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THE STUDY OF MODERN WRITING MEANS ON DOCUMENTS WITH SPECTROSCOPIC METHODS

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Material analysis of writing means is very important part of forensic examination of the questioned documents. Mostly is it used to confirm/refute the authenticity of the document or dating the time of document formation. Nowadays, commonly used writing means can be divided to ballpoint, ink and gel pens, according to the nature of their writing fluid cartridge. The various group of writing means differ in ink composition and principle of supplying writing materials on a substrate. During examination of the document usually routine analysis such as optical microscopic methods are applied first. Their preliminary results can facilitate the choice of other methods which are needed to submit a sample. Widely used are spectroscopic (mostly non-destructive) and chromatographic (destructive) methods. The aim of our study was to utilize a combination of suitable spectro-

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scopic methods in IR region and XRF spectroscopy in order to develop the most appropriate methods of measurement and subsequent data processing in identification of the writing resource. The database of 19 model samples of different kinds of blue pens applied on paper substrate was created. More attention was fixed on micro-FTIR and FTIR analysis. We focused on searching for the optimum technique enabling the analysis of thin lines on a paper substrate and subsequent separation of the spectrum of writing means. It was established what is the minimum required number of measurements from a single sample. In the spectra, the correlation/difference between groups of writing means (ball, gel and roller ball pens) and between individual means within a particular group were studied. The results were supplemented by elemental analysis and by XRF method.

Introduction

Material analysis of writing means is a very important part of forensic examination of the documents. Mostly it is used to confirm/refute the authenticity of the document. Today generally used writing means can be distinguished according to their filling as the ballpoint (B), roller ball (R) and gel pens (G). Particular groups vary in their composition and in principle of feeding the ink on the substrate. In examination of a document routine analysis, such as optical microscopy, are applied first. The obtained preliminary results may facilitate the choice of additional methods (non-destructive or semi-destructive) and chromatographic (destructice) methods.

Experimental

Sample Preparation

All 19 blue pen samples (Table I) were collected based on the market research of most used current writing materials in Slovakia. From our ballpoint, gel and roller ball pen collection we prepared model samples (starting database) on various substrates (different kinds of paper — non-coated paper Whatman and commonly used office paper and aluminium board). The chemical formulations of inks samples were unknown.

Experimental Methods

The samples were subjected to optical examination and spectroscopic analysis. Spectra in the IR region and XRF spectra were measured. FTIR (Fourier Transform Infrared Spectroscopy) give us information about the presence of

organic groups in the examined samples. However, in the spectrum obtained the bands originating from the ink often overlap with the strong absorption bands of the paper. Therefore, it is necessary to further mathematically process the results using a database of reference spectra of writing means. The ability to scan the selected points of writing record by microscope with FTIR and the examination without the need of prior preparation of the sample are important advantages of this method. X-ray fluorescence (XRF) spectrometry is a method used for routine, non-destructive chemical analysis of materials of various shapes and forms. It works on wavelength-dispersive spectroscopic principles that are similar to an electron microprobe (EPMA) and several other instrumental methods involving interactions between electron beams and X-rays with sample (SEM, EDX, XRD). The portable X-ray device is capable of performing multi-elemental analysis from magnesium to uranium in concentrations from ppm to 100 % directly in the air without having to use additional attachments, such as vacuum pump.

Optical Microscopy

Lines of writing means deposited on paper were optically examined using microscope integrated with micro-FTIR assembly. The lines were captured with integrated CCD sensor and saved in JPEG format with 250× magnification (Fig. 1). Appropriate light conditions were provided by lighting from the front of the sample.

