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Document authentication at molecular levels using desorption atmospheric pressure chemical ionization mass spectrometry imaging

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Molecular images of documents were obtained by sequentially scanning the surface of the document using desorption atmospheric pressure chemical ionization mass spectrometry (DAPCI-MS), which was operated in either a gasless, solvent-free or methanol vapor-assisted mode. The decay process of the ink used for handwriting was monitored by following the signal intensities recorded by DAPCI-MS. Handwritings made using four types of inks on four kinds of paper surfaces were tested. By studying the dynamic decay of the inks, DAPCI-MS imaging differentiated a 10-min old from two 4 h old samples. Non-destructive forensic analysis of forged signatures either handwritten or computer-assisted was achieved according to the difference of the contour in DAPCI images, which was attributed to the strength personalized by different writers. Distinction of the order of writing/stamping on documents and detection of illegal printings were accomplished with a spatial resolution of about 140 μm. A Matlab® written program was developed to facilitate the visualization of the similarity between signature images obtained by DAPCI-MS. The experimental results show that DAPCI-MS imaging provides rich information at the molecular level and thus can be used for the reliable document analysis in forensic applications. © 2013 The Authors. Journal of Mass Spectrometry published by John Wiley & Sons, Ltd.

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Keywords: document authentication; desorption atmospheric pressure chemical ionization; imaging; ambient ionization; mass spectrometry

Introduction

Authentication of questionable documents has been an active research topic for several decades in forensic analysis.[1] Handwriting verification has been widely used for authentication of signatures on important documents. Usually, handwriting features such as the character shape and the style of writing are important information used for handwriting identification.[2] Alternatively, handwriting verification can be achieved based on ink analysis by using advanced instrumental methods such as thin layer chromatography (TLC),[3–5] liquid chromatography (HPLC),[6–9] gas chromatography (GC),[10] inductively coupled plasma-mass spectrometry (ICP-MS),[11] liquid chromatography-mass spectrometry (HPLC-MS),[12] gas chromatography–mass spectrometry (GC-MS),[13–15] Raman spectroscopy[5,16] and Fourier transform infrared spectroscopy[17] etc. Due to the high sensitivity of instrumental analysis, these methods generate rich chemical information and allow improved accuracy of document authentication. Tolerating complex matrices present in actual samples, ambient mass spectrometry[18–20] is of increasing interest for the high throughput analysis of actual samples, because little or no sample pretreatment is required. Many techniques such as desorption electrospray ionization (DESI),[18,21] direct analysis in real time (DART),[19,22,23] low-temperature plasma (LTP),[24,25] electrospray assisted laser desorption/ionization (ELDI),[26–28] dielectric barrier discharge ionization (DBDI)[29] and easy ambient sonic ionization (EASI)[30–32] have been reported for rapid analysis of complex samples on ambient surfaces with minimal or no sample pretreatment. These features make ambient mass spectrometry an attractive tool for imaging applications.

DESI[33], DART[34] and EASI[35] have been used for handwriting verification through the mass spectrometric analysis of ink traces. Compounds in painting materials have been sensitively detected

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using LTP-MS,[36] without noticeable damage to the artwork. Clearly, the imaging applications, especially for signature differentiation and writing age recognition, require high sensitivity, high specificity to identify analytes and non-destructive analysis. Desorption atmospheric pressure chemical ionization (DAPCI) has the advantage of high sensitivity for direct analysis of samples in ambient conditions,[37–41] and has been used for rapid imaging of melamine in egg samples with a spatial resolution of 250 μm.[42] DAPCI imaging is reported here for the first time for its use in document authentication at the molecular level.

Experimental section

Experiments were carried out using a Thermo Finnigan LTQ-XL mass spectrometer (San Jose, CA) coupled with a homemade DAPCI source. The general principle of the DAPCI source has been previously described elsewhere.[37–41] A voltage of +3.5 kV was applied to a stainless steel needle with a diameter of 0.05 mm to maintain an ambient corona discharge. DAPCI can be operated in a toxic-reagent-free, gasless mode under ambient conditions with high humidity.[38] Gasless DAPCI was applied to obtain molecular images of letters freshly written on paper surfaces. To facilitate the DAPCI process, nitrogen gas with a gentle flow rate of 250 ml/min (0.15 MPa) was used to produce the vapor of pure water as the chemical reagent for the DAPCI source. As an exception, methanol/water (1:1, v/v) mixture was used for the experiments on the detection of illegal printing. The vapor phase reagent ions were directed to impact the sample surfaces to produce analyte ions for mass analysis. The image was built based on the mass spectral data, which were sequentially acquired by scanning the document surface in the x-direction and y-direction. Nine mass scans performed in a full MS scan mode (*m/z* 50–600) at the same sampling spot were averaged as a final mass spectrum. A total of 0.63 s, including the ion injection time of about 50 ms, was required as the minimal time to produce the final mass spectrum for each sampling point. The scanning step in x-direction was set between 10 and 500 μm. The scanning step in y-direction was 500 μm for most cases, although a step of 10 μm was applied for high spatial resolution imaging. For low-resolution (500 × 500 μm) applications such as the stamp imaging analysis, the analysis time for imaging an area of 1.0 cm^2 is about 5 min. The Sufer® software (Golden Software, Inc. Colorado, USA) was used by following the directions in the software manual to create the molecular image in two-dimensional coordinates. Other information about chemical reagents, instrument operation and data processing is described in the Supporting Information.

