POSSIBILITIES TO DIFFERENTIATE BALLPOINT PEN INKS BY SPECTROSCOPIC AND CHROMATOGRAPHIC TECHNIQUES

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Within criminalistics examinations of documents characterization of ballpoint inks compositions is very important. These ballpoint inks are usually containing a mixture of solvents, resins, dyes and pigments, their nature and proportion being specific to each producer brand.

*The aim of this study was to evaluate the possibility to discriminate amongs the samples of two sets of ballpoint pen inks, provided from various manufacturers, by corroborating data obtained by spectrometric and chromatographic methods, such as UV-VIS-NIR, FT-IR, X-ray fluorescence spectroscopy and thin layer chromatography, all of them being recognized as forensic documents. An original approach is offered by using the chromatic CIE L*a*b* analysis of both inks such as and their extracts in methanol.as well as by correlation of these data with the results obtained by the other techniques.*

Keywords: forensic, ballpoint inks, FT-IR spectroscopy, chromatic analysis, X-ray fluorescence spectroscopy, thin-layer chromatography

1. Introduction

Analysis of ballpoint pen inks of questioned documents is often required in the field of forensic science in order to identify the writing implement used in the commission of a crime. Usually such examinations of ballpoint pen inks are entrusted to the laboratory in the form of a written sample on paper [1].

The ability to differentiate between inks can allow the forensic scientist to evaluate the authenticity of a suspicious document. Although it is difficult to determine whether an individual pen was used to write a document, it is feasible to identify the brand of pen. This requires some kind of classification or discrimination among the different brands of inks [2].

Modern inks contain many substances aiming to improve ink characteristics. Obviously, the most important component is the coloring material, which comes in the form of dyes, pigments or their combination. Dyes are soluble

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in the liquid body of the ink, which is also known as the vehicle. On the other hand, pigments are finely ground multi-molecular granules that are insoluble in the vehicle. The vehicle, whose composition affects the flowing and drying characteristics of the ink can consist of oils, solvents and resins [3].

In routine examinations of inks, non-destructive analytical methods, such as microscopic and optical ones, are primarily applied. These methods allow chosen parameters of the ink to be characterized, such as its colors, luminescence and absorption of radiation. Samples may be differentiated on the basis of transmission, reflection and fluorescence spectra obtained for inks deposited on the surface of paper. However, in order to identify the ink, it is necessary to determine its type and composition, using methods of physico-chemical analysis. Among these methods, thin-layer chromatography and capillary electrophoresis are applied most often. They are simple to use, require only a small amount of sample for examination, and at the same time they are characterized by a high degree of selectivity and repeatability of results, but isolation of the sample from the substrate of the document (i.e. the paper) by means of solvent extraction is necessary, which leads to at least some damage to the examined document [4, 8-12].

Ultraviolet-visible-near infrared spectrophotometry (UV-Vis-NIR) and Fourier Transform Infrared Spectrometry (FTIR) can be also used to pen brand differentiation. Identification of an ink formulation may be important for questioned document examination. Knowledge of ink formulas can help to determine the authenticity of a document, including age and presence of any changes to the document [5-7, 14].

X-ray fluorescence spectrometry as an analytical technique which examines the elemental contents of a small sample and provides information about pigments and fillers, is more sensitive to higher atomic weight elements than SEM/EDX. Nevertheless the depth of X-ray penetration as well as the beam diameter influence on the results obtained for multilayer materials [4, 8-9].

Spectroscopic methods such as Fourier transform infrared spectroscopy, X-ray fluorescence spectroscopy, UV-VIS spectroscopy and chromatography technique, was successfully applied in the analysis of inks [13].

This paper aims to assess the possibility of discriminating in a forensic analysis of a series of ballpoint pastes of blue and black colors, from various sources, by corroborating the data obtained by spectrometric methods, such as FT-IR spectroscopy, X-ray fluorescence spectroscopy, UV-Vis-NIR spectroscopy in diffuse reflectance mode completed by chromatic analyses in CIE-L*a*b* system and thin-layer chromatography, all of them being recognized as efficient techniques used in forensic investigations.

