UDK 543.422.3 + 535.343.32 –54.061: 547.97: 686.862.5 doi: 10.33609/2708-129X.89.07.2023.26-39

IDENTIFICATION OF TRIARYLMETHANE, PHTHALOCYANINE AND XANTHENE IN A MIXTURE OF DYES BY ELECTRON ABSORPTION SPECTROSCOPY.

Posilskyi O.O.[1], Artamonova H.V.[1]*, Trunova O.K.[2]

[1]Kyiv Scientific Research Institute of Forensic Expertise of the Ministry of Justice of Ukraine, 6 St. The Brodsky family Street, 03057 Kyiv, Ukraine
[2]V.I.Vernadsky Institute of general and inorganic chemistry of the National Academy of Sciences of Ukraine,
32/34 Academic Palladin ave., 03142 Kyiv, Ukraine
**e-mail: hanna1artamonova@gmail.com*

In the work, the qualitative composition and differentiation of 43 samples of ballpoint pen pastes of different colors was investigated (blue-violet – 29 samples, pink-violet – 3 samples, blue – 3 samples, black – 5 samples, green – 1 sample and red –2 samples) by the method of electronic absorption spectroscopy. The results of the study showed that each paste can be distinguished by studying the nature of their absorption spectra, which arises due to the presence of different functional groups. It was established that most of the analyzed paste samples contain pigments based on triarylmethane, phthalocyanine, xanthene dyes or their mixture. Certain absorption maxima correspond to each type of dyes. The broad and most intense band at λ~590 nm, which was detected for all samples, corresponds to triarylmethane dyes. The band at λ~670 nm corresponds to phthalocyanine dyes. The presence of absorption bands in the green range (λ~520–560 nm) indicates the presence of xanthene dyes in the composition of the pastes. Using the method of photoluminescence spectroscopy upon excitation of IR luminescence in the green region of the spectrum (λ=530 nm) it is shown that 11 blue-violet, 5 black and one red pastes exhibit bright luminescence due to the presence of crystal violet and some other triarylmethane dyes in their composition. Weak luminescence was detected for three blue pastes. No luminescence response was observed for the other tested pastes, which is due to the presence of phthalocyanine dyes in these pastes, the absorption of which overlaps with the luminescence spectra of triarylmethane dyes. The obtained data can be used to create a reference base for identifying and differentiating the composition of ballpoint pen pastes of modern manufacturers and establishing their classification and identification differences.

Keywords: dyes, UV-Vis absorption spectroscopy, absorption spectra of solutions, ballpoint pen paste.

INTRODUCTION. The dynamics of the expansion of the stationery market and the variety of writing instruments increase the identification and diagnostic studies necessary for forensic investigations of document materials, especially when establishing their forgery. Despite the growing trend towards electronic communication, handwritten documents are still widely used in financial, legal and personal relationships. During the forensic investigation of writing materials (especially when establishing the forgery of documents), a common task is to establish their family (group) affiliation.

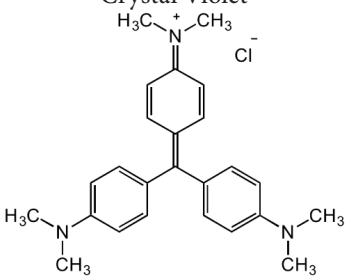
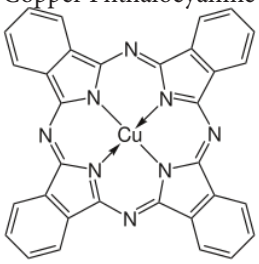
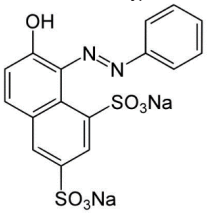
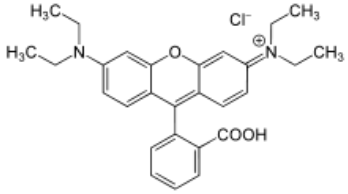
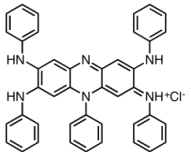
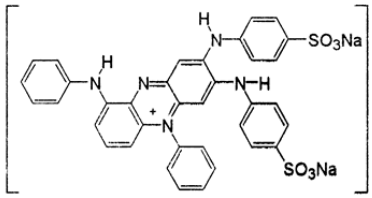
Most of the entries in the documents are made with ballpoint pens equipped with rods with colored paste. The component composition of pastes is diverse and in many cases is a commercial secret of the manufacturer, however, in industrial production, the composition of writing materials is quite standardized (ballpoint pen pastes of the same brand have the same chemical composition). Modern pen pastes are complex multicomponent mixtures consisting of various ingredients, most of which are organic compounds – dyes (or pigments), solvents, polymer resins, fatty acids, biocides, surfactants, corrosion inhibitors, thinners, emulsifiers, buffers and many other additives designed to improve characteristics (consistency, viscosity, polymerization, drying, etc.) [1–4]. Dyes in the composition of ballpoint pen pastes are, as a rule, in a solvent based on glycols or benzyl alcohol and make up to 50% of the total composition of pastes. Chemical analysis of ballpoint pen pastes can reveal useful information about their composition (the presence of organic and inorganic components), which, in turn, allows their group classification, differentiation, and also to establish the antiquity of the creation of documents [5–8].

