EXAMINATION OF THE PRESCRIPTION OF A DOCUMENT AS A WAY TO IDENTIFY MALFEASANCE

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Abstract

The article discusses the signs of artificial and natural aging of documents under the influence of temperature and humidity changes. It is shown that the use of technologies for artificial aging of documents can create risks of concealing malfeasance, leading to economic, technological damage and health. Methods for detecting signs of artificial aging and the possibility of using physicochemical methods of analysis to detect falsification are discussed.

Keywords: forensic chemistry, document dating, chromatography, Raman spectroscopy

I. Introduction

Representatives of the Ministry of Justice of the Russian Federation at the International Scientific and Practical Conference "Topical Issues of Forensic Examination of Documents" reported that over 50% of all calls to the forensic examination center on issues of forensic technical examination of documents are examination of document dating. And this is not surprising, since almost everyone, without exception, in a wide variety of areas of life is faced with forgery of the terms of documents.

Very often, such falsifications, even for seemingly harmless reasons, contain a corruption component.

Paragraph 35 of the Decree of the Plenum of the Supreme Court of the Russian Federation “On judicial practice in cases of bribery and other corruption crimes” dated July 9, 2013 No. 24 expressly states that “the subject of a crime under Article 292 of the Criminal Code of the Russian Federation is an official document certifying the facts that entail legal consequences in the form of granting or deprivation of rights, imposition or release from obligations, changes in the scope of rights and obligations. Such documents should include, in particular, sheets of temporary disability, medical books, examination sheets, record books, salary certificates, protocols of procurement commissions, vehicle registration certificates. Thus, as of September 3, 2021, 56 students were expelled from St Petersburg University from 2018 to 2021 due to falsified medical certificates. According to information dated July 7, 2020, the Urals Investigative Department of the Investigative Committee opened a criminal case against the Perm Institute of Railway Transport, whose administration forged all students' records in order to obtain state accreditation.

More trivial cases of document forgery occur in the field of labor relations. Often at the place of work, employees may encounter the so-called "black bookkeeping", when the director offers to sign documents "backdated". It is in this way that in everyday life an employment contract, a job description, a knowledge test protocol is often drawn up, which sometimes leads to sad consequences. So, for example, when investigating accidents with a fatal outcome or causing grievous bodily harm, the investigating authorities require the issuance of protocols on testing knowledge. If the employer does not provide them with a backdated date, then he faces criminal liability. It is not surprising that the court is also overloaded with an impressive amount of forged papers, since the parties in those cases where decent sums are at stake (cases of bankruptcy, inheritance, purchase and sale of real estate, etc.) are ready to go for even the most risky tricks hoping to win the case.

The seeming possibility to draw up the necessary document "backdating" creates numerous additional risks in the sphere of production, economy and public life. There is an illusion of the possibility of concealing theft or the true cause of harm to health or environmental crime.

The presence of methods for establishing the true prescription of a document is an effective form of preventing the numerous risks of malfeasance by officials. Chromatographic methods are most often used to determine the age of a stroke, despite the fact that, recently, there has been a tendency to replace them with spectroscopic methods [1, 2].

The fundamental basis of chromatographic methods is the study of the temporal dynamics of changes in the concentration of certain components in the ink composition. A list of components that are considered volatile has been compiled. Generally, these are 2-phenoxyethanol, glycerol, triethylene glycol, tetraethylene glycol, hexylene glycol, benzyl alcohol, phthalic anhydride, diphenylamine, Michler's ketone, etc. 2-Phenoxyethanol is used most often for analysis purposes since its chromatographic dynamics are the most stable and obvious. A typical scene of the evaporation dynamics of volatile components of writing materials is described, for example, in [3]. Chromatographic methods based on the evaporation of volatile components have a number of limitations, including the inability to analyze the age of strokes that are older than 1.5–2 years (the evaporation period of volatile components). In attempts to overcome this limit by searching for new components with a longer evaporation time or optimizing sampling parameters such as the paper sheet type, sampling tube, extraction temperature, extraction time, sample mass, and desorption time have been applied [4, 5, 6]. It is claimed that these methods allow increasing the depth of chromatographic analysis by up to 5 years.

Evaporation may not be the only method to change the concentrations of components. The dynamics of the content of conditionally volatile components of writing materials in the presence of moisture may also be caused by the processes of interaction of components with each other and with paper components [7].

The natural difference in atmospheric pressure is another factor in natural aging, which is not embraced by systematic studies. The evaporation of aqueous solutions of the components of writing materials should also accelerate in the case of a decrease in atmospheric pressure. Considering the above assumption that the components of the writing composition evaporate in dilute aqueous solutions, the pressure drop factor can seriously influence the rate of ink degradation.

This work is devoted to the analysis of some factors of natural and artificial aging of documents and methods for their detection using spectral methods.

II. Methods

Chromatographic and chromato-mass spectrometric studies were carried out on the Kristall-5000 gas chromatography-mass spectrometry complex with a flame ionization detector (FID) and a mass-selective detector (MSD). The introduction of samples was carried out using a pyrolytic attachment (in the case of MSD) and a solid sample injector in the case of FID. The MSD channel was equipped with a device for cryofocusing of gas mixture components. The study was conducted using chromatographic columns CR-5 30 m x 0.32 mm x 0.5 μm for FID and CR-5 ms 30 m x 0.32 mm x 0.25 μm for MS. The components were identified based on the results of gas chromatography-mass spectrometry measurements using the Chromatec Analytic and NIST libraries.

