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Examination of paper and toner in page insertion/substitution cases using TLC, GC-MS and FT-IR microspectroscopy

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The comparison of paper and toner of each sheet (or certain pertinent pages) of a multi-page document produced with toner-based electrophotographic technology may help: (A) to determine if there have been page insertions or page substitutions; or (B) to test a hypothesis that multiple documents, which were supposed to come from different sources, have a common source.

This article shows that a combination of three analytical methods, thin-layer chromatography (TLC), gas chromatography-mass spectrometry (GC-MS), and reflectance Fourier transform infrared (FT-IR) microspectroscopy, provides high discriminating power with regard to both paper and toners that cannot be distinguished by non-destructive (optical) techniques. These three analytical methods may allow the examiner to achieve a high level of certainty when evaluating which of two competing hypotheses is more probable:

- **(Case A) the "prosecution" hypothesis, H_p, that certain pages in the document have been substituted, or the "defense" hypothesis, H_d, that no page substitution has occurred since the initial production of the document;**
- **(Case B) the "prosecution" hypothesis, H_p, that multiple documents, which were supposed to come from different sources, have a common source, or the "defense" hypothesis, H_d, that all the documents came from their respective origins as indicated on the documents.**

Introduction

Forensic document examiners are often asked to determine whether there is evidence showing that one or more pages of a multi-page document produced with toner-based electrophotographic technology were inserted or substituted. A common approach that is used to discover indications of page substitution involves non-destructive physical examinations including visual, microscopic and other optical examinations [1-4]. These types of non-destructive physical examinations include, but are not limited to: examining handwritten information and/or writing ink[1] (if present) on the document; identifying and comparing the printing or reproduction process; establishing whether or not the same typeface has been used throughout; assessing page format (alignment, spacing), "trash" marks, print quality, and toner morphology (using a proper magnification) from page to page; examining optical characteristics of paper and toner, such as color, fluorescence (when illuminated by short- and longwave UV light), and infrared absorption/lu-

[1]This may allow discrimination between inks appearing (or pens used) on pertinent pages of a multi-page document. For example, in some cases, the microscopic examination may reveal a peculiar pattern of burr striations and/or other "defects" present within the confines of written strokes that might allow the examiner to individualize the writing instrument through its performance characteristics. If such a writing instrument was used to produce entries on various documents that were supposed to come from different sources and/or be produced a long time period apart (*e.g.*, years apart), this would indicate that the documents have a common source and were not prepared a long time period apart as purported.

minescence; examining watermarks and security fibers that might be embedded in the paper; and examining and comparing staple holes, indentations or marks from the paper transport mechanism, etc. If the non-destructive physical methods did not provide the examiner with sufficient evidence to determine whether or not there have been page insertions/substitutions, analytical (physical and chemical) methods should be used for examining and comparing the paper of the pertinent pages of the document, as well as the toner used to produce machine-generated texts on the pages of the document.[2]

Multiple analytical procedures for analyzing paper and toners have been published and some of these publications have been referred to in the American Society for Testing and Materials (ASTM) International guides [1-3]. Thin-layer chromatography (TLC) has been used for the analysis of black toners containing dyes mixed with the carbon black pigment [5,6]. Color toners have been analyzed by TLC [7,8] and gas chromatography-mass spectrometry (GC-MS) [9]. The majority of publications regarding the analysis of black toners include the use of pyrolysis GC-MS [10,11], scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) [10,19], and various types of Fourier transform infrared (FT-IR) spectroscopy [10-14]. Recently, FT-IR microspectroscopy (a microscope attachment allows the infrared beam to be focused on an extremely small area) has been extensively used for the characterization and differentiation of black toners [15-20,25]. A combination of optical microscopy and spot color tests has been used for many years in paper fiber analysis allowing the type of fibrous raw materials used for making the paper of documents to be determined [21]. Various components of paper, such as tinting materials, optical brighteners [22], and sizing components of paper [23], can be separated and detected by TLC and used to discriminate between paper samples. A number of other analytical methods have been used for the analysis and comparison of paper, including X-ray diffraction [24], IR spectroscopy [24-26], and pyrolysis GC [27].

This article shows that TLC, GC-MS and reflectance FT-IR microspectroscopy, especially when these three analytical methods are used in combination, typically provide high discriminating power with regard to both paper and toners that cannot be distinguished by non-destructive (optical) techniques. The procedures of using TLC, GC-MS and reflectance FT-IR microspectroscopy for the analysis of paper and toner are described in detail below.

Methods and Materials

Toner and Paper Samples – Black toner samples consist of prints from various Hewlett Packard office machines (most of the samples, which cover a period of approximately 8 years, are from HP LaserJet 3030 All-in-One, HP LaserJet P3005d, and HP LaserJet P3015 printers). White paper samples include HP Office paper (92 brightness, 20 lb weight, manufactured in USA), A4 copy paper (unknown manufacturer), OfficeMax Multi Purpose paper (96, 20 lb, USA), HP Color Inkjet paper (96, 24 lb, USA), and OfficeMax Laser paper (96, 24 lb, USA). Other samples of toner and paper, as well as their FT-IR spectra, TLC and GC-MS chromatograms discussed in this article, relate to some of the actual case examinations conducted by this author.

Sampling Device – A hypodermic needle-like apparatus, the Harris Micro-Punch™ (Electron Microscopy Sciences, Hatfield, PA), which removes *ca.* 0.5-mm samples (micro plugs) of paper and toner-on-paper. The bored out paper and toner samples are removed with a plunger.

Extracting Vessels – Grace 2-mL (12 x 32 mm) capped, screw thread, standard mouth clear vials containing Alltech 100-microliter glass inserts with self-centering polyethylene springs.

TLC Materials and Procedure – Toner and paper samples (1 to 3 micro plugs) were extracted in dimethylformamide (*ca.* 1 microliter) for 5 to 15 minutes, and the extracts were applied on high performance (HP) TLC silica gel 60-F_{254} (10 x 10 cm) pre-coated glass plates (Merck, Germany). The plates were developed sequentially using two mobile phases: first acetone:hexane = 1:4, followed by (after the plate was allowed to dry for about 5 minutes) ethyl acetate:isopropanol:water:acetic acid = 30:15:10:1.[3] Resulting chromatograms were observed and photographed (after

[2]Other materials, such as writing inks, if present on pertinent pages of a multi-page document, should also be analyzed and compared using analytical methods, but in the present article only the examination of paper and toner will be considered.

each development) under daylight and UV light (254 and 365 nm).