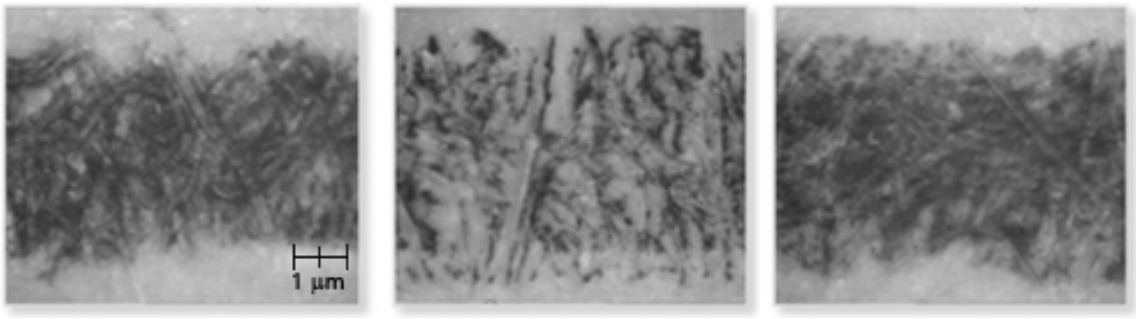

Fig. 1 Microscopy images of ink lines (magnification 250×) — left: gel pen; in the middle: ballpoint pen; right: roller ball pen

FTIR Spectroscopy

The samples were measured using EXCALIBUR series, FTS 3000 MX (Digilab, USA) spectrometer with ATR adapter with diamond crystal in a wavenumber range of 4000-600 cm^{-1}. Micro-FTIR spectra were measured using IR microscope Varian 610-3R Series (Digilab, USA) coupled with the above FTIR spectrometer and micro-ATR system with diamond crystal. Locations of the

measured place of sample were monitored using Capture Sample Application. The spectra were measured using Varian Resolution Pro software.

Table I Experimental samples (ballpoint, gel and roller ball pens)

Sample	Filling	Tip diam. mm	Manufacturer	Other specifications		
				Ser. No.	Distributor	Importer
B1	paste	?	Slovakia	4411 Jumbo	ŠEVT a.s.	
B2	paste	?		4444	ŠEVT a.s.	KOH-I-NOOR
B3	paste	?		4443	ŠEVT a.s.	KOH-I-NOOR
B4	paste	?			PLUS Želiezovce	
B5	paste	0.8	Pentel (France)	BKL78	ŠEVT a.s.	
B6	paste	?	Pentel (Taiwan)	KFLT8	ŠEVT a.s.	
B7	paste	0.7	Pentel (Japan)	BKS7H	ŠEVT a.s.	
B8	paste	1	Pentel (Japan)	BKL10	ŠEVT a.s.	
B9	paste	?	PILOT (Japan)	BLS-G2-5		
B10	paste	1	Parker (France)	ISO 12757-2	Activa s.r.o. SR	
G1	gel	1.6	Pentel (Japan)	K186		
G2	gel	0.7	Pentel (Japan)	LF7	ŠEVT a.s.	
G3	gel	0.4	Pentel (Japan)	KFGN4	ŠEVT a.s.	
G4	gel	0.7	Pentel (Japan)	BGR7	ŠEVT a.s.	
G5	gel	0.7	Parker (France)		Activa s.r.o. SR	
R1	ink	0.7	Germany	ISO 14145-2		
R2	ink	0.3	Stabilo (Germany)			
R3	ink	0.5	SaKOTA (China)	ADH 0488		SaKOTA s.r.o.
R4	ink	0.7	Parker (France)		Activa s.r.o. SR	

XRF Spectroscopy

Elemental composition was obtained using hand-held XRF-spectrometer X-MET5100 (Oxford Instruments). The relative contents of elements were evaluated using Xmet software under general condition (high voltage 15 keV).

Results and Discussion

Optical Microscopy

Based on the different thickness of lines, the studied set of samples may be divided into seven groups. Distribution of samples according to thickness of lines on plain paper is shown in Table II. While group 1 consists of samples of the thinnest lines, group 7 contains the sample with the thickest lines. A higher group number means a thicker line.