The expansion of the market of writing devices and the lack of reference data on their composition necessitates the creation of a data array for the analysis and identification of samples of ballpoint pen pastes. Therefore, today it is relevant to conduct a study of ballpoint pen pastes of modern manufacturers using the methods of electronic absorption spectroscopy, which will allow obtaining information about the composition of their dyes and establishing their classification and identification differences.

Depending on the type of solvent and its interaction with the dye, dyes and/or pigments are produced. It is known from literary sources [9, 10] that dyes are, as a rule, organic compounds with conjugated aromatic structures that contain chromophores and auxochromes (aromatic systems, double bonds, bonds containing nitrogen, carbon atoms, oxygen or sulfur). In the composition of pastes, either one main component or a mixture of coloring substances can be used. The distinction between dyes in ballpoint pen pastes is considered based on the analysis of absorption spectra. The value of absorption coefficients is used to differentiate and identify dyes, and deviations from the reference values can allow us to evaluate the purity of the compound and the presence of even impurities of other dyes. Therefore, the method of UV–vis absorption spectroscopy is widely used to differentiate and identify a certain class of dyes in the study of ballpoint pen pastes. According to UV–vis absorption spectroscopy, the dyes of ballpoint pen pastes can be classified into different chemical classes, the most common of which are: triarylmethane (blue-violet, black pastes; λ_{max} = 550–625 nm); phthalocyanine (blue-violet, black, green pastes; λ_{max} = 625–715 nm); azo dyes (black, green pastes; λmax = 385–480 nm); xanthene (red pastes, λ_{max} = 540–560 nm); azine dyes (black pastes, λ_{max} = 550–580 nm) (Table 1) [2, 9–13].

Table 1.

Classification and examples of dyes used in ballpoint pen pastes.

№	Dye class	Structural fragments of dyes	Example
1.	**Arylmethane dyes (mainly triarylmethane)** are compounds in which hydrogen atoms are replaced by aryl rings (for example, common triarylmethane dyes are crystal violet, methyl blue, malachite green). Triphenylmethane dyes have relatively low light fastness and can decompose under the influence of light.	–N=N–, aryl rings	Crystal Violet 
2.	**Phthalocyanine dyes** contain a structure based on tetrabenzoporphyrazine and form stable complexes with transition metals (for example, Copper Phthalocyanine, Solvent Blue 64). Most blue ballpoint pen pastes contain copper phthalocyanine. Phthalocyanine compounds are some of the dyes most resistant to the action of light and temperature of pastes.	Tetrabenzoporphy-razine Cu(II)	Copper Phthalocyanine 
3.	**Azo dyes** contain an azo bond –N=N–, a benzene and naphthalene ring (for example, Acid Orange 10, Solvent Black 47, Reactive Red 180, etc.); azo dyes undergo photodegradation rather quickly and form isomers under the influence of temperature.	–N=N–, benzene, naphthalene structure	Acid Orange 10 
4.	**Xanthene dyes** contain a xanthene core. These include fluorescein, eosins and rhodamines. Xanthene dyes are usually fluorescent (yellow to pink or bluish-red in color). The light fastness of the chromophoric system of xanthene dyes is particularly low.	–N=N–, aryl rings	Rhodamine B 
5	**Azine dyes** based on nigrosine are acid dyes belonging to the class of azines (pyridines) or anilines (aminobenzene). They are used mainly in the composition of black pastes (for example, Acid Black).	 Structure of the major component of dye nigrosin	Acid Black 2 

ISSN 2708-129X. Укр. хім. журн., 2023

The most common among synthetic dyes are triarylmethane dyes due to their versatility and bright colors – from red/purple to blue/green. The chromophoric system of this class of dyes consists of three conjugated aromatic rings linked to a central carbon atom, while the exact color depends on the number and nature of the auxochromic groups. For example, methyl violet consists of a mixture of tetra-, penta-, and hexa-N-methyl para rosaniline, while crystal violet contains only N-hexamethyl pararosaniline. Methyl blue, also known as Acid Blue 93, is characterized by three benzenesulfonyl substituents on the amine groups, which ensure its good solubility in water. It is the presence of various chromophonic groups (conjugated aromatic system and/or conjugated rings) in the dye molecule that allows them to be recognized by analyzing absorption spectra by the intensity of the absorption bands and the position of the maximum of the absorption wave. [14, 15].

The differentiation of specific dyes within their chemical class based on the results of UV–vis absorption spectroscopy is in most cases complicated due to the low informativeness and closeness of their spectra, however, it allows differentiation of pastes that have the same qualitative, but different quantitative composition of dyes [16, 17]. It should also be noted that the analysis of a specific dye in the strokes of ballpoint pen pastes in documents according to the UV–vis absorption spectroscopy is quite problematic, since the influence on the records of various factors (temperature, radiation, humidity, etc.) that can cause changes in the structure of dyes and, accordingly, in their absorption spectra, is unknown [8].

The use of UV–vis absorption spectroscopy makes it possible both to study the qualitative composition of the pastes under investigation and to establish the amount of each component in their composition, which makes it possible to conduct identification studies of writing materials.

