TECHNICAL NOTE

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A Simple Method for Sampling Photocopy Toners for Examination by Microreflectance Fourier Transform Infrared Spectrophotometry

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ABSTRACT: A simple method for sampling photocopy toners by thermal transfer to metallic stubs is described. The sampling causes only negligible destruction to the photocopy original. The toner material transferred to a metallic stub is analyzed by microreflectance FTIR. This method shows a good reproducibility, is sensitive and applicable to small areas on the transferred material.

KEYWORDS: questioned documents, photocopy toner, sampling, infrared spectroscopy, microreflectance FTIR, document examination

Many different techniques have been reported in the forensic science literature for comparing photocopy toners and these methods were recently reviewed [*1*]. However, the sample handling has often been relatively difficult. A simple method for removing a sample of toner from paper for examination by pyrolysis gas chromatography has been reported by Munson [*2*]. The method involves transferring the toner to a glass sampler by pressing a hot microscope slide onto the photocopy. The transferred toner is scraped from the glass for further examination.

In this study, the toner material is transferred in a similar way to a metallic stub for direct examination by microreflectance fourier transform infrared spectrophotometry (microreflectance FTIR). The whole examination is very fast and requires only a few minutes.

Experimental

The Transfer of Toner Material

Metallic stubs designed for use in a scanning electron microscope (SEM) were used to lift samples of toner from the paper. These stubs are cylindrical in form, with a diameter of 10 or 13 mm and a height of 5 mm; the material is aluminum. The surface of stubs was washed with ethyl acetate prior to use. Ethyl acetate easily removes toner material from metallic surface and stubs can therefore be reused repeatedly.

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A stub is placed over the sampling area. The backside of the stub is heated by pressing a hot soldering iron (ERSA 150, 150 watts, with exchangeable tip) equipped with stainless steel cylindrical tip, 10 mm in diameter. The soldering iron was connected to a transformator (isolation transformator, 0-250V/3A). The voltage applied was 130 V, which resulted in an equilibrium temperature at the tip of about 200°C. The temperature was measured by touching the soldering tip with a fine thermocouple. The transfer of toner material was carried out for 1 minute. An example of toners transferred to an aluminum stub is shown in Fig. 1*a*. The appearance of the transferred toners is similar to that reported by Munson [*2*]. Only a small part of the toner material is transferred from a photocopy to a metal stub. The text on the original photocopy is clearly readable and the damage to the original text is seen normally only under a microscope. Paper fibers were never observed in the toner material on the metal surface when the transferring procedure was carried out with different kinds of dry toners on different papers. The heating procedure described above generally did not cause any visible destruction to the photocopy paper. A choice of higher supply voltage and consequently higher tip

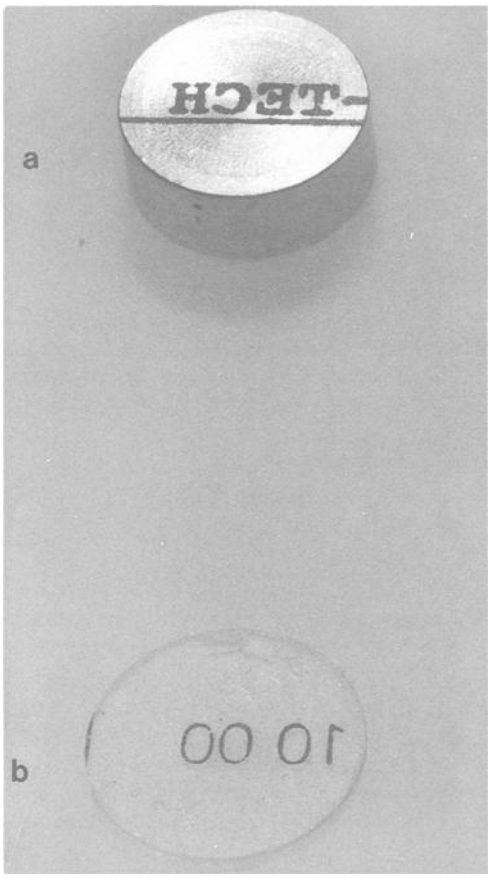

FIG. 1—a) *Aluminum stub with a sample of toner material transferred. The transfer was achieved by heating the stub for 1 minute with a soldering iron, equipped with cylindrical tip, 10 mm in diameter. The equilibrium temperature reached 200°C.* b) *KBr pellet with a sample of transferred toner. This sample is suitable for microtransmittance FTIR.*