Results and discussion

Determination of age of written material

Determination of age of written material is an imperative demand in forensic laboratories. Several methods such as HPLC[6,8,9] and GC-MS [10,14] have been used for the determination of the age of handwriting based on the decomposition of ink dyes. It is extremely difficult to differentiate the time sequence of two documents if they are prepared within a very short period of time, because the overall difference (e.g. the material loss caused by the evaporation of ink, etc.) existing between the documents could be very small. In some cases, additional contents are illegally added to the document with the same pen immediately after the agreement is reached. Using most techniques, it is also difficult to validate the changes in chemical composition over time. Detecting and thus visualizing the tiny differences require high sensitivity of analytical tools. As reported previously[20,38,43], DAPCI shows high sensitivity for detection of small concentrations of analytes on surfaces without sample pretreatment. This makes DAPCI an attractive tool to determine slight differences between signatures prepared by the same person at different times.

Figure 1a shows DAPCI-mass spectrometry (DAPCI-MS) spectrum directly recorded from a horizontal line drawn on the back surface of a graph paper using a blue marker pen. Among many signals detected, the peak at *m/z* 136, which is absent from the blank spectrum, is of the highest intensity (4.89×10^6 cps), indicating that this signal might be ascribed to the major component of the blue ink. The peak was tentatively interpreted as protonated $C_5H_5N_5$, because the peak showed up at *m/z* 136.06164 (uncertainty < 2 ppm) in the mass spectrum obtained using a well-calibrated LTQ-orbitrap mass spectrometer for exact mass measurement. Upon CID, the precursor ions (*m/z* 136) yielded ionic fragments of *m/z* 119, 108 and *m/z* 94 (Fig. 1b), probably caused by the loss of NH_3, N_2 and CH_2N_2, respectively. So far, the ions of *m/z* 91 were

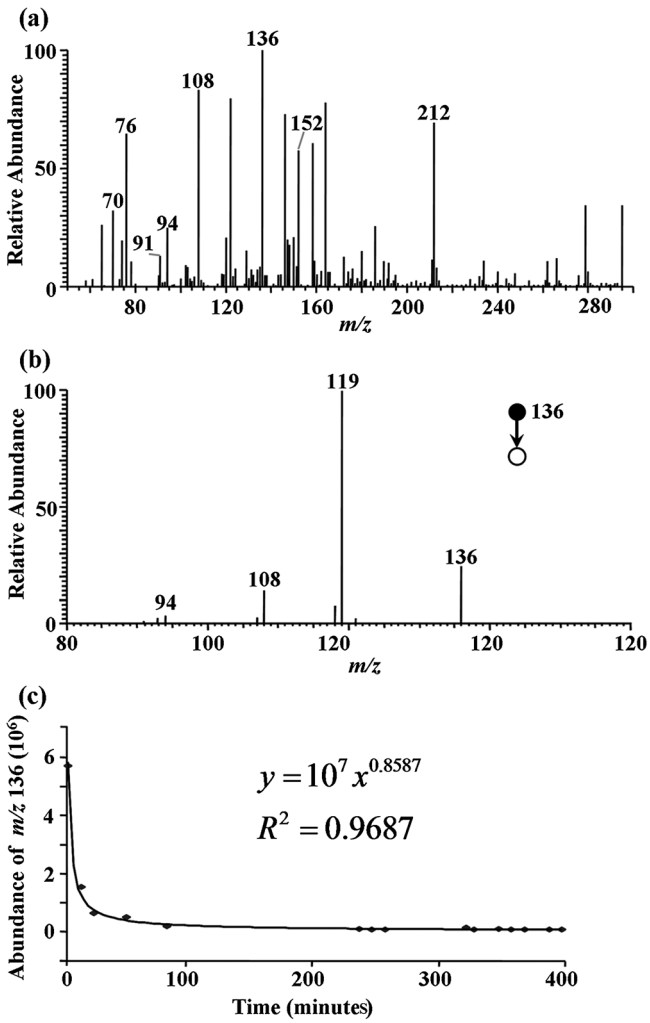

Figure 1. Differentiation of document writing time by DAPCI-MS. a: Mass spectrum of the ink used for handwriting, b: The MS/MS spectrum of the ions of *m/z* 136; c: Degradation of extracted ion (*m/z* 136) chromatogram. Each data point was averaged from five sampling spots on the ink trace.

identified as protonated butanediol using data of CID experiments and exact mass measurement. To avoid potential conflict of interests with the ink producer, further identification of either the ions of *m/z* 136 or other ink components was not attempted.

