THE INFLUENCE OF CLIMATIC FACTORS ON THE PROCESSES OF NATURAL AND ARTIFICIAL AGING OF DOCUMENTS

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Abstract

A distorted date of a document is a factor of strong social and public risks, leading to erroneous court decisions and undermining confidence in the judicial system as a whole. Document forgeries are common in the public relations sphere. Often, at the workplace, employees may encounter so-called "black accounting". If the employer provides them with a date issued "retroactively", then there is a possibility of evading criminal liability. The most popular category are bankruptcy cases (about 40% in total). The next are cases on collection of penalties, debt (8%), followed by cases with share of 5% on invalidation of tax authority decisions; on collection of unjust enrichment, etc. Chromatographic methods, most often used in methods for determining the age of a document. Almost all researchers, by default, assume that the components of the writing materials evaporate, and the main factors limiting this process are temperature and illumination.

In spite, the authors suggested that during the storage of documents, not pure components, but their diluted aqueous solutions evaporate. Water is a volatile liquid. The source of this water is the surrounding atmosphere and its good absorbent in the form of paper sheet cellulose.

Another factor of natural aging is the natural drop in atmospheric pressure. In the case of a decrease in atmospheric pressure, the evaporation of aqueous solutions of the components of writing materials should also accelerate.

The number of humidity and pressure cycles was determined based on a decrease in the level of the chromatographic signal of the studied samples. The results presented in our work show that frequent and deep changes in natural humidity and pressure accelerate the evaporation of volatile and soluble components of ink, leading to accelerated aging of the document. Overcoming this problem will help to significantly improve the quality and validity of court decisions in all types of cases under consideration and reduce the risks of obtaining erroneous court decisions.

Keywords: climatic factors, aging of documents, atmospheric pressure, humidity

I. Introduction

Document forgeries are common in the public relations sphere. Often, at the workplace, employees may encounter so-called "black accounting", when the director suggests signing documents "retroactively". When investigating accidents with a fatal outcome or causing serious

harm to health, investigative bodies require the issuance of protocols on knowledge testing. If the employer provides them with a date issued "retroactively", then there is a possibility of evading criminal liability. Therefore, it is very common to make a document or make an addition, correction "retroactively".

A distorted date of a document is a factor of strong social and public risks, leading to erroneous court decisions and undermining confidence in the judicial system as a whole.

To compile the most complete picture of the categories of cases, in the resolution of which an examination of the limitation period of the application of document details is carried out, a small table can be shown.

Table 1: *Categories of cases, in which an examination of the limitation period of a document is most often required.*

Court cases	number of cases	%
on bankruptcy of an individual	9	24%
on bankruptcy of a legal entity	6	16%
on collection of penalties, debt for undelivered goods	3	8%
on invalidation of a tax authority decision	2	5%
on collection of unjust enrichment, interest for the use of other people's money	2	5%
on invalidation of transactions	2	5%
on invalidation of a contract for work	2	5%
on invalidation of a pledge agreement	1	3%
on termination of a purchase and sale agreement	1	3%
on invalidation of a surety agreement transaction	1	3%
on recognition of ownership of real estate	1	3%
on bankruptcy of an individual entrepreneur	1	3%
on invalidation of an interest-free loan agreement	1	3%
on invalidation of a purchase and sale transaction for non-residential premises	1	3%
on exclusion from the composition of participants in a limited liability company	1	3%
on collection of debt, penalties under a purchase and sale agreement	1	3%
TOTAL	**37**	**100%**