2. Experimental

A number of 7 ballpoint pen inks have been purchased, four blue and three black, to form a collection, available now in Romania, with their specifications shown in table 1.

Table 1

Code	Pen Name	Ink manufacturer
Specification of blue ballpoint inks		
1A	AIHAO	CHINA
2A	BIC	FRANCE
3A	CORVINA51	ITALY
4A	PELIKAN	GERMANY
Specification of black ballpoint inks		
5N	BIC	FRANCE
6N	PELIKAN	GERMANY
7N	PENTELSUPERB	EUROPE

2.1. FT-IR analysis

To highlight the vibrational behavior of molecular bonds existing in the composition of ballpoint pen inks, infrared spectra have been studied for all the samples deposited as a film on a KBr window, and then analyzed by transmission, using a spectrometer FT-IR type Paragon 1000, provided by Perkin-Elmer. Infrared spectrum was recorded for each sample between 400 cm^{-1} and 4000 cm^{-1}.

2.2. UV-Vis/chromatic analysis

Based on UV-Vis spectrometry the chromatic analysis of the samples has been performed in two distinct ways: in reflection mode for the inks such as and in absorption for their methanolic extracts.

In the first case, all the samples were deposited on a square sheet of paper of 2x2 cm size. These samples were analyzed using a Jasco 670 spectrometer in he UV-Vis domain, from 300-800nm, provided with a diffuse reflectance integrating sphere, a similar clean square sheet of paper being used as reference.

In the second case, each sample was deposited on a fragment of white paper, forming a square of 1 cm side, then inserted into a 5 mL glass tube and extracted with methanol. For complete extraction of ink components from paper matrices they were vigorously shaken for 1 min. Dye components were completly dissolved in methanol. The methanol extracts were analyzed using the same instrument but now in absorbance mode, with methanol used as the reference solvent.

The objective analysis of sample color has been performed by using the soft-ware on CIE L*a*b*system provided by Jasco.

2.3. Thin-layer chromatography

Methanolic extracts were spot on TLC plates (made by Merck Art. 5721, Kieselgel 60, without a fluorescence indicator) using micro capillary about 1.5 cm from one end of the plate. Each inks group was spotted on a separate TLC plate and spots were placed at a distance of 2 cm from each other, and they had 3 mm diameter.

The dye components were separated using two developing solvent systems as detailed in literature [3, 9-11, 14]: solvent system I of ethyl acetate/ absolute ethanol/distilled water (70:35:30 v/v), and solvent system II of n-butanol /absolute ethanol / distilled water/acetic acid (18:2:2:1 v/v).

Two sample sets were formed from each ink group, the first set was placed in a developing tank with solvent system I and the second set was placed in another tank with solvent system II. The tanks were closed tightly for 30 min.

The chromatograms were removed from the developing tanks and allowed to dry, and then they were examined under normal incident daylight.

2.4. X-ray fluorescence spectroscopy

Elemental composition of ballpoint inks was analyzed using X-ray fluorescence spectrometry. Measurements were made with an X-ray type spectrofluorimeter EAGLE III, μProbe, in vacuum, in the following conditions: excitation source - X-ray generator (Rh); voltage - 40 kV, current - 200 μA; detector - Si(Li) monocapilar with 300 μm spot; time constant of 17 μs.

Ink samples were carbonized in the crucible and then placed into the spectrometer. Eight measurements were made for each ink sample.

3. Results and discussion

3.1 FT-IR spectroscopy

The IR spectra of inks showed a large peak at 3200 cm^{-1} to 3600 cm^{-1}, this indicating the presence of associated OH groups in the inks formulations [5].