The decay process of a freshly prepared signature was followed by monitoring the signal levels of the peak at *m/z* 136 in the full MS scan experiments, and a curve of signal response as a function of the aging time was obtained. As shown in Fig. 1c, the signal level of the peak at *m/z* 136 decreases to *ca*. 20 % during 30 min. After aging in the air for about 50 min, the signal intensity in the mass spectrum became stable. Note that a signal drop (>10%) was observed during DAPCI experiments if the sampling spot was continuously sampled for more than 5 min. To avoid such a signal drop, each data point shown in Fig. 1c was averaged from five sampling spots randomly selected from the ink trace. To minimize the interference of shifting the sampling spot, each sample spot was closely located on the plane with a distance of 2 mm, and each spot was sampled for only 10 s. Figure 1c also shows that the signal levels (*m/z* 136) obtained by DAPCI-MS can be time resolved. A good temporal resolution of 1 min can be achieved for a fresh signature prepared within 30 min in this experiment. Accordingly, the images obtained during this stage can be differentiated (from each other). Similar kinetic results (Fig. S1) obtained by using four types of different inks on four types of paper surfaces confirm the method reported here is unlikely to be valid only for the cases tested.

To challenge DAPCI detection of writing time for aged signatures, images were obtained using the mass spectral data recorded from two signatures made 4 h previously. Note that the major difference between the two signatures was that one of the letters C (Fig. 2a) was written 10 min earlier than the other (Fig. 2b). Unquestionably, this difference between the two optical images cannot be easily seen. In the images obtained using the DAPCI-MS, the time difference was made obvious by the use of many different signals. For example, for the peak at *m/z* 136, the image of the letter C (Fig. 2c) differs from that (Fig. 2d) prepared 10 min later in many places which are indicated by different colors. Similar results were also obtained using other signals such as *m/z* 70, 94 and *m/z* 152, which were of lower intensity levels than the intensity of the peak at *m/z* 136 in the full scan MS spectrum. Theoretically, the chemical components in the ink are homogeneously suspended in the mixture. Thus, DAPCI-MS shows its potential for studying the dynamic aging process of handwritings.

Discrimination of forged signatures

Discrimination of forged signature in questionable documents is of substantial significance in forensic analysis. For a preliminary test, the letter 'Q' was written twice (Fig. S2a, b) by one person, and this letter was imitated (Fig. S2c) by another person. From the optical images, it is difficult for people by eye to tell the difference between these letters. In the images obtained by DAPCI-MS, operated under ambient condition (*ca*. 65% relative humidity) without using solvent and discharge gas, the similarities and differences between these letters are clearly visualized. The two letters written by the same person show similar contours of DAPCI images obtained with certain *m/z* values (shown in Fig. S2d, S2e). However, the imitated letter shows different contours from the two authentic ones. This is because the way different people apply pressure to a pen is different, resulting in a difference in the distribution of certain *m/z* in the ion images. The imitated letter is different as shown in Fig. S2 d–f. The characteristics of the images of the letter written by the same person are visible, allowing differentiation of the authentic letters from the forged one with ease. In addition, as shown in Fig. S3–S9, detection of forged signatures has been successfully demonstrated using more examples, including signatures prepared by four individuals using four types of papers and four types of different pens. These data show that the method established here is of acceptable repeatability for detection of forged signatures.

Authentic signatures may be scanned into a computer and then printed out without changing the size and shape

