

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/236186711>

Forensic Analysis of Laser Printed Ink by X-ray Fluorescence and Laser-Excited Plume Fluorescence

ARTICLE in ANALYTICAL CHEMISTRY · APRIL 2013

Impact Factor: 5.64 · DOI: 10.1021/ac400378q · Source: PubMed

CITATIONS

5

READS

61

6 AUTHORS, INCLUDING:



Po Chun Chu

Hong Kong Baptist University

3 PUBLICATIONS 18 CITATIONS

SEE PROFILE



Bruno Yue Cai

ANA Artwork Material Analysis

5 PUBLICATIONS 26 CITATIONS

SEE PROFILE



Nh Cheung

Hong Kong Baptist University

53 PUBLICATIONS 938 CITATIONS

SEE PROFILE

Forensic Analysis of Laser Printed Ink by X-ray Fluorescence and Laser-Excited Plume Fluorescence

Po-Chun Chu,^{†,§} Bruno Yue Cai,^{†,§} Yeuk Ki Tsoi,[‡] Ronald Yuen,[¶] Kelvin S.Y. Leung,[‡] and Nai-Ho Cheung^{*,†}

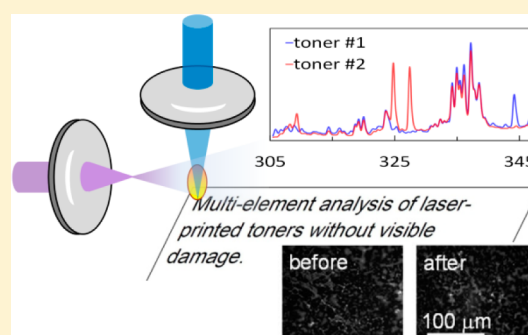
[†]Department of Physics, Hong Kong Baptist University, Kowloon Tong, Hong Kong, China

[‡]Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong, China

[¶]Thermo Scientific, Niton Analyzer Asia, Unit 11-15, 9/F, Tower 1, Grand Central Plaza, Shatin, New Territories, Hong Kong, China

S Supporting Information

ABSTRACT: We demonstrated a minimally destructive two-tier approach for multielement forensic analysis of laser-printed ink. The printed document was first screened using a portable-X-ray fluorescence (XRF) probe. If the results were not conclusive, a laser microprobe was then deployed. The laser probe was based on a two-pulse scheme: the first laser pulse ablated a thin layer of the printed ink; the second laser pulse at 193 nm induced multianalytes in the desorbed ink to fluoresce. We analyzed four brands of black toners. The toners were printed on paper in the form of patches or letters or overprinted on another ink. The XRF probe could sort the four brands if the printed letters were larger than font 20. It could not tell the printing sequence in the case of overprints. The laser probe was more discriminatory; it could sort the toner brands and reveal the overprint sequence regardless of font size while the sampled area was not visibly different from neighboring areas even under the microscope. In terms of general analytical performance, the laser probe featured tens of micrometer lateral resolution and tens to hundreds of nm depth resolution and atto-mole mass detection limits. It could handle samples of arbitrary size and shape and was air compatible, and no sample pretreatment was necessary. It will prove useful whenever high-resolution and high sensitivity 3D elemental mapping is required.



Imagine a laser-printed will stating, “The entire estate shall be vested unto John.” was illicitly modified to read, “The entire estate shall be vested unto John, Peter, and Mary in equal shares.” This contended will would require forensic analysis. Today, the volume of laser-printed documents that require forensic examination is enormous. Wills, deeds, contracts, certifications, and terrorist letters are examples.¹ Worse still, given the high quality of laser printing, criminal modifications can evade most morphological examinations.^{2,3} Chemical information about the printed ink is therefore necessary, yet the analysis has to be nondestructive to preserve the legal specimen.

