

CASE REPORT

QUESTIONED DOCUMENTS; CRIMINALISTICS

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Establishing of Chemical Composition of Printing Ink

ABSTRACT: The subject of the examinations was primarily court tax marks of 50 and 200 PLN, which were suspected not to be genuine. Both inks on the questioned marks as well as comparative genuine marks and inks sent by the manufacturer were analyzed. No information about their chemical composition was available from manufacturer. In the examinations, infrared (IR), visible, X-ray fluorescence, and Raman spectrometry were used. The examinations showed that inks and glue on the marks of both values were the same as samples of those sent by the manufacturer. Discrepancies in some results were observed probably due to contamination, that is, an accidental presence of the foreign substance on the surface (e.g., sweat, saliva while sticking the marks to the surface or physical handling of the documents). It was concluded that there are original (genuine) court tax marks.

KEYWORDS: forensic science, criminalistics, printing inks, court tax marks, infrared spectroscopy, Raman spectroscopy, visible spectroscopy, X-ray fluorescence

Writing or printing materials used for producing documents, such as ballpoint paste, fluid ink, toner, and printing ink, are often the subject matter of physicochemical examination for forensic purposes.

The examination of writing or printing materials superimposed on the paper background is necessarily limited to comparative qualitative analysis. The reason for this is not only the lack of exact information as to the composition of the materials, protected by law, but also the process of drying of the material on the surface which results in the discrepancy between the composition of the material superimposed on the document and its composition prior to the superimposition. The changes brought about by the drying process are dependent on various conditions and are difficult to evaluate.

As the sample provided for the analysis is usually small, the combination of spectroscopic and microscopic methods is required (1–6). In a few cases, the extraction of the sample is necessary, but the damage done to the document is so insignificant that the principle applied in forensic sciences for nondestructive method of analysis is essentially maintained (7–9).

The subject of the current examinations was uncommon documents, that is, court tax marks, whose authenticity had been questioned. The documents were handed in by the same person, at different times and in different places. The results of technical examination pointed at their authenticity. Physicochemical examination of the inks and the glue present on the marks was called for to support the claim of the authenticity.

The aim of the experiment was to obtain information as to the composition of the inks and the glue provided by the manufacturer

and of those present on the questioned marks and the comparison of both.

Materials and Methods

The subject of the examinations was comparative inks (F1–F6) supplied by the manufacturer and marks from four court summons and comparative marks also supplied by the manufacturer. The marks of the value of 50 and 200 PLN were analyzed. The superimposition on each kind of the mark consists of three graphic elements: inscription (A), pattern (B), and background (C). Each element is printed with a different ink; six different types of ink were used in the examination: four dark-blue ones, one light-blue one, and one yellow-brown one. For printing the 200 PLN value mark, three kinds of dark-blue ink are used, and for printing the 50 PLN mark, light-blue, dark-blue, and yellow-brown inks are used, as shown in Fig. 1.

The elemental composition of the comparative inks was examined by means of X-ray fluorescence spectrometry, using an ED 2000 spectrometer produced by Oxford Instruments Ltd. (Abingdon, Oxfordshire, UK). The polymer composition of inks and glue on the marks was analyzed by infrared (IR) spectrometry method (FTS 40Pro spectrometer with the microscope UMA 500, produced by Digilab [Bio-Rad/Digilab, Cambridge, MA]). For comparative inks and inks in the marks, visible and Raman spectra were obtained. For the visible spectra, a microspectrophotometer was used (Zeiss Axioplan 2 microscope [C. Zeiss, Oberkochen, Germany], detector DAD, software programs Tidascop and J&M Spectralys 1.81 [J&M Analytik AG, Essingen, Germany]). For the Raman spectra, a Raman spectrometer Renishaw InVia with microscope (Renishaw, Wotton-under-Edge, Gloucestershire, UK) and the excitation sources of 514, 633, and 785 nm were used. Both of these provided information about the pigment composition. For each ink, 10 measurements were made. The reproducibility was estimated by visual comparison of spectra.

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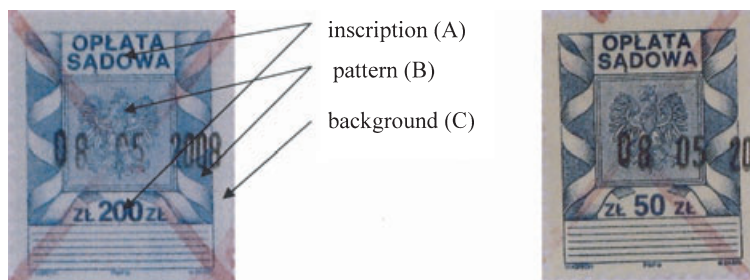


FIG. 1—Graphical elements on court tax marks.