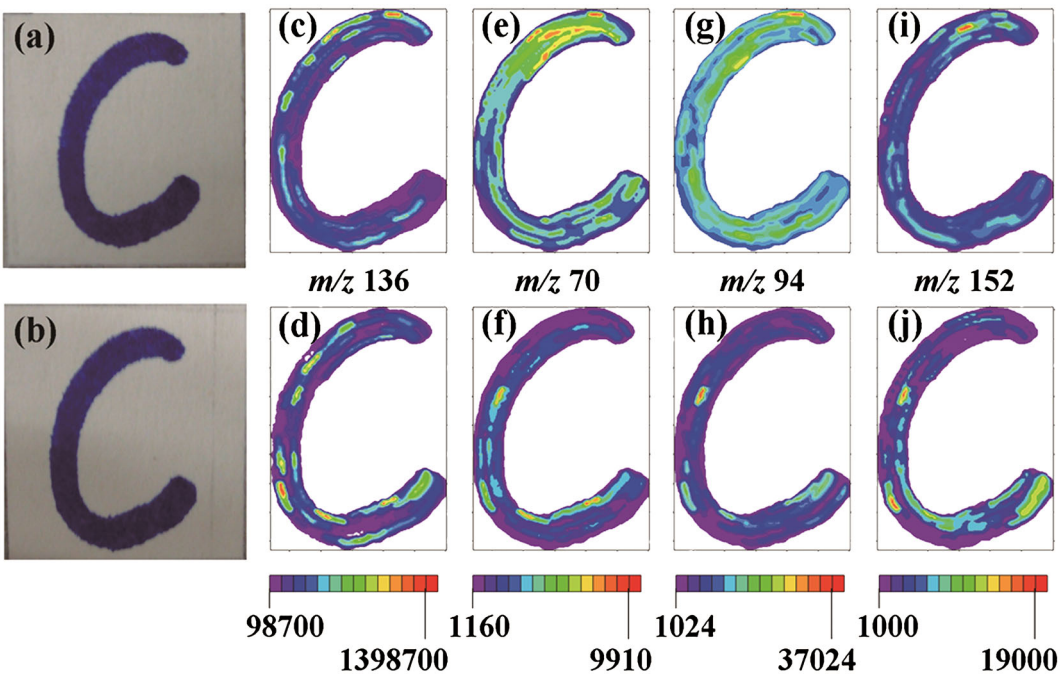

Figure 2. Recognition of two 'C' letters 4 h after being created. The optical images obtained from the letter 'C' written 10 min earlier (a) than the other (b) tell no significant difference. DAPCI images obtained using the peaks at *m/z* 136, 70, 94 and *m/z* 152 for the letter given in a and b are shown in the sequence of c and d, e and f, g and h, i and j, respectively.

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information. The printed signature can be re-filled with a pen, even the same ink used for the authentic signature. This is an advanced case of forged signature and challenges many techniques for fast, reliable and non-destructive detection. In this study, an original signature '*BinHu*' (Fig. 3a) was imitated by another person (Fig. 3b), and also converted to an electronic version by a scanner for printing. Once the electronic version of the signature was printed on a paper surface, it was re-filled using the same pen (Fig. 3c), ensuring that the optical image appearances of these signatures were exactly the same. After imaging by DAPCI-MS with *m/z* 136 as the analytical signal, the authentic signature (Fig. 3d) can be easily distinguished from the signatures written by another person (Fig. 3e) and/or the re-filled signature using the printed signature as a template (Fig. 3f). Note that the composition of the ink left in the signatures would also change with time due to the aging. However, our data suggested that the forged signatures differed from the authentic ones by the contour of the DAPCI images obtained with certain *m/z* values, while the contour of the DACPI images would remain unchanged for the authentic signatures made at different times. These data show that DAPCI-MS can detect the slight difference among forged signatures prepared with computer-assisted skills. Note that DAPCI can be operated in a toxic reagent free, gasless mode, with no significant sensitivity loss. In such a case, the document is preserved in its current state during the analysis, because no solvent or matrix is spiked into the document during the experiment.

Analysis of a stamped document

Documents can be authenticated by a signature and/or stamping with a seal. The latter is a popular legal formality for contracts or other important documents, especially in Asian countries such as China. For many cases, in the real world, it is often necessary to determine if the document was stamped before or after the text was written, because stamping a document before writing/printing violates the legal formality. Thus, for document authentication, it is essential to determine the order of stamping and writing/printing. The '*x*' written before (Fig. S10a) and after stamping (Fig. S10b) was analyzed. The two optical pictures show no difference which can be readily recognized by the human eye. In a blind test, a total of 20 people working in either a local government office or the department of our institute could not distinguish these two stamped writings. In contrast to the optical images, the DAPCI-MS images display the obvious difference between these two stamped writings. For example, the letter '*x*' can be clearly seen when '*x*' was written after the stamp was applied (Fig. S10c). However, no obvious trace of '*x*' is observed when the letter was written before the stamp was applied (Fig. S10d), because the ink for writing the letter '*x*' was masked by the stamp oil in this case, resulting in a significant signal drop in the mass spectra and leading to a blank trace of the letter '*x*' in the DAPCI-MS image.

To further validate the capability of DAPCI-MS for detection of the order of stamping and writing, further experiments were performed to analyze the seal stamps made on a document which had 'ZXL' written on it before (Fig. 4a) and after stamping the seal with Chinese characters (Fig. 4b). Typical DAPCI-MS spectra were recorded from the blank area (colored white in Fig. 4a, b), the seal oil (colored red in Fig. 4a, b) and the handwriting ink (colored black in Fig. 4a, b) on the same paper. In the blank mass spectrum (Fig. S11), many signals were detected from the paper surface. However, the signals detected from the blank paper differ from those detected from the seal oil (Fig. S12) or the handwriting ink (Fig. S13). The seal oil was characterized by the peaks such as *m/z* 137, 170 and 184, while the ink was dominated by the peak signals including *m/z* 70, 136, 146 and 164. The mass spectra recorded from the places where the ink was on the top of the seal oil show abundant signals of *m/z* 108,136, 146, 180 and *m/z* 212 (Fig. S14). Based on CID data matching (data not shown), it was confirmed that the peak at *m/z* 136 was the major peak of the DAPCI-MS of the ink. As shown in Fig. S15, a peak at *m/z* 137 rather than *m/z* 136 was recorded with enhanced intensity on the DAPCI-MS spectra recorded from the places where the seal oil