The most popular category are bankruptcy cases (about 40% in total). The next most popular category are cases on collection of penalties, debt for undelivered goods (8%), followed by cases with the same share of 5% on invalidation of tax authority decisions; on collection of unjust enrichment, interest for the use of other people's money; on invalidation of transactions; on invalidation of a contract for work. Chromatographic methods, most often used in methods for determining the age of a document, demonstrate high dispersion of results and not always satisfactory convergence. Almost all researchers, by default, assume that the components of the writing materials evaporate as a result of evaporation, and the main factors limiting this process are temperature and illumination. Some works compare the influence of abstract factors of natural and artificial aging on the measurement results [1-5]. The authors of [6] were the first to suggest that such an opinion is erroneous. The temperature factor, of course, affects the rate of degradation of the writing composition, although in natural conditions of room storage its fluctuations usually do not exceed several degrees. Light exposure, as a rule, is also limited by the dark conditions of storing documents in folders and cabinets. However, in some cases, the amount of 2-phenoxyethanol in the process of chromatographic analysis begins to increase over time according to chromato-mass spectrometry data [7]. This phenomenon is difficult to explain by temperature

or light fluctuations. An alternative hypothesis explaining this fact is the underestimation of such an important factor of natural aging, which, according to the authors, should be changes in atmospheric humidity [6]. This reasoning arose in connection with the fact that, having compared data on the volatility of glycerin and 2-phenoxyethanol, the authors [6] drew attention to the fact that both components are absolutely non-volatile substances, have very high boiling points (240-290 C), very low equilibrium vapor pressures, especially glycerin, which is one of the most non-volatile liquids in nature, and 2-phenoxyethanol at room temperature, according to some data from open sources, is a crystalline substance at 26 C, according to others - at 13 C. [8]

In [6] it was suggested that during the storage of documents, not pure components, but their diluted aqueous solutions evaporate [9]. Unlike 2-phenoxyethanol and glycerol, water is a volatile liquid. The source of this water is the surrounding atmosphere and its good absorbent in the form of paper sheet cellulose [10]. In this case, the natural aging period of the ink will be determined not so much by the duration and temperature of storage, but by the frequency and depth of changes in natural atmospheric humidity. This assumption explains the non-monotonic behavior of the time dependence of 2-phenoxyethanol [7]. During periods of high humidity, a larger amount of easily evaporating 2-phenoxyethanol aqueous solution is formed.

Another factor of natural aging that has not been covered by systematic research is the natural drop in atmospheric pressure. In the case of a decrease in atmospheric pressure, the evaporation of aqueous solutions of the components of writing materials should also accelerate. Considering the above assumption that the components of the writing composition evaporate as part of diluted aqueous solutions, the factor of pressure drops can seriously affect the rate of ink degradation. Pressure and humidity, in contrast to elevated temperature and intense light radiation, represent a separate group of natural climatic factors that do not have a destructive effect on the paper base of the document and on the ink dyes. In this regard, the authors [6] propose to introduce the concept of "accelerated" aging along with the concepts of "artificial" and "natural" aging. This is aging caused by increased exposure to climatic factors during the storage of the document and does not cause the destruction of paper and writing materials.

II. Experimental procedure

Randomly selected writing compositions of both certain brands and unknown brands were used for the study.

Chromatographic and chromatograph mass spectrometric studies were performed on a Crystal-5000 GCMS complex with a flame ionization detector (FID) and a mass detector (MS). Samples were introduced using a pyrolytic attachment (in the case of MS) and a solid sample dispenser in the case of FID. The MS channel is equipped with a device for cryofocusing of gas mixture components. The study was conducted using CR-5 chromatographic columns 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. Components were identified based on the results of GCMS measurements in the Chromatec Analytic and NIST libraries. The modeling of humidity processes was carried out in a climatic chamber "heat-humidity" M 0/100-1000 KTV in the range of maintaining humidity from 40% to 80%, at a temperature of +25 °C (accuracy of humidity control: 3%. , temperature ± 5 C). The choice of the humidity range was determined by typical differences for the city of St. Petersburg.

During one cycle of studies, samples of strokes applied to office paper were kept for 3 hours in a climatic chamber at a relative humidity of 80%, then 3 hours at a humidity of 40% or natural drying in the air for 24 hours.

The number of humidity cycles was determined based on a decrease in the level of the chromatographic signal of the studied samples to background values or until reaching a horizontal plateau.

