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Instantaneous chemical profiles of banknotes by ambient mass spectrometry



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Instantaneous chemical profiles of banknotes by ambient mass spectrometry

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Using two desorption/ionization techniques (DESI and EASI) and Brazilian real, US\$ dollar, and euro bills as proof-of-principle techniques and samples, direct analysis by ambient mass spectrometry is shown to function as an instantaneous, reproducible, and non-destructive method for chemical analysis of banknotes. Characteristic chemical profiles were observed for the authentic bills and for the counterfeit bills made using different printing processes (inkjet, laserjet, phaser and off-set printers). Detection of real-world counterfeit bills and identification of the counterfeiting method has also been demonstrated. Chemically selective 2D imaging of banknotes has also been used to confirm counterfeiting. The nature of some key diagnostic ions has also been investigated *via* high accuracy FTMS measurements. The general applicability of ambient MS analysis for *anti*-counterfeiting strategies particularly *via* the use of “invisible ink” markers is discussed.

Introduction

Banknote counterfeiting is a major type of financial crime. This illegal and potentially profitable practice has been expanding worldwide both in quantity and sophistication.¹ US dollars, owing to their global circulation, have been the greatest target for counterfeiting, but since the introduction of the euro as the common currency in the European Union, counterfeiting of euro banknotes has also become a great threat. In Brazil, after the economic stability achieved with the introduction of the real (R\$) currency in 1994, there has also been an increasing growth in banknote counterfeiting and sophistication. Forensic laboratories in law-enforcement institutions worldwide are therefore confronted with an increasing demand to analyze larger numbers of samples with faster responses and with reliable verdicts for samples fabricated with greater sophistication than ever before. Frequent improvements in computational image-capturing devices, image-processing software and copying and printing equipment have contributed to the increasing diversity and sophistication of the counterfeiting process. To confront this worldwide economic threat, it has been mandatory to develop more effective security items as well as analytical techniques able to perform rapid and ideally automated high throughput screening of banknote authenticity.

Spotting of counterfeit banknotes by the general public has relied mostly on sensory tests based on the look, feel and tilt angle, but the most sophisticated counterfeit notes often escape these subjective tests. An increasing number of security items such as sophisticated security papers, latent images, watermarks, magnetic strips, special printing techniques, holograms and areas

with IR or UV light responses are therefore being applied, with a consequent increase in production costs. Counterfeiting uses mainly computational reproduction methods, which include image-capturing in electronic media (scanners), processing (software) and printing (laser, ink-jet, off-set) or direct photocopying. Owing to the diversity of counterfeiting methods and their increasing dissemination and sophistication, and counter-reactions from the counterfeiters based on knowledge of the security items employed, new security items and techniques must constantly be created or improved for the law enforcement agencies to stay “one step ahead”. Although sensory inspection of security items and optical evaluation of image quality and patterns are most desirable and can still detect most counterfeit banknotes, chemical analysis of banknotes, especially if new security tests are based on chemical fingerprinting screening, may provide an automated, fast and reliable approach able to detect forgery of increasing quality with reliable results.

Chemical fingerprinting of banknotes could fulfill these requirements but it has been only sporadically tested by forensic laboratories. Microscope ATR-infrared spectroscopy applied at several colorful selected areas,² for instance, has been shown to provide an effective method for chemical analysis of euro banknotes able to characterize and distinguish between original and counterfeit samples. IR spectroscopy and gas chromatography coupled to mass spectrometry (GC-MS) have also been used to correlate the chemical profiles of colored toner samples to the color photocopiers and the toner extracted from counterfeit banknotes.³ Mass spectrometry⁴ and laser desorption mass spectrometry⁵ have also been used to detect colorants and pigments on banknotes. The main target of chemical analysis of banknotes has not been focused on counterfeiting, but rather on the detection of contamination by illegal drugs.⁶

Recently, a series of desorption/ionization techniques for direct ambient mass spectrometry analysis has been introduced.⁷ These revolutionary techniques have provided fast chemical profiles with unprecedented simplicity and speed. Ionization is performed in the open atmosphere followed by mass