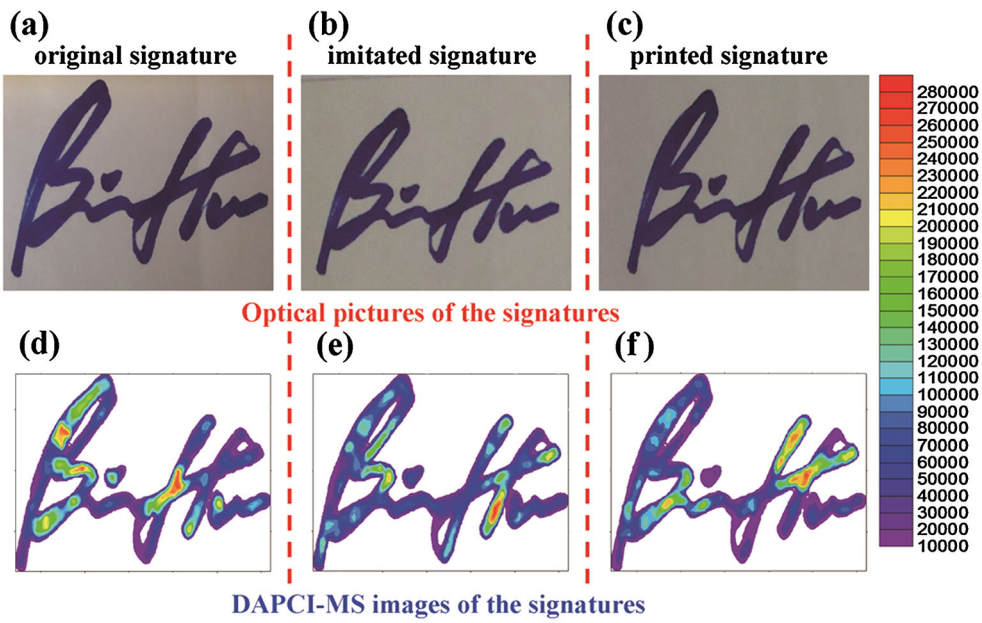

Figure 3. Detection of forged signatures by DAPCI-MS imaging. a, d: original signatures; b, e: imitated writings; c, f: facsimiled writings on a printed copy by using the same pen. (the peak at *m/z* 136 was monitored for analysis).