The purpose of this study is to generalize the data of the analysis of strokes of ballpoint pen pastes of different colors in documents by the UV–vis absorption spectroscopy method. The obtained data can be used to create a reference base for the identification and differentiation of the composition of ballpoint pen pastes of modern manufacturers.

EXPERIMENT AND RESULTS DISCUSSION. For the analysis of modern writing materials, 43 samples of ballpoint pen pastes of different colors were used: blue-violet (29), blue (3), black (5), pink-violet (3), red (2), green (1).

Research on the presence or absence of luminescence of pastes in individual fragments of document images according to the degree of absorption or reflection of the IR range of the spectrum was carried out using the spectral luminescence magnifier «Regula 4177» (λ=870–940 nm) upon excitation of IR luminescence in the green region of the spectrum at λ= 530 nm. The UV–vis absorption spectroscopy method was used to determine the qualitative composition of the dyes of the samples of ballpoint pen pastes under study. Using a scalpel, parts of strokes of paste samples were cut from documents together with paper fibers. Dimethylformamide (DMF) was used as a solvent for extracting pastes (pH=6) due to its effectiveness in dissolving most ballpoint pen inks. DMF solutions with pH = 6 were obtained by adding formic acid dropwise. pH was measured on a Thermo Scientific Orion Star A111 Benchtop Meter. The absorption spectra of extracts of

strokes of samples 1–43 were recorded on a Shimadzu 2600 spectrophotometer in the visible region of the spectrum (250–750 nm) in quartz cuvettes (l = 1 cm).

For research, all samples were divided into 6 groups depending on the color of the paste (Table 2).

Table 2.

Spectral and luminescent properties of ballpoint pen paste samples.

№ sample	Presence of fluorescence	λ_{max} (nm), visible area	Primary dye class
		Blue-violet pastes	
1	+	597.5, shoulder ~ 550	Triarylmethane
2, 6	+	592, shoulder e ~ 550	
3	+	595, shoulder ~ 550	
4	+	593, shoulder ~ 550	
5, 8, 11	+	590, shoulder ~ 550	
7	+	592.5, shoulder ~ 550	
9	+	590.5, shoulder ~ 550	
10	+	589, shoulder ~ 550	
12	–	595, 671, shoulder ~ 710	A mixture of triarylmethane and phthalocyanine
13	–	595, 670 nm, shoulder ~ 710	
14	–	592, 671, shoulder ~ 710	
15	–	592.5, 671, shoulder ~ 710	
16	–	589.5, 670.5, shoulder ~ 710	
17	–	590, 671, shoulder ~ 710	
18	–	593, 671, shoulder ~ 710	
19, 25	–	591.5, 670.5, shoulder ~ 710	
20	–	591.5, 671, shoulder ~ 710	
21, 28	–	591.5, 671.5, shoulder ~ 710	
22	–	592.5, 670.5, shoulder ~ 710	
23	–	593, 671, shoulder ~ 710	
24	–	593.5, 671, shoulder ~ 710	
26	–	593, 671.5, shoulder ~ 710	
27	–	591.5, 671, shoulder ~ 710	
29	–	596.5, 669, shoulder ~ 710	

Table 2.

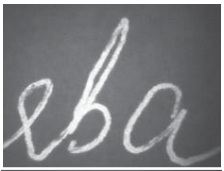
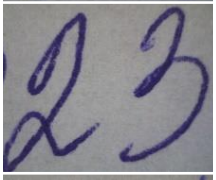
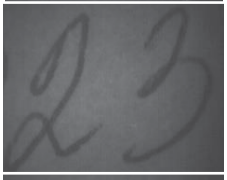
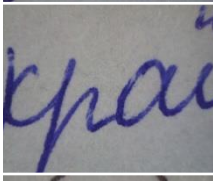
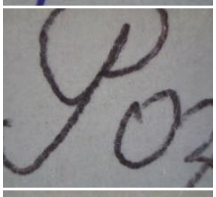
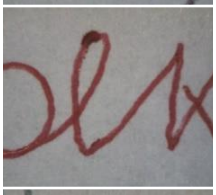
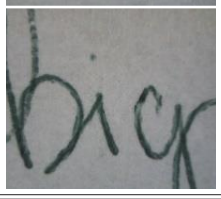
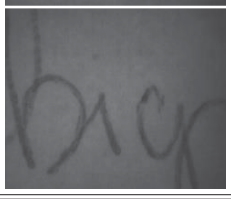
		Blue pastes	
30	weak	595.5, 668.5	Phthalocyanine
31	weak	598.5, 669	
32	weak	597.5, 670	
		Pastes are black	
33	+	420, 595	Triarylmethane
34	+	421.5, 591	
35	+	421, 589	
36	+	587.5	
37	+	421, 594.5	
		Pink-purple pastes	
38	+	562, 670, shoulder ~ 520	A mixture of triarylmethane and xanthene
39	+	561.5, 671, shoulder~520	
40	+	561.5, shoulder ~ 710	
		Red pastes	
41	–	446.5, 536, shoulder ~ 497	Xanthenic
42	+	444, 559, shoulder ~ 520	
		Green pastes	
43	–	605, 671, shoulder ~ 445	A mixture of triarylmethane and phthalocyanine

Based on the results of research into the luminescent properties of experimental samples (Table 3), it was established that 11 blue-violet pastes (samples 1–11), 5 black pastes (samples 33–37) and one red paste(sample 42) exhibit quite bright luminescence, and 3 blue pastes (samples 30–32) – a weak one. No luminescent response was observed for other pastes (samples 12–29, 41, 43).