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spectrometric characterization directly from sample surfaces with little or no sample preparation or pre-separation procedures. The field was pioneered with desorption electrospray ionization (DESI)⁸ and direct analysis in real time (DART)⁹ but a variety of related techniques are currently available including ASAP,¹⁰ ELDI,¹¹ EESI,¹² DAPPI,¹³ and EASI.^{14,15} Both DESI¹⁶ and EASI¹⁷ have also been used to investigate ink manuscripts with regard to ink composition and aging. In addition, DESI-MS¹⁸ as well as DART-MS¹⁹ and DAPPI²⁰ have seen extensive use in the detection of counterfeit drugs, including 2D chemical-selective images of the tablets.¹⁸ Ambient MS seems therefore to be an attractive alternative for banknote inspection at the molecular level due to its ability to provide direct, fast and highly specific molecular signatures and chemical selective images from printed surfaces. DESI-MS and/or EASI-MS have already been applied with success in other forensic areas such as the detection of adulteration of oils,²¹ perfumes,²² and biofuels,²³ and the forensic applications of ambient mass spectrometry have recently been reviewed.²⁴ Herein we investigate, *via* EASI-MS and DESI-MS, the ability of ambient mass spectrometry to allow chemical fingerprinting of banknotes, and discuss the general application of this approach for similar cases such as drug packages and tax labels and invisible bar codes.

Experimental

Chemical reagents and samples

Methanol of HPLC grade was purchased from Merck SA (Rio de Janeiro, Brazil) and Aldrich (USA) and used without further purification. Authentic and counterfeit banknotes were analyzed directly by EASI-MS or DESI-MS without any sample treatment. "Real-world" counterfeit banknotes were provided from apprehended samples by the Brazilian Federal Police Department in São Paulo-Brazil between the years 2008 and 2009.

MS data

Easy ambient sonic-spray ionization mass spectrometry (EASI-MS) data in the positive ion mode was collected at the ThoMSon laboratory using either a QTRAP mass spectrometer (Applied Biosystems) or the linear ion trap of a hybrid LTQ FTMS Ultra mass spectrometer (ThermoScientific, Bremen, Germany) with a homemade EASI source, which is described in detail elsewhere.¹⁵ The EASI and DESI sources are similar in design, with the EASI source being simplified to operate without an applied voltage in the sonic spray ionization²⁵ mode. Typical operation conditions were as follow: flow rate of acidified (0.1% formic acid) methanol of 20 mL min⁻¹, nebulizing gas back pressure of *ca.* 30 bar, curtain gas pressure of 5 bar, de-clustering potential of 100 V probe, tip-to-banknote samples distance of *ca.* 2 mm, and capillary-banknotes-entrance angle of *ca.* 30 degrees. High resolution and high accuracy EASI-FTMS data were collected using the ICR cell of a 7.2T LTQ FTMS Ultra mass spectrometer with a mass resolving power of *ca.* 400 K at *m/z* 400 by summing 100 microscans. DESI-MS data were acquired at the Aston Laboratory (Purdue University) using a Thermo Fisher LTQ (San Jose, CA, USA) linear ion trap mass spectrometer, equipped with a custom-built automated DESI ion source based on

a design by ProSolia (Indianapolis, IN, USA). The main LTQ operating parameters were as follows: spray voltage 5 kV; no automatic gain control; MS injection time 250 ms; and 2 microscans were summed. The DESI source used nitrogen sheath gas pressure 7 bar; scattering angle *ca.* 10° and an acidified (0.1% formic acid) methanol-water 9:1 solution was sprayed at volumetric flow rates of 1.5 mL min⁻¹ at a nitrogen pressure of *ca.* 150 psi. DESI-MS imaging was carried out using an automated stage moving in an x,y plane in relation to a static extended bent capillary, which is described in detail elsewhere.²⁶ The size of the spray spot, under the normal DESI experimental conditions used, was measured to be *ca.* 250 × 250 μm² or less.²⁷ The pixel size was 200 × 200 μm². Total time for imaging acquisition was *ca.* 20 min/cm². The area covered during imaging was mapped by 100 × 100 pixels.

Chemometric analysis

EASI-MS data of the banknote samples were extracted using Analyst 4.1 (Applied Biosystems). Mass spectral data were accumulated, centered and aligned to generate a final data matrix of all samples for ions ranging from *m/z* 100 to 1000. To classify the banknotes, principal component analysis (PCA) was performed, for simplicity, on the total EASI-MS data with no omission of background or impurity ions. The Pirouette v. 3.11 program was used.