Table 1: *Conditions for obtaining chromatograms of mass spectrometric detection*

Seq No.	Element	Parameters
1	Pyrolytic evaporator P4	Temperature: 200 °C, 5 min, temperature elevation rate 2,500 °C/min
2	Cryofocus module	Temperature: initial -40 °C, final 280 °C, 5 min at 2,000 °C/min
3	Column thermostat	Temperature: 1. 150 °C, 5 min 2. heating up to 270 °C at a rate of 22 °C/min 3. 270 °C, 10 min
4	Carrier gas (helium, qualification 6.0)	Pressure 93 kPa Column 1.0 ml/min Velocity 40.1 cm/s

The samples (each about 1 cm long) were introduced into a pyrolytic evaporator with a cryofocusing module (L-CO2). The samples should be placed in the pyrolytic evaporator for 5 min. The samples are analyzed on a KhromatekKristall 5000 gas chromatograph with a mass spectrometric detector (GC-MS) and a flame ionization detector (GC).

Raman spectroscopy studies were conducted using the Horiba LabRAM Evolution HR Raman spectrometer with a confocal Raman microscope instrument with laser sources 532 nm, two diffraction gratings (600 g/mm and 1,800 g/mm), manual XY stage. The instrument was controlled using the LabSpec 6 software. The evaluation of the temporary degradation degree of the ink dye was carried out according to the methods and results of papers [8,9,10,11].

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Simulation of humidity processes was performed in the “heat-humidity” M 0/100-1000 KTV climatic chamber within the range of maintaining humidity from 40% to 80% at a temperature of +25 °C (humidity adjustment accuracy: 3%, temperature ± 5 °C). The choice of humidity range was determined by the characteristic differences for the city of Saint Petersburg.

During one cycle of studies, stroke samples applied to office paper were kept for 2 hours in a climatic chamber with a volume of 50 liters at a relative humidity of 80%, and then they were kept for 3 hours at a humidity of 40% or natural air drying was fulfilled for 24 hours. The number of humidity cycles was determined based on the decrease in the chromatographic response level of the studied samples to background values or until reaching a horizontal plateau.

The signs of accelerated aging of documents were detected using GC-MS measurements, Raman spectroscopy, and optical microscopy using a MIKMED-6 microscope with a built-in webcam.

III. Experimental

When falsifying a document, an attempt is often made to artificially “inflate” its age and give it the appearance of a document with a long shelf life. Traditional methods of artificial aging are heating and exposure to sunlight or ultraviolet light. Signs of such artificial aging are easily established during the usual observation of props in a microscope (Fig. 1).

Chromatographic signs of artificial aging are expressed in a decrease in the intensities of the main signals of the volatile components of writing materials to background values. The dynamics of evaporation of solvents is considered on the example of writing compositions presented in Table 2.

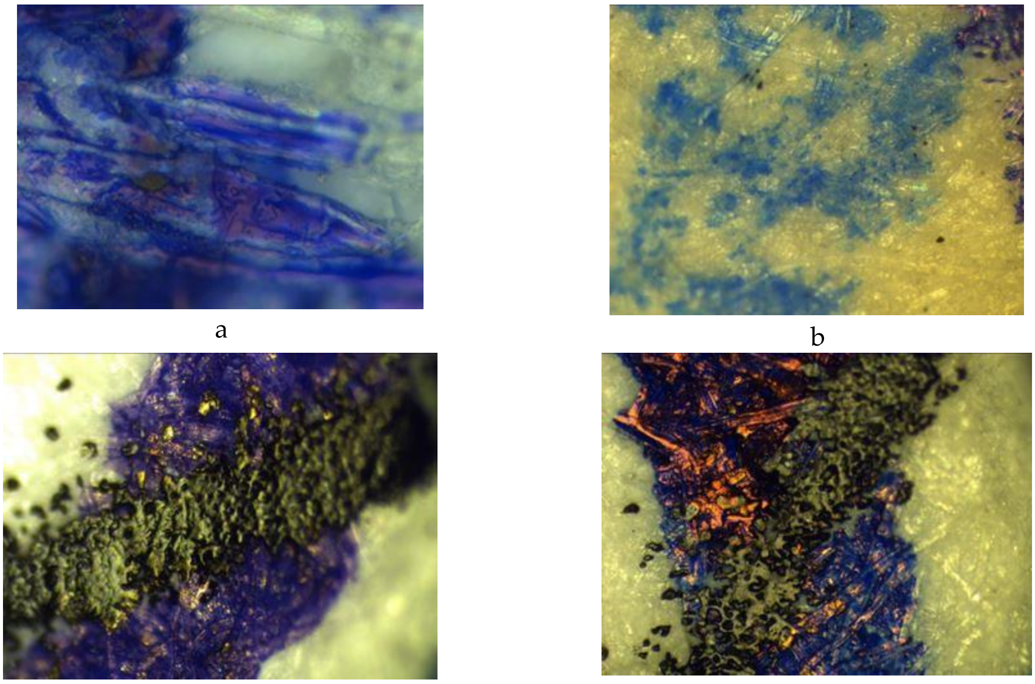


Fig. 1: *(a) - micrograph of a stroke of a handwritten inscription made with a ballpoint pen, (b) the same stroke subjected to heating to 90°C., (c) a micrograph of a printed text toner, (d) the same toner heated to 90°C.*

Table 2: *Characteristics of the writing compositions selected for the experiment*

Number writing composition	Type (according to Raman spectra)	Type (by composition)	Solvent under consideration	Retention time, min
№5	A	capillary	Tetraethylene glycol	13,676
№3	B	Ball	2-phenoxyethanol	10,823
№7	C	Gel	Glycerol	7,365

