

Analyzing Brazilian Driver's License Authenticity by Easy Ambient Sonic-Spray Ionization Mass Spectrometry

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Abstract

Fast and unequivocal methods of questioned document analysis are essential in forensic science. Here, a desorption/ionization technique, EASI-MS, was assessed for its ability to investigate questioned driver's licenses (DL). Two suspects DL, displaying the same personal data in the proper fields (name and ID numbers), but with different individual photos, showing similar impressions on microscopic analysis, and authentic standards documents specimens were used as test cases. Profiles from authentic DL surface were dominated by a set of few minor ions, mainly from the plasticizers bis(2-ethylhexyl)phthalate and dibutylphthalate. The seized suspect counterfeit DL on points from personal data and photo were, however, dominated by abundant diagnostic ions of m/z 463, 507, 551, 595, 639, 683, which confirmed counterfeiting. Surfynol® and Nonoxynol-9®, which are common constituents of inkjet printing, were detected in the counterfeiting areas by high-accuracy EASI(+)-FT-ICR MS. The EASI-MS technique is shown therefore to offer an attractive tool for forensic investigation of questioned documents.

Keywords

Forensic Sciences, Questioned Documents, Ambient Mass Spectrometry, Easy Ambient Sonic-Spray

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Ionization Mass Spectrometry, EASI-MS

1. Introduction

The analysis of potentially forged printed documents, such as driver's licenses, is an important area in forensic science [1]. In an attempt to hamper the action of counterfeiters, the Brazilian Government introduced a new driver's license in 2006 that features several security items with sophisticated graphic characteristics. Brazilian driver's licenses are produced by first printing a background or blank document at the official federal institution on security paper in which all of the security items, including a two-dimensional holographic strip, chalcography and micro letters, are present. The owners' personal data and photo are then printed on this blank document in the official state institutions responsible for assigning driver's licenses. Counterfeit licenses that look authentic and display all of the security items can be produced by taking and printing on blank documents from official institutions; this illegal process is known as stolen-blank forgery. Detecting illegally printed data on stolen blank driver's licenses is challenging for criminal experts because the counterfeiters use advanced printing and copying technologies. In addition, the detection of the printing procedure by visual inspection or microscopic analysis is difficult.

In forensic investigations, the use of nondestructive methods of screening and the acquisition of molecular data is crucial to produce unequivocal evidence. To date, diverse analytic methodologies have been applied. For example, FTIR [2] has been applied to analyze Japanese passports and Mossbauer and X-ray fluorescence [3], ATR-infrared spectroscopy [4] and Raman spectroscopy [5] [6] have been used to analyze banknotes. All such tools are non-destructive and cheap forensic approaches, particularly when chemometrics tools are used [7]; however, instrumental operations requirements and data processing may make the spectroscopic application in questioned documents analysis complex. Gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/mass spectrometry (LC/MS) have also been used to characterize, for instance, the ink composition of banknotes [8]-[12], but the pretreatment procedures required for GC/MS and LC/MS are time-consuming and may irreparably damage the samples [13]. Laser-based mass spectrometric ionization methods such as matrix-assisted laser desorption/ionization (MALDI) and nanoparticle-assisted laser desorption/ionization (NALDI) are attractive because they minimize banknote destruction and provide high spatial resolution [14]; however, these techniques are operated in a vacuum that may require the specimens to be cut or folded to fit in the source.

Recently, a new class of ionization techniques for ambient mass spectrometry [15]-[18] has been developed. These techniques allow for the desorption, ionization, and mass spectrometry characterization of volatile and nonvolatile analytes directly from their natural surfaces and matrices in an open atmosphere with little or no sample preparation. Hence, they are attractive tools for the direct characterization of questionable documents and allow rapid, accurate and minimally destructive chemical profile screening. Several of these ambient ionization techniques, such as desorption electrospray ionization (DESI) [19], easy ambient sonic-spray ionization (EASI) [20], direct analysis in real time (DART) [21] and electrospray laser desorption ionization (ELDI) [22], have already been used to study chemicals on the surfaces of printed documents. For instance, DART-MS was employed to screen the surface of banknotes [23]. Recently, ELDI-MS was used to rapidly distinguish authentic from counterfeit US dollar bills and New Taiwan dollar banknotes [24]. EASI-MS was used for the nearly instantaneous, reproducible, and non-destructive characterization of Brazilian vehicle documents [1] and first [25] and second generation Brazilian banknotes [26].