Results and discussion

Authentic R\$ banknotes of variable denominations

To test the ability of both EASI-MS and DESI-MS to fingerprint banknotes, we first analyzed authentic Brazilian real (R\$) banknotes of different nominal values (different designs and color profiles, see inserts in Fig. 1) as well as homemade counterfeit samples prepared by scanning authentic bills and printing copies using either laser jet, inkjet or phaser printers and common laser print paper (white alkaline paper).

Authentic R\$ banknotes of all denominations were tested, and Fig. 1 shows representative EASI(+)-MS for three common R\$ bills. Note that many different spots of the bill surface were examined but quite similar EASI-MS data were obtained throughout the whole printed surface. In general, total ion current for the R\$ bills was substantially low and most ions in the low *m/z* region are likely due to solvent and surface contaminants (see below). EASI-FTMS detects, however, a series of diagnostic ions of *m/z* 391, 413, 429, 803 and 819 in all the R\$ samples analyzed. Blank EASI-MS spectra using white paper and also a sample of authentic R\$ banknote paper²⁸ showed very low abundance "paper" ions (mostly of *m/z* 193 and 223 but with variable profiles)¹⁶ that were undetectable from the banknote surfaces.

As Fig. 2 illustrates, similar chemical profiles with little variation as a function of banknote denomination or specific spots on the printed note surface were also observed for the DESI-MS experiment. Note the set of background ions probably due to solvent and surface contamination (*m/z* 304 for cocaine) and the series of diagnostic ions of *m/z* 391, 413, 429 and 803 and 819 due to the banknote plasticizer (see below). Therefore, regardless of the banknote nominal value and their contrasting artistic and

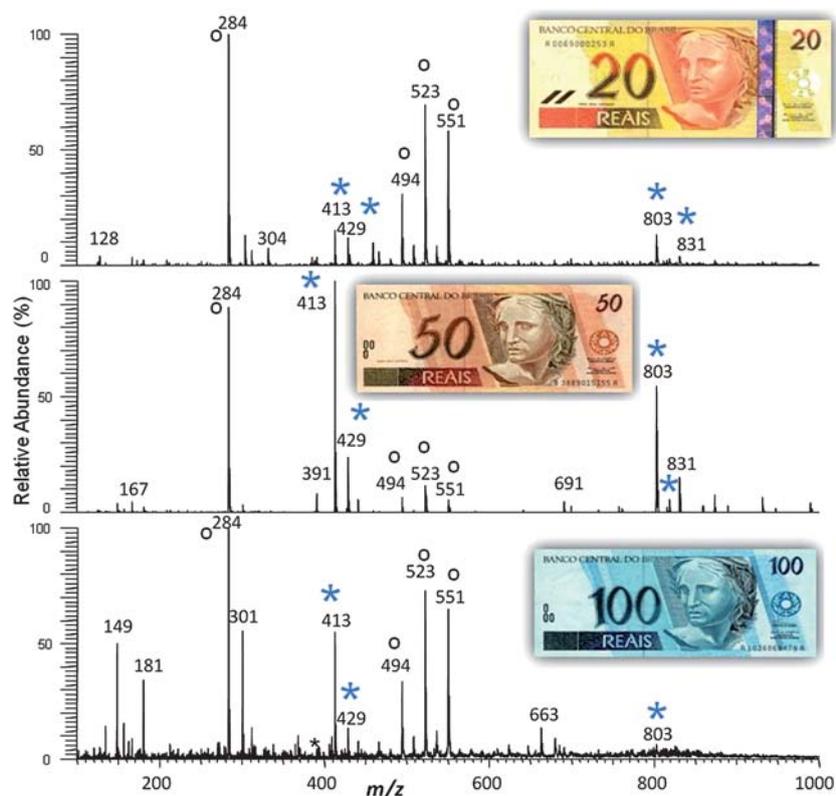


Fig. 1 Illustrative EASI(+)-MS of Brazilian R\$ banknotes of three different denominations obtained at printed areas. Background ions (o) as well as a series of diagnostic ions (*) of m/z 413, 429, 803 and 819 are marked.

color patterns as well as the age or degree of use of the notes, both EASI-MS and DESI-MS appear to provide a characteristic chemical signature for the whole bill surface for authentic Brazilian R\$ banknotes due to the detection of a set of diagnostic ions (m/z 391, 413, 429 and 803 and 819). Note that hand grease from the manipulation of these bank notes should mainly add human triacylglycerides (TAG) but these molecules with masses around 900 Da²¹ escaped detection with the solvent systems used in all notes investigated, even for the oldest ones.