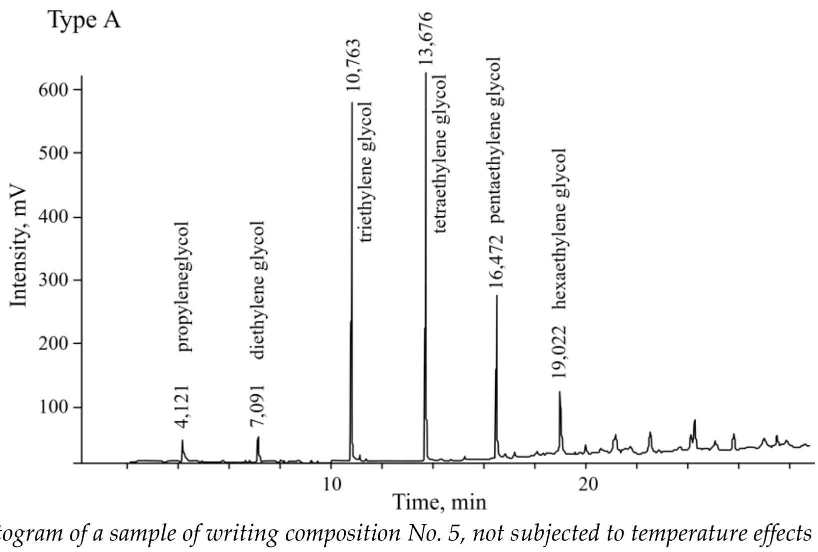


Fig. 2: *Chromatogram of a sample of writing composition No. 5, not subjected to temperature effects*

From the chromatogram shown in Fig. 2, tetraethylene glycol was chosen for further analysis, since it has the most intense peak, respectively, its concentration in the writing composition is maximum.

A graph of the dependence of the change in the area of the peak corresponding to a given solvent on the chromatogram, on the time of storage in "natural" conditions is shown in Fig. 3.

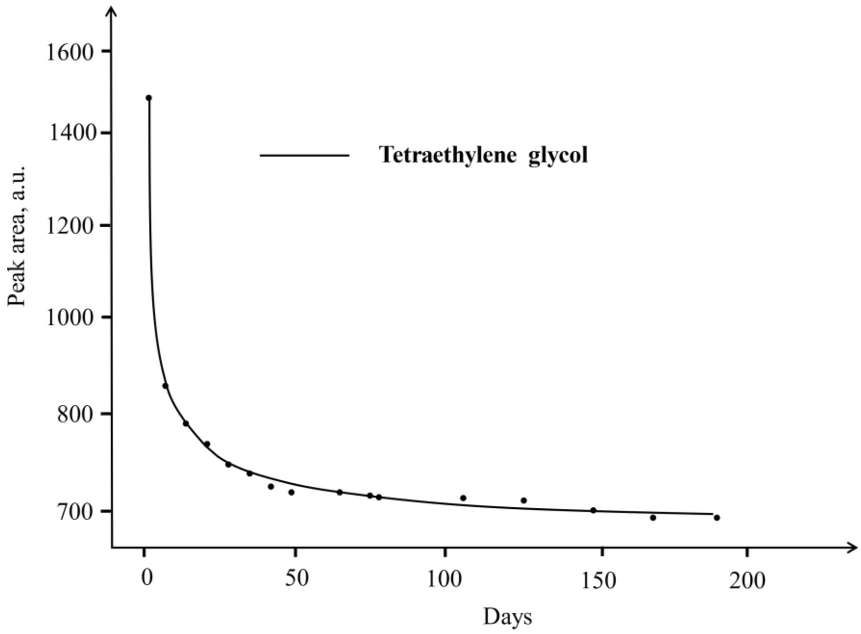


Fig. 3: *Plot of tetraethylene glycol peak area vs. storage time under "natural" conditions*

It can be seen from Fig. 3 that the main part of the solvent evaporates already after a month of storage of the sample under natural conditions. To study the effect of temperature on the rate of evaporation of solvents, the samples were subjected to temperature effects in various modes. The results are presented in Table 3 and in Fig. 4.

Table 3: *Correlation of heating time, at various temperatures and storage time at "natural" conditions*

60 degrees		Number of days at "natural" storage	90 degrees		Number of days at "natural" storage
Heating time	Peak area		Heating time	Peak area	
7,25	905,19	3	8,5	460,97	9
22,75	644,30	5	23,5	204,82	35
35,25	239,19	27	32,5	127,46	76
43,75	159,79	54	56,0	69,72	more 120