Regarding the chemical composition of the tested pen inks, by viewing FT-IR spectra (fig. 1) it can be presumed that almost all the 7 ballpoint pen pastes present multiple functional groups (e.g. hydroxyl, carbonyl, amino, nitro, ester/ether groups). For instance, all the 7 ballpoint pen inks present the strong band of carbonyl (C=O) from 1720-1725 cm^{-1}, and an intensive peak at about 1170 cm^{-1}, characteristic for the asymmetrical bending vibration of C-O-C bonds. This last band completed by the appearance of the symmetric vibrations of C-O-C from about 940 cm^{-1} (more evident for the samples 1A, 3A, 4A and 6N) confirms the presence of saturated ethers in ink composition. Beside this aliphatic ethers the strong band for all ink samples observed at 1245cm^{-1} - 1294 cm^{-1} could also suggest the presence of aromatic ethers (Ar -O) (e.g. 1A sample presents the intensive band at 1294 cm^{-1}). The strong band which appeared between 1580-1600 cm^{-1} represents

a clear evidence of some amino groups (ν_{N-H}). This last aspect is confirmed by the appearance of ν_{C-N} from about 1050-1100 cm^{-1}. Another peak that can be observed in almost all the samples is the peak from 1380 cm^{-1} which can be assigned to the N-O groups. The spectra also exhibited peaks at the region of 2857 cm^{-1} to 2900 cm^{-1} indicating the CH_3 and CH_2 stretching bond vibrations.

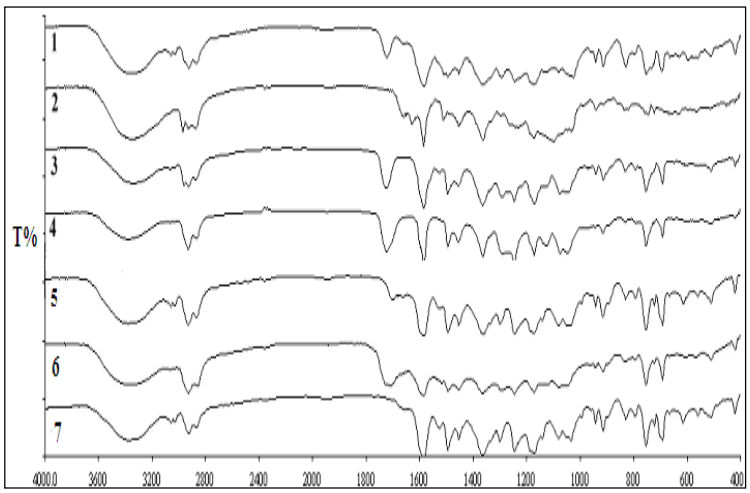

Fig. 1. IR spectra of all ballpoint ink samples

It follows that for each ink brand some specific fingerprints can be detected, for instance the region specific to carbonyl group, which appear at 1722 cm^{-1}, 1725 cm^{-1}, 1724 cm^{-1} for blue inks (1A, 3A, 4A, respectively), while for black inks appear at 1703 cm^{-1} (5N, 7N) and 1714 cm^{-1} (6N). However, it is rather difficult to assess the identity of an ink brand by simple using infrared spectra, and it should be completed by complementary techniques, more specific for a particular color as it is electronic spectroscopy in visible domain.

3.2. UV-Vis/chromatic analysis

Color perception has been debated for many years and, as in any evaluation that relies on human senses, the essence of analysis remains subjective. However, with the evolution of computerized color systems and controlled artificial light sources, a more objective method to differentiate color is available. Currently, there are many excellent software packages that translate detailed, color formulas into mathematical calculations [15].

The International Commission on Illumination (called CIE) completed the first phase of CIELAB in 1931. It initially was developed as an objective, color evaluation method using a light source, a sample, and an observer [15].

In 1976, the CIE recommended the CIE L*a*b*, or CIELAB, color scale for use. It was intended to provide a standard, approximately uniform color scale

which could be used by everyone so that color values could be easily compared [16].