Laser printer toners are composed of polymeric binders and inorganic components.⁴ The polymers were best analyzed by Fourier-transform infrared (FT-IR) spectroscopy.⁵ While FT-IR generally required scraping toner from the document,⁶ the total reflection version was nondestructive and had been used to sort toners though at reduced precision.⁷ Complementary analysis of the inorganic components was therefore desirable. The inorganics were the pigments as well as the charge and magnetic controllers. They had been successfully analyzed by laser-ablation inductively coupled-plasma mass-spectrometry (LA-ICPMS),^{8,9} yet two issues remained. First, the questioned documents might not fit inside the small sealed chamber.¹⁰ Second, for those that fit, the technique was destructive to the

extent that the ablated spot of about 150 μm diameter was stripped of all ink.¹⁰

To be less destructive and atmosphere compatible, the low temperature plasma version of mass spectrometry may be an option,¹¹ but all-optical probes will have an edge if their analytical sensitivity can rival. Below, we will show that the forensic problem could be satisfactorily addressed by an all-optical two-step approach: an initial screening by portable X-ray fluorescence (XRF) to be followed by a novel second step based on laser-excited atomic fluorescence (LEAF) of desorbed ink in laser-ablated plumes. We will show that the plume-LEAF technique, or PLEAF for short, was not restricted by the conventional one-wavelength-one-transition specificity. Instead, multielements could be detected.

EXPERIMENTAL SECTION

Materials. We picked four toner samples, Hewlett-Packard black toner CC364X (coded H1) and Q5949X (coded H2), Panasonic black toner DQ-TU35D (coded P), and FujiXerox black toner CT 200539 (coded F). They were selected because

Received: February 4, 2013

Accepted: April 10, 2013

Published: April 10, 2013

of their widespread use and their similarity in composition (H1 and H2). Toners were printed on white A4 copier papers (HP Everyday Paper, 80 g/m², Order No. Q2400A) using four respective printers.

ICPMS. The elemental composition of nonprinted toner powders was analyzed by ICPMS to establish analyte concentrations for reference. It was performed by adding 7 mL of concentrated HNO₃ (Aristar, BDH, UK) to a weighed portion of the toner powders. Digestion was carried out in a temperature programmed ETHOS One Advanced Microwave Digestion System (Milestone S.r.l., Sorisole, Italy). After cooling, the digest was diluted to 25 mL with Milli-Q (18.2 MΩcm Millipore, Billerica, MA, USA) water for subsequent elemental determination by ELAN DRC II ICPMS (PerkinElmer, Waltman, MA, USA). Elemental content was quantified against calibrated response curves prepared from 1000 g L⁻¹ stocks (VHG, Manchester, NH, USA). Printed ink was also analyzed by digesting weighed portion of printed samples.

XRF. XRF analysis was performed with a portable probe (Thermo Scientific Niton XL3t GOLDD+). The probe head was brought in contact with the ink surface. The probed area was 8 mm in diameter. The probe was set to mining mode for panoramic scans and consumer product mode for heavy metals. Exposure was 90 s for one spectrum when the voltage was scanned from low (<19 keV) through mid (19–23 keV) to high (>23 keV) ranges with 30 s in each.

PLEAF. PLEAF analysis was carried out using the setup shown schematically in Figure 1. It was a two-laser-pulse probe

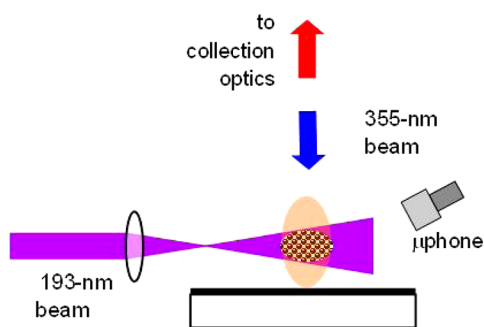


Figure 1. Schematics of the PLEAF setup as viewed from top.