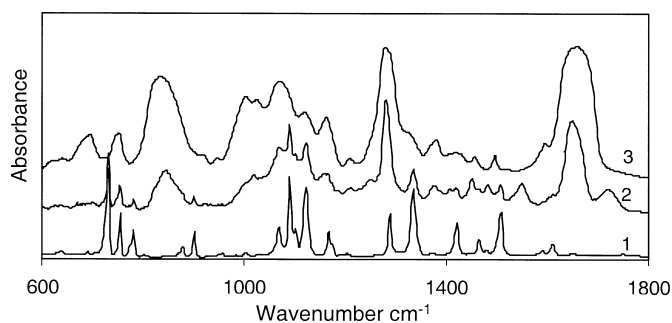


FIG. 2—IR spectra of F6 comparative ink (2), nitrocellulose (3), and copper phthalocyanine (1).

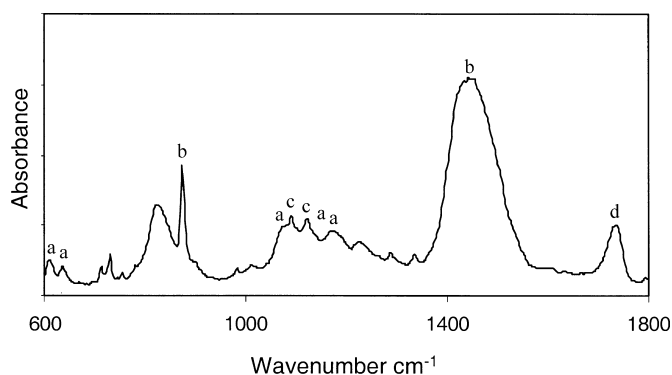


FIG. 3—IR spectrum of F3 comparative ink (a, barium sulphate; b, carbonates; c, copper phthalocyanine; and d, polyester).

Results and Discussion

On the examined and the comparative marks, regardless of the value, there was used the same kind of glue. The polymer basis of glue was vinyl acetate.

The information obtained from spectra in IR (Figs 2 and 3), Raman, and X-ray made it possible to divide the comparative inks (F1–F6) into groups depending on the particular feature (Table 1).

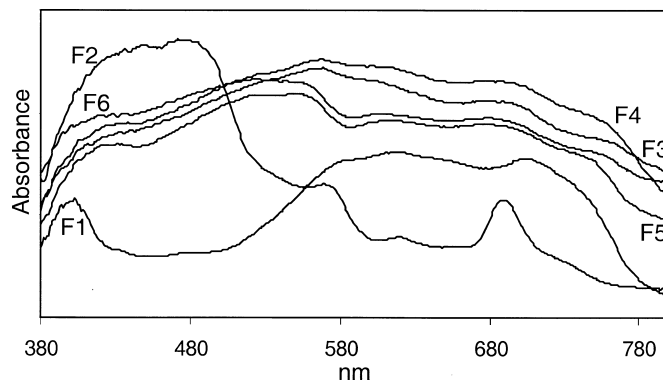


FIG. 4—Visible spectra of F1–F6 comparative inks.

The polymer basis was nitrocellulose (dark-blue inks F5 and F6, light-blue F1, and yellow-brown F2) or unidentified ester (dark-blue inks F3 and F4). The inks contained only an organic pigment (copper phthalocyanine [dark-blue inks F5 and F6, light-blue F1]) or an organic pigment (copper phthalocyanine) and inorganic pigments (barium sulphate) and some carbonates (dark-blue inks F3 and F4). For the yellow-brown ink F2, it was not possible to determine the kind of pigment used—it is probably an organic pigment, such as hydrochloride pigments being suggested by the high content of chlorine. The high content of copper indicates that copper phthalocyanine is the main pigment in inks F1, F5, and F6, the high content of calcium indicates that the main pigment in ink F3 is calcium carbonate, and the high content of sulphur indicates barium sulphate as the main pigment in ink F4. Visible spectra (Fig. 4) did not differentiate samples F3, F4, F5, and F6. As a result of all applied spectrometric methods, it was not possible to differentiate between inks F5 and F6 (Table 2). The possible differences between these inks are solely connected with the quantitative and not the qualitative content. Qualitative differences in the element composition are visible for inks F3 and F4 (Table 1).

Raman spectra of the comparative inks (F1–F6), obtained by excitation under radiation of the wavelength of 785 nm, are similar to the spectra of ink from graphic elements (A–C) on marks of

TABLE 1—The color and composition of the comparative inks (F1–F6).

Ink	Color	Elements	Resin	Pigments/Fillers
1	Light blue	Cu, S, Si, Fe, Ca, Zn, Zr	Nitrocellulose	Copper phthalocyanine
5	Dark blue	Cu, S, Ca, Si, Ti, Zr, Fe	Nitrocellulose	Copper phthalocyanine
6	Dark blue	Cu, S, Ca, Si, Ti, Fe, Zr	Nitrocellulose	Copper phthalocyanine
3	Dark blue	Ca, Y, V, S, Cu, Sr, Si, Ba	Polyester	Barium sulphate, carbonates, copper phthalocyanine
4	Dark blue	S, Si, Y, Ca, Fe, Cu Sr, Ba, V	Polyester	Barium sulphate, carbonates, copper phthalocyanine
2	Yellow-brown	Cl, S, Si, Cu, Zn, Zr, Ca	Nitrocellulose	Unknown

TABLE 2—A comparison of the composition of the comparative inks (F1–F6).