In this study, we examined the ability of EASI-MS to identify a real and challenging case of document forgery. In this case, printed data were added to an original blank driver's license, on which all of the security items were present, thus constituting illegal data insertion.

2. Materials and Methods

2.1. Materials

HPLC-grade methanol and formic acid were purchased from Burdick & Jackson (Muskegon, MI). Two suspect driver's licenses were provided by Dr. Octávio Eduardo de Brito Alvarenga at the Criminalistic Institute, Technical-Scientific Police Superintendency from São Paulo State, Brazil. The two driver's licenses displayed the

same personal data in the proper fields (name and ID numbers) but had different individual photos and showed relatively similar impressions on microscopic analysis. The authentic license of the owner was provided by the police investigators, but the forged license was of high quality and could not be clearly identified using the existing standard methods. A set of three samples of authentic driver's licenses were analyzed for comparison with the two seized samples.

2.2. EASI-MS

Experiments were initially performed on a single quadrupole mass spectrometer (LCMS-2010EV; Shimadzu Corp., Kyoto, Japan) equipped with a home-made easy ambient sonic-spray ionization (EASI) source (**Figure 1(A)**). Acidified methanol (0.1% formic acid) at a flow rate of 20 $\mu\text{L}/\text{min}$ and N_2 at 100 psi were used to form the sonic spray in the positive ion mode (EASI(+)-MS). The entrance angle of the capillary relative to the sample surface was around 45° . Each driver's license sample (authentic and suspected forged samples) was directly analyzed by EASI(+)-MS, without sample pretreatment in the same three points on the sample surfaces (**Figures 1(C)-(E)**). To confirm the molecular formula of the compounds detected on the surface of the seized driver's license, an EASI source operated in the positive ion mode was also coupled to an ultrahigh-resolution and ultrahigh accuracy Fourier transform-ion cyclotron resonance mass spectrometer (FT-ICR MS, Thermo Scientific, Bremen, Germany, **Figure 1(B)**). Mass spectra were accumulated over 100 microscans centered and aligned using the Xcalibur 2.0 software (Thermo Scientific). The elemental compositions and isotopic patterns of the molecules were assessed using m/z values. The EASI source coupled to the FT-ICR MS system used similar conditions to those applied in the single quadrupole mass analysis. Details on the EASI source and its operation (**Figures 1(A)** and **Figures 1(B)**) are provided elsewhere [20] [27].

