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Direct analyte-probed nanoextraction (DAPNe) coupled to matrix-assisted laser desorption ionization (MALDI) for examination of the ink chemistry on documents

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ABSTRACT

Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) has been coupled to direct analyte-probed nanoextraction (DAPNe) through use of nanomanipulation for the analysis of ink chemistry on documents. DAPNe is first used to extract ink from the document and then deposits the sample on the MALDI plate. Through this method, cutting the document for MALDI-MS analysis is avoided. DAPNe extracts ink from documents with minimal to no visible destruction. Specific dyes and binding agents in the extracted ink are monitored with mass spectrometry. Different matrices, 1, 5-diaminonapthalene (DAN), 2, 5-dihydroxybenzoic acid (DHB), and silver nanoparticles, were tested to compare intensity enhancement of the mass spectra signals. The advantages of using MALDI-MS coupled to DAPNe are shown by characterizing Crystal Violet, Basic Yellow 2, Rhodamine B, and polyethylene glycol from red and blue pens, black pen, and a black inkjet printer cartridge.

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1. Introduction

The evaluation of inks on questioned documents is crucial, especially when the manipulation and falsification of manuscripts is involved. These counterfeit documents include passports, checks, letters, contracts, identification cards, social security cards, and many more. Once dispensed, the chemistry of the ink changes as it ages. The amount of solvents in the ink will decrease over time and other agents such as dyes, resins, and vehicles will oxidize as the ink ages [1]. Identifying the presence of ink solvents and how much the dye and other agents have oxidized, the age of the ink can be used to determine the authentication of the document in question [1,2]. Analysis of the ink chemistry helps differentiate if the questioned document is authentic or an imitation. Since a counterfeit document in question typically becomes evidence, a nondestructive approach with minimal alteration is necessary in order to preserve the document in its most pristine state.

Over the past few years, several techniques have been used to analyze inks and documents. Common, but destructive, methods to analyze ink on documents are separation techniques such as gas chromatography [3–5], liquid chromatography [6,7], and thin-layer chromatography [8,9]. These chromatographic techniques are destructive due to the required sample preparation methods including cutting strips [8], micropunching holes [9], and pulling ink-bearing fibers [10] from the document. Once destroyed, those pieces are then placed in a solvent to remove the ink where the ink-infused solvent is then further analyzed. Although the aforementioned separation methods output reliable data, the sample is used up in the analysis and precious or historical documents are not amendable to the technique. Utilizing direct analysis techniques require minimal to no sample preparation, saving time. These techniques include, direct analysis in real time mass spectrometry (DART) [11], desorption electrospray ionization (DESI) [12], easy ambient sonic-spray ionization mass spectrometry (EASI-MS) [13] and liquid extraction surface analysis (LESA) [14]. The issue that arises when using these techniques is that full documents cannot be analyzed with minimal destruction. A large amount of surface area is required when using DART and DESI which becomes more destructive [11–13]. Although EASI-MS uses a milder ionization/direct desorption method with a voltage free apparatus, the sampling area is very confined. LESA operates in an enclosed workstation that also limits sample size [14,15]. Nondestructive methods allow the opportunity to resample the document several times with minimal to no alteration. A direct sampling method that can analyze full documents in a nondestructive manner will be greatly beneficial to the forensic science community.

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Laser desorption has proven to be a powerful tool for colorant analysis in art and ballpoint pens in addition to colorant and pigment analysis of ink jet printer inks [16,17]. Coupling the technique to mass spectrometry yields a large amount of chemical and structural information [8]. This has led to the use of matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) for analyzing the ink chemistry from documents and identifying specific dyes [10,16,18–23]. Although insoluble pigments may not be analyzed, the binding agents (i.e., glycols, triethanolamine) in the ink formula may be characterized using MALDI-MS. No visible damage, from the interaction of the laser, has been reported when analyzing ink directly from the document [10,23]. Although this technique is beneficial to forensic document analysts, saves time, and is efficient, the size of the sample plate is constricted and limits document size. Utilizing only MALDI-MS for this application can be destructive to the document due to its plate size limitation. Analyzing full documents can require cutting and fixing an area of the document to the sample plate. Thus, there is some limitation of MALDI-MS in analyzing full documents.

Recent articles have shown success in coupling direct analyte-probed nanoextraction (DAPNe) with nanospray ionization mass spectrometry (NSI-MS) for ink on document analysis [2,24]. This technique has also been used for biological [25,26] and drug residue [27,28] applications. DAPNe is a nanomanipulation technique that directly extracts miniscule amounts of analyte from a variety of surfaces with minimal to no visible damage [2,24]. The nanomanipulator is fixed on the stage of a high-powered microscope and contains a removable tip emitter that is pre-filled with an extraction solvent. There are however a few drawbacks in using NSI-MS with DAPNe. NSI-MS requires a coated tip in order to transfer ions from solution into the gas phase for mass analysis [29]. The tip emitter is typically coated (e.g., AuPd) which is more expensive when analyzing many samples. NSI-MS also requires accurate positioning to the MS source leading to longer preparation time. The major disadvantage of utilizing NSI is sample consumption. The continuous flow of NSI means that the sample is constantly being consumed [30–32]. Therefore, a large amount of sample is wasted. Not all mass spectrometers can constantly analyze ions. For example, a quadrupole ion trap (QIT) cannot accept any more ions once it reaches ion volume capacity. Coupling DAPNe with MALDI-MS instead can lead to several advantages. Since the tip emitters do not need to be coated for MALDI-MS analysis, they can be pulled in the lab for quick use instead of ordering them commercially pre-coated, thus reducing cost. Since MALDI-MS uses a pulsed laser, it ablates ions as needed and no sample is wasted [32]. It is important to not "throw away" ions, especially for ultra-trace analyses. MALDI-MS can often provide data from sub-femtomole amounts of sample loading, achieving high levels of sensitivity [17,32]. MALDI-MS is also advantageous due to its high tolerance to salts and buffers (physiological levels of salts), unlike NSI.