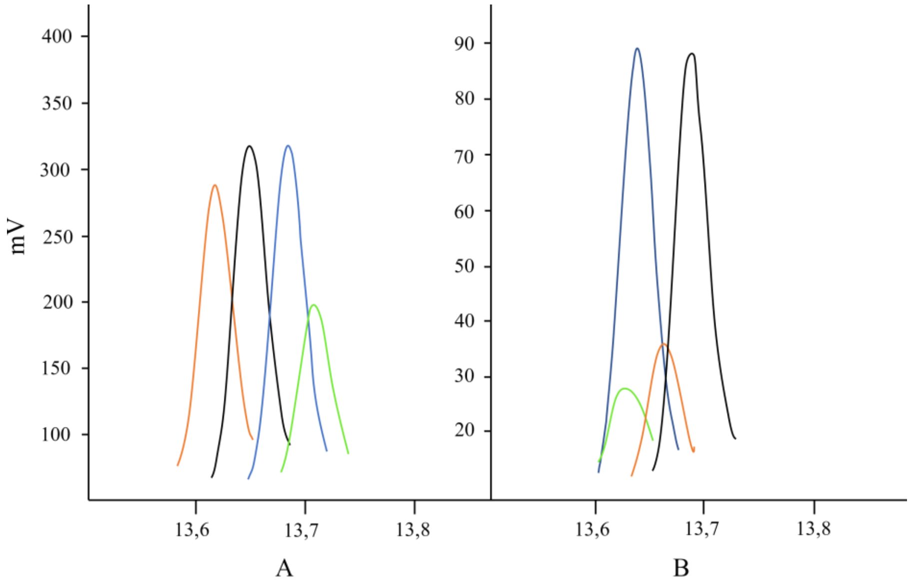


Fig. 4: *The enlarged area of the peak of tetraethylene glycol on the corresponding chromatograms obtained after exposure to temperatures (60 and 90 degrees), chromatograms obtained from samples at different heating times are highlighted in different colors:*
A. 60 degrees; blue -7.25; black - 22.75; red - 35.25; green - 43.75;
B. 90 degrees; blue -8.5; black - 23.5; red - 32.5; green - 56.0 (heating time is indicated in hours

As the temperature increases, the rate of evaporation of tetraethylene glycol also increases accordingly. After 56 hours of heating at 90 degrees, virtually all of the solvent had evaporated. Similarly, for other types of writing compositions.

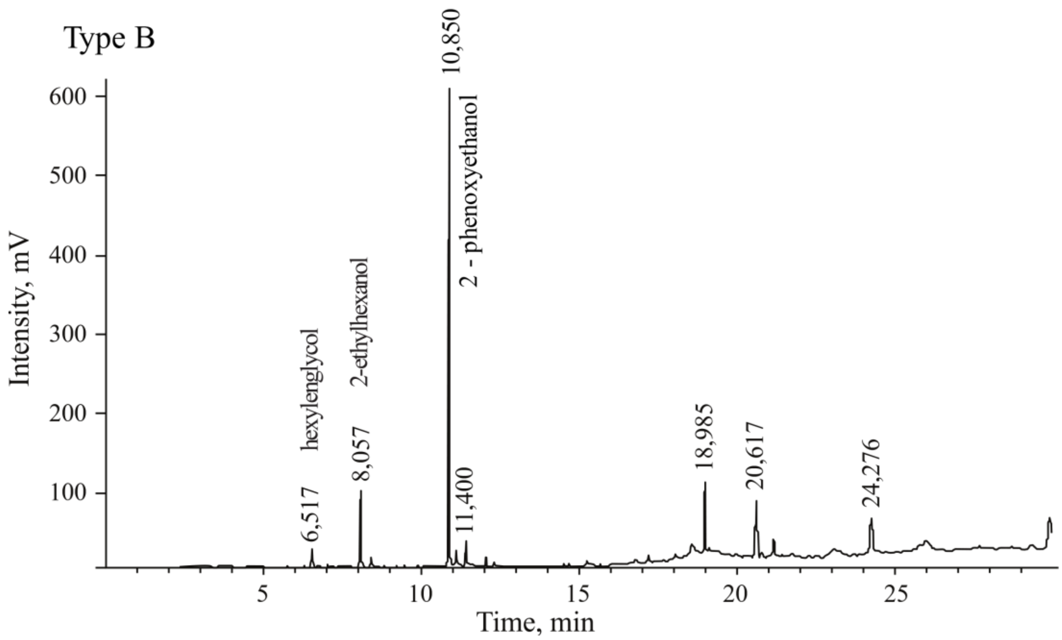


Fig. 5. *Chromatogram of a sample of writing composition No. 3, not subjected to temperature effects.*

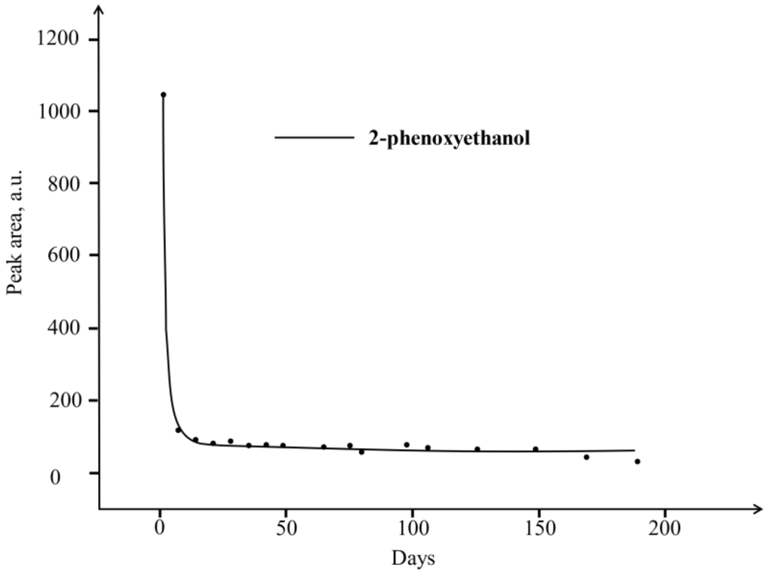


Fig. 6: *Plot of peak area corresponding to 2-phenoxyethanol versus storage time under natural conditions*

Table 4: *Correlation of heating time, at various temperatures, and storage time under natural conditions for 2-phenoxyethanol*

60 degrees		Number of days at "natural" storage	90 degrees		Number of days at "natural" storage
Heating time	Peak area		Heating time	Peak area	
7,25	158,86	5	8,5	135,01	7
22,75	112,34	8	23,5	87,50	14
35,25	77,89	20	32,5	53,74	80
43,75	56,42	80	56,0	36,11	more 120