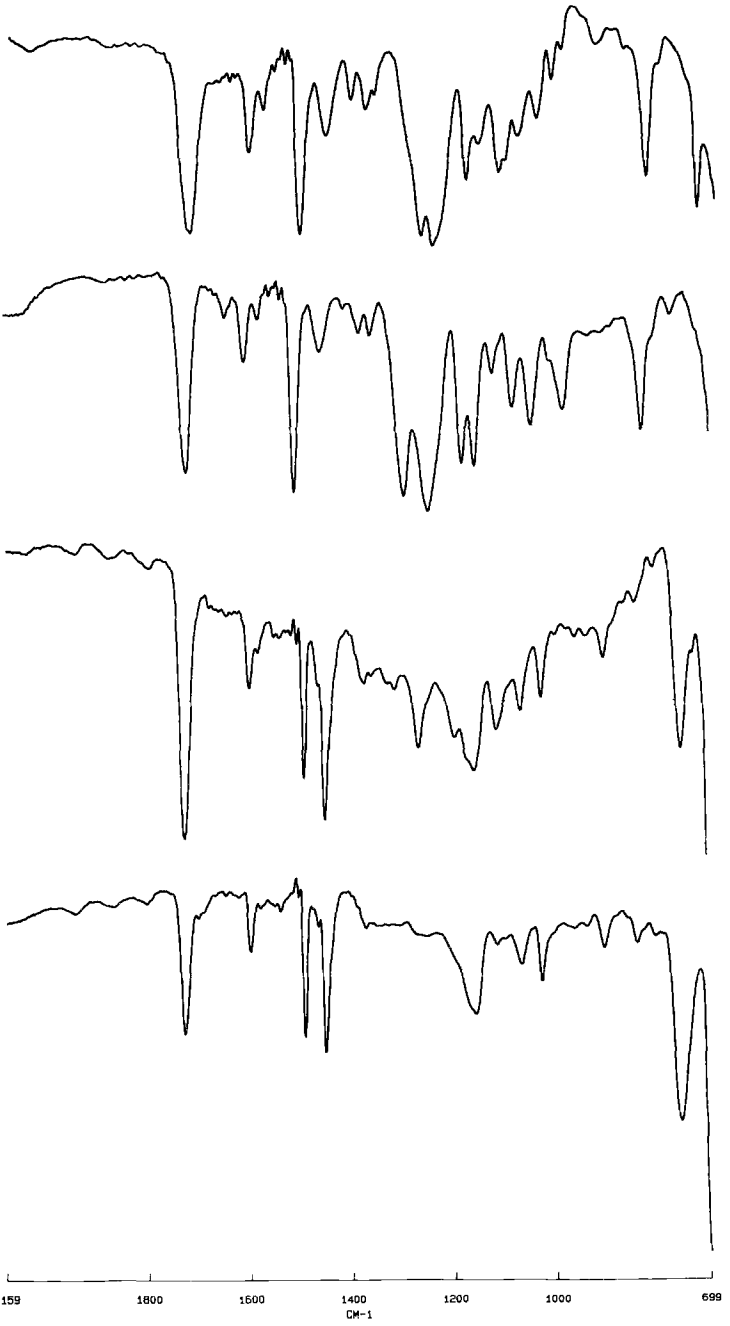

FIG. 2—*Microreflectance FTIR spectra of four different black toners. From top—Canon 5060, Océ 1850, 3M 536 Copier and Mita DC 1205. Only a part of the whole spectra is shown. The area measured was about 0.5 × 0.3 mm.*

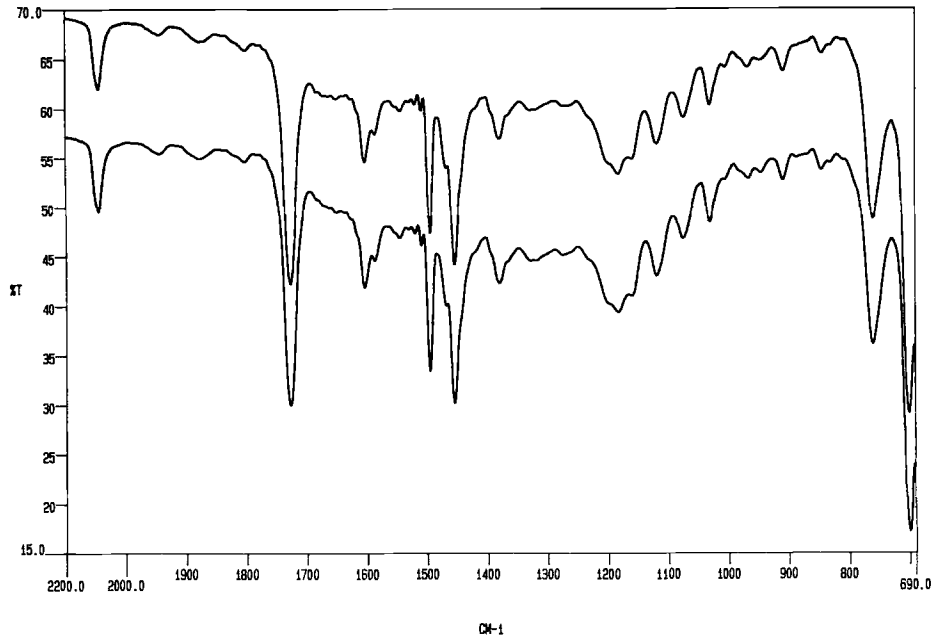

FIG. 3—*Microreflectance FTIR spectra of toner from two suspect documents. Each spectrum is an average of two separate measurements on different areas of materials transferred to metallic stubs. The two materials were indistinguishable by this technique.*

temperature resulted in a yellow discoloration of the paper. A document treated with ninhydrin will be discolored in the whole contact area. Wet toners cannot be transferred thermally to a metal stub.