By coupling MALDI-MS with direct analyte-probed nanoextraction (DAPNe), analyzing the chemical footprint of inks on full documents can be made possible. The aim of this research is to demonstrate the ease of analyzing the ink chemistry on documents from different pens and printed documents with DAPNe coupled to MALDI-MS. Different matrices added to the extracted ink sample, was used to compare absolute intensities of ink components such as dyes and binding agents. These matrices include 1, 5-diaminonapthalene (DAN), 2, 5-dihydroxybenzoic acid (DHB), and silver nanoparticles. The absolute intensities of these matrices were compared to the absolute intensity of samples with no matrix. For the first time, MALDI-MS has been transformed into a nondestructive technique for ink on document analysis.

2. Materials and methods

2.1. Reagents and solvent preparation

The solvents used are 18 Ω Millipore water (Milli-Q Plus; Billerica, MA) and optima LC/MS methanol (Fischer Scientific; Fair Lawn, NJ). The matrices used are 1,5-diaminonaphthalene (Sigma Aldrich; St. Louis, MO), 2,5 dihydroxybenzoic acid (Sigma Aldrich; St. Louis, MO), and silver nanoparticles (99.999% purity, SPI Supplies; West Chester, PA). Blue and red pens (Société Bic S.A.; Shelton, CT), Uniball black pen (Newell Rubbermaid; Downers Grove, IL), deskjet (Black 60) ink cartridge (HP; Alto, CA), and A4 type copy paper were commercially obtained.

The extraction solvent used for all ink chemistry was methanol:water (1:1, v/v). Matrix spotting (0.5 μL per sample spot) was completed with 20 mg/mL of 2,5 dihydroxybenzoic acid (DHB) and 1,5-diaminonaphthalene (DAN), dissolved in a 70:30 mixture of acetonitrile: water (v/v). The matrix, silver nanoparticles, were deposited on the sample using soft-landing ion mobility (SLIM) [33–36].

2.2. Instrumentation and sampling technique

The nanomanipulator is fixed on the stage of a high-powered microscope, illustrated in Fig. 1. It contains a removable, borosilicate glass, tip emitter that is pre-filled with an extraction solvent. Borosilicate glass (with filament) were used to create these tips with an outer diameter (o.d.) of 1.2 mm, i.d. 0.69 mm, and length of 10 cm (item #: BF120-69-10). The tip emitters were pulled in the lab using a P-2000 laser-based micropipette puller (Sutter Instrument; Novato, CA). This system integrates a CO_2 laser-based heat source to create different inner diameter (i.d.) tip sizes. A program with a heat setting of 280, velocity setting of 30, a pull setting of 0, and a delay setting of 200 was used to create these tip emitters. With this program, the average i.d. of the tip emitters was 42 μm. The i.d. of the tip emitters was determined using an FEI Quanta 200 environmental scanning electron microscope (SEM). Two tip emitters were created from each borosilicate glass capillary. Once made, the capillary was then cut to 2.5–3 cm for nanopositioner.

The piezoelectric–controlled nanomanipulator consists of an L200 nanomanipulator (DCG Systems; Richardson, TX) mounted on a Nikon AZ 100 (Nikon Instruments Inc.; Melville, NY) microscope stage. The range of motion for the joystick controlled nanomanipulator is 12 mm in the x- and z-direction and 28 mm in the y-coordinates. The translational resolution for fine and course mode are 5 nm and 100 nm, respectively. A PE2000b four-channel pressure injector (MicroData Instrument Inc.; S. Plainfield, NJ) was used to perform injection and aspiration.

The samples were made by drawing a line with different pens and printing text on copy paper. Fig. 2 show micrographs that illustrate the process used for ink extraction. The tip emitter was first filled with 10 μL of extraction solvent. A 5 μL solvent droplet of Millipore water was then placed on the ink (Fig. 2(b)). The tip emitter was positioned, using a joystick controller, where a miniscule amount of extraction solvent was injected via pressure injector (5 psi) into the droplet. While the droplet was still holding its tension, the extraction solvent induces liquid phase microextraction where components from the ink diffuse into the solvent. After 15–20 s the solvent droplet is then extracted (at 10 psi) back into the tip. As shown in Fig. 2(c), this extraction method has a low impact on the document and ink where a watermark is left at most. The sample in the tip is then dispensed on a glass slide or MALDI plate (at 35 psi) where a matrix may be added or analyzed as is with laser