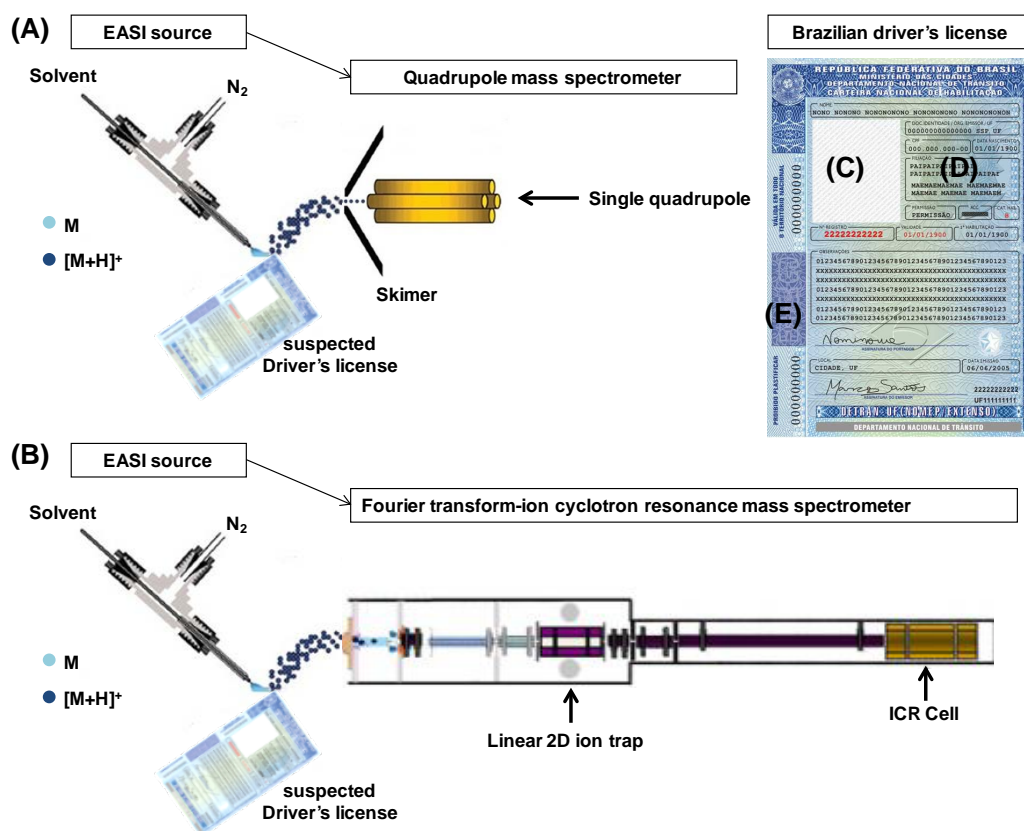


Figure 1. Schematic diagrams of the (A) EASI-MS and (B) EASI-FT-ICR MS voltage-free ambient mass spectrometry screening of driver's licenses, (C) surface area of the illegally printed photo, (D) surface area of the illegally printed personal data on the original blank document and (E) surface area corresponding to the original blank document of the driver's license [26] [27].

3. Results and Discussion

3.1. EASI(+)-MS

Figure 2 shows the EASI(+)-MS chemical profiles of both authentic and forged seized driver's licenses. Three different areas along the surface of the documents were analyzed (photo, personal data and blank document). The authentic license (**Figures 2(A)-(C)**) had similar chemical profiles at all three areas, indicating that EASI(+)-MS fingerprints provide a characteristic chemical signature for the original driver's license. In these spectra, a series of diagnostic ions, m/z 284, 301, 368, 391, 413, 429, 494, 522, 550, were detected. This set of diagnostic ions has been detected and reproduced in others official Brazilian printed documents, such as banknotes [25] [26] and vehicle registration documents [1]. Most dyes used in the official printing process are expected to be deeply and/or strongly adsorbed to the security driver's license paper, therefore, the EASI charged droplets desorb small amounts of chemicals from the top of document; hence, there is a low abundance of ions and a low total ion current produced from original printed documents [28].

As **Figure 2(D)** and **Figure 2(E)** show, EASI(+)-MS of the photo and personal data areas of the seized driver's license revealed a unique and characteristic chemical profile compared with the same area of the authentic driver's license (**Figure 3(A)** and **Figure 3(B)**). The diagnostic ions of the counterfeit license areas were of m/z 463, 507, 551, 595, 639, 683 and 727, which were detected in the m/z 400 - 800 range. There is a difference of m/z 44 between most ions, which is typical for polyethylene glycol (PEG) oligomers containing $(C_2H_4O)_n$