GC-MS – Paper samples (1 to 3 micro plugs) were extracted in *ca.* 2 microliters of chloroform for about 15 minutes. Toner samples (1 to 3 micro plugs) were extracted in *ca.* 10 microliters of chloroform for approximately 1 hour.[4] Extracts were analyzed using an Agilent 6850 gas chromatograph equipped with a split/splitless injection system interfaced with an Agilent 5975C mass selective detector.

GC Conditions and MS parameters:

Column: DB-5MS, 30 m x 0.25 mm ID x 0.25-micrometer film thickness (cross-linked 5%-phenyl-95%-dimethylpolysiloxane)

Liner: splitless, single-taper, deactivated glass wool

Carrier: Helium (column flow 1 mL/min)

Oven program: Isothermal for 1.2 min at 35°C, program 15°C/min to 270°C and hold for 10 min

Injection: *ca.* 1 microliter, pulsed splitless, T=260°C

Pressure pulse: 120 kPa until 1.2 min

Purge flow to split vent: 30 ml/min at 1.2 min

GC/MS transfer line: 280°C

Tune: autotune

Scan range: 45 - 450 atomic mass units (amu)

FT-IR Microspectroscopy – Mid-infrared spectra were obtained using a Perkin Elmer AutoIMAGE™ FT-IR microscope system including a Spectrum GX FT-IR spectrometer. The paper blank and toner-on-paper samples (0.5 mm in diameter) were placed on a piece of Scotch removable double-sided tape. The side of the tape that did not bear the samples was attached to the gold-coated glass mirror (used to calibrate the FT-IR in reflectance mode by running background spectra) mounted on the stage of the FT-IR microscope.

FT-IR Measurement Conditions – For each sample analyzed, the measurement area was focused and defined directly on the on-screen live visible image of the sample using a 100 µm × 100 µm aperture. After the measurement area was chosen, the AutoIMAGE microscope system was switched from viewing (35 W tungsten halogen illuminator) to infrared mode and an IR spectrum was recorded. All the infrared spectra were recorded in reflectance mode in which the surface of the sample was illuminated by the mid-IR energy (FT-IR microscopy uses reflecting optics to focus the infrared light onto small samples) and the light reflected from the sample was collected and focused on the detector. The spectra were recorded in the 4000–700 cm^{-1} region (100 scans, 4 cm^{-1} resolution) using a liquid-nitrogen-cooled MCT detector sensitive from 700 cm^{-1} to beyond 4000 cm^{-1}. For each toner sample (0.5 mm in diameter) analyzed, the measurement area was a 100 µm × 100 µm square. The 100 µm × 100 µm measurement area was chosen, under the microscope, in a portion of the sample where: 1) the toner completely covers the paper; and 2) the distribution of the toner on the paper is most homogeneous.

Results and Discussion

FT-IR Microspectroscopy

Toners are very fine powders consisting primarily of a pigment (such as carbon black used in black toners), a binder that fixes the pigment to the paper (usually an organic polymer resin), and additives used to improve the properties of the toner. As seen under the microscope, toner coverage of paper on micro plugs of toner on paper taken from documents is typically non-homogeneous;

[3]Since the early 1980s, the author has been using these two mobile phases for the TLC analysis of both paper and photocopier toners [5].

[4]Some toner samples might create a gray suspension while being extracted in chloroform, especially if the vial was agitated during the extraction process. The suspended toner particles, if sampled by the syringe and injected in the GC, will irreversibly contaminate the liner requiring a liner change. To prevent this from happening this author increased both the volume of the extracting solvent (about 10 microliters) and time of extraction (1 hour). Additionally, care is taken not to agitate the vial during the extraction process and the aliquot of the extract is gently taken (avoiding stirring the extract) by the needle of the syringe from the upper portion of the extract (not from the lower portion of the extract that is close to the toner samples lying at the bottom of the vial). Other options to prevent suspended toner particles from sampling by the syringe and subsequently getting into the liner may include the use of an extracting solvent that does not dissolve the resins of toners (*e.g.*, acetonitrile) and/or the use of micro-centrifuge to centrifuge (separate) the extract from toner particles.

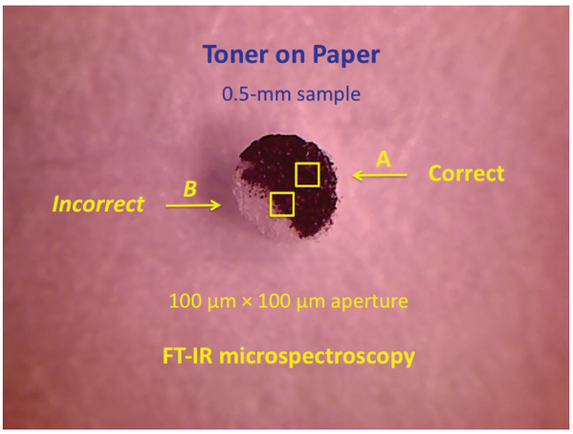

Figure 1. 0.5-mm sample of toner on paper photographed at 40x.

i.e., there are darker and lighter "clouds" of toner on paper, as well as areas of paper completely uncovered by toner.

Figure 1 shows a typical 0.5-mm sample (micro plug) of toner on paper photographed at 40x.

When choosing a measurement area for recording an IR spectrum of a sample of toner on paper, it is necessary to ensure that the measurement area is completely filled with/covered by toner (see Figure 1: the area indicated by the "A" arrow), *i.e.*, it does not contain any exposed areas of paper not covered by toner. If the measurement area contains patches of paper not covered by toner (see Figure 1: the area indicated by the "B" arrow), then the resulting IR spectrum will be a mixture of the IR absorption bands of both paper and toner. In such a case, some absorption bands of the binder of toner might disappear inside more intense absorption bands of cellulose and other components of paper. In other words, IR spectra obtained for the "A" and "B" measurement areas shown in Figure 1 may well be drastically different. Hence, it follows that if two toner-on-paper samples taken from the same printed entry are compared, and a measurement area for one sample contains toner only, and a measurement area for the other sample contains both toner and paper, the analyst might erroneously conclude that the compared toner samples represent the toners of different formulations.