pioneered by us. Experimental details had been reported.^{12–14} Briefly, a Nd:YAG laser pulse (Continuum Surelite II, 355 nm, 10 Hz, 9 ns) was focused normally onto a 100 μm diameter spot at the surface of the printed ink to form a plume. The laser fluence ranged from 60 mJ cm⁻² for mild ablation to 17 J cm⁻² for destructive ablation. We avoided sampling an area twice by translating the document. Seven microseconds later, the ablated

plume was intercepted transversely by an ArF laser pulse (Lumonics Ex 748, 193 nm, 10 Hz, 10 ns) with fluence of 42 mJ cm⁻² over a spot of 2 mm × 4 mm (height × width). The ArF laser pulse vaporized the toner particulates in the plume to produce analyte atoms. The trailing portion of the same 193 nm laser pulse induced the various analytes to fluoresce.^{12,15} Fluorescence emissions were collected along a tilted direction to avoid the reflected 193 nm light and imaged onto the entrance slit of a 0.5 m spectrometer (Acton SpectraPro-500) equipped with a gateable intensified charge-coupled device (ICCD, Andor iStar). The ICCD was gated on 40 ns after the 193 nm pulse and stayed on for 220 ns. Unless stated otherwise, the full width of each captured spectrum was 40 nm; the instrumental resolution was about 150 pm which was preserved in all off-line spectral smoothing. The acoustic signal generated in the pulsed laser ablation was also monitored to gauge the extent of sample destruction.¹⁶

Profilometry. The geometry of ablated craters could be characterized by scanning profilometry. For that purpose, inks were printed on smooth transparencies (3 M Transparency Film, Order No. PP2900) and the ablated craters were scanned with a profilometer of 0.1 nm z-resolution (Veeco Dektak 150).

Chemometrics. Principal component analysis was done with MATLAB. K-means statistics were computed using Weka.

RESULTS AND DISCUSSION

We first analyzed the four brands of nonprinted toner powders by ICPMS. The results were tabulated in the Supporting Information (Table S-1). We then used the portable XRF probe to scan the printed ink. We found that XRF could tell the iron-rich H1 and H2 samples from F and P (Supporting Information, Figure S-1). Telling H1 from H2 was more difficult; XRF could detect the higher zinc content in H2, but the signal-to-noise ratio was less than three when the font size of the printed letters was 20 and smaller. Telling F from P was still more challenging; while XRF could identify the copper-rich F toner, signal dropped below noise for letters of font size 20 and smaller (Supporting Information, Figure S-2).

We used the PLEAF probe for more discriminating multielement analysis. Readers may wonder how multielement analysis could be possible given the one-wavelength-one-transition specificity of conventional LEAF. Reference to photofragmentation fluorescence spectroscopy (PFF) may help to clarify the issue.¹⁷ In PFF, a precursor molecule absorbed an energetic uv photon. Because molecular absorption bands were broad, excitation wavelength could be imprecise. The excited molecule then dissociated to produce electronically excited atomic fragments of the analyte. Their subsequent radiative decay gave rise to fingerprint spectral lines. LEAF of vaporizing particulates was similar to PFF. The dispersing species in a high-density vapor plume were akin to the

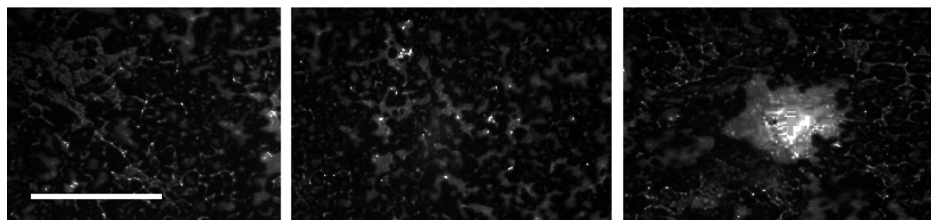


Figure 2. Micrographs showing printed ink surfaces that were not irradiated (left) and ablated by a single 355 nm laser pulse at 320 mJ cm⁻² (middle) and 17 J cm⁻² (right). Scale bar = 100 μm.