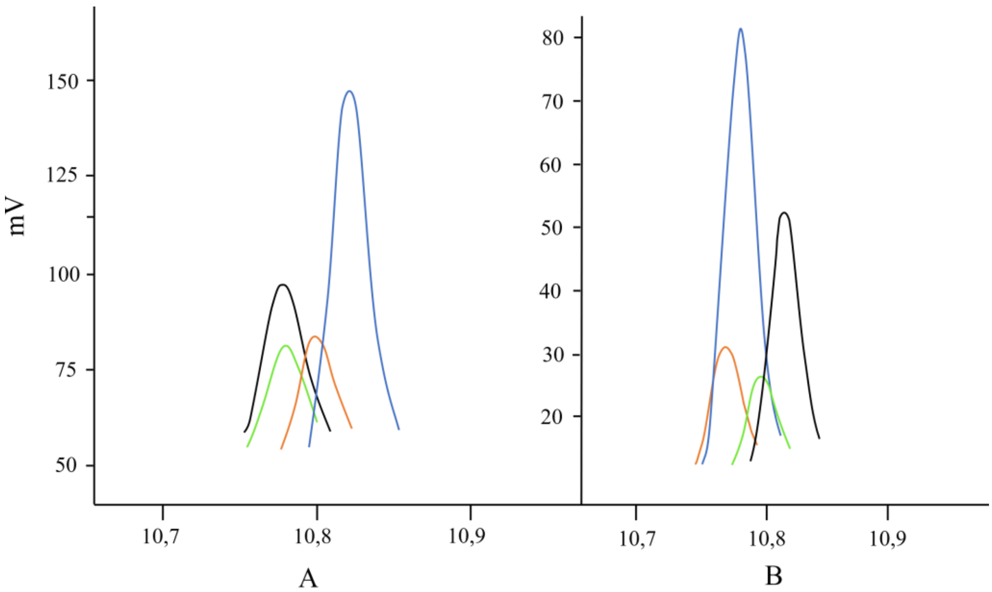


Fig. 7: *The enlarged area of the peak of 2-phenoxyethanol on the corresponding chromatograms obtained after exposure to temperatures (60 and 90 degrees), chromatograms obtained from samples at different heating times are highlighted in different colors:*
A. 60 degrees; blue -7.25; black - 22.75; red - 35.25; green - 43.75;
B. 90 degrees; blue -8.5; black - 23.5; red - 32.5; green - 56.0 (heating time is indicated in hours).

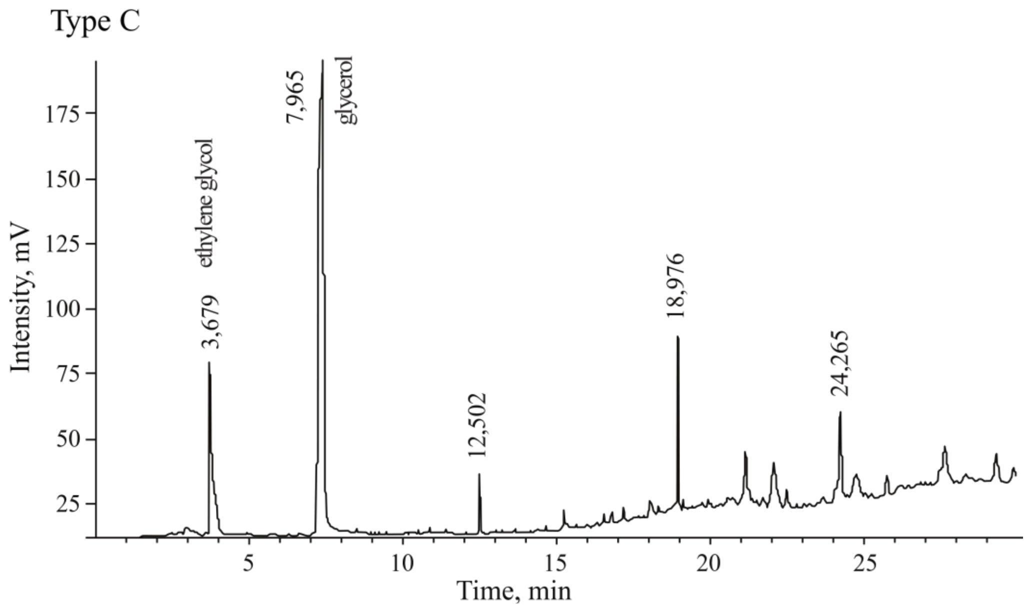


Fig. 8: *Chromatogram of a sample of writing composition No. 7, not subjected to temperature effects*