The results of this study show that, if applied correctly, the reflectance FT-IR microspectroscopy is sensitive and reliable enough to discriminate between toners of different formulations, even those produced by the same manufacturer. Thus, the black toners produced by Hewlett Packard and used in the cartridges for the HP LaserJet 3030 All-in-One printer and HP LaserJet P3015 printer, respectively, have similar but clearly differentiable IR spectra shown in Figure 2.

The capabilities of the reflectance FT-IR microspectroscopy in the analysis of toner and paper are further illustrated in Figures 6 and 10 that follow.

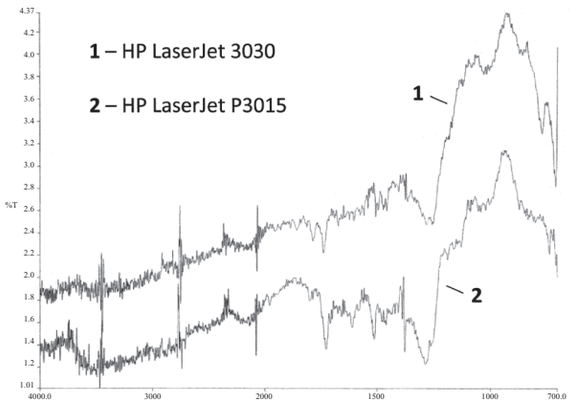

Figure 2. FT-IR spectra of two HP black toners. Note that the FT-IR spectrum of toner 1 has a doublet of intense bands at 712 and 775 cm^{-1} that are both absent in the FT-IR spectrum of toner 2. Besides, the FT-IR spectrum of toner 2 has two bands at 1515 and 1610 cm^{-1} that are both absent in the FT-IR spectrum of toner 1. These differences between the spectra show that the toners have different qualitative compositions.

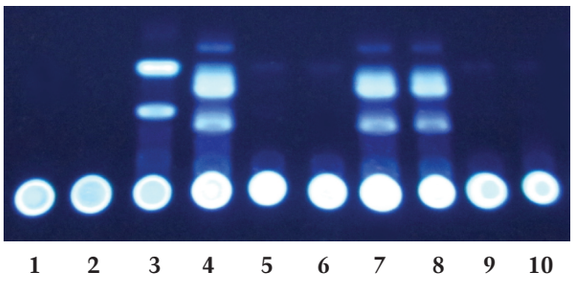

Figure 3. The thin-layer chromatogram obtained for the paper and toner-on-paper samples (photographed under long-wave UV light, 365 nm): 1 – HP Office paper; 2 – A4 copy paper (unknown manufacturer); 3 – OfficeMax Multi Purpose paper; 4 – HP Color Inkjet paper; 5 – OfficeMax Laser paper; 6 – toner (HP LaserJet P3015 printer) on OfficeMax Laser paper; 7 – copy paper (unknown manufacturer); 8 – toner (HP LaserJet P3005d printer) on the copy paper (unknown manufacturer); 9 – OfficeMax Laser paper; 10 – toner (HP LaserJet 3030 All-in-One printer) on OfficeMax Laser paper.

Thin-Layer Chromatography

Figure 3 shows the results of the TLC separation of 6 samples of different papers and 3 samples of HP black toners used in HP monochrome printers series P3015, P3005, and 3030, respectively (photographed under long-wave UV light, 365 nm).

As seen from Figure 3, the 6 different paper samples showed 4 different TLC profiles and thus the 6 paper samples can be separated into at least 4 groups, each containing paper with a different optical brightener. The black toner samples used in the 3 HP monochrome printers (series P3015, P3005, and 3030) were not differentiated using this TLC procedure. However, these 3 toners were differentiated by FT-IR microspectroscopy (see Figure 2 above) and GC-MS (see Figure 5 below).

Gas Chromatography-Mass Spectrometry

In scan acquisition mode, GC-MS allows separation, detection and characterization of both toner and paper's volatile solid ingredients potentially including non-reacted reagents and low molecular weight components of natural and synthetic resins used in paper and toner manufacturing, as well as multiple proprietary additives contained in paper and toner.

As an example, Figure 4 shows the GC-MS chromatograms of the paper samples taken from the HP Office paper and the A4 copy paper—the two types of paper that were not differentiated by the TLC analysis (see Figure 3).

The significant difference between the GC-MS chromatograms ("profiles") of the two papers (HP