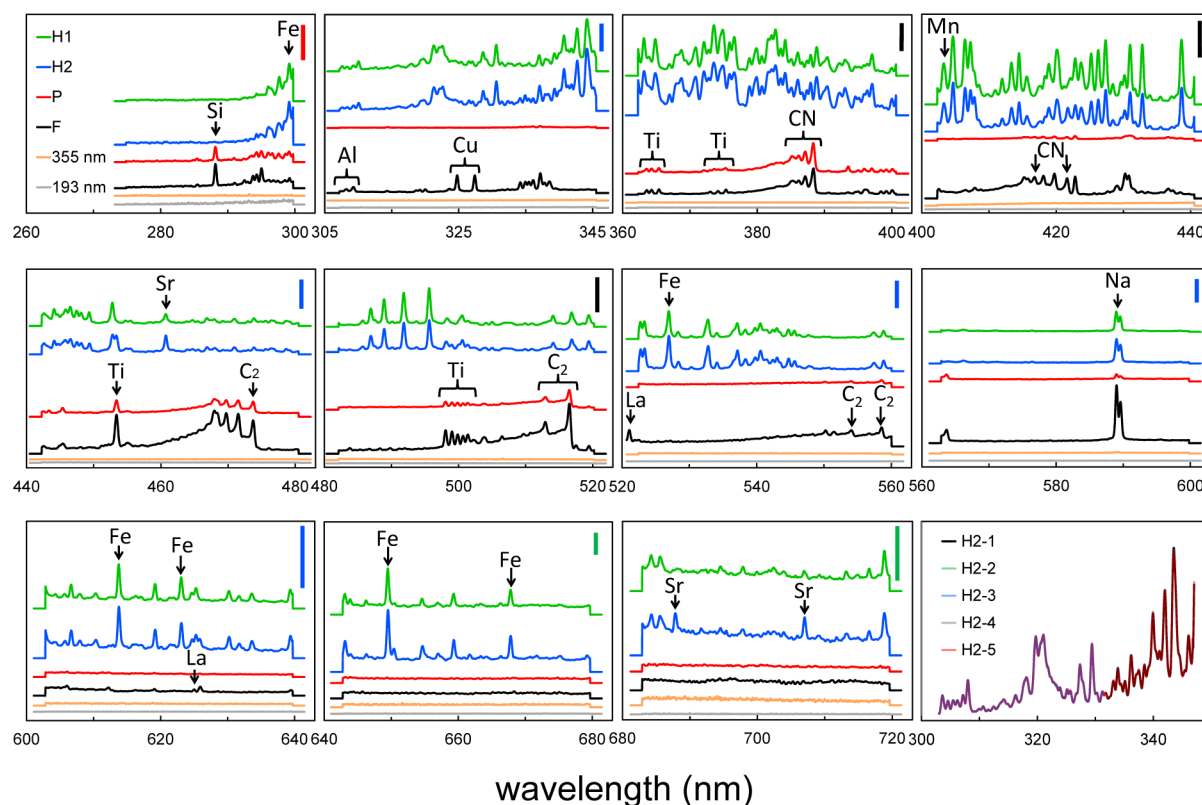


Figure 3. PLEAF spectra of four laser-printed inks coded H1 (green curve), H2 (blue curve), P (red curve), and F (black curve). Spectra produced by the 355 and 193 nm laser pulse alone are shown in orange and gray, respectively. Each spectrum was accumulation of 200 events. Vertical scale bars in # CCD counts: black (1 000 000), blue (500 000), green (100 000), and red (20 000). The bottom right panel shows five PLEAF spectra of H2 ink to illustrate reproducibility; each was an accumulation of 200 shots over fresh sample spots and the spectral area was normalized to one. Experimental conditions are as stated in the text except 355 nm fluence was 320 mJ cm^{-2} and the ICCD was gated on 30 ns after the laser pulse for the case of 355 or 193 nm laser alone.