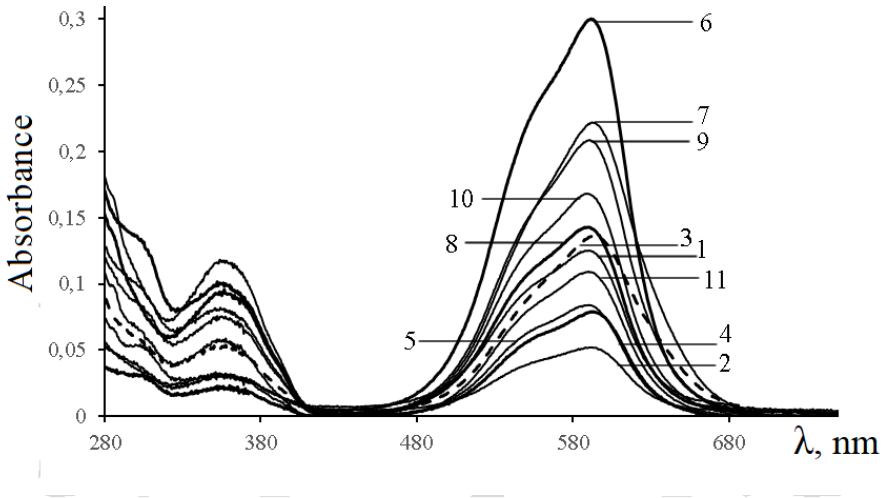
An interesting fact is that the samples of blue-violet pastes behave differently in IR radiation: sample 1 has luminescent activity, and sample 12 does not. Obviously, this is due to the different composition of the pastes. The IR luminescence of sample 1 is provided by the presence of crystal violet and some other triarylmethane dyes in its composition. Sample 12 contains a phthalocyanine dye, which leads to the quenching of the luminescence of the sample due to the overlapping of the absorption of the phthalocyanine dye and the luminescence of triarylmethane dyes [18].

Table 3.

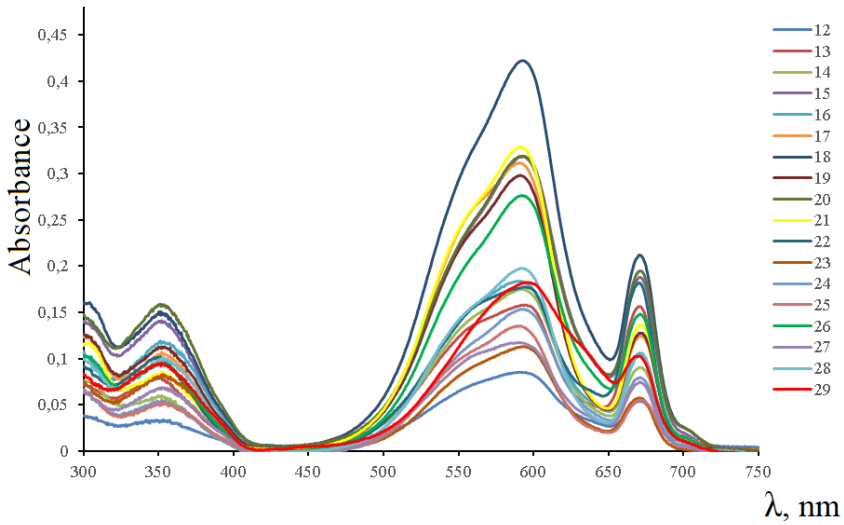
Examples of luminescence of selected samples of paste strokes.

№ sample	The color of the paste	Photo in white light	Photo in IR rays
1	Blue-violet		
12	Blue-violet		
30	Blue		
34	Black		
41	Red		
43	Green		

The in Figures 1–3 show electronic absorption spectra of dye extracts of ballpoint pen pastes in DMF. UV–vis absorption spectra of blue-violet pastes have a similar appearance and are characterized by the presence of pronounced maxima in the UV region at λ_{max} ~ 365 nm and in the visible region at λ_{max} ~ 590 nm with a pronounced shoulder in the region of 550–600 nm. The peak positions are typical of the class of triaryl-methane dyes, such as methyl violet and its analogue crystal violet. Thus, the spectrum of standard methyl violet (95% purity), taken by us under the same conditions, has λ_{max} = 597 nm and a shoulder



a



b

Fig. 1. UV-VIS spectra of extracts of blue-purple ballpoint pen strokes: samples 1–11 (a), samples 12–29 (b). The color of the absorption band corresponds to the sample number.

at 550 nm. It should be noted that the spectrum of sample 3 has a slightly different shape, which differs from the rest of the pastes. Upon microscopic examination of sample 3, it was established that the strokes of the blue-purple paste contain clusters of black dye, that is, this paste is not a single-component one, but contains a mixture of arylmethane dyes and/or azo dyes. In addition, the possibility that the storage conditions of the document led to partial decomposition of the dye is not excluded.