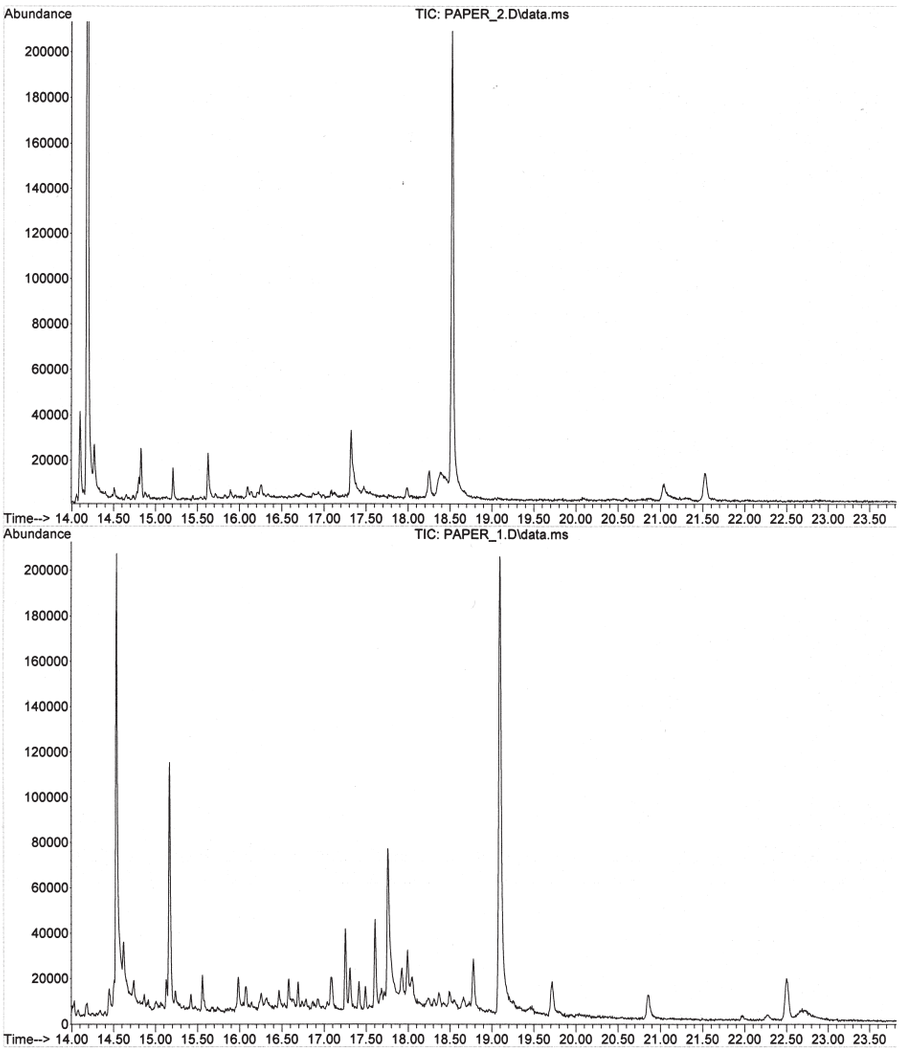

Figure 4. GC-MS chromatograms of paper samples taken from the HP Office paper (lower chromatogram) and A4 copy paper (upper chromatogram).

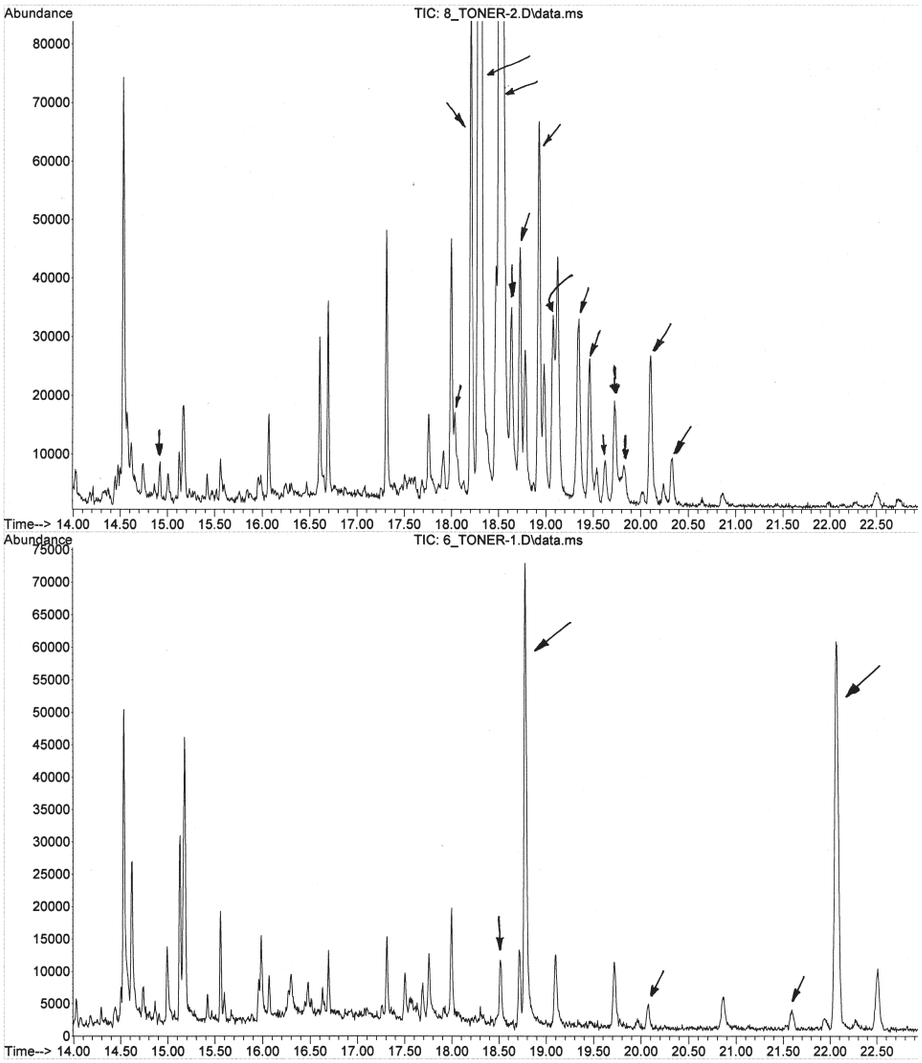

Figure 5. Comparison of the GC-MS chromatograms of toner-on-paper samples taken from entries printed with the HP P3005d (upper chromatogram) and HP P3015 (lower chromatogram) printers. The peaks indicated by the arrows represent the components of the toners. The other peaks on the GC-MS chromatograms represent the components extracted from the paper.

Office paper and A4 copy paper) not discriminated by TLC (see Figure 3), clearly demonstrates the high discriminating power of the GC-MS technique that typically allows the analyst to distinguish between paper samples in cases when the TLC and non-destructive physical examinations might not reveal any difference between the paper samples.

Figure 5 shows the GC-MS chromatograms of two samples of black toner on paper taken from the texts printed using the HP P3015 and HP P3005d printers.

As seen from Figure 5, the two toners that were not differentiated by the TLC analysis (see Figure 3) were clearly differentiated by the GC-MS analysis that showed that the toners have drastically different chemical compositions.

Case Examinations

The following two case examinations show the capabilities of the analysis of toner and paper by TLC, GC-MS, and reflectance FT-IR microspectroscopy in determining whether there have been page substitutions (see *Case Example 1*) and in testing a hypothesis that two documents, which were supposed to come from different sources, have a common source (see *Case Example 2*).