Detection of signs of accelerated aging of documents was carried out using GCMS measurements, and optical microscopy using a MIKMED-6 microscope with a built-in web camera. The calculation of the correlation coefficients (Pearson coefficients) of the intensity of the

chromatographic response and the number of cycles of humidity changes was calculated using the formula:

$$Rxy = \frac{\dot{n}\sum_{i=1}^{n} x_i y_i - \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i}{\sqrt{\left(n\sum_{i=1}^{n} X_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2\right) \times \left(n\sum_{i=1}^{n} y_i^2 - \left(\sum_{i=1}^{n} Yi\right)^2\right)}} \quad (1)$$

where Xi are the serial numbers of the humidity change cycles, Yi are the corresponding values of the chromatographic peak intensity. The relative dispersion (σ%) of the chromatographic response intensity was calculated using the formula

$$\sigma\% = \frac{\sigma_{a\delta c}}{\bar{y}} \times 100\% \quad (2)$$

where

$$\sigma_{abs} = \sqrt{\frac{\sum(\bar{y}-y_i)^2}{n(n-1)}} \qquad \bar{y} = \frac{\sum_{i=1}^{n} y_i}{n}$$

The pressure drop processes were simulated in a sealed chamber with a volume of 2 liters. The vacuum was created using a diffusion pump H-250/2500 with a depth of up to 0.133 Pa. The duration of one cycle is 24 hours. The number of pressures drop cycles was determined based on the decrease in the chromatographic signal level of the studied samples to background values or until reaching a horizontal plateau. Detection of signs of accelerated aging of documents was performed using GCMS measurements and a MIKMED-6 microscope with a built-in web camera. The dynamics of individual components was studied.

III. Research results

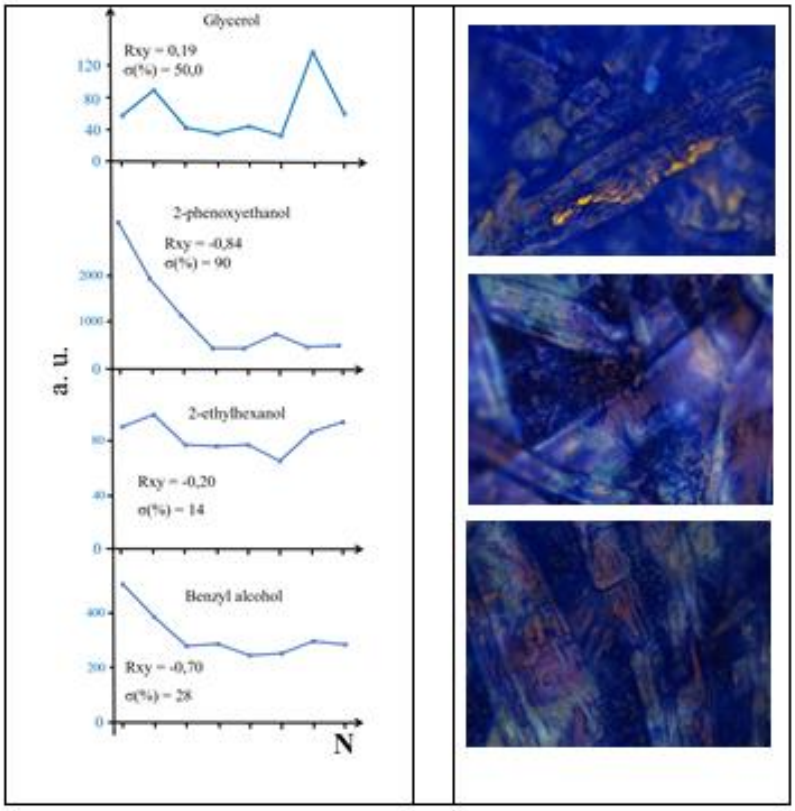
The average results of measuring the GC dynamics of individual components of the writing composition under the influence of humidity changes are given in Table 2. On the right are microscopic images of the surface of the ballpoint ink stroke obtained at the beginning of the process, in the middle and at the end.