In the UV–vis absorption spectra of the

pastes of samples 12–29 compared to samples 1–11, the absorption maxima in the UV region have a hypsochromic shift of ~25 nm and, in addition, another maximum appears in the visible region at λmax ~670 nm with a shoulder at ~710 nm The appearance of the last band is due to the presence of phthalocyanine and/or arylmethane dyes in the composition of the pastes. Thus, according to [19, 20], the characteristic absorption spectrum of phthalocyanine dyes consists of a band in the region of 325–350 nm and an intense peak at ~700 nm. However, slight differences in the position of the absorption maxima and the uniform shape of the spectra of the studied samples of blue-violet pastes suggest that they contain similar components of coloring substances that have a slight difference in structure.

The blue pastes (samples 30–32) have two absorption bands in different ranges: a narrow intense band with λ_{max} ~ 350 nm and a less intense broad band split into 2 components (Q-band) with λ_{max} at 600 and 670 nm (Fig. 2, a). The Q band is characteristic of the phthalocyanine macrocycle and is responsible for the color of the dye. Its presence in the UV–vis absorption spectra is due to π–π* transitions in the cyclic aromatic system. In addition, in the absorption range of the Q-band, changes in the spectra can be associated with the presence of dimers of phthalocyanines formed by the interaction of molecules through delocalized π-electrons and hydrogen bonds [21].

The spectra of the samples of black ballpoint pen pastes (Fig. 2, b) in the visible region have one broad structured band, the absorption maximum of which occurs in the range of 587.5 –595 nm with a higher energy shoulder at ~ 550 nm. The general form of the spectra and the shape of the lines are similar to the most studied triarylmethane dye – crystal violet [22]. It should be noted that for all studied samples there is no significant difference in the frequency of maximum absorption, but for samples 33, 35 the intensity of absorption increases significantly, which may be due to an increase in the concentration of the dye in the specified samples, or its aggregation.

The spectra of the samples of pink-violet ballpoint pen pastes (Fig. 3, a) have absorption bands exclusively in the visible region with λmax at ~ 560 nm and a well-defined shoulder at ~ 520 nm, although a peak at 670–67 nm appears in samples 38 and 39 , the intensity of which is almost 6 times lower than for the 560 nm band. Probably, the pink color of these samples is due to the presence of xanthene dye rhodamine B (λ_{max} rhodamine = 556 nm [23]) in the composition of the pastes. The absorption bands in the range of 520–560 nm are caused by n-n* transitions between lone electron pairs and n-bonded electrons of the benzoid structure of rhodamine B with increasing ring conjugation with the opening of the five-membered lactone ring [23, 24]. A small additional band at 670 nm can be identified as a band belonging to a phthalocyanine compound (probably Blue 38 dye) that gives the pastes a purple tint. That is, the color of the samples of pink-purple pastes is due to the presence of a mixture of xanthene and phthalocyanine dyes in their composition.

In the UV-VIS spectra of the green paste, the band in the region of 600–710 nm is split into two components (λ_{maxI} = 605 nm, λ_{maxII} = 671 nm) and has a small shoulder at 708 nm. This indicates that the green paste contains phthalocyanine dyes such as Copper Phthalocyanine, Solvent Blue 64, as well as blue trialmethane dyes (Crystal Violet, Methyl Blue).