Comparing the findings with the manufacturers data (if they are listed), writing means of the type G (gel filling) and in particular of the type R (ink filling) compared to type B (paste filling) with the same tip diameter create thicker lines because of better penetration into the substrate. Therefore, line thickness does not always correspond to the expected value.

Table II Distribution of writing means based on their line thickness

Group	1	2	3	4	5	6	7
Samples	B9	B4	B1	B5	B10	G5	G1
	G3		B2	B6	G2	R1	
			B3	B8	G4	R4	
			B7	R3	R2		

FTIR Spectroscopy

Analysing FTIR spectra the characteristic absorption bands in the spectrum of writing means measured on the aluminium substrate was identified and subsequently the presence of these characteristic absorption bands in the spectrum of the writing means deposited on different papers (blank paper, and Whatman paper) were searched for.

The FTIR spectra of pure inks were measured as thin layers on aluminium substrates, which makes it easier to find the principal characteristic absorption bands of writing mean. The FTIR spectra of all 19 samples on aluminium substrate were measured using ATR-diamond crystal technique.

The spectrum of aluminium substrate (Fig. 2) does not contain the absorption bands which are observed in IR spectra of writing means.

Each group of samples contains characteristic absorption bands. These absorption bands correspond to the vibrations of different groups of atoms. Almost all samples are distinguishable by the presence of the characteristic absorption

bands in their FTIR spectra. For example, the peak at 1360 cm^{-1} can be found only in the inks from ballpoint pens. This absorption can be attributed to $–SO_2$-OX group (X – alkali metal ion), which is in dye Acid Blue 1. The presence of the peak at 1169 cm^{-1} in all samples except for G1 and G3 types of fillings indicates that the gel and roller ball pens contain this dye too. The next present dye can be Methyl Blue, which contains $–SO_2–OH$ group with band at 1080-1010 cm^{-1}. This band is apparent in almost all of spectra, except of spectra of samples B10 and G1.

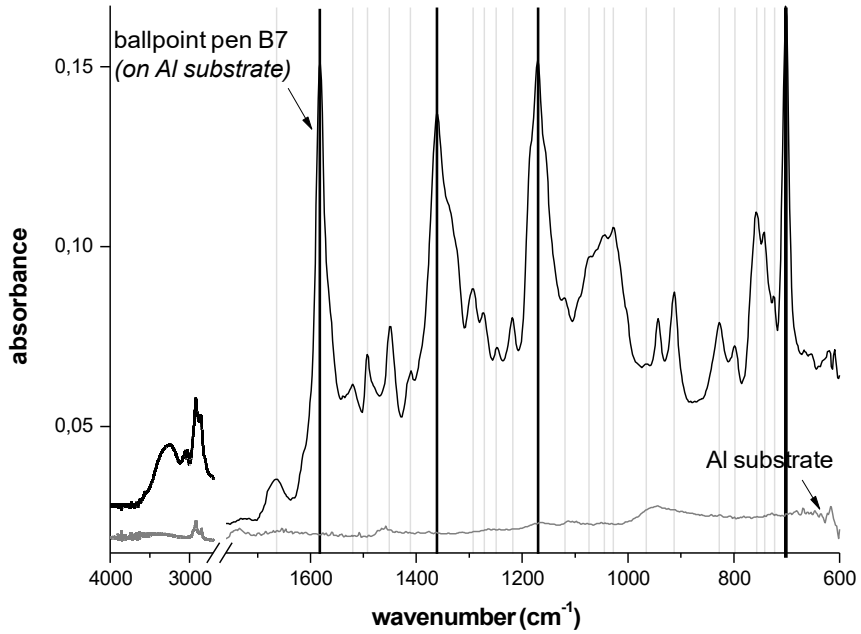

Fig. 2 FTIR spectrum of sample B7, measured on aluminium substrate

Significant peak at 1585 cm^{-1} can be assigned to the $–COO^-$ vibrations of oleic acid and is found in most samples. Oleic acid belongs to common part of the writing means of pens with ball, and acts as a lubricant, driers and regulator of the viscosity in writing means.