Acquiring mass spectra using the high resolution and high accuracy ICR cell of the LTQ FTMS instrument, as well as examining the fragmentation profile as revealed by EASI-FTMS/MS (not shown), allowed us to identify the nature of the diagnostic ions for the R\$ banknotes. They were found to correspond mainly to the plasticizer bis(2-ethylhexyl)phthalate (M) detected as $[M + H]^+$ of m/z 391; $[M + Na]^+$ of m/z 413; $[M + K]^+$ of m/z 429, $[2M + Na]^+$ of m/z 803 and $[2M + K]^+$ of m/z 819.

For the background ions, for instance, the ion of m/z 494 was attributed to the dihexadecyl dimethyl quaternary ammonium salt ($C_{16}H_{31})_2N^+(CH_3)_2$ probably due to hand manipulation. Such salts are common in personal care products, wherein they are often added as softeners.²⁹ The ion of m/z 284 is due to contamination by a $C_{19}H_{41}N$ aliphatic amine (as revealed by high accuracy m/z data) whereas those of m/z 523 and 551 are common lab contaminants from detergents.²⁹ The ion of m/z 304, which was sometimes detected, corresponds to protonated cocaine as evidenced by EASI-FTMS and probed by EASI-FTMS/MS data (not shown).³⁰ Cocaine is a common contaminant of banknotes in circulation.²⁶

Fig. 3 displays representative EASI-MS fingerprints for the three types of homemade counterfeit samples. As compared to the authentic bills, ions with much higher abundance were easily detected for these counterfeit bills. The spectra were also very characteristic; those for inkjet and phaser bills displayed a broad oligomeric series of ions from m/z 300–900 and from m/z 700–1300, respectively, whereas those for laserjet bills showed a less diverse set of marker ions, the most characteristic being those of m/z 629, 734, 793 and 835. Note in Fig. 3 the highly contrasting EASI-MS chemical signatures for the homemade counterfeit bills as compared to those in Fig. 1 for the authentic bills. Again, high accuracy EASI-FTMS analysis allowed us to assign these marker ions to ethoxylated (repeating ions separated by 44 m/z units) or propoxylated (58 m/z units) alcohols detected mainly as $[M + Na]^+$ (Fig. 3). EASI-MS data was also very reproducible as several authentic samples and counterfeit samples analyzed on different days displayed similar profiles.

The EASI-MS data of Fig. 1 and 3 can be compared to the DESI-MS data of Fig. 2. Note that both DESI-MS and EASI-MS provide distinct chemical signatures for each sample type. Both techniques were also able to detect similar sets of diagnostic ions. For the inkjet printers, characteristic sets of oligomeric markers (mainly ethoxylated alcohols) centered around m/z 600 and separated by 44 m/z units were detected by both EASI-MS and DESI-MS. The counterfeit laser print bill analyzed by DESI-MS (Fig. 2) was produced by a laser printer from a different brand to that used to collect the EASI-MS data (Fig. 3); hence, both profiles were distinctive but very different from those of laserjet printers and authentic bills. In the DESI-MS profile for