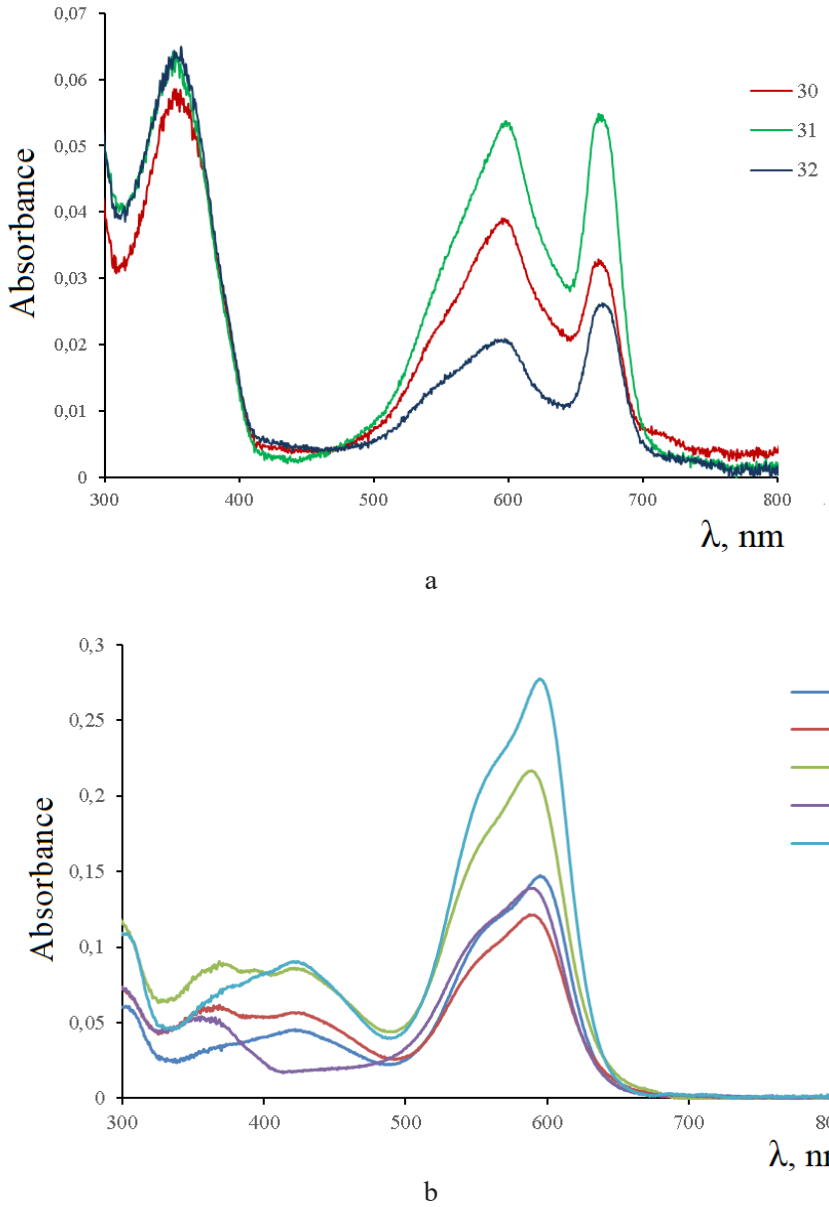


Fig. 2. UV-VIS spectra of extracts of blue (a) and black (b) ballpoint pen strokes (samples 30–32 and 33–37, respectively). The color of the absorption band corresponds to the sample number.

Low-intensity bands at ~ 450 nm are also observed for all three samples (Table 1), which is probably due to the presence of a yellow component molecularly similar to tartrazine in the composition of the pastes [25]. At the same time, the combination of blue and yellow dyes determines the green color of the paste of sample 43.

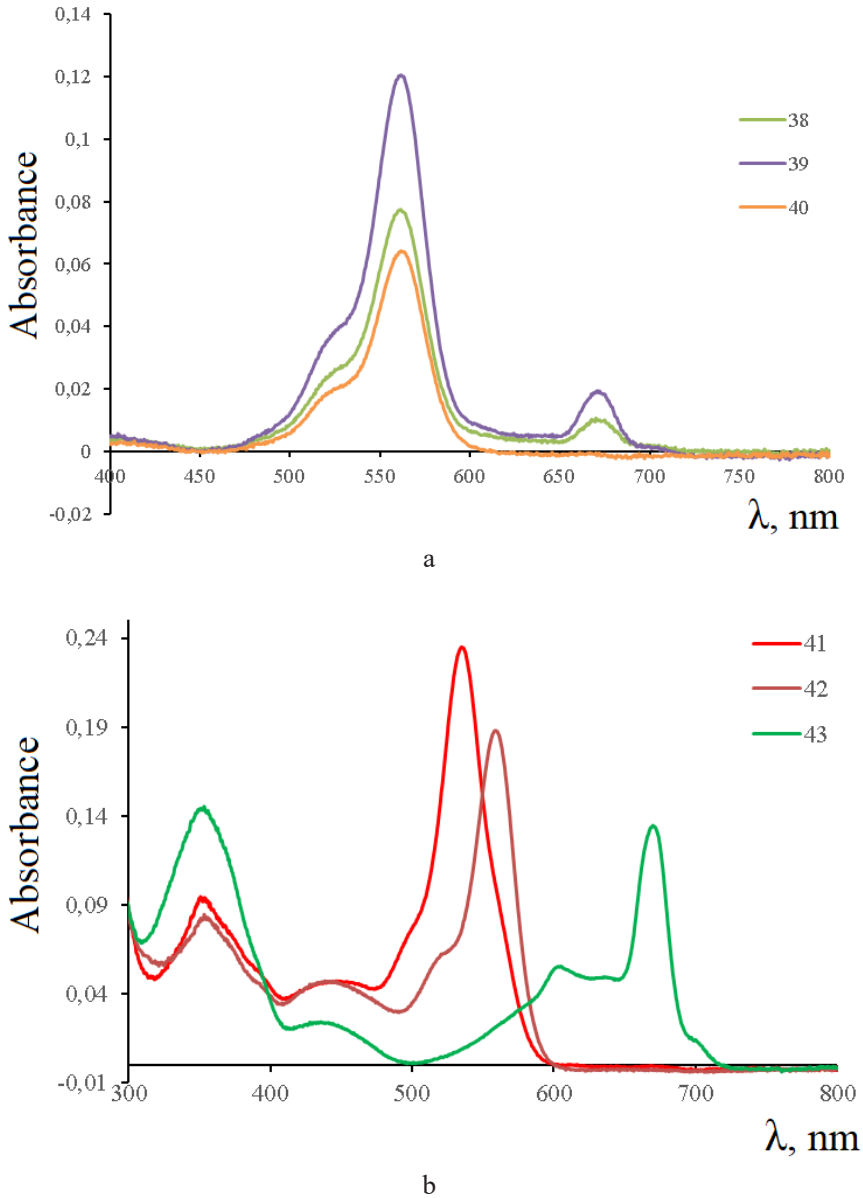


Fig. 3. UV-VIS spectra of extracts of pink-purple (a), red and green (b) ballpoint pen strokes (samples 38–40 and 41–43, respectively). The color of the absorption band corresponds to the sample number.