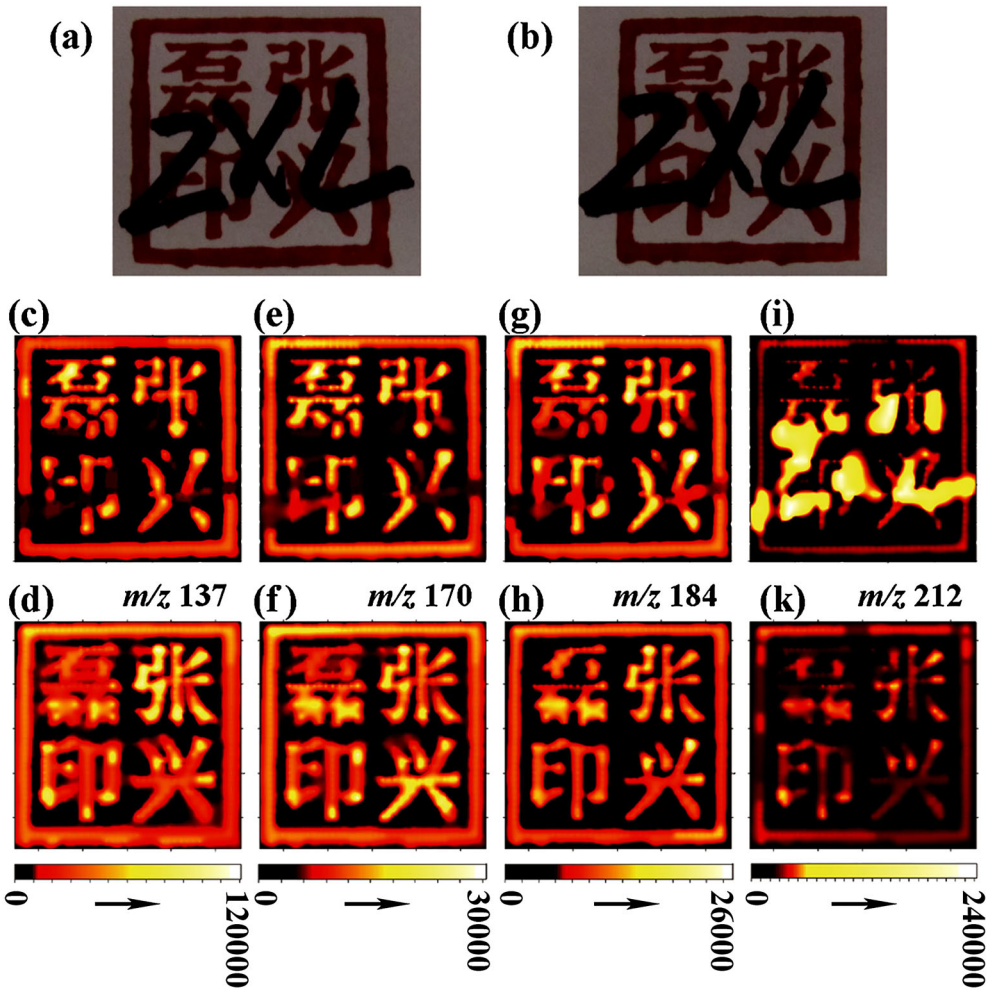

Figure 4. Differentiation of seal-ink overlapping sequences by DAPCI-MS. a: optical images of a seal stamped before signature; b: optical images of a seal stamped after signature; c, e, g and i: the DAPCI images of the seal stamped before handwriting signature base on the data of *m/z* 137, 170, 184 and 212; d, f, h, k: the DAPCI images of the seal stamped after handwriting signature base on the data of *m/z* 137, 170, 184 and 212.

was on the top of the ink. More interestingly, the signal intensity levels of *m/z* 212 increased on the overlapping areas where the ink was on the seal oil.

In Fig. 4a, the DAPCI experimental data show that the Chinese characters of the seal stamp are clearly visible in a two-dimensional image (Fig. 4c) when using characteristic signals such as *m/z* 137 which is found in the seal oil. By contrast, the same Chinese characters are not clearly discernable when using the signal of *m/z* 137 (Fig. 4d) recorded from the picture shown in Fig. 4b. Similar results were reproduced using different signals such as *m/z* 170 (Fig. 4e, f) and *m/z* 184 (Fig. 4g, h), showing that the differences observed in the DAPCI-MS images were not caused by measurement biases. In comparison with the DAPCI images obtained using the signal of *m/z* 212 (Fig. 4i, k), the overlapping areas of the 'ZXL' letters are highlighted in the DAPCI image, but only slightly indicated from the picture shown in Fig. 4a. These data demonstrate that the sealing order can be made clear by DAPCI-MS. The characteristic ions of the ink were not used for DAPCI imaging to avoid the erroneous determination caused by intended disposal for the overlapping areas. Note that these images were obtained at low spatial resolution, as the seal stamps were scanned by DAPCI-MS with a step of 0.5 mm. For practical use, although it takes a longer time (see discussion later), it is recommended that the stamp be scanned with a smaller step size since the maximum resolution of DAPCI can make the details visible at high spatial resolution (a high spatial resolution about 0.1 mm can be obtained by decreasing the diameter of the discharging tube). However, the current results demonstrate that DAPCI-MS is of interest for use in the authentication of documents to clarify the order of stamping and writing without sample pretreatment.

Detection of illegal printing

A word/phrase or even a paragraph may be added into a signed document for illegal purposes. In such a case, the extra words are usually printed by another printer using different printing oils. For a demonstration, some small black boxes (1 cm × 1 cm) were printed on the same paper surface (Fig. 5a) using three different printers, and they served as samples for DAPCI-MS analysis. A total number of 60 samples (20 each set) were printed by an HP laser jet printer (HP 1320, Hewlett-Packard Co., USA), a TOSHIBA laser jet printer (TOSHIBA e-studio600, TOSHIBA Co., Japan) and a Canon inkjet printer (Canon iX4000, Canon Inc., Japan) for DACPI-MS analysis. The DAPCI mass spectral fingerprint of the blank paper was recorded for reference (Fig. 5b). As shown in Fig. 5c, d and e, the DAPCI mass spectra of the samples prepared by different printers differed from each other, showing characteristics of different printing oils. On a 3-D plot of PCA

