.06
8		1.45	12.64	18.33
10	0.77		16.25	
12			19.91	26.22
15		2.67		
16			27.05	34.42
18				37.18
20		3.26	35.28	40.84
30	1.53	5.03	42.67	
45		6.72		
60	2.15	8.16		
90		10.64		
120	3.76	13.57		
180	5.54			
240	8.06			
300	12.31			
420	15.69			

[a] All ink entries were written on single-side glossy paper (basis weight: 40 g/m^2); temperature was controlled at 363.15 K (90 °C) by DL302 temperature and humidity controlling box.

The width of entry was measured again after dry of entry. In order to ensure the same location of the same stroke was measured, the locations in strokes, which prepared for measure, were marked with pencil before the first measurement.

The diffusion percentage was then obtained according to the following formula:

$$M = \frac{X_2 - X_1}{X_1} \times 100\%$$

M denotes the diffusion percentage, X_1 denotes the original width value of entry, and X_2 denotes the width value of entry treated by chemical reagent. According to the formula, the diffusion percentage of SO_4^{2-} can be obtained.

3. Results and discussion

3.1. Influence of humidity on the diffusion of SO_4^{2-}

In order to find out the influence of humidity on the diffusion of SO_4^{2-}, the samples written on five types of paper using five different brands of iron gall inks were put into DL302 temperature and humidity controlling box. The temperature was controlled respectively at 323.15 K (50 °C), 333.15 K (60 °C) and 363.15 K (90 °C), and relative humidity was controlled respectively at 70%rh, 75%rh, 85%rh and 90%rh.

The diffusion percentages were calculated respectively according to formula. Data showing the diffusion percentage of SO_4^{2-} used in iron gall ink were listed in Tables 1–7. The typical curve showing the influence of humidity on the diffusion of SO_4^{2-} used in Ostrich brand of the iron gall ink (data from Table 1) was shown in Fig. 2. The results showed that humidity had varying impacts on the diffusion percentage. From the results, it can be determined that for this ink, a higher humidity was associated with a bigger diffusion percentage of SO_4^{2-}. Conversely, the lower the humidity, the smaller the diffusion percentage of SO_4^{2-} was determined to be. These differences were likely caused by different adsorption of water molecules. The greater the humidity of environment, the more the number of water molecules adsorbed by the gap between the paper fibers, and the more favorable the diffusion of SO_4^{2-}. Therefore, the humidity of conditions, where entries selected for