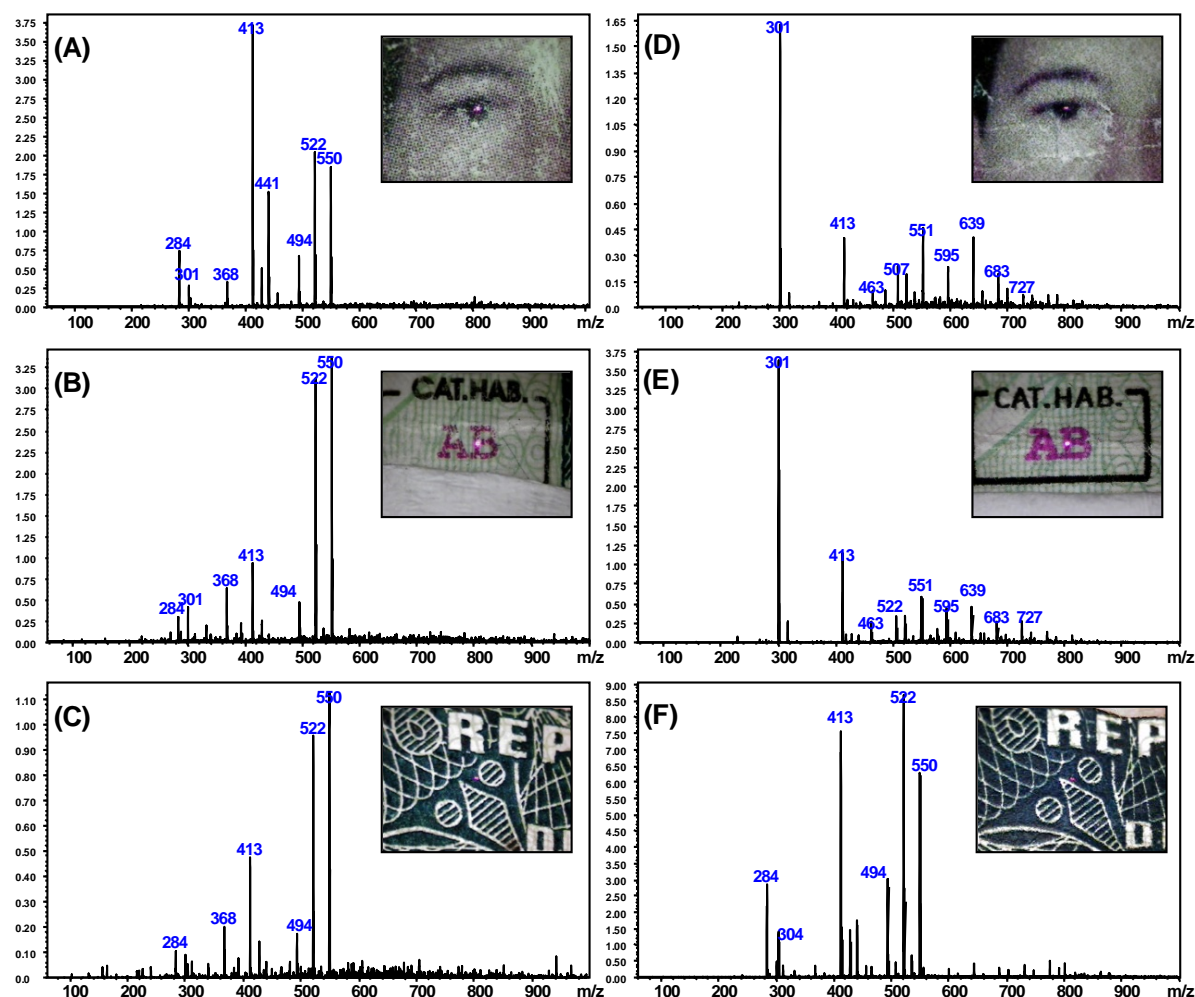


Figure 2. EASI(+)-MS for (A)-(C) authentic and (D)-(F) counterfeit Brazilian driver's licenses: (A) Photo field; (B) Data field; (C) Logo field; (D) Photo field; (E) Data field; (F) Logo field.