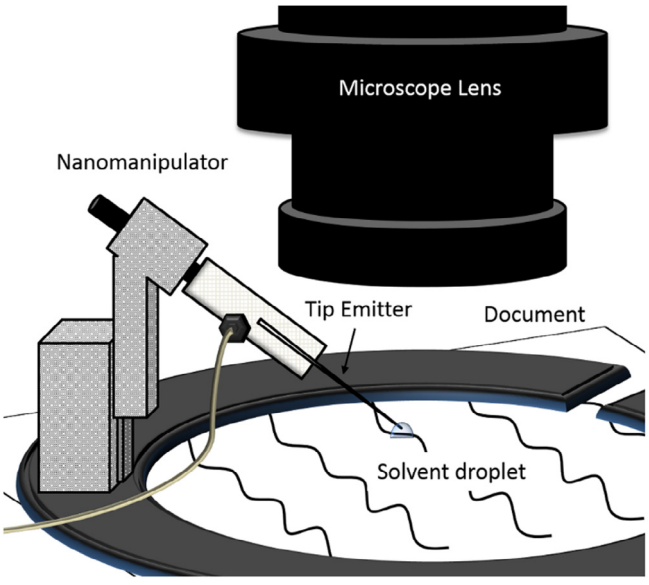


Fig. 1. Schematic of nanomanipulator extracting ink from a document.

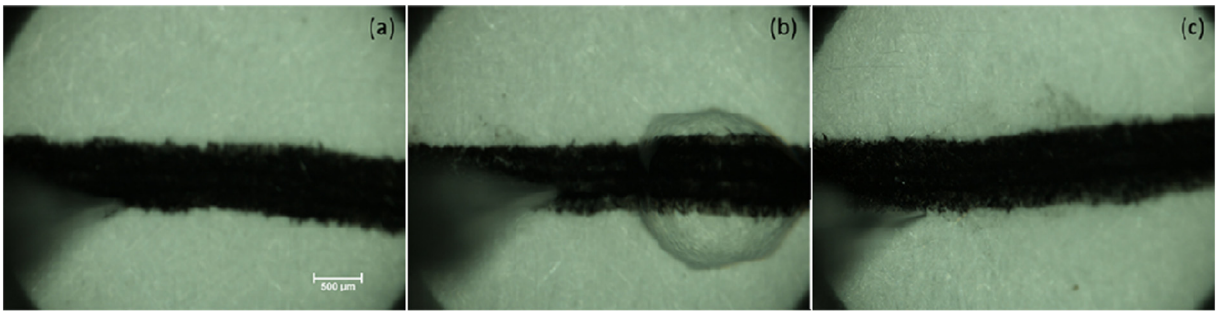


Fig. 2. Micrographs of ink extraction from a black pen where (a) is before, (b) is during, and (c) is after extraction.

Table 1
Different matrices used compared to no matrix for ink samples from a blue pen.

Sample	Matrix	Peaks	*m/z* (±0.003)	Absolute Intensity
Blue ink	DAN	Crystal Violet	372.243	23,409,836
			358.400	21,868,852
			344.213	7,442,623
		Basic Yellow 2	268.181	31,180,328
	DHB	Crystal Violet	372.246	74,745,290
			358.230	39,934,480
			344.213	8,891,072
		Basic Yellow 2	268.181	57,641,278
	Ag	Crystal Violet	372.246	6,261,736
			358.230	3,574,888
			344.215	834,033
		Basic Yellow 2	268.130	43,683
	None	Crystal Violet	372.244	315,163,934
			358.400	79,098,360
			344.953	33,606,557
		Basic Yellow 2	268.140	5,743,443

Table 2
Different matrices used compared to no matrix for ink samples from a red pen.

Sample	Matrix	Peaks	*m/z* (±0.003)	Absolute Intensity
Red ink	DAN	Rhodamine B	443.272	532,279
			415.200	227,334
			399.156	11,200
	DHB	Rhodamine B	443.238	161,179,361
			415.175	19,164,619
			399.195	321,965
	Ag	Rhodamine	443.236	171,806
			415.205	41,905
			399.900	1,353
	None	Rhodamine	443.235	27,478,689
			415.204	12,290,164
			399.172	1,142,623

desorption ionization. The technique of extracting from a sample and depositing onto a glass slide for MALDI-MS analysis, with the nanomanipulator, was first conducted by Phelps et al. [37] for the analysis of single organelles. The direct extraction technique has also been previously discussed in other articles [2,24,37]

After spotting the samples with a matrix, the slides were analyzed by a MALDI-LTQ-XL-Orbitrap (Thermo Scientific; San Jose, CA). This instrument is equipped with an intermediate pressure MALDI source (75 mTorr) using a 337 nm N_2 laser (MNL 100; Lasertechnik; Berlin, Germany). Automatic gain control (ACG) was on for all samples. Each sample was scanned from a *m/z* range of 100–2000 in positive mode. The laser power used for irradiating samples using DHB and DAN was 10 µJ (laser fluence of 0.83 J/cm^2, 30 × 40 µm spot size). Laser energies ranging from 10 to 80 µJ was conducted on printer ink with no matrix. The spectra obtained for blue, red, and black pen (with no matrix) was conducted using a laser energy of 25 µJ, 35 µJ, and 15 µJ, respectively. The data was processed using Xcalibur v 2.2 (Thermo Scientific; San Jose, CA) and image processing was performed with ImageQuest v 1.01 (Thermo Scientific; San Jose, CA). This process was replicated three times for each matrix used. It is important to note that error was not added for absolute intensity values due to the lack of quantitation abilities of this process. The nanomanipulator extracts an unknown amount of ink from a paper substrate, which cannot be determined, leading to large error values for absolute intensities [1,2,24]. Thus, Tables 1–4 only displays one set of values for absolute intensities.