The results presented in Table 2 show that periodic exposure of a document to humid air results in strong dispersion of the chromatographic signal. For various ink components and mathematical processing methods, the relative signal dispersion can vary from 18 to 1000 percent or more. The Pearson coefficients of signal intensity change with increasing number of humidity cycles can also be in a wide range from values close to +0.7 to -0.8 or more.

Most of the studied samples demonstrate a consistent decrease in the content of soluble ink components in a stroke with increasing number of humidity change cycles. 2-phenoxyethanol and benzyl alcohol demonstrate a stable dynamics of content decrease in a stroke with increasing number of humidity – drying change cycles. 2-ethylhexanol can react to humidity changes in different directions. Glycerol, in all cases, exhibits strong dispersion of chromatographic peak intensity values and low Pearson coefficient values. In approximately half of the studied cases, for most components, the first wet aging cycle leads to a significant increase in the content of the volatile component in the chromatographic response. Then this content decreases systematically as the number of cycles of drops increases. This behavior of the components strongly resembles the effect noted in [7].

It is evident that artificial modeling of humidity fluctuations in the range of 40-80% leads, in some cases, to accelerated aging of ink according to the criterion of the content of volatile components in it. In other cases, it leads to the appearance of uncontrolled strong fluctuations in the values of chromatographic peaks.

Table 2: *Research of the GC dynamics of individual components of the writing composition under the influence of humidity changes*



The results of the microscopic study show that signs of wet accelerated aging appear on the materials of documents in an implicit form, which does not allow the document to be clearly identified as "artificially aged". There are no areas of melting, bleeding and chipping of the dye, yellowing and uneven fluorescence. This explains some of the anomalies previously discovered by researchers during chromatographic studies of the age of ink [7]. And refutes the opinion about the insignificant influence of the humidity factor on the evaporation rate of high-boiling components of ink [11]. The porous nature of the ink stroke and the paper base on which it is applied results in the penetration of components that are fluid at the time the stroke is applied into the volume of the paper sheet, creating a diffuse region at the paper-stroke boundary. It is obvious that the action of capillary forces causes processes similar to the separation of components of an extract on a thin-layer chromatography plate [12].

The amount and rate of evaporation of poorly soluble and low-volatile components depend on the ratio of their solubility in water and the equilibrium vapor pressure. One can see the relationship between the average values of the correlation coefficients Rxy and T, S\P and N (the number of humidity cycles, Table 3). Glycerol, which has unlimited solubility in water and virtually zero volatility at room temperature, probably falls out of this relationship. Both factors act in opposite directions, which creates uncertainty in the result.

Changes in atmospheric pressure, similar to changes in humidity, can accelerate the process of evaporation of volatile components. When the pressure decreases, the evaporation rate of all substances included in the composition of paper materials and writing compositions increases. It is logical to expect that the dynamics of the content of volatile components of writing materials will have a picture similar to changes in humidity.

The test results are given in Table 4.

Table 3: *Relationship between the dispersion indices of the chromatographic signal and the physicochemical properties of the solvent [8,13,14,15].*

	S - solubility in water, g/l	**T boiling point, C**	**P-equilibrium vapor pressure at 20C (kPa)**	**S/P**	**Pearson's coefficient r_{xy}**	**Dispersion % σ**
2-phenoxyetanol (PE)	26	244	5,2*	5,0	-0,52÷-0,84	45÷303
Glucerol (G)	unlimited	290	0,4 (at 50C)	∞	-0,14÷-0,39	29÷63
Ethylhexanol (EH)	0,7	185	7,33	≈0,1	-0,2 ÷+0,7	14÷64
benzyl alcohol (BA)	40	205	12,7	3,1	-0,08÷-0,7	18÷67

Table 4: *Results of studies of the dynamics of the content of volatile components due to pressure changes using the chromatograph mass spectrometry method.*