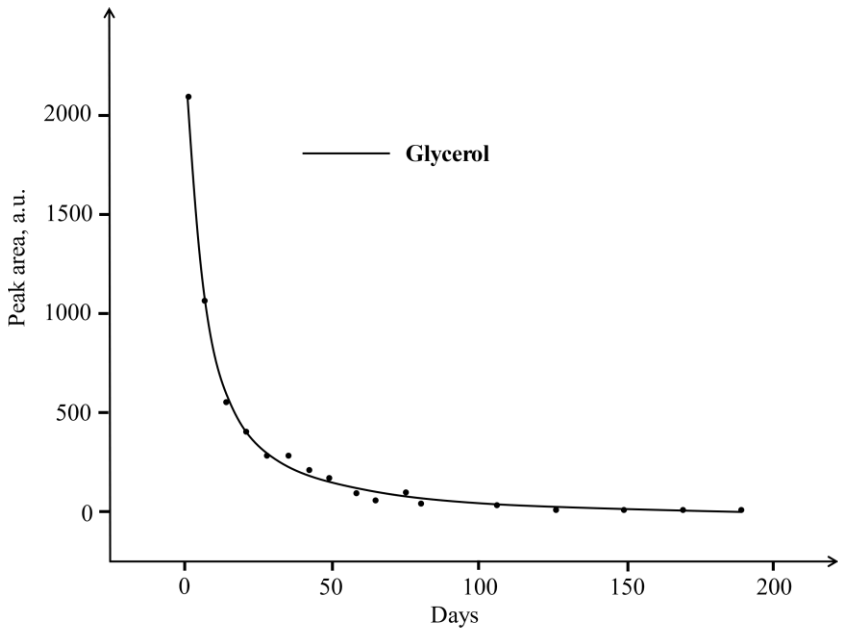


Fig. 9: *Plot of peak area corresponding to glycerol versus time of storage under natural conditions*

Table 5: *Correlation of heating time, at various temperatures and storage time under natural conditions for glycerol*

60 degrees		Number of days at "natural" storage	90 degrees		Number of days at "natural" storage
Heating time	Peak area		Heating time	Peak area	
7,25	1304,53	5	8,5	1210,52	6
22,75	1216,86	6	23,5	1087,54	8
35,25	1208,50	6	32,5	589,46	14
43,75	1134,10	7	56,0	284,17	30

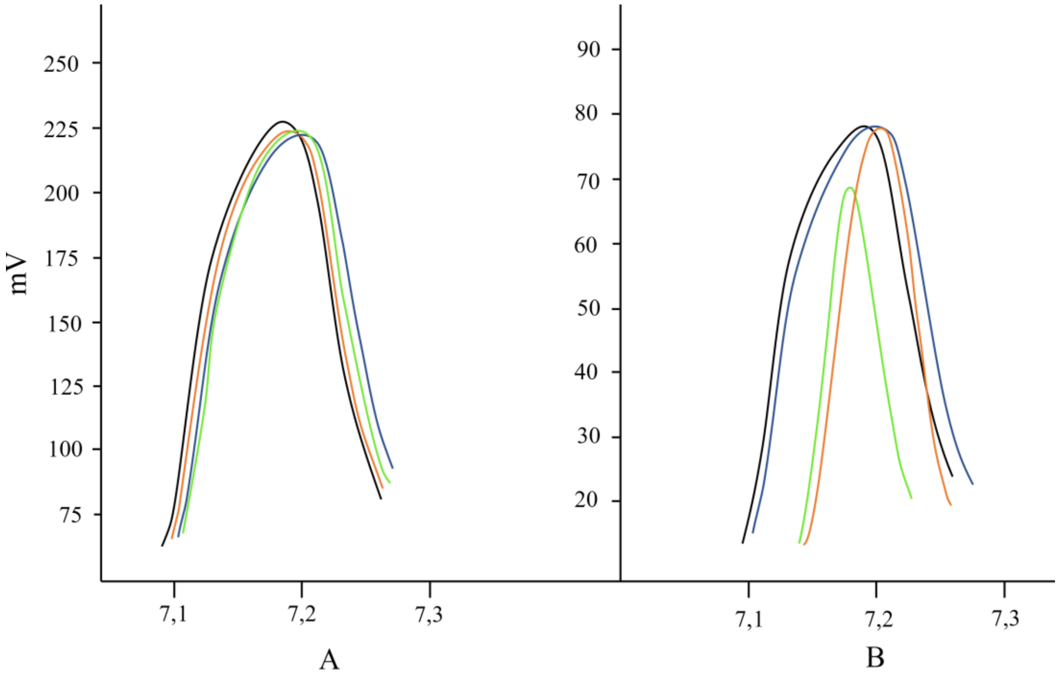


Fig. 10: *The enlarged area of the glycerin peak on the corresponding chromatograms, after exposure to temperatures (60 and 90 degrees), chromatograms obtained from samples at different heating times are highlighted in different colors:*
A. 60 degrees; blue -7.25; black - 22.75; red - 35.25; green - 43.75;
B. 90 degrees; blue -8.5; black - 23.5; red - 32.5; green - 56.0 (heating time is indicated in hours).

All the main volatile components of letter materials demonstrate the same dynamics of evaporation under the influence of temperature. As the temperature increases, the evaporation rate of the component also increases accordingly. After 56 hours of heating at 90 degrees, virtually all of the solvent has evaporated. Thus, the temperature factor is an effective method of artificial aging of a document, the essential drawback of which, according to the counterfeiter, is the easy detection of its features with a conventional microscope.

Therefore, in recent years, experts are increasingly confronted with new methods of artificial aging, which do not have a visually and microscopically detectable effect on the microstructure of paper and details of writing materials.

Such methods include treatment in a climatic chamber with changes in humidity and evaporation of volatile components in the form of dilute aqueous solutions.

Humidity fluctuations can accelerate the evaporation of volatile components in writing materials without changing the microstructure of the document.

Tests in the climatic chamber were carried out on a series of samples shown in Table.6.

