Determining the sequence of crossed lines by FT-IR-ATR-Microscopy

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Introduction
In recent years, due to the widespread use of laser printers and photocopiers, offences in connection to documents of questioned origin have become more frequent. The similarity of physical and chemical properties of printer toners and pen inks makes the solution of these cases a difficult task for forensic experts, because in most instances only minor differences can be identified. Fraud, counterfeiting, blackmailing, and threatening letters are a few of the crimes requiring discrimination and identification of printers and inks. Concerning fraud cases the examiner has to find out whether the original document had been altered. In case of counterfeit documents, the sequence of crossed printed text and pen ink line needs to be determined in order to answer the frequently asked question: ‘Which was first: autography or printed text?’ This question used to demand lengthy investigation from the experts and the answer given by conventional methods was more or less subjective. Infrared microATR, in contrast to conventionally used optical microscopy techniques, is a simple, fast, and non-destructive method for analysis. It does not require sample preparation and provides an objective result, leaving the documents intact. This note describes the application of the microscopy-based infrared ATR for the chemical determination of thin layers on the surface of documents. Printer toners and pen inks usually create surface layers of a few µm thickness that can be investigated in-situ by this new method. In addition to the analysis of their physical character, the chemical analysis of printer toners and pens inks is considerably helpful for forensic examination.
Method of experiment

Spectra were collected with a Bruker VERTEX 70 Fourier transform infrared spectrometer equipped with a Bruker HYPERION 2000 microscope with a 20x ATR objective (Figure 1.). To identify the region of interest in a document, the ATR objective is used in the visual mode. During the infrared analysis the documents are contacted by the tip of the germanium (Ge) crystal (100 µm in diameter), after the ATR objective was switched to the infrared mode. With this approach, infrared spectral information is gathered only from the surface layer of the sample to about ~1/2 µm depth. To illustrate the trace of this contact, Figure 2 shows minor, faint, and round-shape imprints of the ATR crystal on the surface of a letter from a document of interest. All measurements were performed for 30 sec at 4 cm⁻¹ resolution. Bruker Optics’ Opus 5.5. software was used for manipulation of the resultant spectra (e.g. baseline correction, atmospheric compensation etc.).

In relation to questioned documents, the most common and indistinguishable samples are the black printed and black handwritten documents. Examination of these samples by other optical analytical methods is very problematic due to the low contrast of different black inks. In order to demonstrate the strength of FT-IR-ATR-microscopy for this task, only black toners of laser printers and black pen inks were used. Samples were printed with three different laser printers brands and a number of different models (2-14) from each brand. Handwritten samples were made with three different black pens. For determination of the sequence of crossed lines we used two clearly distinguishable laser printer toners for our experiments. The lines printed by the two printers crossed each other or in the other example were crossed by a line drawn with pen ink.

Results and discussion

Analysis of printed documents

The main component of dry black printer toners is polymer resin which creates a few micron thick black surface layer on the paper. This layer can be analyzed by FT-IR microATR without removal of the ink from the paper substrate of the document. Figure 3.A shows a typical spectrum of paper with its characteristic bands of cellulose fibers. Figure 3.B shows the spectrum of printer toner I. Here, the peaks of cellulose are absent from the spectrum of the printed document. Printed matter can be investigated in situ by making contact with the ink with ATR crystal and collection of the infrared spectrum without interference from the paper. Because the penetration depth of the infrared radiation for ATR with a germanium crystal is limited to about 1/2 µm, the analysis depth is smaller than the thickness of the printed layer.

Analysis of handwritten documents

On a handwritten document, liquid pen inks penetrate into the micro fibers of paper, so that the upper side of the micro fibers of paper are saturated with pen ink. Therefore, the infrared spectrum of this region of the document reveals spectral features of the paper as well as of the ink. To illustrate this problem, Figure 4 shows the spectrum of paper (A) and the spectrum of pen ink (B). In the spectrum of the
handwritten document (C), characteristic infrared peaks of pen ink are superimposed with those of paper. However, since several absorption bands of pen ink and paper are separated, the characterization of pen inks is still feasible.

Determination of the sequence of crossed lines
By the identification of the upper layer, the sequence of crossed lines of printer toners or printer toner and pen ink can then be determined. To find the exact positions of line crossing points within the documents, the ATR objective was used in the visual mode. For analysis of the chemical composition of the surface layer, the infrared spectra were measured after the ATR objective was switched to the infrared mode. Two documents were printed with two different laser printers.

Printers can sometimes be distinguished by the unique imprint of dots that make up the printed numbers and letters. Figure 5 shows that the determination of the sequence of the dots from Printer toner I and text from Printer toner II with optical microscopy is nearly impossible.

In order to identify the top layer, the crossing point was measured by FT-IR micro ATR (Figure 6). In B and C, the spectra of the pure printer toners are shown. The spectrum of the line crossing (A) shows high similarity with the spectrum of printer toner I. The characteristic bands of printer toner II are missing. This result reveals that toner I was printed on toner II, and moreover that the penetration depth of the infrared radiation was smaller than the thickness of each printed layer. Figure 7A presents the ATR infrared spectrum of a crossing line point, taken in the same way, but after the sequence of printing was changed. Here, the spectrum reveals only spectral features from toner II (B) with none of the specific features from toner I (C). In the case of a crossing of printed subjects and a pen ink line (Figure 8.A-B), the top layer cannot be recognized by visible inspection. Figure 9A shows the ATR spectrum at the line crossing point, when the toner line is above the pen ink line. The spectrum is very similar to the spectrum collected from printed toner B, since the penetration depth of infrared radiation is smaller than the thickness of the printed layer. The characteristic bands of pen ink (C) are missing in the spectrum. Figure 10A shows the spectrum of the crossing line point of lines, where the pen ink line was drawn above the toner line. Since the penetration depth of infrared radiation is larger than the thickness of the pen ink layer; the spectrum combines features of the pen ink and the printer toner.

Advantages of microscopy-FT-IR-ATR technique
These results demonstrate that FT-IR ATR-microscopy is a very suitable technique for the examination of printed and handwritten documents. The technique allows for identification of different types of printer toners and pen inks.
by their chemical fingerprints. Further, the sequence of crossed lines can be determined by measuring the surface layer at the line crossing point of the documents. Lastly, the measurement does not destruct the document and does not require sample preparation. This instrumental analytical method is objective and easy to interpret facilitating the forensic comparison of documents.

Figure 8 A-B: Optical microscopy image of printed documents. A The dots typed by Printer I are above the text written by pen ink; B The text written by pen ink is above the dots typed by Printer I.

Figure 9 A-B-C: A IR spectra of a crossing point of printed matter and pen ink line when the dots typed by printer I are above the text written by pen ink; B Printer toner I; C pen ink

Figure 10 A-B-C: A IR spectra of a crossing point of printed matter and pen ink line when the text is written by pen ink is above the dots typed by Printer I; B pen ink; C Printer toner I.

Figure 10 A-B-C: A IR spectra of a crossing point of printed matter and pen ink line when the text is written by pen ink is above the dots typed by Printer I; B pen ink; C Printer toner I.