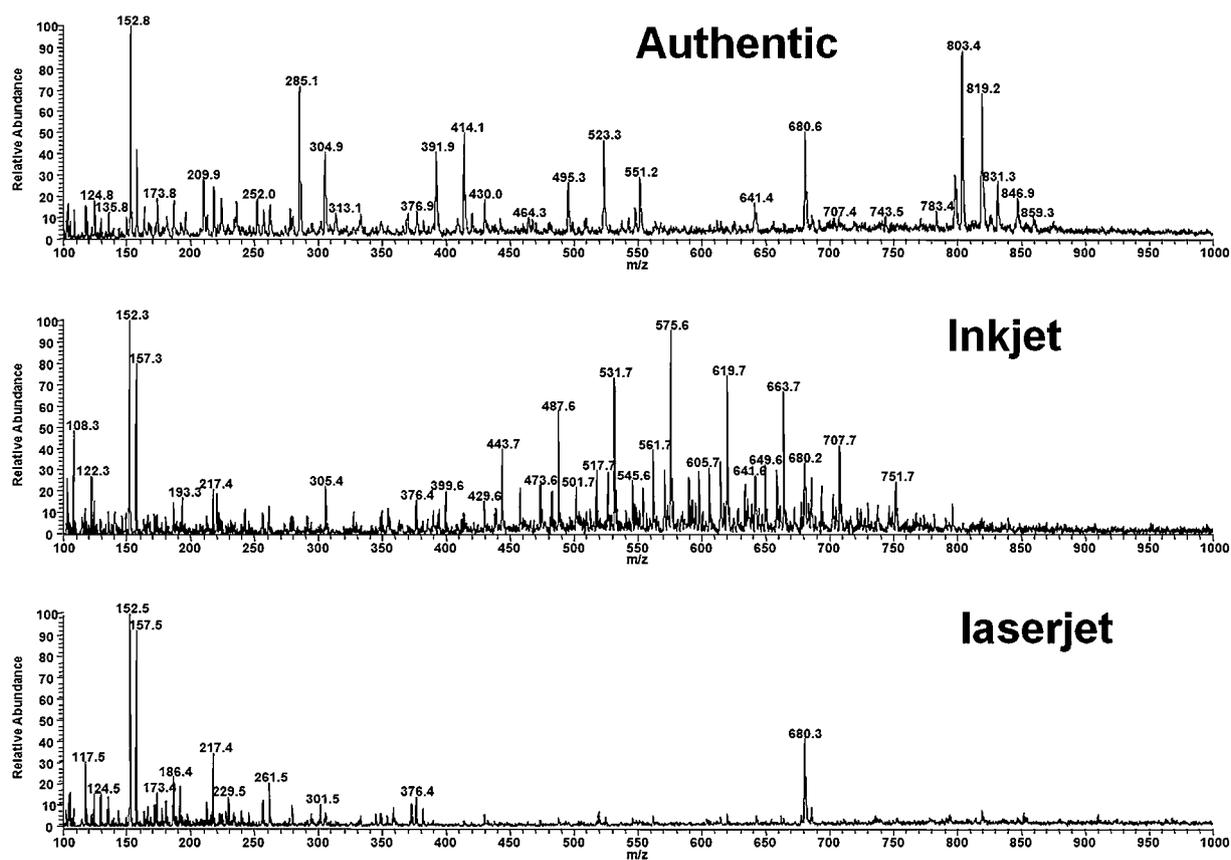


Fig. 2 DESI(+)-MS of an authentic Brazilian R\$ banknote and homemade counterfeit banknotes made by using inkjet or laserjet printers.

the laser printer, a single and dominant diagnostic ion of m/z 680 was detected (Fig. 2), whereas the laserjet printer used in the EASI-MS experiment produced a richer set of major ions (Fig. 3).

For the authentic bills, although different samples, operators, instruments and ambient desorption/ionization techniques and their specific settings were used in the two laboratories, the same set of diagnostic ions was detected by both EASI-MS (Fig. 1) and DESI-MS (Fig. 2), most particularly those of m/z 391, 413, 429, 803 and 819 arising from the banknote plasticizer and from a common biocide.

Dollar and euro banknotes

Authentic samples of dollar and euro banknotes were also analyzed by EASI-FTMS (Fig. 4). Note that the set of diagnostic ions of m/z 391, 413, 429 and 803 and 831 that characterize the Brazilian R\$ banknotes were nearly undetected. The chemical profiles of the euro and dollar bills are unique and dominated by much more abundant oligomeric distributions of ions arising mainly from propoxylated alcohols separated by 58 m/z units. These distributions are quite distinctive for both the euro and dollar bills. The distribution for the euro bills is centered around m/z 900 and the oligomers are detected mainly as $[M + Na]^+$ whereas that for the dollar bills is less diverse, and centered around m/z 500 being detected mainly as $[M + H]^+$.

“Street” counterfeit bills

To test the ability of ambient mass spectrometry to detect “real-world” samples, 50 representative samples of R\$ banknotes apprehended by the Brazilian Federal Police and classified as either authentic or counterfeit by classical forensic approaches (based on sensory tests and optical inspection) were analyzed by EASI-MS. Fig. 5 summarizes the results in a 3D PCA plot (see below). As observed for the homemade samples (Fig. 3), the EASI-MS chemical profiles of the street counterfeit samples (not shown) differ markedly from the characteristic chemical signatures systematically observed for the authentic samples (Fig. 1). As evidence for the reliability of ambient MS data to identify the counterfeiting method, all street bills classified as inkjet or laserjet counterfeit by EASI-MS had been also classified as such by microscopic inspection by an expert in the forensic laboratories of the Brazilian Federal Police. A unique chemical signature was also observed for some samples identified by microscopic inspection as being manufactured by a higher quality method using most likely off-set printing. Note that visual inspection of such high quality counterfeit samples is more intricate and can lead to false negatives.