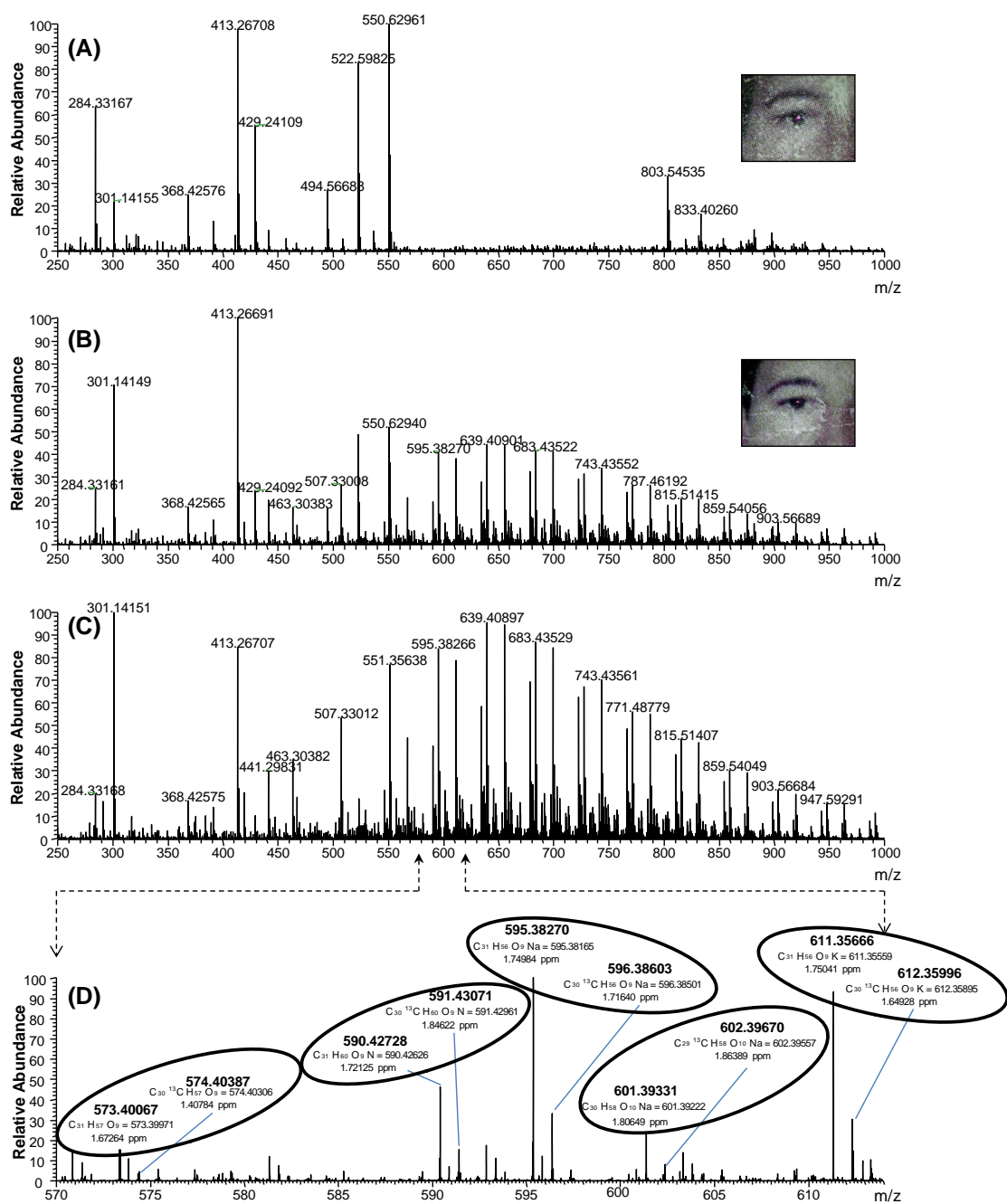


Figure 3. Accurate, high resolution EASI(+)-FT-ICR MS for: (A) Original driver's license photo areas; (B) Forged driver's license photo areas; (C) Spectra subtraction of (B)-(A); and (D) Spectra expansion from m/z 570 - 620 showing the counterfeiting markers and their characteristic ^{13}C isotopologue patterns.

repeating units. The EASI(+)-MS chemical profile of the blank document in the seized driver's license (Figure 2(F)) is similar to that of the authentic driver's license (Figure 2(C)). This result supports the hypothesis that the photo and personal data were inserted using an unofficial printer on the original blank document diverted or stolen from an official institution. An ink jet printer was likely used, as indicated by the PEG ions [29].

3.2. EASI(+)-FT-ICR MS

The forged samples were also analyzed by EASI(+)-FT-ICR MS, as shown in Figure 3, to conduct a thorough

characterization of the marker ions via the determination of their molecular formula. EASI(+)-FT-ICR MS analysis gave similar chemical profile of the authentic driver's license photo field as EASI(+)-MS analysis (**Figure 2(A)**) with the same set of diagnostic and blank ions characteristic of official Brazilian documents analyzed in positive ion mode, considering all regions of the official documents (**Figure 3(A)**) compared to **Figures 2(A)-(C)**). The EASI(+)-FT-ICR MS ion of m/z 391 was established as protonated bis(2-ethylhexyl)phthalate (DHEP), $[C_{24}H_{39}O_4]^+$, m/z 413 corresponded to $[C_{24}H_{38}O_4Na]^+$ and m/z 429 to $[C_{24}H_{38}O_4K]^+$. Similarly, the ions of m/z 803 and 819 were assigned to the Na^+ and K^+ -bound dimers of DHEP, $[C_{48}H_{76}O_8Na]^+$ and $[C_{48}H_{76}O_8K]^+$, respectively. The m/z 301 ion, $[C_{16}H_{22}O_4Na]^+$, with an error of approximately 1.71 ppm, is dibutyl phthalate (DBP). Therefore, DEHP and DBP function as diagnostic markers of the authentic driver's licenses and are likely constituents of common plasticizers typically found in offset printing inks [30] used by official Brazilian institutions to produce official documents [1] [26] [27].