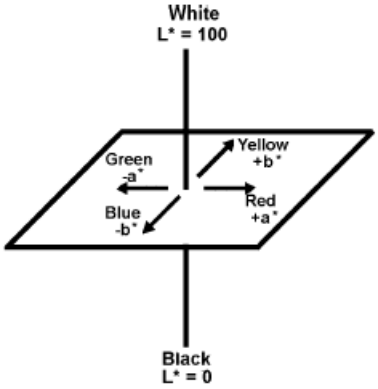

Fig. 2 Diagram representing the CIELAB color space

The CIELAB color scale is an approximately uniform color scale. In a uniform color scale, the differences between points plotted in the color space correspond to visual differences between the colors plotted. The CIELAB color space is organized in a cube form, with the following significance of geometrical parameters, which is also represented in Fig. 2 [17]:

L* - represents the luminosity of the color (***L**** = 0 yields black and ***L**** = 100 indicates diffuse white; specular white may be higher);

a* - position between red and green axis (negative values indicate green, while positive values indicate red colors);

b*- position between yellow and blue axis (negative values indicate blue and positive values indicate yellow colors);

C* - chroma (distance from the luminosity axis) is an indication on homogeneity or complexity of the chromophore composition;

h^* - hue angle, reflecting the proportion of colours provided by a* and b* parameters.

The CIELAB color scale may be used on any object whose color may be measured. It is used extensively in many areas. As was intended, it provides a standard scale for comparison of color values.

In this case, CIE L*a*b* based analysis of the investigated samples can provide valuable tools in discrimination of different inks within the same colouristic pallet by means of all five parameters provided by the soft-ware.

The trichromatic analysis of the samples investigated will be discussed in detail based on parameters collected in the tables 2 and 3 for the ink samples such as and for their extracts in methanol solutions.

For the inks deposited on a paper support the diffuse reflectance spectra provided no significant differences in luminosity parameter, L*, its values ranging between 31 and 37 units regardless the sample or its color.

Table 2

Trichromatic parameters of sample ballpoint pens inks deposited on a square sheet of paper

Sample	L^*	a*	b*	C*	h^*
1A	34.61	20.50	-20.90	29.28	314.45
2A	33.11	16.86	-24.04	43.77	298.16
3A	33.15	26.53	-34.81	27.26	307.31
4A	37.24	36.77	-52.30	63.93	305.11
5N	33,04	8,75	1,88	8,95	12,10
6N	31,58	6,66	-1,65	6,86	346,05
7N	33,13	7,91	4,63	9,17	30,33

However, a* and b* parameters have different values both between blue - black samples and within the same color samples. Indeed, while all a* parameters exhibit positive values for all the samples, b* values are negative as expected for blue inks, 1A – 4A (between 20 and 53), and either positive (5N, 7N) or negative (6N) and rather small for black inks. The proportion between blue and red colors are revealed by the hue angle, which is located near 290^o (pure blue) for blue inks (298 – 314), while for black inks it is ranging between – 14 (6N) and + 30 (7N), that is bellow or above the positive abscise. Another point of discrimination is provided by chroma, C*, which is between 27 and 64 units for blue inks and much smaller, between 6 and 9 units for blue inks. As high values for chroma indicate quite pure colors, one can conclude that the blue ink 4A consists in a fewer chromophor agents, while the other inks have a more complex composition, as in case of sample 1A. Even smaller values for chroma of black inks are also in agreement with a higher complexity of chromophor mixture.

An interesting approach is offered when compare these trichromatic parameters with those obtained from analysis of corresponding methanol extracts (table 3). In this case one can distinguish between the contribution of dyes, which are mostly soluble in methanol, and that of pigments, which will not be extracted. As in previous case, the luminosity parameter is not relevant to discrimanate among the inks, its higher values in solution being the result of appropriate dilution for optimal registration of spectra in absorbance mode. However, the other parameters are specific to various samples, and in some cases are different from those obtained from reflactance spectra of inks. Indeed, while b* prameters remained negative for all four blue inks as expected, they are now all negative for the three black inks as well, this suggesting extraction in solution of dominant blue dyes from these last samples.