Chemometric analysis

To statically test the performance of EASI-MS fingerprinting for R\$ banknote analysis, PCA data treatment was performed. Fig. 5 shows a scatter plot of $PC1 \times PC2 \times PC3$ for the total

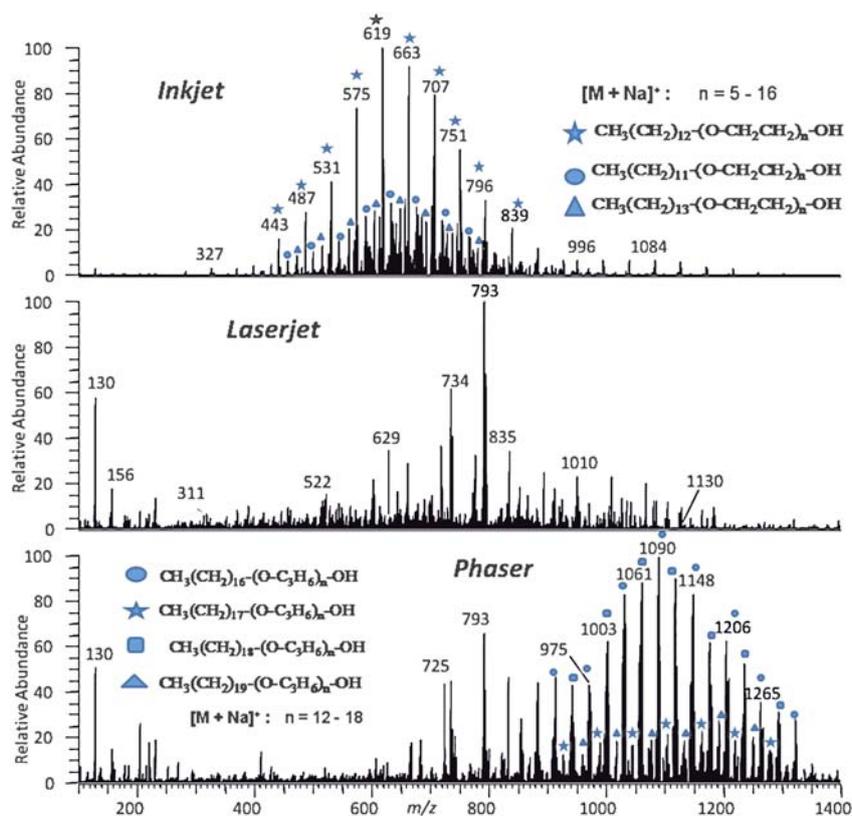


Fig. 3 EASI(+)-MS of homemade counterfeit banknotes made by using inkjet, laserjet and phaser printers. The oligomeric series of ethoxylated and propoxylated alcohols identified in these bills are marked.

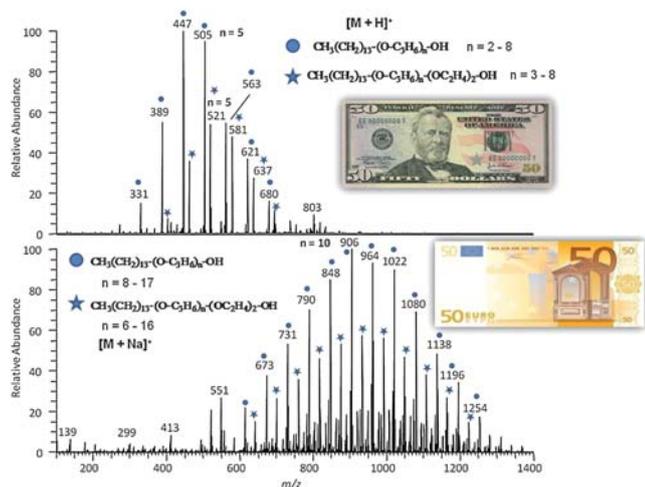


Fig. 4 EASI(+)-MS fingerprints of authentic dollar and euro banknotes. The main identified oligomeric series of ethoxylated/propoxylated alcohols are marked.