CONCLUSIONS. Using the method of electronic absorption spectroscopy, the qualitative composition and differentiation of 43 samples of ballpoint pen pastes of different colors was investigated. The UV-Vis characteristics of the main paste dyes were determined. A comparison of the spectra showed that the main absorption maxima relate to different structural and group affiliations of the dyes and depend on their chemical characteristics. It has been

proven that most of the analyzed pastes contain dyes based on triarylmethane, phthalocyanine, xanthene dyes or their mixture. The obtained data are useful for conducting research on ballpoint pen pastes to identify classification and identification differences and will be included in the spectrum database of ballpoint pen pastes for further diagnosis and identification of pastes received for research.

AKNOWLEDGEMENT. The work was carried out with the financial support of the Ministry of Justice of Ukraine within the scope of the research work of the Kyiv Scientific Research Institute of Forensic Expertise «Development of a methodology for determining changes in the chemical composition of dyes over time in the presence of crossing requisites».

ІДЕНТИФІКАЦІЯ ТРИАРИЛМЕТАНУ, ФТАЛОЦІАНІНУ ТА КСАНТЕНУ В СУМІШІ БАРВНИКІВ МЕТОДОМ ЕЛЕКТРОННОЇ АБСОРБЦІЙНОЇ СПЕКТРОСКОПІЇ

О. О. Посільський [1], Г. В. Артамонова [1]*, О. К. Трунова[2]

[1]Київський науково-дослідний інститут судових експертиз,
вул. Сім'ї Бродських, 6, Київ 03057, Україна
[2]Інститут загальної та неорганічної хімії ім. В. І. Вернадського НАН України,
просп. Академіка Палладіна, 32/34, Київ 03142, Україна
**e-mail: hanna1artamonova@gmail.com*

У роботі досліджено якісний склад та проведено диференціацію 43-х зразків паст кулькових ручок різного кольору (синьо-фіолетового – 29 зразків, рожево-фіолетового – 3 зразки, синього – 3 зразки, чорного – 5 зразків, зеленого – 1 зразок та червоного – 2 зразки) методом електронної спектроскопії поглинання. Результати дослідження показали, що кожну пасту можна відрізнити, вивчаючи характер спектрів їхнього поглинання, яка виникає через присутність різних функціональних груп. Встановлено, що більшість проаналізованих зразків паст містять у своєму складі пігменти на основі триарилметанових, фталоціанінових, ксантенових барвників або їхні суміші. Кожному типу барвників відповідають певні максимуми поглинання. Широка та найбільш інтенсивна смуга – при λ~590 нм, яку виявлено для всіх зразків, – відповідає триарилметановим барвникам. Смуга при λ~670 нм відповідає фталоціаніновим барвникам. Наявність смуг поглинання у зеленому діапазоні (λ~520–560 нм) свідчить про наявність у складі паст ксантенових барвників. Із використанням методу фотолюмінесцентної спектроскопії при збудженні ІЧ-люмінесценції в зеленій області спектру (λ=530 нм) показано, що 11 синьо-фіолетових, 5 чорних та одна червона пасти проявляють яскраву люмінесценцію через присутність в їхньому складі кристалічного фіолетового та деяких інших триарилметанових барвників. У трьох пастах синього кольору виявлено слабку люмінесценцію. В інших досліджуваних пастах люмінесцентного відгуку не спостерігали, що пов'язано з наявністю в цих пастах фталоціанінових барвників, поглинання яких перекриваються зі спектрами люмінесценції

триарилметанових барвників. Одержані дані можна використати для створення довідкової бази для ідентифікації і диференціації складу паст кулькових ручок сучасних виробників та встановлення їхніх класифікаційних та ідентифікаційних відмінностей.

Ключові слова: барвники, електронна спектроскопія поглинання, спектри поглинання розчинів, паста кулькової ручки.