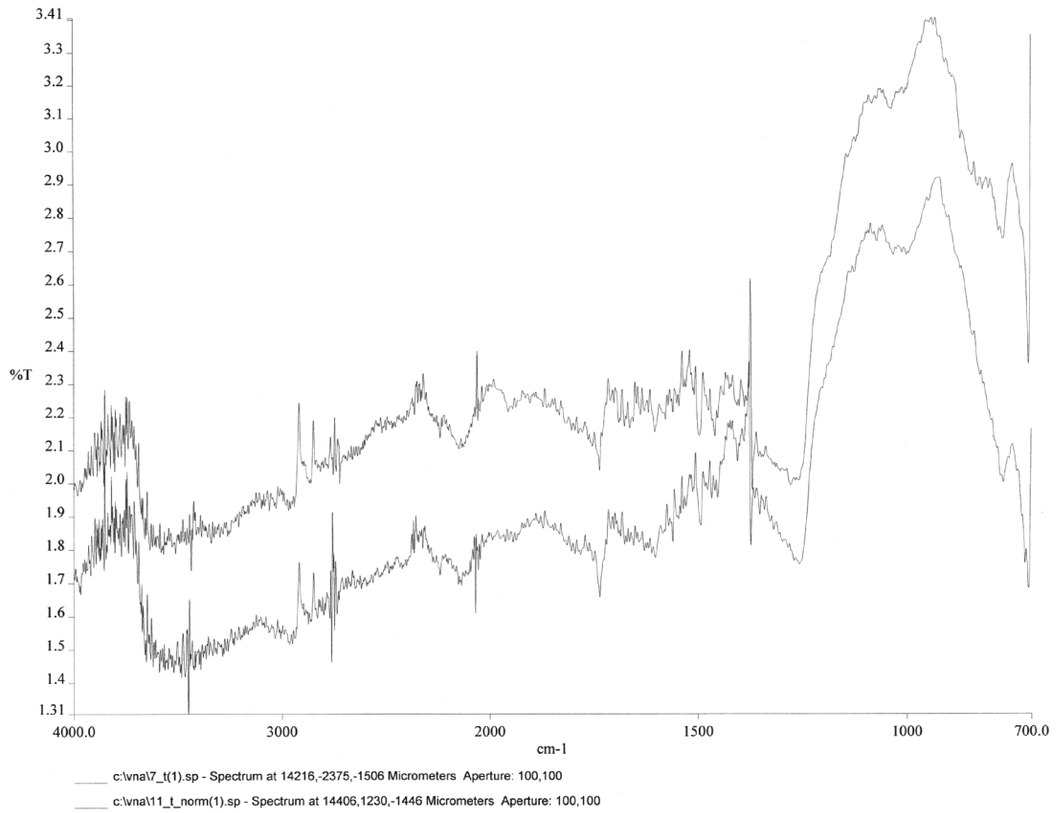

Figure 6. Comparison of the FT-IR spectra of toner-on-paper samples taken from pages 7 (upper spectrum) and 11 (lower spectrum) of the questioned document.

Case Example 1

In a civil case, the key issue was whether the first 9 pages in the 11-page document dated in 2004 had been substituted approximately 6 years later, after the lawsuit was filed in late 2010. The expert retained by the plaintiff used a conventional ("macro") *Attenuated Total Reflectance (ATR) FT-IR* spectroscopy to compare 0.5-mm samples of the toner[5] taken from the questioned document and concluded that two different toners were used: toner 1 - to produce the printed texts on pages 1-9 and toner 2 - for texts on pages 10 and 11.

This author, retained by the defendant, analyzed the toner samples (taken from the questioned document) using *reflectance FT-IR microspectroscopy* (the procedure is described in the *Methods and Materials* section) and determined that all the toner samples tested showed matching FT-IR spectra. As a typical example, Figure 6 shows FT-IR spectra of the toner-on-paper samples taken from pages 7

[5]To this author's knowledge, there are no peer-reviewed publications that would recommend using "macro"-ATR FT-IR (a variant of ATR FT-IR spectroscopy that does not use an IR microscope) for the analysis of micro-objects, such as 0.5-mm samples of toner on paper. It is this author's opinion that micro-objects, such as 0.5-mm samples of toner on paper, cannot be reliably compared by "macro"-ATR FT-IR spectroscopy for at least two reasons:

1. The area of the ATR crystal illuminated by the IR beam and used to record the IR spectrum of a sample (it is called the *analytical spot size* in FT-IR) is typically significantly larger than 0.5 mm in diameter. Therefore, an IR spectrum of a 0.5-mm sample of toner on paper *a priori* will be unpredictably distorted by some extraneous information originated from the measured (by the IR detector) area surrounding the 0.5-mm sample.
2. As the coverage of paper by toner typically varies significantly from sample to sample, the resulting IR spectra of such samples (having different ratios of the areas of paper covered and not covered by toner) will also vary significantly. Each of such spectra will be a mixture (overlap) of the IR absorption bands of both the paper and the toner (see the discussion relating to Figure 1 above).

and 11 of the questioned document (the spectra are overlaid for ease of their comparison).

Additionally, the TLC analysis of toner samples showed that the same violet dye (in addition to the carbon black pigment) was present in all toner samples tested. Finally, the GC-MS analysis of the toner samples showed that all pages of the document were printed using toner which contained 24 components detected by the GC-MS procedure used in this case (as a typical example of the GC-MS data obtained for the pertinent pages of the document, Figure 7 shows the GC-MS chromatograms recorded for toner-on-paper samples taken from pages 7 and 11).