The ions of m/z 284 $[C_{19}H_{42}N]^+$, m/z 368 $[C_{25}H_{54}N]^+$, m/z 494 $[C_{34}H_{72}N]^+$, m/z 522 $[C_{36}H_{76}N]^+$, and m/z 550 $[C_{38}H_{80}N]^+$ were attributed to quaternary ammonium cations (**Table 1**). Specifically, m/z 494.56688 is attributed to dimethyl-dihexadecyl-ammonium, m/z 522.59825 to dimethyl-hexadecyl-octadecylammonium and m/z 550.62961 to dimethyl-dioctadecyl-ammonium (or distearyl-dimethyl-ammonium) with errors of less than 2 ppm. These are common contaminants encountered in modern mass spectrometry using spray based ionization techniques [31].

The EASI(+)-FT-ICR spectra of the forged document showed diverse and characteristic chemical profiles (**Figure 3(B)**) for the two specific areas analyzed, the photo and added personal data (**Figure 2(D)** and **Figure 2(E)**). Spectra subtraction for the photo area and blank ions show the diagnostic ions specific to the illegally printed photo (**Figure 3(C)**). Spectra expansion from m/z 570 - 615 (**Figure 3(D)**) shows a set of five diagnostic ions and the characteristic ^{13}C isotopologue patterns. An oligomeric distribution separated by 44 Da is also present. **Figure 3(D)** shows the protonated molecule of m/z 573.40066, $[C_{31}H_{57}O_9]^+$, and its corresponding ammonium, sodium and potassium adducts, that is, m/z 590.42732 $[C_{31}H_{56}O_9NH_4]^+$, m/z 595.38266 $[C_{31}H_{56}O_9Na]^+$ and m/z 611.35661 $[C_{31}H_{56}O_9K]^+$, respectively, all corresponding to nonylphenol ethoxylate (nonoxynol-9), $C_{31}H_{56}O_9$ [32]. Nonoxynol-9 is commonly used in micro-emulsion surfactant based inks used in electrophotographic imaging apparatuses and in a transfix apparatus in solid ink jet printing [33]. PEG derivatives are common components of inks and function as lubricants for the printer heads [34]. The m/z 601.39331 ion in **Figure 3(D)**, identified as $[C_{30}H_{58}O_{10}^{23}Na]^+$, and its isotopologue ion m/z 602.39670, $[C_{29}^{13}CH_58O_{10}^{23}Na]^+$, are likely related to a family of ethoxylated surfactants sold under the commercial name of Surfynol, which is used to improve the quality of water-based inks in inkjet printer cartridges [35] [36] and has diverse applications in ink composition [37]. **Table 2** summarizes the attributes for the five most abundant ions in the Gaussian distribution

Table 1. EASI(+)-FT-ICR MS spectra acquired from an authentic driver's license photo field (**Figure 1(C)** and **Figure 3(A)**).

m/z	Relative abundance	Theoretical mass	Error (ppm)	Formula	Identification
550.62961	100	550.6285	1.97	$[C_{38}H_{80}N]^+$	[QAC] ⁺
413.26708	96.62	413.2662	2.06	$[C_{24}H_{38}O_4Na]^+$	[DEHP-Na] ⁺
522.59825	83.29	522.5972	1.95	$[C_{36}H_{76}N]^+$	[QAC] ⁺
284.33167	62.15	284.3312	1.75	$[C_{19}H_{42}N]^+$	[QAC] ⁺
429.24109	53.88	429.2402	2.15	$[C_{24}H_{38}O_4K]^+$	[DEHP-K] ⁺
803.54535	32.37	803.5432	2.62	$[C_{48}H_{76}O_8Na]^+$	[2DEHP-Na] ⁺
494.56688	26.35	494.5659	1.92	$[C_{34}H_{72}N]^+$	[QAC] ⁺
368.42576	24.32	368.4251	1.84	$[C_{25}H_{54}N]^+$	[QAC] ⁺
301.14155	21.02	301.1410	1.71	$[C_{16}H_{22}O_4Na]^+$	[DBP-Na] ⁺
391.28515	12.98	391.2843	2.22	$[C_{24}H_{39}O_4]^+$	[DEHP-H] ⁺
819.51931	5.23	819.5172	2.6	$[C_{48}H_{76}O_8K]^+$	[2DEHP-K] ⁺

QAC: quaternary ammonium cations; DBP: dibutyl phthalate; DEHP: bis(2-ethylhexyl)phthalate.