F4	F5	F6	F3
PS	NS	NS	F3
	NS	NS	F4
		S	F5

S, similar; NS, not similar; PS, partly similar.

TABLE 3—A comparison of Raman spectra of the comparative inks (F1–F6) and the corresponding inks (A–C) on court tax marks.

Mark	Inks	Excitation			
		514	633	785	
50 PLN	C	2	S	NS	S
	B	4	S	S	S
	A	6	NS	NS	S
200 PLN	C	1	NS	S	S
	B	3	S	S	S
	A	5	NS	S	S

S, similar; NS, not similar.

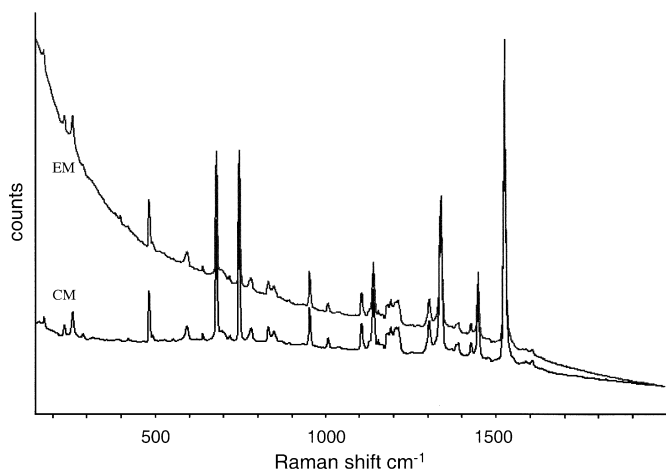


FIG. 5—Raman spectra (633 nm) of the comparative material (CM; ink F4) and the evidence material (EM; B ink on 50 PLN mark).

both values (Table 3). Raman spectra obtained for the comparative inks F3 and F4, regardless of the wavelength of the excitation radiation, are similar to the spectra of ink used in both types of marks (Fig. 5). For the excitation wavelength of 514 nm, no similarities between spectra were found for inks F5 and F6 and the corresponding spectra of inks from inscriptions (A) on marks of both values and similarly between spectra of the comparative ink F1 and the spectrum of the background (C) ink from the mark of the value of 200 PLN. While examining mark of 50 PLN under the excitation wavelength of 633 nm, no similarity was found between spectra for ink F2 and for the ink in the background (C), similarly as between spectra for ink F6 and the ink in the inscriptions (A) (Fig. 6). However, the observed discrepancies were not repeatable and did not occur in all examinations of the marks of this particular value. Possibly, superimposed substances, such as sweat and fat, may have resulted in the lack of the similarity between the obtained spectra. Both the marks and the summons with glued marks were prone to contamination, that is, the superimposition of trace amounts of foreign substances during the process of sticking the marks and of the physical handling of them.

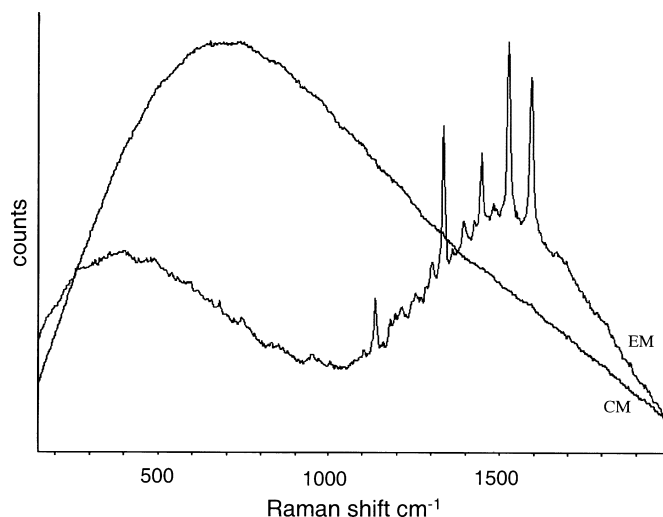


FIG. 6—Raman spectra (633 nm) of the comparative material (CM; ink F6) and the evidence material (EM; A ink on 50 PLN mark).

Conclusion

As a result of the performed examination, it was found out that the glue on the questioned marks and the inks used in their preparation were similar with the comparative material, which strongly suggested their authenticity. The application of micromethods without the need of extraction of a sample enabled us to examine the ink directly on the summons in a nondestructive manner. However, the evaluation of the influence of possible contamination on the results of examinations was difficult for unknown treatment of documents in the past.

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