Table 3

Trichromatic parameters of sample ballpoint pens inks extracted with methanol

Sample	L*	a*	b*	C*	h*
1A	88.95	6.21	-17.44	18.51	289.60
2A	80.44	3.62	-21.80	33.81	279.92
3A	79.68	10.83	-32.02	22.10	288.69
4A	81.42	17.02	-27.82	32.62	301.46
5N	72.45	20.46	-28.11	34,76	306.05
6N	78.79	22.56	-26.20	34.58	310.73
7N	70.20	23.19	-30.34	38.19	307.38

This is in agreement with the values for hue angle which are now all around 300^o specific to quite pure blue both for blue and black ink extracts and higher values of chroma for black than for blues inks extracts. Such a behaviour is a clear indication on a dominant proportion of black pigments, such as black carbon, in the samples 5N and 7N, which are insoluble in any solvent, and thus not extractible in methanol.

3.3. Thin-layer chromatography

The R_f value and color tones of the bands separated by TLC analysis of the methanolic extracts are listed in tables 4 - 7 and the chromatograms are shown in Fig. 3 - 6.

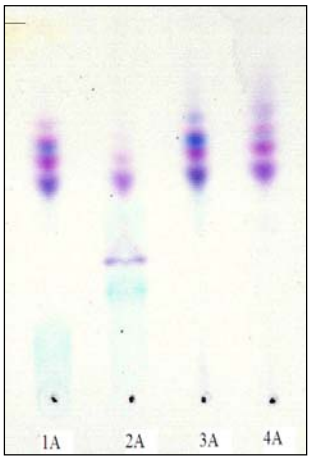

Fig. 3 - Plate of blue inks developing in solvent systems I

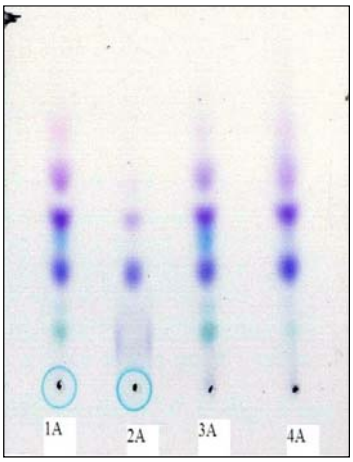

Fig. 4 - Plate of blue inks developing in solvent systems II

Table 4

TLC results of blue inks, solvent system I, under normal incident daylight

Solvent I							
Ink 1A	R_f	Ink 2A	R_f	Ink 3A	R_f	Ink 4A	R_f
Pale Blue	0.00	Pale Blue	0.40	Pale Purple*	0.02	Purple/Blue	0.30
Pale Blue	0.30	Blue/Purple	0.46	Blue/Purple	0.47	Purple	0.50
Blue/Purple	0.47	Pale Purple	0.52	Purple	0.55	Blue/Purple	0.57
Purple	0.55	Blue/Purple	0.65	Blue	0.62	Purple/Blue	0.75
Blue	0.62	Pale Blue*	0.75	Blue/Purple	0.67	Pale Purple*	0.80
Blue/Purple	0.67			Pink	0.70		
Pink	0.70			Purple*	0.72		
Purple	0.72			Pale Purple*	0.75		
Pale purple*	0.77						

Table 5

TLC results of blue inks, solvent system II, under normal incident daylight

Solvent II							
Ink 1A	R_f	Ink 2A	R_f	Ink 3A	R_f	Ink 4A	R_f
Pale Blue	0.00	Pale Blue	0.00	Pale Purple	0.05	Purple	0.36
Blue/Purple	0.34	Pale Purple	0.18	Pale Blue	0.26	Pale Blue	0.42
Blue	0.38	Purple	0.34	Blue/Purple	0.34	Purple	0.44
Blue/Purple	0.44	Pale Purple	0.44	Blue	0.38	Purple	0.52
Purple	0.52			Blue/Purple	0.44	Pale Purple	0.60
Pale Purple	0.60			Purple	0.52		
				Pale Purple	0.60		