Table 3
Different matrices used compared to no matrix for ink samples from a black pen.

Sample	Matrix	Peaks	*m/z* (±0.003)	Absolute Intensity
Black ink	DAN	PEG*	777.506	1,370,024
		Crystal Violet	372.361	132,173
	DHB	PEG*	805.443	67,361,761
		Crystal Violet	372.185	56,921
	Ag	PEG*	673.370	1,631,147
		Crystal Violet	372	Not seen
	None	PEG*	821.422	638,065
		Crystal Violet	372.349	67,872

* The most intense peak was chosen.

Table 4
Different matrices used compared to no matrix for ink samples from black printer ink.

Sample	Matrix	Peaks	*m/z* (±0.003)	Absolute Intensity
Printer ink	DAN	PEG*	1155.710	39,877
	DHB	PEG*	1259.718	13,307,377
	Ag	PEG*	n/a	Not seen
	None	PEG*	n/a	Not seen

* Most intense peak was chosen.

For silver matrix studies, a soft-landing ion mobility (SLIM) chamber was used to deposit silver nanoparticles on top of the samples. SLIM uses a combination of cluster formation via laser ablation to soft land silver nanoparticles on a substrate [34]. The average sizes of one or more metal nanoparticles landed ranges from 10–500 nm [33]. A silver rod (99.999% purity; SPI Supplies; West Chester, PA) was laser ablated for silver nanoparticle deposition via 532 nm Nd:YAG laser (Minilite; Continuum; Santa Clara, CA) at 1 and 2 Torr He buffer gas for a deposition time of 60 min. Soft landing silver nanoparticles with the SLIM system has been previously discussed in more detail in a patent by Verbeck et al. [33] and in a most recent publication by Walton et al. [34].

3. Results and discussion

3.1. Ink pens

To evaluate the DAPNe-MALDI technique, an ink sample was analyzed from a blue pen. After extraction, the chemical footprint of the ink sample was first imaged with no matrix and then analyzed with different matrices using MALDI-MS. Crystal Violet and Basic Yellow 2 (bis [4-(dimethylamino)phenyl]methaniminium chloride) were the dyes observed for the blue pen. The mass spectrometric species for Crystal Violet dye and its degradation products include $[M]^+$, $[M\text{-}CH_3 + H]^+$, and $[M\text{-}2CH_3 + 2H]^+$ [28–40] corresponding to *m/z* 372.244 ± 0.003, 358.400 ± 0.003, 344.953 ± 0.003, respectively, and for Basic Yellow 2 is $[M]^+$ representing *m/z* 268.14 ± 0.003. [38]. Fig. 3 shows the image of a blue pen, with no matrix added, where *m/z* 372.244 ± 0.003 is isolated. The red spots indicate high intensities of that peak whereas the blue areas indicate lower intensities. Fig. 4(a) shows the spectrum

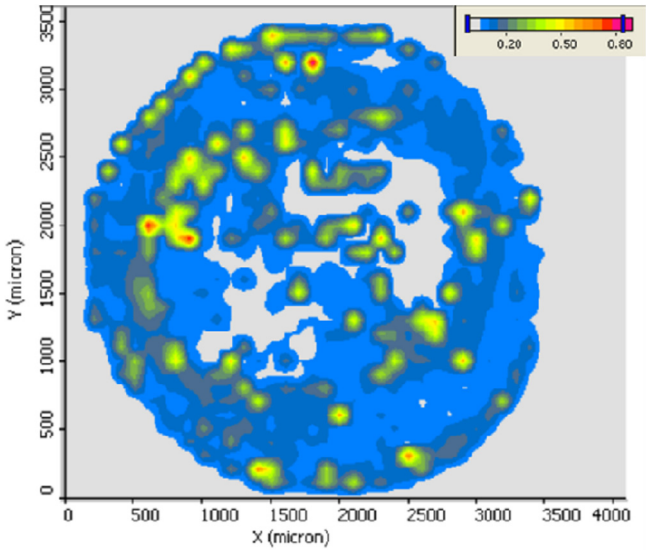


Fig. 3. A MALDI-MS image of an ink extraction from a blue pen with no matrix, scale bar indicated (top right) where red represents high intensity of a specific peak and blue represents low intensity of that peak.

obtained from a red region without added matrix. Not using a matrix gave the highest intensity peaks for Crystal Violet due to its strong UV absorption characteristic. Samples with added matrix had lower intensities for the 372.244 peak. Even though Crystal Violet was able to undergo absorption without a matrix, Basic Yellow 2 was not. Fig. 4(a), inset, shows that Basic Yellow 2 does appear but at very low intensity compared to Crystal Violet. The ratio difference of Basic Yellow 2 to Crystal Violet when not using a matrix and using DAN as a matrix is 0.0182 and 1.3319, respectively. This may be due to the low molar absorptivity of Basic Yellow 2 at the wavelength of the laser compared to Crystal Violet [29]. Therefore a matrix must be used to enhance its signal. As seen in Table 1, DHB has the most reduced matrix assisting effect and highest absolute intensity for *m/z* 268.181 ± 0.003.