dissociating molecules except no precursor molecules were required.¹⁸

PLEAF was highly sensitive. Only miniscule sample mass was needed for analysis. Figure 2 shows the ablated crater. As can be seen, at a 355 nm laser fluence of 320 mJ cm^{-2} , destruction was not visible even under the microscope. The etched thickness per shot was only 700 nm or 5% of the ink layer and 20% of the roughness of the substrate surface. This was to be contrasted against the 50 J cm^{-2} used in typical LA-ICPMS when the ink layer was stripped.^{8,10}

We captured numerous single-shot PLEAF spectra of the printed toners. The average of 200 such spectra for each toner is shown in Figure 3 in the form of an array of panels. Each panel corresponded to the 40 nm spectral window of a CCD frame. The full array covered the entire visible spectrum. Within each panel, the traces corresponded to the PLEAF spectra of H1 (green), H2 (blue), P (red), and F (black) toners. Also shown are the spectra generated by the 355 nm laser alone (orange) and the 193 nm laser alone (gray). All six traces were offset vertically for clarity. The leading and trailing pixels were zeroed to indicate the baseline. The vertical intensity scale was optimized for each panel; the color-coded scale bar on the top right was in CCD counts (see caption). We presented these averaged spectra because they were highly reproducible and could be used as reference spectra for later comparisons. Their reproducibility is illustrated in the bottom-right panel of Figure 3 when five 200-shot average spectra of the same toner are shown, vertically magnified. Further

illustration of reproducibility is shown in Figures S-3 and S-4 in the Supporting Information.

As can be seen from Figure 3, and especially from the last magnified panel, the spectral features were enormously rich. While graphical clarity dictated the labeling of only a small fraction of the atomic and molecular analytes, the other unlabeled features were also identified (Supporting Information, Table S-2). The panoramic spectra clearly demonstrated the multianalyte detection capability of PLEAF. One might be tempted to associate multielement excitation with laser-induced plasmas, but the 193 nm laser fluence of 42 mJ cm^{-2} was unlikely to cause breakdown. Moreover, no plasma continuum emissions were seen, and no sensible plasma temperature could be deduced. For example, on the basis of the H2 spectra (blue trace), the Boltzmann temperature T deduced from the Sr I 687.8 and 689.3 nm lines was 0.4 eV while that deduced from the Fe I 646.3 and 667.8 nm lines was 26 eV. Should a temperature of 26 eV be real, emissions from states higher than 6.4 eV (energy of 193 nm photon) would be readily visible, yet none were seen. For instance, the strong Fe I 646.9 nm (upper state at 6.75 eV) and Zn I 636.2 nm (upper state at 7.744 eV) transitions were not seen. Quite the contrary, all our observations were consistent with the model of 193 nm photoexcitation.^{18,19}

Another notable feature of Figure 3 was the synergy of the two laser pulses. The spectra produced by either laser alone were weak and featureless (the bottom orange and gray traces). When operated in tandem, the sensitivity was orders of