* slightly visibile under normal incident daylight

The analysis of data collected in tables 4 and 5 for blue inks results in the following observations:

- all the four samples have different numbers of components of different colors separated at various R_f ; however the differences between members of pairs of inks, 1A – 3A and 2A – 4A, respectively, are not significant;

- for the first pair of inks, 1A – 3A, a number of 9 – 8 components could be distinguished, while for the pair 2A – 4A only 5 components are separated; this behavior is in agreement with the tricromatic analysis, when chroma for the former pair of inks is smaller than for the later, thus confirming a higher complexity if the chromofor mixture in the first case;

- the best separating and discrimination results have been obtained using solvent system I.

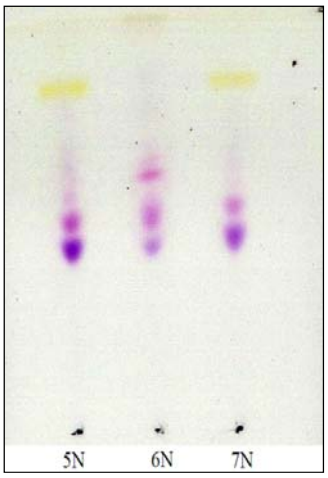

Fig. 5 - Plate of black inks developing in solvent systems I

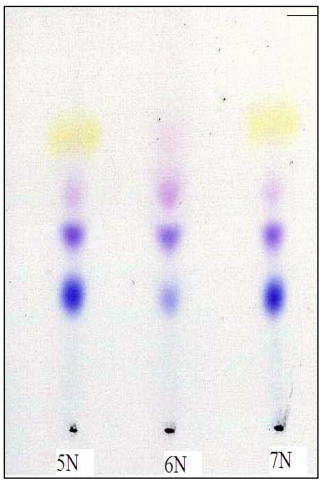

Fig. 6 - Plate of black inks developing in solvent systems II

Table 6

TLC results of black inks, solvent sistem I, under normal incident daylight

Solvent I					
Ink 5N	R_f	Ink 6N	R_f	Ink 7N	R_f
Pale Purple	0.00*	Pale Purple	0.00*	Pale Purple	0.00*
Purple	0.29	Purple	0.27	Purple	0.29
Purple	0.41	Pale Purple	0.37	Purple	0.41
Purple	0.50	Purple	0.45	Purple	0.50
Pale Purple	0.58*	Purple	0.58	Pale Purple	0.58*
Yellow	0.75*	Pale Purple	0.66*	Yellow	0.70*
Yellow	0.83	Purple	0.79*	Yellow	0.83
		Pale blue	0.83*		
		Yellow	0.91		

Table 7

TLC results of black inks, solvent sistem II, under normal incident daylight

Solvent II					
Ink 5N	R_f	Ink 6N	R_f	Ink 7N	R_f
Purple	0.00*	Purple	0.00*	Purple/Blue	0.00*
Purple	0.22*	Purple	0.20*	Purple	0.22*
Purple	0.27*	Purple	0.25*	Purple	0.27*
Blue/Purple	0.33	Pale Purple	0.32	Blue/Purple	0.33
Purple/Pink	0.38	Purple	0.38	Purple/Pink	0.38
Pale Purple	0.45	Pink	0.43	Pale Purple	0.45
Yellow	0.51	Pale Purple	0.51	Yellow	0.51
Yellow	0.69	Pale Blue	0.88*	Yellow	0.64
		Yellow	0.96*	Pale Yellow	0.70*

* slightly visibile under normal incident daylight

The analysis of data collected in the tables 6 and 7 for black inks extracted in methanol revealed the following aspects:

- for the three samples very complex chroamtograms are obtained, with 7 – 10 components separated, most of them at similar R_f for different samples, therefore this technique is not appropriate to differentiate among black inks;
- the best separating and discrimination results have been obtained using solvent system II.