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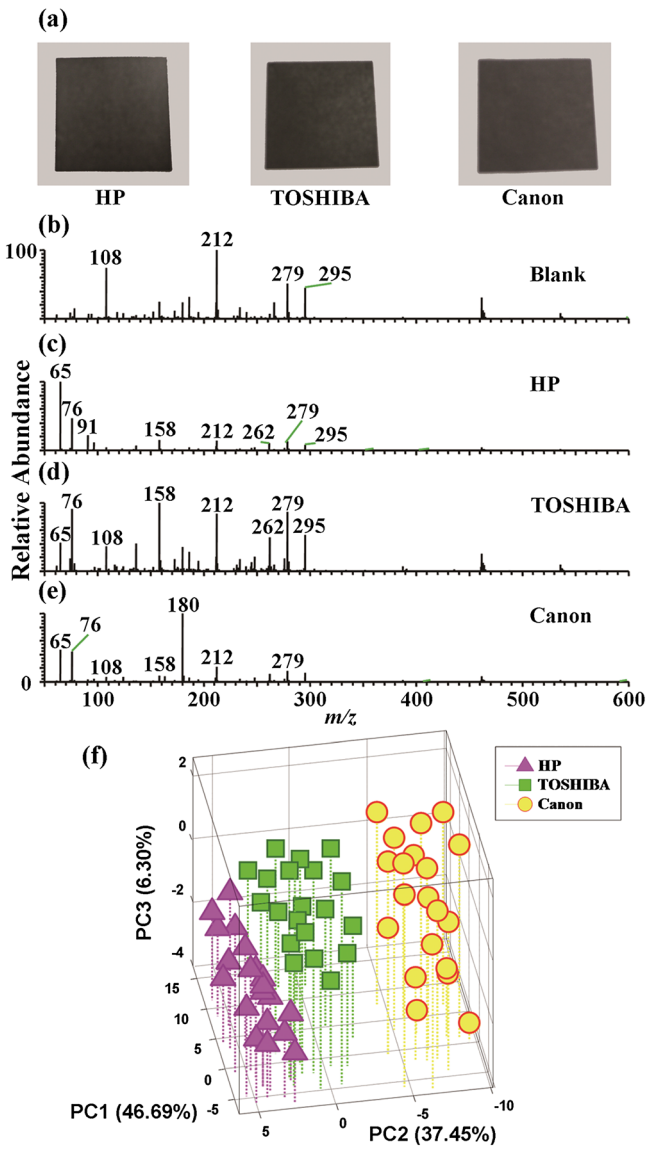

Figure 5. Detection of illegal printings using DAPCI-MS combined with PCA. a: optical pictures of the printings; b–e: mass spectra of different printer surfaces: blank, HP, TOSHIBA and Canon; f: score plot of PC1-PC2-PC3.

results (Fig. 5f), these 60 samples were clearly classified into three clusters, where 90.44% of the total variations were represented and the percentages of variance explained by PC1, PC2 and PC3 were 46.69%, 37.45% and 6.30%, respectively. The PCA loadings obtained are also shown in Fig. S16. As read in the loading plots, the ions of *m/z* 65, 76, 180 and 212 highlighted in the loading plot of PC2 might be differential signals for detection of the origins of printings.

Spatial resolution

For a given object, the spatial resolution of DAPCI-MS is critical for the imaging quality and affects the total time for imaging. Similar to DESI technique, the plume of the primary ions generated by corona discharge forms an irregular ellipse desorption/ionization region on the surface of the sample.[18,21] The spatial resolution of DAPCI-MS was reported to be 250 μm for imaging melamine on the surface of an egg slice. [42] The spatial resolution of DAPCI is mainly related to the diameter of the discharge tip and the gas flow. By reducing the diameter of the discharging tube and using the gentle nitrogen gas flow, better resolution can be obtained without significant loss of sensitivity. To experimentally measure the spatial resolution of DAPCI, a dried paper surface soaked with oxalic acid aqueous solution (10 ppm) was chosen, because oxalic acid is a typical non-volatile compound and yields good signals in the negative ion detection mode. The predominant peak detected at *m/z* 89 was ascribed to the deprotonated oxalic acid (Fig. 6a), which generated a major fragment of *m/z* 61, by the loss of CO (inset of Fig. 6a). The small peaks at *m/z* 43 and *m/z* 71 might be generated from contaminants on the paper surface. A paper strip with a width (w) of 2220 μm was used as a sample, across which the plume of the primary ions was scanned continuously with a step of 10 μm from the left side of the paper until reaching the margin of the right side. The characteristic fragment ions of *m/z* 61 from the parent ions of *m/z* 89 were recorded during the scanning, showing the variation of signals of oxalic acid along the distance (Fig. 6b). Note that only the paper surface area overlapped by the ellipse region can be sampled for production of analyte ions. Once the signal of *m/z* 61 appeared in the mass spectrum, the corresponding spot was marked as