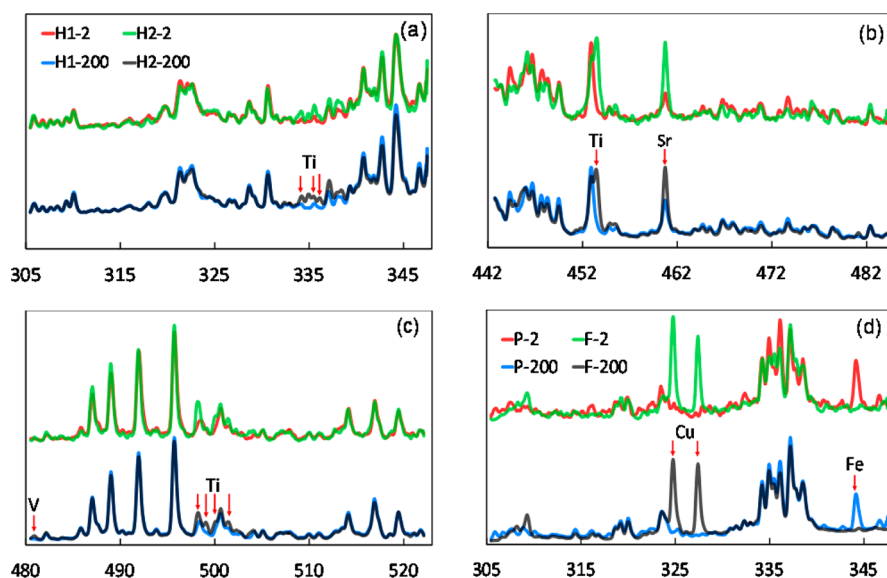


Figure 4. Normalized PLEAF spectra of 2-shot average (red and green traces) and 200-shot average (blue and gray traces). The two groups were offset vertically for clarity. The spectral regions shown in panels (a) through (c) were used in the principal component analysis of ink types H1 and H2. The spectral region shown in panel (d) was used in the principal component analysis of ink types P and F. Distinguishing spectral features are Ti 334.2, 335.5, 336.1 and 453.3, Sr 460.7, V 480.8, Ti 498.2, 499.1, 500.0 and 501.4, Cu 324.8 and 327.4, and Fe 344.1 nm lines.

magnitude enhanced. To quantify the sensitivity, we estimated the mass detection limits. They were a few atto-moles to a hundred atto-moles for a range of analytes (Supporting Information, Table S-3).

The excellent sensitivity meant fewer laser shots and less target destruction. We successfully sorted the four toners based on 2-shot average PLEAF spectra. The tale-telling spectral regions are shown in Figure 4. Panels (a) through (c) highlighted the difference between H1 and H2. Panel (d) contrasted F against P. For each panel, the top red and green traces are 2-shot spectra of the contrasting toners while the bottom blue and gray traces are the corresponding 200-shot reference spectra. All spectra were normalized to unit area. For the 2-shot spectra, the relative uncertainty of telltale features was within 20%. (For example, the standard deviations in the intensity of the Cu 324.8 and 327.4 nm lines in the F ink spectra were 16 and 14% respectively. That of the Ti 377.0 nm line was 10%.) These distinguishing features were labeled. Their brightness was indicative of the analyte concentration. For example, among the four toners, F had the brightest Cu 324.8 and 327.4 nm lines. Meanwhile, both ICPMS and XRF also showed that the F toner carried the most copper (Supporting Information, Table S-1 and Figure S-1). This kind of consistency among PLEAF, ICPMS, and XRF was found to be true for most other analytes except one. Panel (d) of Figure 4 shows that the P toner contained significantly more iron than the F toner. This agreed with XRF but differed from ICPMS. We subsequently did ICPMS analysis of the printed toners and found that the printed P toner was indeed more iron-rich (Supporting Information, Table S-4). Apparently, the printing process affected the toner chemistry.

We did principal component analysis using the 2-shot PLEAF spectra.²⁰ The clusters of 1870 samples are shown in Figure 5. The K-means sorting statistics are also tabulated. As can be seen, sorting was 100% correct in all cases.

As a final experiment, we attempted to tell the printing sequence of overlapping printed characters. This was required in the original forensic assignment when one wanted to know if

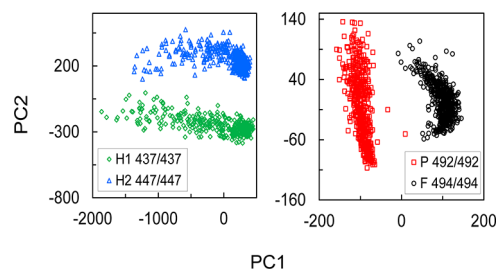


Figure 5. Principal component clusters of ink types H1 (green diamonds), H2 (blue triangles), P (red squares), and F (black circles) based on 2-shot averaged PLEAF spectra shown in Figure 4. H1 and H2 were sorted on the basis of spectra from 305.5 to 522.0 nm. P and F were sorted on the basis of spectra from 321.8 to 330.1 nm. K-means sorting statistics of correct identifications are also shown.

the comma after John was printed over the period. We prepared samples with F toner printed on extended area of P toner, as well as samples with the printing order reversed. We again started with an XRF scan. We found that XRF could barely resolve toners printed on opposite side of the paper, as in double-sided printing. Its limited depth resolution could not discriminate ink layers printed on the same side (Supporting Information, Figure S-5).