EASI-MS data. For simplicity, no subtraction of background or impurity ions was performed. Note the grouping of the authentic samples and their clear separation from the three major types of counterfeit samples. Even better separation was noted, however, when background and impurity ions were omitted, or when focusing on sets of diagnostic ions, but this data treatment requires the intervention of an expert.

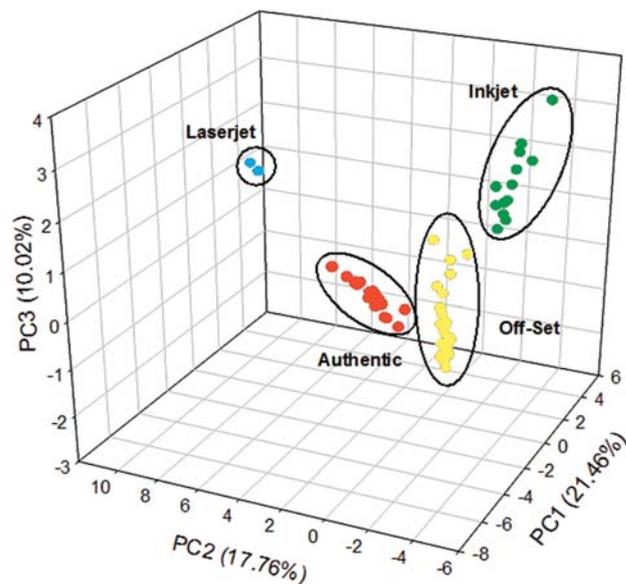


Fig. 5 3D PCA of the EASI(+)-MS data of authentic and counterfeit “street” confiscated Brazilian RS banknotes.

Ambient MS 2D imaging

As already discussed, the data of inkjet counterfeit bills are dominated by a characteristic oligomeric cluster of ions (Fig. 2

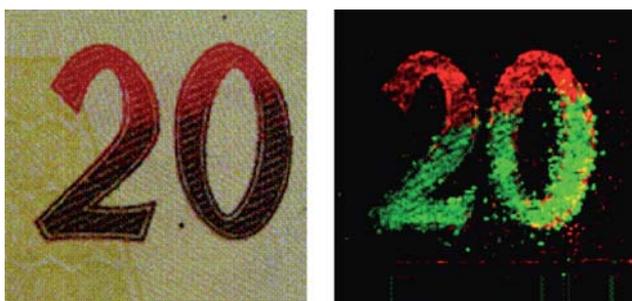


Fig. 6 (Left) R\$ 20 inkjet counterfeit bill photography of a $ca. 2 \times 2$ cm² area around number 20 and (right) chemically selective DESI(+)-MS 2D image of the same area produced by monitoring the intensity of trace but diagnostic ions for the red (m/z 122) and brown (m/z 597) counter regions along number 20.

and 3) attributed mainly to ethoxylated alcohols. However, by creating selective 2D ion images of portions of the notes, minor but diagnostic ink ions could be identified. Fig. 6 illustrates this feature for an inkjet R\$ 20 bill for which ink ions were identified for the red (m/z 122) and brown (m/z 597) colors of the number 20. Note that such 2D imaging provides an unquestionable confirmation of the counterfeit nature of such bills since the same ion-selective 2D DESI-MS data collected from an authentic bill produced a fully dark image (not shown).

Fig. 7 also illustrates the use of selective 2D ion images for an authentic US\$ 5 bill analysis. In this case DESI-MS in the