Generally, all the 19 samples could be classified into three main groups. In contrast to spectra of the samples R and G, spectra of the samples B contain the absorption bands at 1492, 1360, 943 and 701 cm^{-1}. It is difficult to distinguish between samples G and R. However, the spectra of samples G contain absorption band at 1223 cm^{-1}, which is missing in the spectra of samples R. Based on detailed analysis of FTIR spectra of all 19 pure inks on aluminium substrate, they can be divided into 13 distinguishable groups, which are listed in Table III.

Table III Distribution of writing means based on the presence of characteristic absorption bands

Group	1	2	3	4	5	6	7	8	9	10	11	12	13
Samples	G1	G3	G5	G2	R1	R2	R3	B1	B3	B6	B9	B10	B7
				G4		R4		B2	B4	B8			

Comparison of Different Methods for Measurement and Evaluations of the FTIR Spectra of Writing Means

The potential of FTIR spectra of writing means deposited on substrates in solid areas and lines for characterization of writing means was evaluated. The characteristic absorption bands of writing materials are better resolved in the FTIR spectra measured on solid areas in comparison with the spectra of lines. The IR absorption of lines is partly overlapped by strong absorption of paper cellulose. For example, in the spectrum of sample B7 (Fig. 3) measured on full area, all peaks in the wavenumbers 1585, 1365, 1173 and 700 cm^{-1} are better resolved than they are in the spectrum measured on lines. In addition, less significant absorption bands at 912, 754 and 740 cm^{-1} can be recognized.

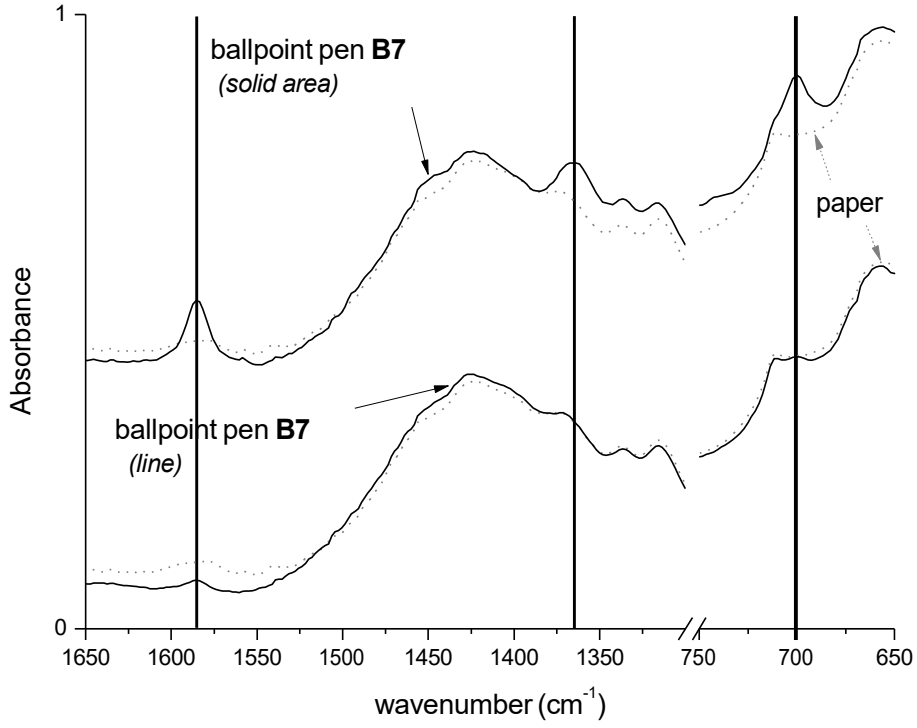

Fig. 3 Comparison of the ATR-FTIR spectra measured on solid areas and on lines (sample B7)

Further, the spectra obtained from the lines of writing means by conventional (macro) ATR-FTIR method and micro-ATR-FTIR methods were compared. For the micro-ATR-FTIR method also the influence of used tips — diamond and germanium — was evaluated. As can be seen in Fig. 4, the micro-ATR-FTIR method provides a better resolution of absorption bands of writing means, for example, at 1585 cm^{-1}.