Some experiments were carried out to transfer toner material to KBr-pellets suitable for microtransmittance FTIR spectroscopy. This was best achieved by placing a KBr pellet on a plane surface and putting a photocopy with the text to be examined over the pellet. A piece of metal with an area similar to the KBr pellet (that is, Al-stub) was laid on the backside of the photocopy in a position corresponding to the text to be transferred. The transfer of toner material was then performed by heating the backside of the metal stub with the soldering iron as described above. Higher temperatures were necessary to transfer toners to KBr pellets. The procedure was more destructive to a photocopy (discoloration etc.) and some toners did not adhere to the KBr lifter. Paper fibers were sometimes observed in the transferred material. KBr-pellets are also fragile and care must be taken not to break them. These disadvantages make KBr pellets less suitable as sample lifters for toners. Figure 1*b* shows a KBr pellet with a toner material transferred thermally.

Measurement of Reflectance FTIR Spectra

Measurements of microreflectance FTIR spectra were performed on Perkin Elmer FTIR spectrophotometer, model 1725 X, equipped with Spectra-Tech IR-Plan™ microscope. The microscope objective was Reflachromate™ (15 × 0.58 N.A.) and the detector was a narrow band 0.25 × 0.25 mm MCT (mercury-cadmium-telluride). The reflectance spectra were normally collected from 0.5 × 0.3 mm spots of transferred toner material on aluminum stubs. Spectra of sufficient quality were obtained for sampling areas of

about 0.1 × 0.1 mm. The resolution was 8 cm^{-1} and the gain was 4. Two hundred scans were averaged for each sample. This required 2 minutes of instrumental time. The reflections from the clean surface of the stubs were used as reference spectra. Perkin Elmer software IRDM was used for data handling.

Results

The microreflectance FTIR of photocopy toners transferred to a metallic stub is a sensitive analytical technique. The IR beam passes the material twice, since the metallic surface reflects most of the incident beam. One lift from the average size typed letter is sufficient for several analyses on various parts of the letter. The analysis is nondestructive and may thus be repeated on the same specimen without limitations.

Figure 2 shows the FTIR spectra obtained for four different kinds of black toners. Only parts of the spectra with the most obvious differences between the samples are shown. The microreflectance FTIR could not be applied to spectra regions below 700 cm^{-1} due to limitations of the detector.

Microreflectance FTIR spectra are similar to conventional FTIR spectra obtained for extracts from the same toner material. Any contribution of specular reflectance from a specimen surface to the spectra seems small.

The reproducibility of this method is good provided that the transfer of toner material is carried out under the same conditions (time, temperature). For best results, several measurements may be performed on various parts of the transferred material and the average spectra calculated. Figure 3 compares toners from two photocopies encountered in routine casework. Each spectrum is a mean of two separate measurements on different parts of the transferred toners. The documents were examined to investigate if they were made on the same photocopier. The spectra in Fig. 3 are indistinguishable by this method, which supports the suspicion of them having the same origin. The agreement between the two toner materials is so good that second derivatives of their FTIR spectra show almost perfect matching. It may also be noted here that both documents were treated with ninhydrin before the examination. This treatment did not seem to influence the results.

Some experiments were carried out in attempts to transfer color toners. The same technique may be used to transfer toners from color photocopies as that of black toners. Because the microreflectance FTIR spectroscopy of toners transferred to metal surfaces is applicable to small areas (under 0.1 × 0.1 mm), the method has a good potential to analyze the separate colors in a copy.

Finally, it can be noted that a toner material transferred to aluminum stubs may be examined by additional techniques used to characterize toners. X-ray microanalysis in a SEM may be performed directly on the stubs as well as the distribution of inorganic particles (for example, Fe) in toners by backscatter electron detector imaging. Toner material may be scraped from metallic stubs for further analyses, for example, by pyrolysis gas chromatography.

References

[1] Totty, R. N., "Analysis and Differentiation of Photocopy Toners," *Forensic Science Review*, Vol. 2, No. 1, June 1990, pp. 1–23.

[2] Munson, T. O., "A Simple Method for Sampling Photocopy Toners for Examination by Pyrolysis Gas Chromatography," *Crime Laboratory Digest*, Vol. 16, No. 1, January 1989, pp. 6–8.

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