REFERENCES

1. Chen H., Meng H., Cheng K. A survey of methods used for the identification and characterization of inks. *Forensic Science Journal.* 2002. **1** (1): 1–14. ISSN:1556–4029.
2. Brunelle R.L., Crawford K.R. *Advances in the forensic analysis and dating of writing ink.* (Charles C Thomas Publisher, 2003).
3. Ezcurra M., Góngora J.M., Maguregui I., Alonso R. Analytical methods for dating modern writing instrument inks on paper. *Forensic Science International*. 2010. **197** (1–3): 1–20. https://doi.org/10.1016/j.forsciint.2009.11.013
4. Allen M. J. *Foundations of forensic document analysis: theory and practice*. (John Wiley & Sons, 2015).
5. Aginsky V.N. Some new ideas for dating ballpoint inks- a feasibility study. *Journal of Forensic Sciences*. 1993. **38** (5): 1134–1150. https://doi.org/10.1520/JFS13517J.
6. Weyermann C., Almog J., Bügler J., Cantu A.A. Minimum requirements for application of ink dating methods based on solvent analysis in casework. *Forensic science international*. 2011. **210** (1–3): 52–62. https://doi.org/10.1016/j.forsciint.2011.01.034.
7. Calcerrada M., García-Ruiz, C. Analysis of questioned documents: a review. *Analytica chimica acta*, 2015. **853**:143–166. https://doi.org/10.1016/j.aca.2014.10.057.
8. Cantu A.A. On the behavior of certain inkaging curves. *Forensic science international.* 2017. **278**: 269–279. https://doi.org/10.1016/j.forsciint.2017.07.011.
9. Zollinger H. *Color chemistry: syntheses, properties, and applications of organic dyes and pigments*. (John Wiley & Sons, 2003).
10. Ziarani G.M., Moradi R., Lashgari N., Kruger H.G. *Metal-free synthetic organic dyes*. (Elsevier, 2018).
11. Weyermann C., Kirsch D., Costa Vera C., Spengler B. Evaluation of the photodegradation of crystal violet upon light exposure by mass spectrometric and spectroscopic methods. *Journal of forensic sciences*. 2009. **54** (2): 333–345. https://doi.org/10.1111/j.1556-4029.2008.00975.x.
12. Nag A., Goswami D. Solvent effect on two-photon absorption and fluorescence of rhodamine dyes. *Journal of Photochemistry and Photobiology A: Chemistry*. 2009. **206** (2–3): 188–197. https://doi.org/10.1016/j.jphotochem.2009.06.007.
13. Myheev Yu.A., Guseva L.N., Ershov Yu. A., Zaikov G.E. Optical spectra of individual molecules of phthalocyanine chromogens. *J. Chemical Physics and Mesoscopy.* 2007. **9** (4): 415–421. ISSN 1727-0227 (Print). [in Russian].
14. Gessner T., Mayer U. Triarylmethane and diarylmethane dyes. *Ullmann's Encyclopedia of Industrial Chemistry*. (2000). https://doi.org/10.1002/1435600 .a27_179.
15. Degano I., Sabatini F., Braccini C., Colombini, M. P. Triarylmethine dyes: Characterization of isomers using integrated mass spectrometry. *Dyes and Pigments*. 2019. **160**: 587–596. https://doi.org/10.1016/j.dyepig.2018.08.046].
16. Hora I.V., Kolesnyk V.A., Popovich I.I. Current issues of forensic forensic examination of documents. *Scientific Bulletin of the Uzhhorod National University. Series: Law.* 2023. **2**(75):163–170. https://doi.org/10.24144/2307-3322.2022.75.2.26

17. Shevchenko T.N., Temerdashev Z. A., Kiseleva, N.V. Identification and determination of aromatic dyes in ballpoint pen inks by HPLC with spectrophotometric and mass spectrometric detection. *Analytics and Control*. 2012. (3): 232–239. ISSN: 2073–1442 (Print). http://hdl.handle.net/10995/42557. [in Russian].
18. Gawad A.A., Salama T.M., Ibrahim I., Meshref M., Mohamed G.G., Zedan A.F. Alleviating Luminescence and Quenching toward Discrimination of Ballpoint Pen Inks Using Spectroscopy and Chromatography Techniques. *Applied Sciences*. 2023. **13** (16): 9300. https://doi.org/10.3390/app13169300
19. Bundina N.I, Galpern M.G., Derkachev V.M., Kopranenkov V.N. *Electronic absorption spectra of phthalocyanine and related compounds. (Cherkasy*, 1989). [in Russian].
20. Bunin D.A., Ndebele, N., Martynov A.G., Mack J., Gorbunova Y.G., Nyokong T. Low-Symmetry Phthalocyanines Bearing Carboxy-Groups: Synthesis, Spectroscopic and Quantum-Chemical Characterization. *Molecules*. 2022. **27** (2): 524. https://doi.org/10.3390/molecules27020524.
21. Farag A.A.M. Optical absorption studies of copper phthalocyanine thin films. *Optics & Laser Technology*. 2007. **39** (4): 728–732. https://doi.org/10.1016/j.optlastec.2006.03.011.
22. Lewis L.M., Indig G. L. Solvent effects on the spectroscopic properties of triarylmethane dyes. *Dyes and pigments*. 2000. **46** (3): 145–154. https://doi.org/10.1016/S0143-7208(00)00049-8.
23. Shabir G., Saeed A. Solvent free, one pot synthesis of symmetric xanthene dyes and their electrochemical study. *Journal of the Chilean Chemical Society*. 2016. **61** (2): 2907–2912. http://dx.doi.org/10.4067/S0717-97072016000200012.
24. Mielgo I., Moreira M.T., Feijoo G., Lema J.M. A packed-bed fungal bioreactor for the continuous decolourisation of azo-dyes (Orange II). *Journal of biotechnology*. 2001. **89** (2–3): 99–106. https://doi.org/10.1016/S0168-1656(01)00319-4.
25. Bhowmik B.B., Ganguly P. Photophysics of xanthene dyes in surfactant solution. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2005. **61** (9): 1997–2003. https://doi.org/10.1016/j.saa.2004.07.031.

Стаття надійшла 09.08.2023.