The ink from a red pen was also analyzed with no matrix and different matrices added. Fig. 5 shows the spectra obtain from using no matrix and different matrices. Table 2 consists of compiled absolute intensity values from the substrate and dyes found in a red pen. Three different chemical components from Rhodamine B were observed. These peaks were *m/z* 443.235 ± 0.003, 415.204 ± 0.003, and 399.12 ± 0.003 corresponding to $[M]^+$, $[M\text{-}CH_3 + H]^+$, and $[M\text{-}CO_2]^+$, respectively (M represents the parent ion) [39]. Although Rhodamine B was characterized adequately with no matrix, DHB greatly enhanced the signal by one order of magnitude (Fig. 5(c)). Matrix effects of DHB and the substrate did not suppress the dye signal. The spectra from Fig. 5(b) and (d) show that using DAN and silver nanoparticles, correspondingly, greatly suppress the signals of interest.

The spectra obtained when analyzing a black pen is shown in Fig. 6, where PEG was the main constituent observed. Table 3 indicates that using no matrix and DAN had more matrix assisting

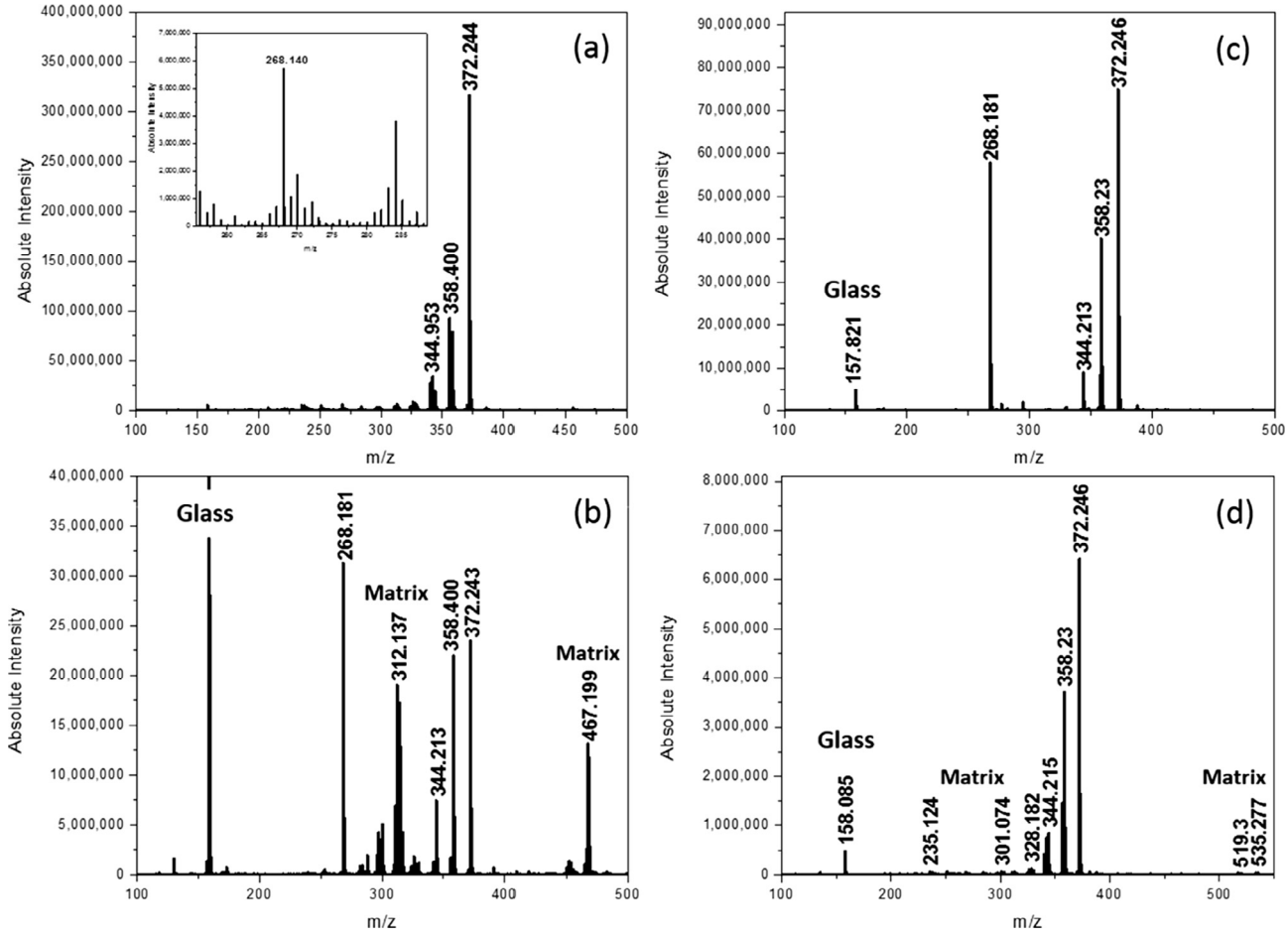


Fig. 4. Spectra of ink sample from Blue pen using (a) no matrix, (b) DAN, (c) DHB, and (d) silver nanoparticles.