Table 2. EASI(+)-FT-ICR MS data acquired from a forged driver's license photo field (Figure 3(C)).

Experimental m/z	Relative abundance	Theoretical m/z	Error (ppm)	Predict formula	Identification
485.34812	7.64	485.3473	1.72	C ₂₇ H ₄₉ O ₇	
529.37442	13.11	529.3735	1.75	C ₂₉ H ₅₃ O ₈	
573.40066	14.43	573.3997	1.66	C ₃₁ H ₅₇ O ₉	Protonated Nonoxynol-9
617.42702	11.16	617.4259	1.78	C ₃₃ H ₆₁ O ₁₀	
661.45323	7.76	661.4521	1.65	C ₃₅ H ₆₅ O ₁₁	
590.42732	42.87	590.4263	1.80	C ₃₁ H ₅₆ O ₉ NH ₄	
634.45358	61.58	634.4525	1.74	C ₃₃ H ₆₀ O ₁₀ NH ₄	
678.47984	72.80	678.4787	1.69	C ₃₅ H ₆₄ O ₁₁ NH ₄	Ammoniated Nonoxynol-9
722.50616	65.57	722.5049	1.74	C ₃₇ H ₆₈ O ₁₂ NH ₄	
766.53242	51.56	766.5311	1.70	C ₃₉ H ₇₂ O ₁₃ NH ₄	
551.35638	80.65	551.3554	1.71	C ₂₉ H ₅₂ O ₈ Na	
595.38266	89.27	595.3817	1.69	C ₃₁ H ₅₆ O ₉ Na	
639.40897	100.00	639.4079	1.72	C ₃₃ H ₆₀ O ₁₀ Na	Sodiated Nonoxynol-9
683.43529	91.98	683.4341	1.76	C ₃₅ H ₆₄ O ₁₁ Na	
727.46161	70.39	727.4603	1.80	C ₃₇ H ₆₈ O ₁₂ Na	
567.33034	46.55	567.3294	1.69	C ₂₉ H ₅₂ O ₈ K	
611.35661	83.73	611.3556	1.66	C ₃₁ H ₅₆ O ₉ K	
655.38292	98.95	655.3818	1.71	C ₃₃ H ₆₀ O ₁₀ K	Potassiated Nonoxynol-9
699.4092	90.39	699.4080	1.68	C ₃₅ H ₆₄ O ₁₁ K	
743.43561	74.41	743.4342	1.85	C ₃₇ H ₆₈ O ₁₂ K	
513.34053	12.04	513.3398	1.44	C ₂₆ H ₅₀ O ₈ Na	
557.36693	19.00	557.3660	1.66	C ₂₈ H ₅₄ O ₉ Na	
601.39329	22.22	601.3922	1.79	C ₃₀ H ₅₈ O ₁₀ Na	Sodiated Surfynol
645.41951	23.04	645.4184	1.66	C ₃₂ H ₆₂ O ₁₁ Na	
689.44577	16.55	689.4447	1.63	C ₃₄ H ₆₆ O ₁₂ Na	

of ions separated by 44 m/z units (Figure 3(B)). The high accuracy and resolution of the m/z measurements from EASI(+)-FT-ICR MS, which is not essential for forensic investigation, was useful here because it identified the molecular formulas of most markers in the counterfeit areas of the illegally printed driver's license.

4. Conclusion

In this case study of counterfeit driver's licenses, EASI(+)-MS provided a direct, rapid, robust, non-destructive and reliable molecular fingerprinting method to screen for authenticity of printed documents. The illegally inserted personal data and photo could be easily distinguished from the original printed areas, which matched those of authentic driver's licenses. The counterfeiting process was also inferred from the characterization of typical constituents of the ink used. In this case, the data suggested the use of an inkjet printer. The simple design of an EASI source uses readily available laboratory parts and, therefore, can be easily implemented on most mass spectrometers using API sources. This rapid and inexpensive implementation in forensic laboratories equipped with such instruments makes routine analysis of questionable printed documents possible.

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