In contrast, PLEAF with its hundreds of nm etch rate could resolve the overprints. We first depth-profiled the ink layers by ablating the same spot repeatedly. The profile showed that the two ink layers mixed extensively (Supporting Information, Figure S-6). We therefore lowered the fluence of the 355 nm ablation laser to 60 mJ cm⁻² to reduce the etch rate to 220 nm per pulse for finer depth resolution. All subsequent PLEAF analysis was done at this lower etch rate.

Figure 6 shows the principal component clusters of 200 samples half of which had F printed on P while the other half was the opposite. Representative 2-shot spectra (top two traces) used in the clustering are shown in the inset. Reference spectra based on 200 shots (bottom two traces) are also shown for comparison. As can be seen, bright Cu 324.8 and 327.4 nm

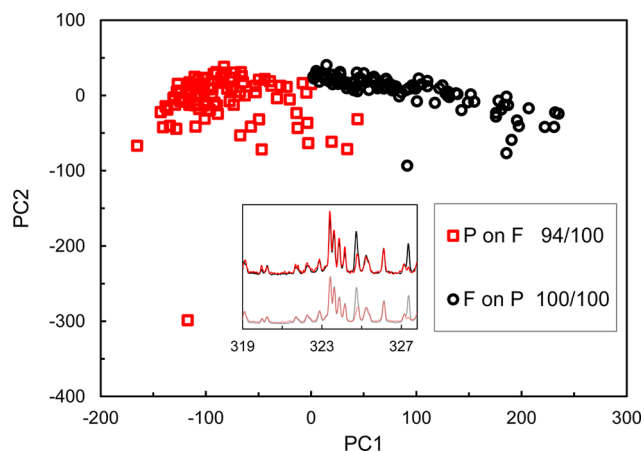


Figure 6. Principal component clusters of two types of laser printed black ink. One type had P ink printed over F ink (red squares). The other type was vice versa (black circles). The analysis was based on 2-shot average PLEAF spectra with λ ranging from 321.8 to 328.4 nm. K-means statistics of correct identifications are shown in the right inset. Left inset is 2-shot PLEAF spectra of P on F (red trace) and F on P (black trace); the corresponding 200-shot average reference spectra are shown at the bottom in paler color. Instrumental resolution was about 40 pm.

emissions were the distinguishing feature of F on P. The corresponding K-means sorting statistics are also listed. Six cases out of 200 were wrongly identified. They were classified as F on P although they were really P on F. We inspected the spectra of all six cases. Surprisingly, they showed bright Cu doublet emissions (Supporting Information, Figure S-7). We suspected the P ink was printed unevenly. The six aberrants were probably holes where the bottom layer of Cu-rich F ink was exposed.

CONCLUSION

In summary, we demonstrated a minimally destructive two-tier approach for multielement forensic analysis of laser-printed ink. The printed document was first screened using a portable-XRF probe. If the results were not conclusive, a discriminatory PLEAF probe was then deployed. The PLEAF probe was based on 193 nm laser-induced fluorescence of analytes in a dispersing plume. It featured tens of μm lateral resolution and 220 nm depth resolution and atto-mole mass detection limits. The sampled area was not visibly different from neighboring areas even under the microscope. The probe could handle samples of arbitrary size and shape, and no sample pretreatment was necessary. Applicability of the technique to other toner brands printed on different papers will have to be further explored. We are also applying the PLEAF technique to analyze works of art and to depth-profile multilayer organic electronic devices. We believe the technique will prove useful whenever high-resolution and high sensitivity 3D elemental mapping is required.