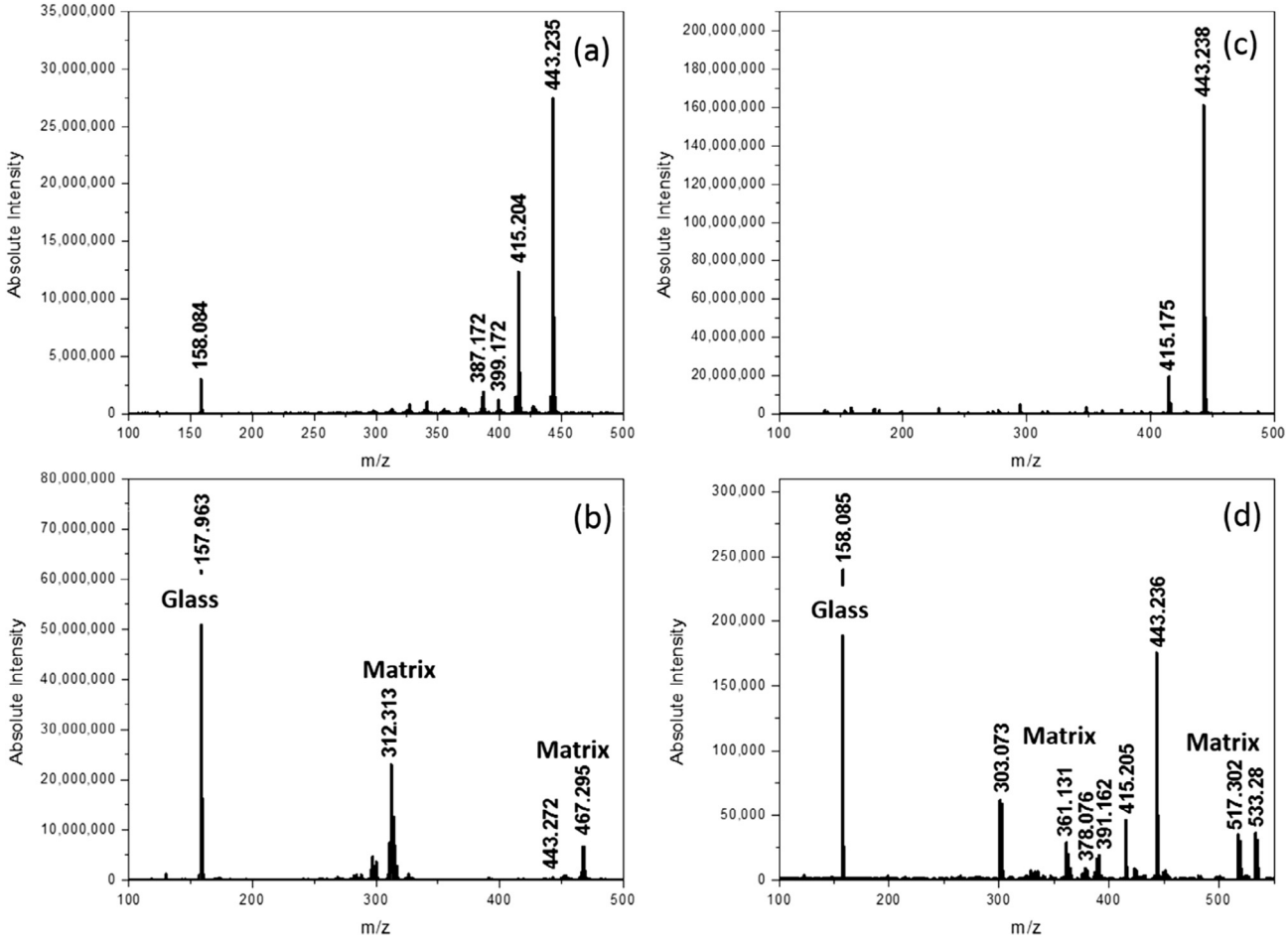


Fig. 5. Spectra of ink sample from Red pen using (a) no matrix, (b) DAN, (c) DHB, and (d) silver nanoparticles.