Table 6. *List of samples subjected to artificial aging by humidity changes.*

Sample name	Writing composition	Dye type according to Raman spectra
101 STABILO Galaxy 818 F	Ballpoint Blue	phthalocyanine
102 NORMAN NOR-01002	Ballpoint Blue	triarylmethane
103 XEPUL ICBP602	Ballpoint Blue	phthalocyanine
104 PAPER MATE ComfortMate Ultra	Ballpoint Blue	triarylmethane

Graphs of the peak areas corresponding to the main components: 2-phenoxyethanol, 2-ethylhexanol, and benzyl alcohol on the number of humidity drops are shown in Fig. . 11 (a-d)

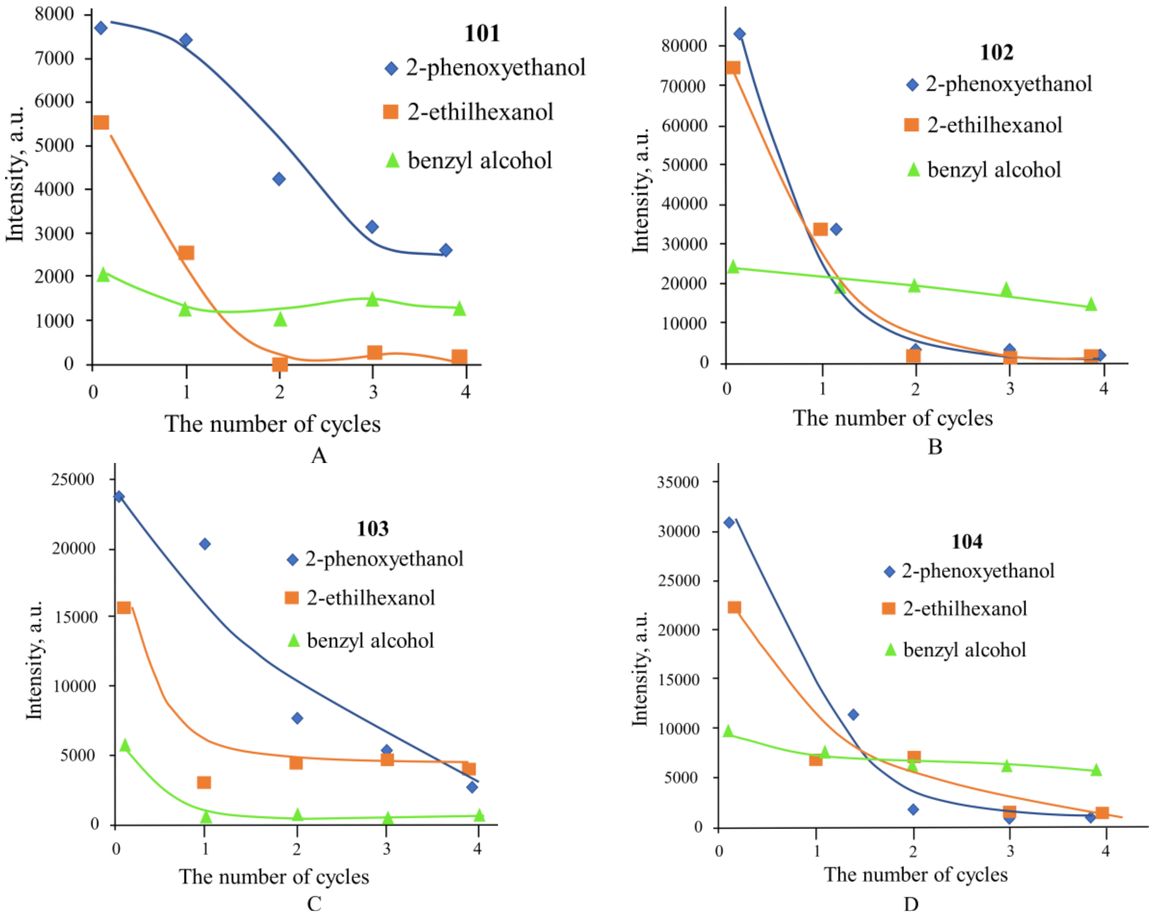


Fig. 11: *Plots of peak areas corresponding to the main components: 2-phenoxyethanol, 2-ethylhexanol and benzyl alcohol on the number of humidity drops.*
A - sample No. 101 STABILO Galaxy 818 F, B -102 NORMAN NOR-01002, C-103 XEPUL ICBP602 D-104 PAPER MATE ComfortMate Ultra

Microscopic images of strokes before and after aging are shown in Table 7.

The influence of the duration of moisture aging on the spectral characteristics of writing compositions is shown in Fig.12.

To evaluate the degree of degradation of the dye, the characteristic lines of the Raman spectrum of dyes were used according to [8,9, 10], Table 8.

Table 7: *Microscopic images of strokes of writing compositions, subjected and not subjected to the wet aging procedure.*

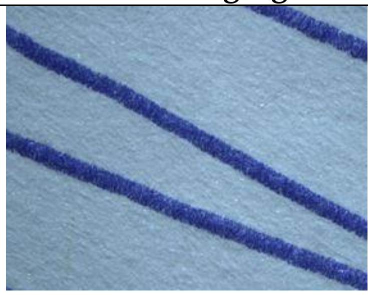
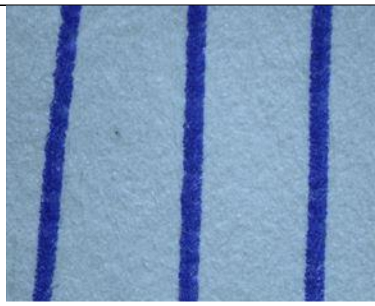
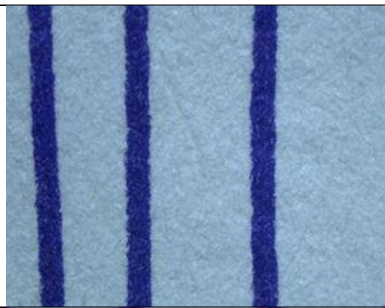
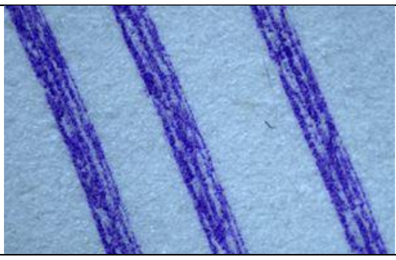
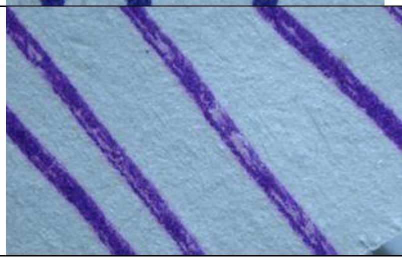
Sample	Before aging	After aging
101		
102		
103		
104		