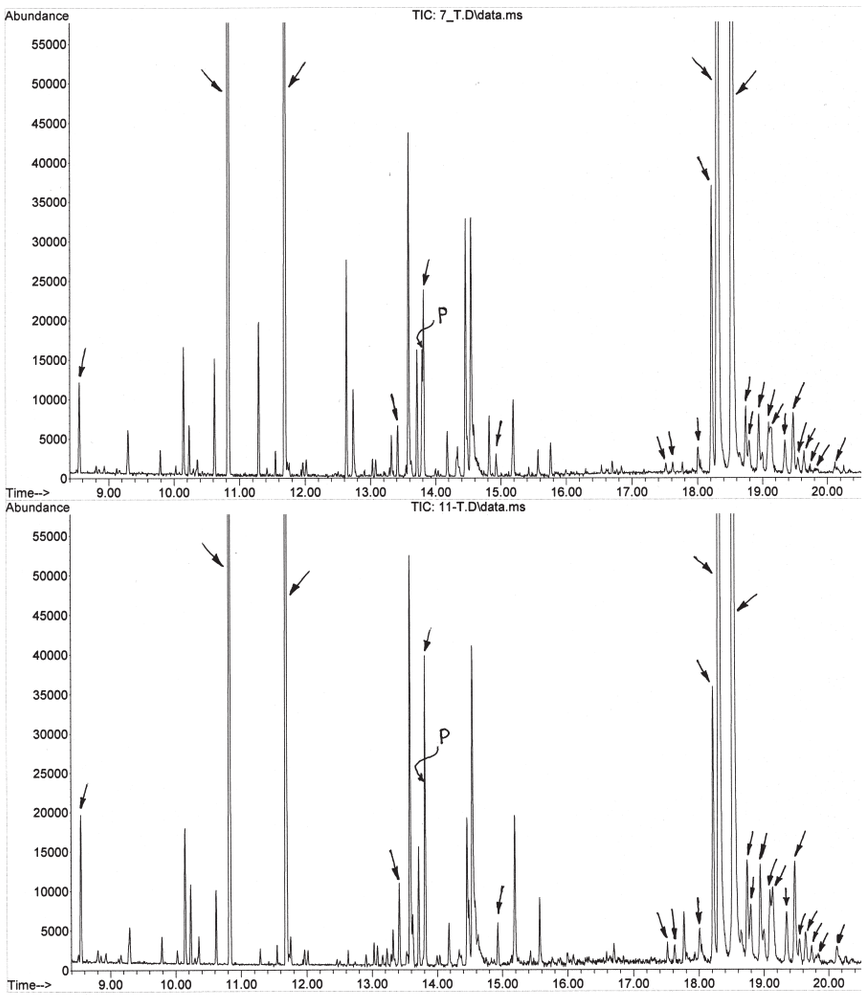

Figure 7. Comparison of the GC-MS chromatograms of toner-on-paper samples taken from pages 7 (upper chromatogram) and 11 (lower chromatogram) of the questioned document. The 24 components of the toner are indicated by the arrows. The other multiple peaks (other than those indicated by arrows) appearing on the two GC-MS chromatograms are the peaks that represent the components of the paper.[6,7] Also, the "*P*" indicates the peak of the paper's component that partially overlapped with the peak of the toner's component having the retention time of approximately 13.8 min.

[6]It is important to note that because paper is a non-homogenous material, no two samples taken from the same sheet of paper will typically have the identical qualitative and/or quantitative composition. Moreover, various areas of a paper document might be differently contaminated, for example, by handling that might leave traces of perspiration or other organic contaminants on those areas of the document that were touched during the handling.
[7]It also should be noted that some components of paper are extracted to a lesser degree from paper blank samples (that do not bear any ink or toner on the document) and to a greater degree from samples taken from areas that bear other materials applied to the paper, such as writing ink, inkjet printing ink, toner, stamp pad ink, etc. It is this author's opinion that the above materials might play a role as catalysers, providing higher yield of extraction for some paper components.

The 24 toner components indicated by the arrows (see Figure 7) create a very complex (virtually unique) combination of components that are unlikely to be coincidentally reproduced by other toner manufacturers. This provides evidence that all of the pages of the document were printed using toner of the same formulation.

Thus, the above FT-IR, GC-MS, and TLC data obtained for the toner samples show no evidence of page substitution in the 11-page questioned document. To the contrary, these FT-IR, GC-MS, and TLC results, coupled with the respective FT-IR, GC-MS, and TLC data obtained for the paper of all the pages of the document[8], provide evidence to support the "defense" hypothesis that no page substitution has occurred in 2010 since the initial production of the document in 2004.[9]

Case Example 2

In a criminal case, the "first generation" copies of two originals were submitted for the forensic document examination instead of the originals that were claimed to be lost. The originals were purportedly produced and copied once (first generation copies) one year apart and in two different offices situated in different countries (one in Europe, the other in Asia). One of the key issues was to check the same-origin hypothesis versus the different-origin hypothesis for these two "first generation" copies, which were designated as documents *Q1* and *Q2*.

The non-destructive physical examinations outlined above: 1) did not reveal any difference between the paper or the toner used to produce the two copies; and 2) showed clear differences between these documents in their trash mark patterns, typefaces, and page formats. As the results of the non-destructive physical examinations were essentially inconclusive, and thus they could not support either the same-origin hypothesis or the different-origin hypothesis, this author took samples of paper and toner from the two documents and examined the samples using reflectance FT-IR microscopy, TLC, and GC-MS.

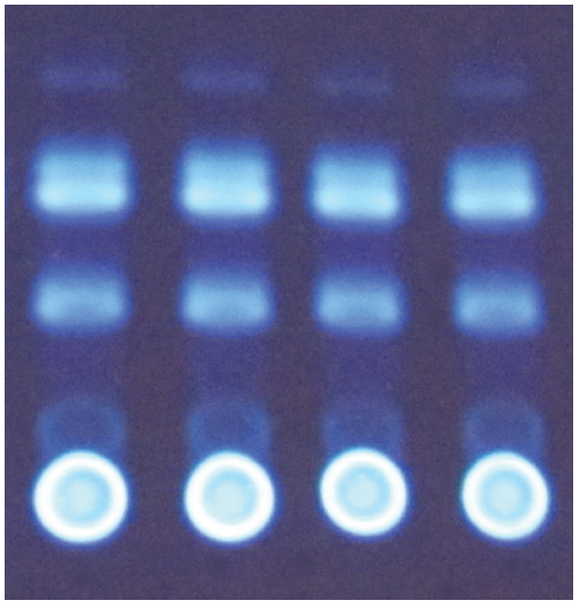

Figure 8. TLC chromatogram of the paper samples taken from two questioned "first generation" copies, *Q1* (lanes 1 and 3) and *Q2* (lanes 2 and 4) (photographed under long-wave UV light, 365 nm).