effects than using DHB and silver nanoparticles. Low-molecular-mass PEG (e.g., PEG 1000) can be analyzed in a straightforward laser desorption experiment without a matrix [41,42]. As PEG becomes more complex, by increasing the molecular mass or if the ink formula contains a mixture of polymers, a matrix will be needed. In Fig. 6(a), the highest mass spectrometric species detected without a matrix is *m/z* 1085.586 ± 0.003. When DAN and DHB is added, the number of PEG ions detected widens. Fig. 6(c) shows an increase in molecular weight of PEG ions detected when using DHB as a matrix. The black pen also contained Crystal Violet dye with absolute intensities of 67,872.346 a.u., 37,716.743 a.u., and 53,728 a.u. for *m/z* 372.247 ± 0.003, 356.215 ± 0.003, and 343.073 ± 0.003, respectively, when no matrix was used (spectrum not shown). Huynh et al. [2] analyzed Uni-ball black pen with DAPNe-NSI-MS. Crystal Violet could only be observed when the ink was extracted with methanol:chloroform (1:1, v/v) and no peaks were observed when using methanol:water (1:1, v/v) as the extraction solvent. Although the absolute intensity values were low, the addition of DHB matrix increased the intensities values by one order of magnitude. The intensity of Crystal Violet could also be increased by using chloroform instead of methanol as the extraction solvent, but this would completely depreciate the signal of PEG [2]. This is because PEG requires heat to be soluble in chloroform. By coupling DAPNe with MALDI-MS instead of NSI-MS, signals from both Crystal Violet and PEG can be effectively observed when using DHB as a matrix and methanol as the extraction solvent.

3.2. Printer ink

Polyethylene glycol (PEG) is a popular ink solvent often used in printer inks due to its lubricating feature for the print heads. PEG ions have a distinct distribution, where each peak is spaced 44 u apart due to the oxyethylene repeating unit $(—OCH_2CH_2—)_n$ and n representing the number of monomeric ions [2]. Each signal can be detected with a proton, sodium, or potassium adduct represented as $[M + H]^+$, $[M + Na]^+$, and $[M + K]^+$, respectively ($M = HO(C_2H_4O)_nH$). PEG as a binding agent has been observed when analyzing HP black ink from a printer cartridge. The same constituent has been found in black Epson ink cartridge [17]. Fig. 7(a) shows PEG ions with sodium adducts. The spectrum shown in Fig. 7(b) shows two different distributions, inner (less intense) and outer (more intense). The outer distribution are PEG ions with sodium adducts and the inner distribution are PEG ions with potassium adducts. This is because the adjacent peaks have a difference of 16 u. The same phenomenon was observed with Anne et al. analyzed PEG using a MALDI-TOF spectrometer [43].

Different laser energies, ranging from 15–80 μJ, were applied. Due to the inefficient nature of PEG, it cannot ionize without a matrix. The molecular species of PEG ions were also not enhanced significantly when using DAN and silver nanoparticles as a matrix (Fig. 7(a)). The matrix, DHB, greatly enriched the absolute intensity signals of the PEG distribution found in printer ink. Table 4 compares the most abundant PEG peak to the signal obtained when using different matrices. The matrix background is significantly higher when DAN is used, especially in the low mass region [44].