Table 8: *Lines selected for plotting temporal dependences and fluctuations corresponding to them*

Writing compound type	Coloring matter	Band position in the Raman spectrum, cm^{-1}	Fluctuation	Ratio
Type A (101)	Alcohol-soluble blue phthalocyanine	1 340	$\nu(C\text{-}C)_{ring}$ $\nu(C\text{-}N)$	1,340/1,266
		1 266	VSO_2	
Type B (102, 104)	Triarylmethane group dyes	729	$\nu(C\text{-}N)$	729/1,587
		1 587	$\nu(C\text{-}C)_{ring}$	
Type C (103)	Blue phthalocyanine pigment	1 340	$\nu(C\text{-}C)_{ring}$ $\nu(C\text{-}N)$	1,340/680
		680	$\nu(C\text{-}C\text{-}H)$	

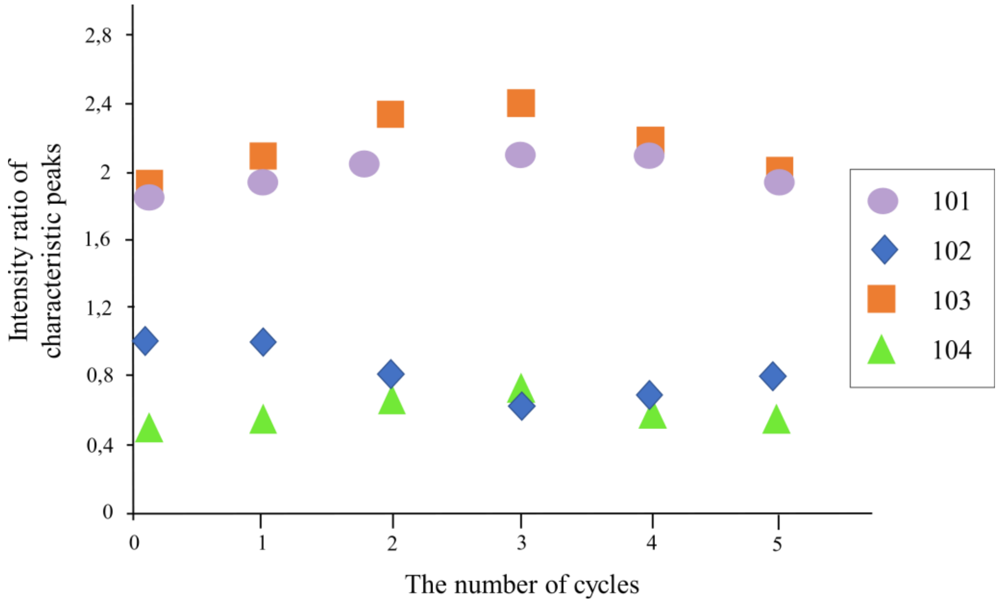


Fig. 12: *Influence of the duration of moisture aging on the spectral characteristics of writing compositions*

In contrast to chromatographic characteristics, moisture aging does not significantly affect the spectral characteristics of writing compositions. Moreover, humidity has the greatest impact at the initial stage (small serial numbers of cycles). Then the spectral characteristics stabilize and approach the original ones. This effect may be associated with the possible overlap of the spectral lines of the dye and volatile components.

IV. Discussion

Summing up the research results, we can conclude:

- artificial thermal aging affects the chromatographic characteristics of writing compositions, simulating the effect of "old" inscriptions containing trace amounts of volatile components. However, the effect of thermal exposure is easily detected by microscopic observation of an artificially aged stroke.

- artificial aging by moisture has the same effect as thermal exposure, but, unlike it, does not lead to a violation of the microstructure of the stroke and paper of the document and is indistinguishable in an optical microscope. This fact can create difficulties in the forensic analysis of the study of artificially aged documents. However, the effect of wet aging has practically no effect on the spectroscopic properties of writing materials, so the simultaneous use of chromatographic and spectral methods will solve this problem. The dynamics of the Raman spectra of writing compositions is determined by the spectral dynamics of the dye, which is the basis of the latter, with the exception of the initial period of aging, which is accompanied by the evaporation of the volatile components of the writing composition.

- the influence of other components of the writing compositions on its spectral characteristics is manifested in the initial period of application to the paper base (up to 6 months). Raman spectroscopy is an effective method for studying the aging processes of writing compositions subjected to the procedure of latent artificial aging with the help of moist exposure in a climatic chamber.

The simultaneous use of two physical and chemical methods for determining the prescription of a document will significantly reduce the risks of forging important official and financial documents and prevent possible damage or effectively contribute to its compensation by searching for the perpetrators.

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