As seen from Figure 8, the TLC analysis of the paper samples shows that both "first generation" copies, *Q1* and *Q2*, were produced using the paper containing the same multi-component optical brightener. Besides, the paper samples taken from documents *Q1* and *Q2* showed matching GC-MS chromatograms and FT-IR spectra.

The TLC analysis of toner samples did not reveal any extractible and detectable component. However, the toner-on-paper samples taken from documents *Q1* and *Q2* clearly showed matching GC-MS chromatograms (see Figure 9) and FT-IR spectra (see Figure 10 that follows).

As seen from Figure 9, GC-MS analysis of the toner samples shows that both "first generation" copies, *Q1* and *Q2*, were produced using toner containing the same five components, designated as components 1 through 5. The other multiple peaks (other than the 5 peaks numbered 1 through

[8]As well as the results of the TLC and GC-MS analyses of ink that show that the ink of the same formulation (and most probably of the same manufacturing batch) was used to initial all the pages of the document.

[9]Theoretically, the same ink (the same pen or another pen containing the ink of the same manufacturing batch), toner (having the same composition and showing the *same* print quality) and paper (copy paper of the *same* composition and showing the *same* wear and tear characteristics [here *the same* means *indistinguishable* from the unquestioned pages 10 and 11 of the document]) could be used 6 years after the initial production of the document in 2004; however, the probability of this happening is small.

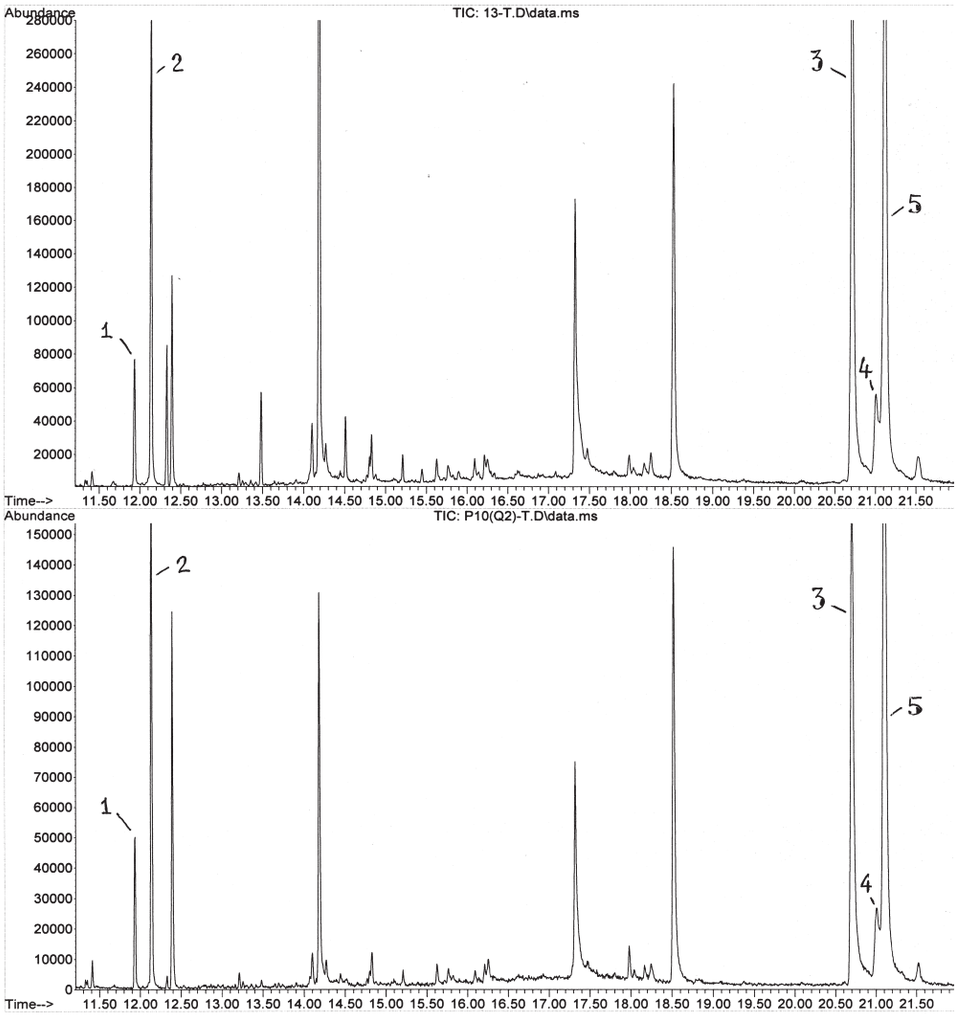

Figure 9. GC-MS chromatograms of toner-on-paper samples taken from two questioned "first generation" copies, *Q1* (upper chromatogram) and *Q2* (lower chromatogram).

5) appearing on the two GC-MS chromatograms are the peaks that represent the components of the paper.[10] Toner components designated as 1 and 2 (see Figure 9) were identified with a high degree of certainty as two isomers of diisocyanato-trimethylcyclohexane (using a 2008 NIST library of mass spectra). The other three toner components (components 3, 4 and 5 in Figure 9) did not have satisfactory matches in the 2008 NIST library of mass spectra used in this case examination and thus they were not "identified", *i.e.*, their chemical names were not determined.[11]

[10]See footnotes 6 and 7 above.

[11]It should be noted that for the purpose of comparison between two toner samples (or, generally, between any two materials used to produce the documents that are to be compared), such as the two toner samples compared in Figure 9 through their GC-MS chromatograms, each toner component (chemical substance) does not need to be identified by its chemical name. Instead, a component can be unambiguously characterized (and thus "identified") by its mass spectrum (which is essentially a unique barcode by itself, *i.e.*, without using a mass spectra library search), even if its mass spectrum does not have a satisfactory match in any of the commercially available libraries of mass spectra. Only a small percentage of millions of existing organic substances have been included in commercially available libraries of mass spectra, and thus only this small percentage of the existing organic substances can be identified by their chemical names using GC-MS analysis coupled with a mass spectra library search. Therefore, two materials (toner, paper, ink, etc.) are considered as having the same component if the peaks of this component on the GC-MS chromatograms of the two materials both have the same retention time and are characterized by the same mass spectrum.