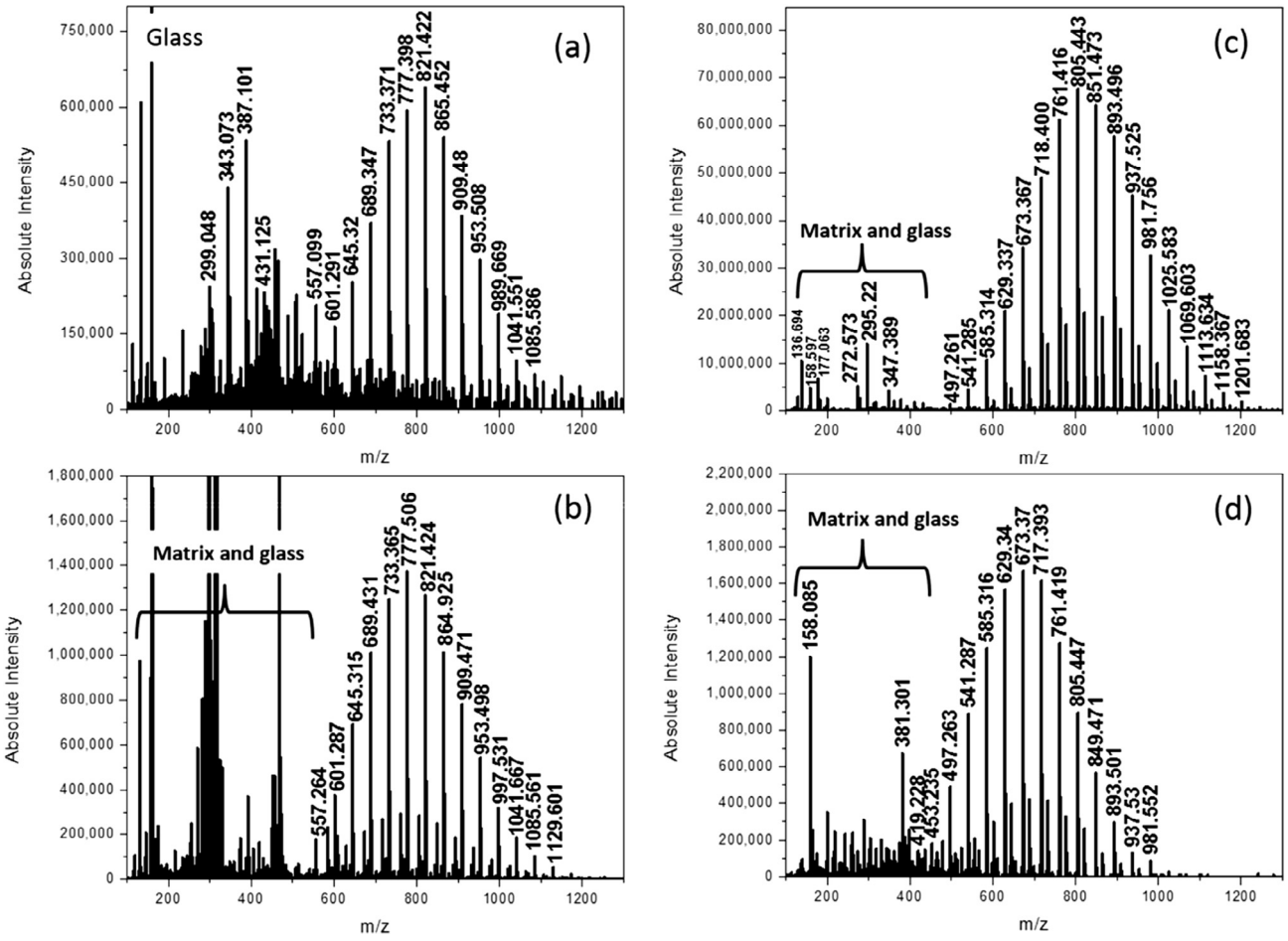


Fig. 6. Spectra of ink sample from a black pen using (a) no matrix, (b) DAN, (c) DHB, and (d) silver nanoparticles.

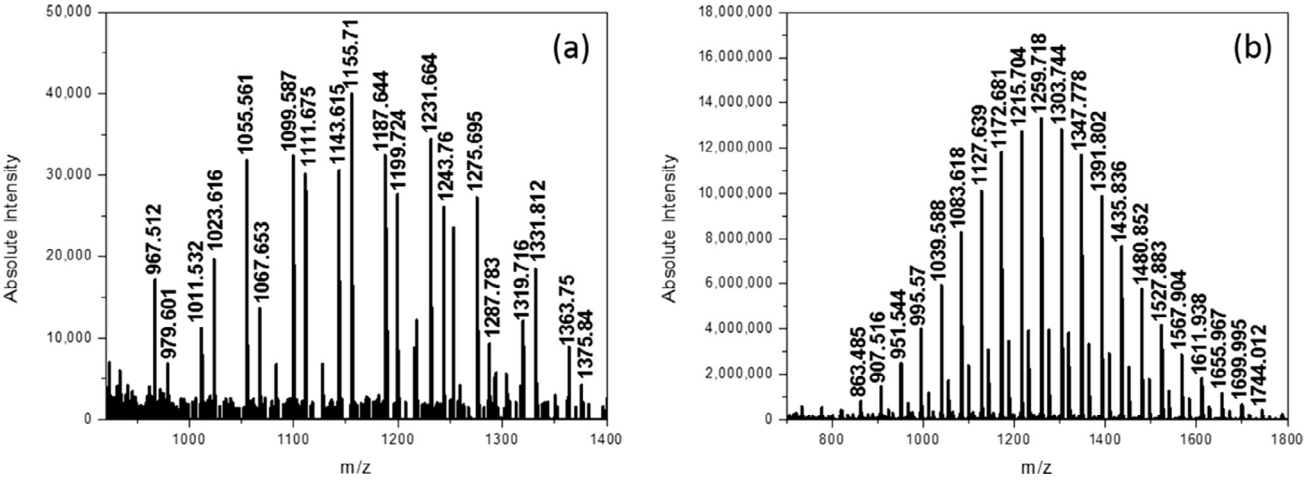


Fig. 7. Spectra of ink sample from black printer ink using (a) DAN and (b) DHB.

4. Conclusion

For the first time, MALDI-MS can analyze ink on documents without the destructive nature of plate size constriction. Common ways to analyze ink on documents, using MALDI-MS, require removal of samples from the document or sample preparations involving evidence-altering of the paper [45]. DAPNe is a great addition for MALDI-MS and ink analysis generally due to its ability to nondestructively extract ink from a document and specifically because it can isolate specific components contained in ink. The latter is achieved by using different extraction solvents. Chloroform may be added to the extraction solvent to extract a higher volume of Crystal Violet dye from the black pen in contrast to methanol which extracts a higher volume of PEG [2]. It is important to note that achieving the same components from a few different pens does not mean the ink formula is the same for those pens,

but a conclusion can be drawn that a particular solvent is able to extract those specific components from different types of inks. Additional studies are also needed to determine the extraction chemistry on different types of paper. Paper that is made up of 100% cotton may contribute more to soaking up and holding the ink, making extraction more difficult [45].

Not only is sample preparation time reduced, sensitivity is maintained and sample volume is not wasted. Printer ink was the only sample that could not be analyzed without a matrix. PEG could not be analyzed effectively without a matrix in printer ink, but by concurrently analyzing printer ink with DHB this problem is solved. DHB proves to be the most proficient matrix used to enhance all molecular ion signals found in red and blue pens, black pen, and printer ink. By combining MALDI-MS with DAPNe, forensic document examiners can obtain the benefits provided by MALDI-MS in a nondestructive nature.

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