ASSOCIATED CONTENT

Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: nhcheung@hkbu.edu.hk. Phone: +852 3411 7034. Fax: +852 3411 5813.

Author Contributions

[§]P.-C.C. and B.Y.C. contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Research Grant Council of Hong Kong under Grant Number HKBU200610, the Science and Technology Development Fund of Macao under Grant Number 032/2010/A2, and the Faculty Research Grant of Hong Kong Baptist University.

REFERENCES

- (1) Fritz, T.; Herry, F.; Partouche, F. Examination of Questioned Documents/Handwriting. In *16th International Forensic Science Symposium Interpol-Lyon, Review Papers*; Daeid, N.N., Ed.; 2011, pp 346–377.
- (2) Tchan, J. S. J. *Imaging Sci. Technol.* **2007**, *51*, 299–310.
- (3) Moussa, C.; Novotny, M. *J. Am. Soc. Questioned Doc. Examiners* **2009**, *12*, 27–33.
- (4) Udristoiu, E. G.; Bunaciu, A. A.; Aboul-Enein, H. Y.; Tanase, I. G. *Instrum. Sci. Technol.* **2009**, *37*, 230–240.
- (5) Merrill, R. A.; Bartick, E. G.; Mazzella, W. D. *J. Forensic Sci.* **1996**, *41*, 264–271.
- (6) Assis, A. C. A.; Barbosa, M. F.; Valente Nabais, J. M.; Custodio, A. F.; Tropecelo, P. *Forensic Sci. Int.* **2012**, *214*, 59–66.
- (7) Tanase, I. G.; Udristoiu, E. G.; Bunaciu, A. A.; Aboul-Enein, H. Y. *Instrum. Sci. Technol.* **2009**, *37*, 30–39.
- (8) Szyrkowska, M. T.; Czerski, K.; Paryjczak, T.; Parczewski, A. *Surf. Interface Anal.* **2010**, *42*, 429–437.
- (9) Trejos, T. Evaluation of the Evidential Value of the Elemental Composition of Glass, Ink and Paper by Laser-Based Micro-Spectrochemical Methods, PhD Thesis, Florida International University, 2012.
- (10) CETAC LSX-500 is an example of LA-ICP-MS with an oversize sample chamber for documents. See http://www.perkinelmer.co.kr/files/pkia4629e3b4d24_3.pdf.
- (11) Liu, Y.; Ma, X.; Lin, Z.; He, M.; Han, G.; Yang, C.; Xing, Z.; Zhang, S.; Zhang, X. *Angew. Chem., Int. Ed.* **2010**, *49*, 4435–4437.
- (12) Ho, S. K.; Cheung, N. H. *Anal. Chem.* **2005**, *77*, 193–199.
- (13) Cheung, N. H. *Appl. Spectrosc. Rev.* **2007**, *42*, 235–250.
- (14) Chu, P. C.; Yip, W. L.; Cai, Y.; Cheung, N. H. *J. Anal. At. Spectrom.* **2011**, *26*, 1210–1216.
- (15) Cai, Y. Minimally destructive multi-element analysis of colorants for forensic applications and artwork authentication, PhD Thesis, Hong Kong Baptist University, 2013.
- (16) Cai, Y.; Cheung, N. H. *Microchem. J.* **2011**, *97*, 109–112.
- (17) Simeonsson, J. B.; Sausa, R. C. *Appl. Spectrosc. Rev.* **1996**, *31*, 1–72.
- (18) Cai, Y.; Chu, P. C.; Ho, S. K.; Cheung, N. H. *Front. Phys.* **2012**, *7*, 670–678.
- (19) Ho, S. K.; Cheung, N. H. *Appl. Phys. Lett.* **2005**, *87*, 264104.
- (20) Chu, P. C. Argon fluoride laser induced plume fluorescence for multi-element analysis: Sensitivity and universality, PhD Thesis, Hong Kong Baptist University, 2013.