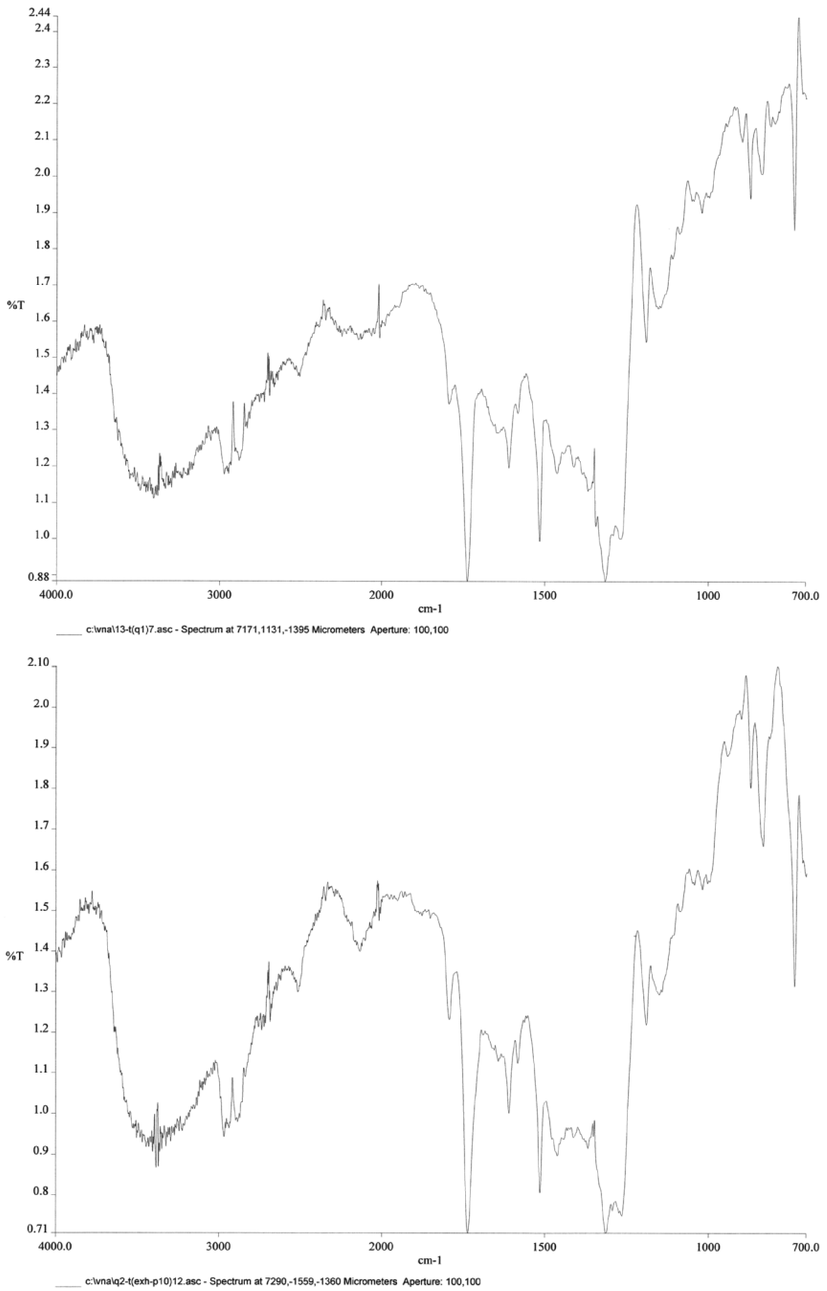

Figure 10. The FT-IR spectra of 0.5-mm toner-on-paper samples taken from document *Q1* (upper spectrum) and *Q2* (lower spectrum).

Figure 10 shows a satisfactory FT-IR spectral match between the toner-on-paper samples taken from documents *Q1* and *Q2*. Slight variations in relative intensities of the absorption bands in the area from 700 to 1000 cm^{-1} is within the range of variations observed for repetitive FT-IR measurements conducted for toner-on-paper samples taken from each document.

Thus, the GC-MS, FT-IR, and TLC data obtained for both paper and toner samples, taken from the two "first generation" copies, *Q1* and *Q2*, coupled with the results of the optical comparative examination of the *Q1* and *Q2* documents, show that these two copies were produced either on the same office machine (photocopier) utilizing dry black toner or on two different of-

fice machines (photocopiers) that both used: A) paper originating from the same source (the same manufacturer); and B) toner of the same formulation (the same manufacturer). These results do not support the "defense" hypothesis that the *Q1* and *Q2* copies were produced one year apart in two different offices situated in different countries (one in Europe, the other in Asia). To the contrary, these FT-IR, GC-MS, and TLC data provide evidence to support the "prosecution" hypothesis that these two copies have a common source (*i.e.*, the copies have been produced in the same office).

Conclusion

This paper shows that a combination of three analytical methods, TLC, GC-MS, and reflectance FT-IR microspectroscopy, increases the ability of the document examiner to differentiate paper and toners that cannot be distinguished by the commonly used non-destructive (optical) techniques.

For those who stand to be defrauded, the high discriminating power of these three analytical methods may prove vital by allowing the document examiner to conclude, with a higher (than it would be without using these analytical methods) degree of certainty, that the combined examination results reveal no evidence to support the contention (the "prosecution" hypothesis, H_p) that any pages of the document have been inserted or substituted. Moreover, in combination with other evidence, it may be possible to conclude, with a high degree of certainty, that the combined examination results support the "defense" hypothesis, H_d, that no page substitution/insertion has occurred since the initial production of the document.

Similarly, the use of TLC, GC-MS and reflectance FT-IR microspectroscopy for comparing paper and toner samples increases the level of certainty of the conclusions made by document examiners in cases in which multiple documents are to be compared to check the same-origin hypothesis versus the different-origin hypothesis.

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