3.4. X-ray fluorescence spectroscopy

Elemental composition of all ballpoint inks is shown in tables 8-9 and illustrated in figure 3 for blue ballpoints.

Table 8

Results of X-ray analysis of blue ballpoint inks

Element % / Sample	S	Fe	Cu	Zn	P	Si	Ti	K	Ca
1A	50.2	0.5	42.4	2.4	4.4	-	-	-	-
2A	78.7	0.7	19.4	1.2	-	-	-	-	-
3A	-	1.0	-	-	92.6	6.5	-	-	-
4A	-	5.3	-	-	61.4	11.8	2.9	3.8	14.8

Table 9

Results of X-ray analysis of black ballpoint inks

Element % / Sample	S	Cu	Zn	Fe	P	Si	Cl
5N	89.3	-	-		10.7	-	-
6N	3.6	10.5	6.7	4.6	-	10.9	63.6
7N	93.1				6.9		

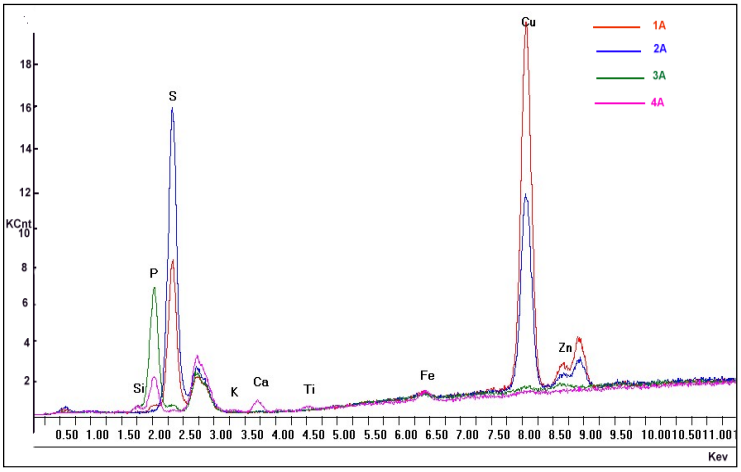

Fig. 3 X-ray fluorescence spactra of blue ballpoints

The analysis of data in tables 8 – 9 revealed the following aspects:

- for the blue inks the dominant elements are sulfur and copper for samples 1A and 2A, while phosphor is dominant for the samples 3A and 4A;

- three of blue inks have dominant mineral pigments, such as CuS and CuZn in case of 1A and 2A samples, while a silica clay mineral could be present in the sample 4A; it seems that in the sample 3A the main cromofor contribution is provided by organic dyes, this explaining the differences observed in chromatic analyses of inks such as and of their methanolic extracts;

- for black inks the sample 6N has dominant mineral contribution from pigments as it was also noticed from comparative tricromatic analysis, while for 5N and 7N dominant are organic dyes, possible including also black carbon.

4. Conclusion

After the author knowledge, this is the first time when a comparative tricromatic analysis of some colored samples registered such as and for their extracts has been applied in order to assess the contributions of pigments and organic dyes used as chromofor agents. This original approach seems to be very efficient in discriminating various brands of ballpoint pen inks when it is sustained by complementary data provided by infrared spectroscopy, thin layer chromatography and elemental analysis performed by X-ray fluorescence spectroscopy.

Following such a procedure, one can discriminate not only amongs inks of different colors, e.g. blue and black, but also within the same coloristic pallet.

To further improve these discrimanting aspects the methodology should also include the TOC analysis of carbon by differentiating the inorganic carbon,

organic carbon and elemental carbon provided by black carbon, thus contributing to significant advances in forensic science.

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