For micro-ATR-FTIR using of both tips — diamond as well as germanium — is advantageous, as IR radiation penetrates into different depth — about 2 μm in the case of diamond, about 0.66 μm in the case of germanium, which allows to

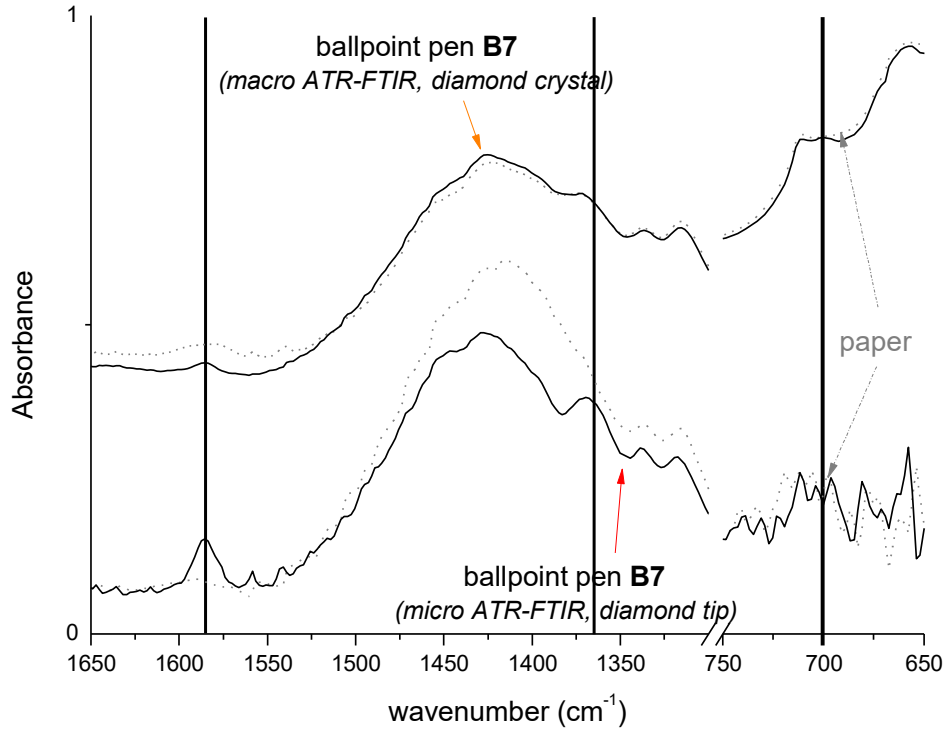

Fig. 4 Comparison of ATR-FTIR and micro-ATR-FTIR spectrum measured on line of sample B7