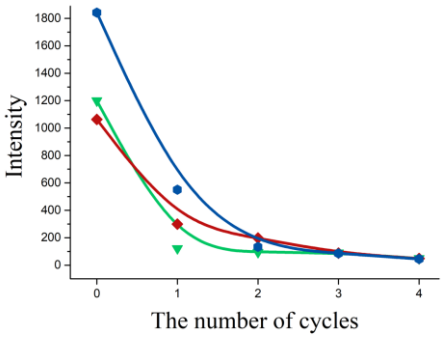
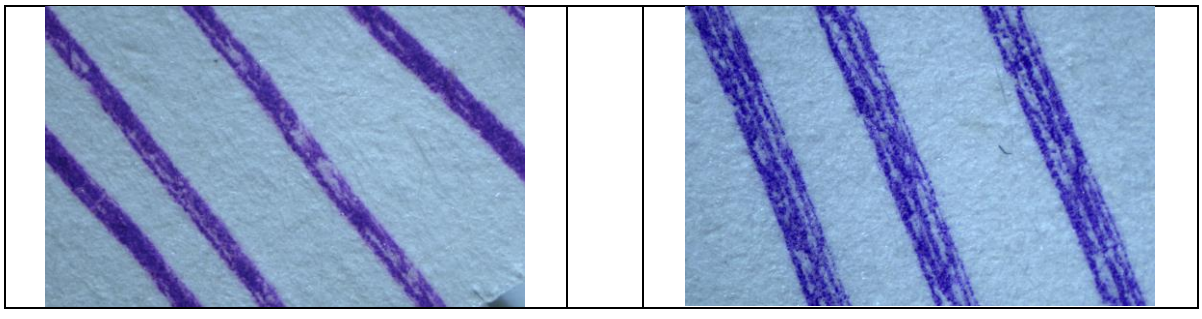
Number of cycles	Time, min	Component	Area	Height	Graph
0	3,513	ethylene glycol	7121,913	1199,834	
	8,370	glycerin	51857,774	1063,293	
	13,873	triethanolamine	6169,034	1841,471	
1	3,503	ethylene glycol	931,818	121,735	
	7,352	glycerin	3935,379	298,879	
	13,784	triethanolamine	1489,906	550,339	
2	3,508	ethylene glycol	671,905	93,477	
	7,023	glycerin	2114,581	198,140	
	13,764	triethanolamine	334,942	133,854	
3	3,511	ethylene glycol	599,203	90,422	
	7,028	glycerin	1105,776	88,140	
	13,760	triethanolamine	234,972	85,834	
4	3,511	ethylene glycol	259,211	48,615	
	7,028	glycerin	874,223	48,434	
	13,760	triethanolamine	134,234	45,616	

Fig. 1 (a, b) shows micrographs of the blue streak before and after the end of the process.



а **в**

Figure 1: *Micrographs of writing ink strokes before the process of artificial aging by pressure (a) and after the end of the aging process (b)*

The results presented in Tables 2 and 4 show a close analogy of the effects of humidity changes and pressure changes on the dynamics of the volatile components of writing materials. Frequent and deep changes in natural humidity and pressure accelerate the evaporation of volatile

and soluble components of ink, introducing a large dispersion into chromatographic measurements.

IV. Conclusion

In world practice, there is a significant gap in understanding the fundamental processes of aging of props. It is meant that it is necessary to expand the list of factors influencing the dispersion of the results of determining the age of a stroke, namely, to fundamentally study humidity, atmospheric pressure, structure and composition of paper, as well as various processes occurring during aging [6].

Thus, currently the applied methods require revision and improvement in connection with new results.

Determination of the absolute and relative age of a document and its details is in great demand among courts and parties in the framework of pre-trial investigation, but it encounters the impossibility of ensuring the quality of examinations due to the imperfection of existing physical and chemical models of aging, ignoring natural climatic factors. These are not random phenomena, but a consequence arising from a misunderstanding that a document is the most important material evidence, especially in civil and arbitration proceedings.

Overcoming this problem will help to significantly improve the quality and validity of court decisions in all types of cases under consideration and reduce the risks of obtaining erroneous court decisions.

Acknowledgment

The work was carried out with the financial support of the Russian Science Foundation, Grant No. 23-23-00365.

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