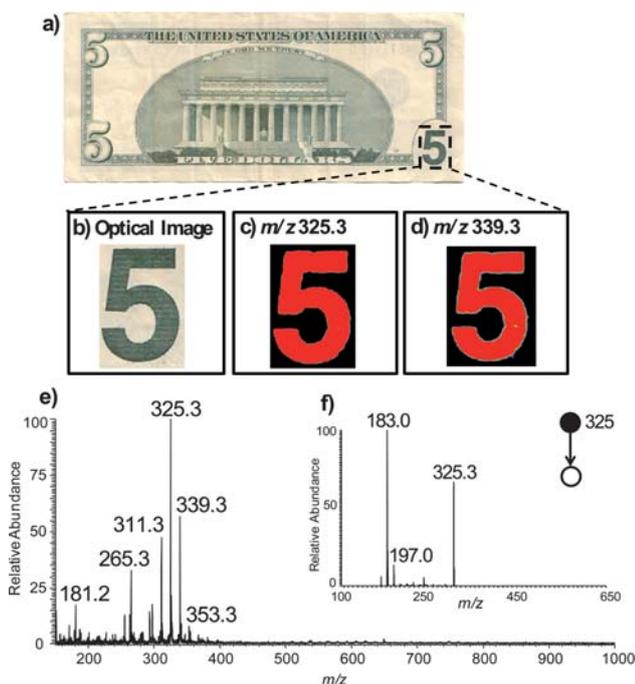


Fig. 7 a) Optical image of an authentic US\$ 5 bill. b) Zoomed in optical image of the number 5 (1.5×1.2 cm area). Chemically selective DESI(-)-MS image for the ions of c) m/z 325.3, identified as dodecylbenzene sulfonate, and d) m/z 339.3, identified as tridecylbenzene sulfonate. e) DESI(-)-MS of the printed area of number five in the authentic dollar bill and f) DESI(-)-MS/MS of the ion of m/z 325.3, identified as dodecylbenzene sulfonate.³¹ The most abundant fragment ion of m/z 183 corresponds to the loss of a neutral decane molecule of 142 Da.

negative ion mode was used, and the spectrum (Fig. 7e) showed a characteristic set of marker ions, mainly those of m/z 311, 325, 339 for number 5. Fig. 7c and d show the exact reproduction of the number 5 by chemically selective 2D DESI imaging. More secure identification can also be performed *via* collision induced dissociation of marker ions, as Fig. 7f illustrates for that of m/z 325.

Final remarks and conclusions

As exemplified herein for Brazilian real, dollar and euro bills, as proof-of-principle cases, and by using two ambient ionization techniques (DESI and EASI) performed in two laboratories using different instrumentation and operating conditions, ambient mass spectrometry seems to provide an unbiased, direct, non-destructive and robust method for the analysis of banknotes. Nearly instantaneous detection of counterfeit samples and the counterfeit printing method seems to be attainable *via* comparison of their characteristic chemical profiles. Ambient MS could be used as a complementary technique to the traditional forensic microscopic inspection and help the expert in the case of dubious or more sophisticated samples. It could also be useful for the forensic scientist to link counterfeit bills to their production sites or to a particular brand, or even to a specific printer. Ambient MS can also be easily automated for high throughput analysis using, for instance, devices similar to those applied for banknote counting.

Effective *anti-counterfeiting* items based on ambient-MS detection could also be developed such as the use of polar (for efficient DESI-MS or EASI-MS detection) but colorless chemical markers (“invisible inks” irreproducible by photocopying or scanning) placed on specific spots on the banknote, which could be changed periodically. The use of unique compositions of plasticizers or ink emulsifiers or polar markers (such as ionic cationic dyes^{16,17} for improved DESI or EASI detection) can also be envisaged for the production of authentic bills with unique chemical signatures. These unknown (by the general public) and invisible diagnostic chemicals could therefore function as effective markers of banknote authenticity, production site or even for the period of production if periodically replaced. The use of similar approaches as a security item in tax labels and packages of valuable products such as high-cost drugs also seems attractive. For drug packages, for instance, the external inspection by ambient mass spectrometry of “invisible ink” spots or even



Fig. 8 (Left) An “invisible stamp” simulated by using black ink and black paper and (right) the image resulting from diagnostic ion-selective development by 2D DESI-MS imaging.

stamps could be used as a rapid and non-destructive screening method of counterfeiting detection of the inviolate sample. To illustrate the principle, we have stamped the Purdue University logo on black paper using black ink to simulate the application of an “invisible” stamp and have revealed the image via 2D DESI-MS using the most abundant crystal violet¹⁷ marker ion of m/z 372 (Fig. 8). One could also propose the use of different invisible inks to make an invisible bar code that would contain key information about the product such as production batch, date and manufacture.

Miniature mass spectrometers able to operate with ambient ionization techniques are also being made more compact and robust.³² Therefore, the use of such hand-portable and affordable instruments would allow on-site (in banks or markets for instance) and wide-spread application of this nearly instantaneous and unbiased chemical fingerprinting method for banknote analysis and chemical security items.

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