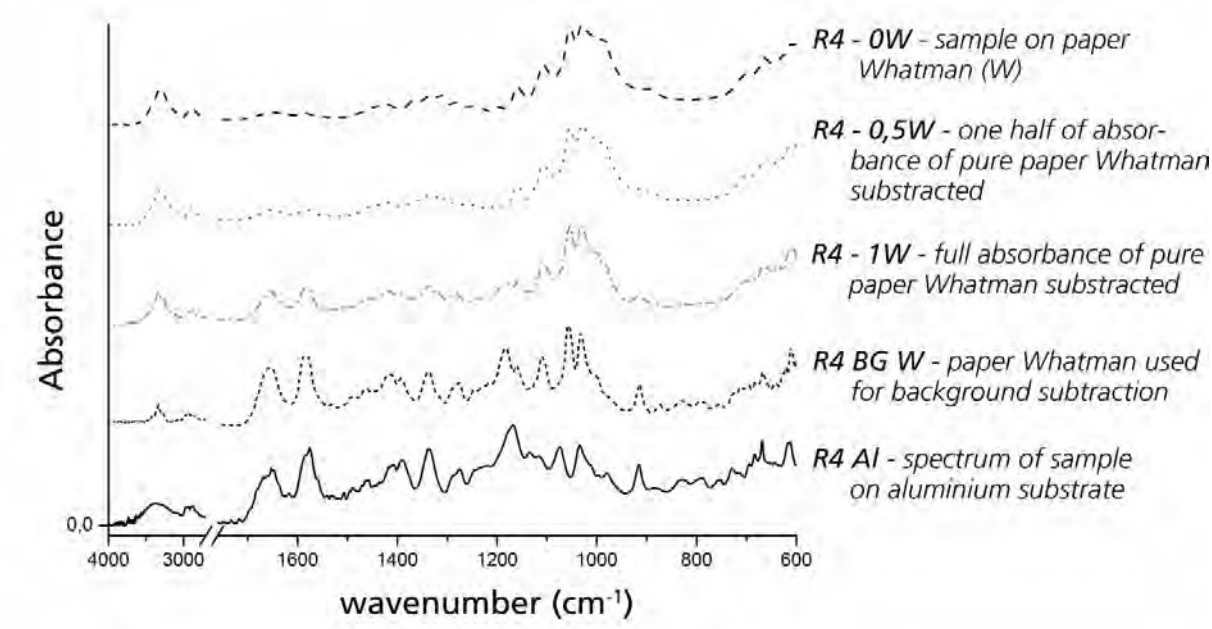

Fig. 5 Comparison of FTIR spectra obtained by different subtraction methods (sample R4, micro-ATR)

analyze writing means penetrated deeper as well as shallower into the paper.

With the aim to overcome the limited recognition of all characteristic absorption bands in the spectra of writing lines on paper in comparison with the

spectra on aluminium substrate, we tried to “subtract” the spectrum of the blank paper from the spectra of inks on paper after measurement and compare the various methods of subtraction (Fig. 5).

XRF Spectra

Different elemental compositions were found for samples of writing means B, G, R. Further differentiation is possible within the individual groups. According to the elemental composition, all 19 samples can be clearly divided into 9 groups (Table IV).

Table IV Distribution of writing materials according to elemental compositions

	B1, B3	B2	B4	B5	B6-B8	B9, G2, G4, G5, R	B10	G1	G3
Al	–	–	–	–	–	–	–	×	–
S	×	–	×	–	×	×	–	–	×
Cr	–	–	×	–	–	×	–	–	–
Mn	–	–	–	×	–	–	–	–	–
Fe	–	–	–	–	–	–	–	–	×
Ni	–	–	–	×	–	–	–	–	–
Cu	×	×	×	×	×	–	–	×	×
Zn	×	×	–	×	–	–	–	–	–

Conclusion

All performed analyzes provided various information about the properties, composition, and possible classification of the sample into certain group. Based on the microscopic examination and determination of common and different features of written record, the writing means can be classified into the 2 groups: ballpoint and gel/roller ball pens.

FTIR spectroscopy proved to be a useful tool in the analysis of the writing means. In examination of writing means by FTIR spectroscopy, the measurement at least on three different positions is recommended. For measurement of spectra of solid areas the method of conventional ATR-FTIR (diamond crystal) is adequate, for measurement of spectra of lines micro-ATR-FTIR method using diamond and germanium tip is more suitable. Exact position of measurement has to be checked microscopically.

Subtraction of spectra of substrate from spectra of writing means on

substrate is feasible; however, the spectrum of substrate should be taken in the closest proximity of the line.

Based on the characteristic absorption bands in the FTIR spectra, the writing means of the group B can be clearly distinguished from the writing means of the groups G and R. Also within these groups certain differences can be observed. Samples of the group of ballpoint pens (B), gel pens (G) and ink pens (R) have different elemental composition determined by XRF spectroscopy.

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