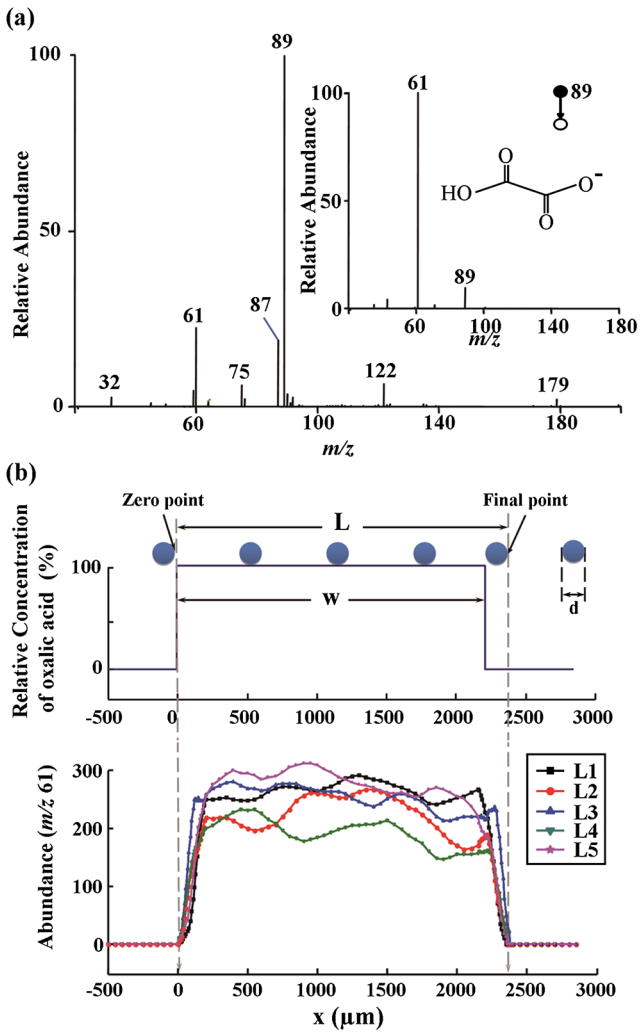

Figure 6. Determination of spatial resolution of DAPCI-MS. a: the DAPCI mass spectrum of the oxalic acid on a paper surface, inset: MS/MS spectrum of *m/z* 89; b: The ion current traces of selected characteristic fragment (*m/z* 61).

the zero point (0). Correspondingly, the point at which the signal of *m/z* 61 disappeared was marked as the final sampling point. The distance between the zero point and the final sampling point is defined as *L*. The diameter of the ellipse region (*d*) equals the distance length (*L*) minus the width of the paper strip (*w*). Since the *L* is read directly from the moving control stage, and the *w* is already known by measuring the width of the paper strip, the diameter (*d*) of ellipse region can be calculated as $d = L - w$. In this study, $w = 2220$ μm; the *L* was measured five times, as shown in Fig. 6b, and the results were 2350, 2350, 2380, 2360 and 2360 μm, respectively. Consequently, the average of *L* was 2360 μm, and $d = L_{ave} - w = 140$ μm. As the ellipse region is responsible for the ion production for each sampling spot, the spatial resolution can be estimated using the diameter of the ellipse region. Therefore, the intrinsic spatial resolution of DAPCI was estimated as 140 μm in this test. This resolution is acceptable for the generation of reasonable results for the authentication of questionable documents.

Repeatability

Signatures maintain the basic characteristics of the writer. To examine the similarity of authentic signatures made under different moods (such as happy, sad, angry, tired and sleepy), five authentic signatures prepared under different conditions and five signatures imitated by another person were subjected for imaging by DAPCI-MS. As shown in Fig. S17a, the optical pictures of these ten signatures are hard to distinguish with high confidence. In the images (Fig. S17b) obtained from the DAPCI-MS spectral data, the authentic signatures are easily differentiated from the forged ones.

A program (detailed in the Supporting Information) has been developed to facilitate the visualization of the similarity of signature images obtained by DAPCI-MS. As a result, the similarity of each signature image was quantitatively obtained, as summarized in Table S1. The data in Table S1 show that the authentic signatures have a similarity larger than 62%, while the similarity between an authentic signature and an imitated signature is smaller than 8%. Once the threshold value of the similarity is set to a given number (e.g. 62%, which is obtained by comparing authentic signatures made under different moods), the forged signatures can be easily recognized automatically by a programmed computer. This makes DAPCI-MS more applicable for actual sample analysis.

Analysis speed

For imaging applications, DAPCI mass spectral data can be directly generated from the object, requiring no sample pretreatment. However, it is necessary to scan the object surface to obtain enough data points for imaging. The analysis time (*t*) required is inversely proportional to the resolution squared (R^2) (i.e. $t = k \times 1/R^2$, k is a factor). For low-resolution imaging (e.g. 0.5 mm, shown in Fig. 4), the total analysis time required to produce useful images is significantly reduced. For imaging a picture with an area of 4.0 cm^2 (such as Fig. 4a) with a resolution of 500 μm, about 20 min was typically used in this study for data recording.

Conclusion

DAPCI-MS imaging has been developed for the authentication of questionable documents. Taking advantage of high sensitivity, DAPCI-MS has a good temporal resolution to detect slight alterations in the ink traces, allowing the time after writing to be determined with high temporal resolution. Molecular images of documents were obtained by scanning the surface of the document in a non-destructive mode under ambient conditions. Reliable differentiation of forged signatures, stamped documents and illegal printings was successfully demonstrated based on the two-dimensional mass spectral images of the objects. In this study, the optimal spatial resolution of DAPCI-MS was estimated to be 140 μm. The relationship between the image quality, spatial resolution and the analysis speed has also been discussed. The experimental results show that DAPCI-MS provides reliable information at the molecular level and thus has the potential for a reliable analysis of questionable documents in forensic applications, provided certain background information is available.

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Supporting information

Supporting information may be found in the online version of this article.

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