



## Technical note

## Direct and non-destructive proof of authenticity for the 2nd generation of Brazilian real banknotes via easy ambient sonic spray ionization mass spectrometry



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## ABSTRACT

Using a desorption/ionization technique, easy ambient sonic-spray ionization coupled to mass spectrometry (EASI-MS), documents related to the 2nd generation of Brazilian Real currency (R\$) were screened in the positive ion mode for authenticity based on chemical profiles obtained directly from the banknote surface. Characteristic profiles were observed for authentic, seized suspect counterfeit and counterfeited homemade banknotes from inkjet and laserjet printers. The chemicals in the authentic banknotes' surface were detected via a few minor sets of ions, namely from the plasticizers bis(2-ethylhexyl)phthalate (DEHP) and dibutyl phthalate (DBP), most likely related to the official offset printing process, and other common quaternary ammonium cations, presenting a similar chemical profile to 1st-generation R\$. The seized suspect counterfeit banknotes, however, displayed abundant diagnostic ions in the  $m/z$  400–800 range due to the presence of oligomers. High-accuracy FT-ICR MS analysis enabled molecular formula assignment for each ion. The ions were separated by 44  $m/z$ , which enabled their characterization as Surfynol® 4XX (S4XX, XX = 40, 65, and 85), wherein increasing XX values indicate increasing amounts of ethoxylation on a backbone of 2,4,7,9-tetramethyl-5-decyne-4,7-diol (Surfynol® 104). Sodiated triethylene glycol monobutyl ether (TBG) of  $m/z$  229 ( $C_{10}H_{22}O_4Na$ ) was also identified in the seized counterfeit banknotes via EASI(+) FT-ICR MS. Surfynol® and TBG are constituents of inks used for inkjet printing.

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## 1. Introduction

The analysis of suspect documents is a highly important area in forensic science. In Brazil, in an attempt to hinder the action of forgers, the Brazilian Central Bank launched in 2010 the 2nd generation of Real currency, which features security items with sophisticated graphics capabilities, imposing stronger obstacles to counterfeiting. However, despite efforts by the Brazilian Central Bank to combat counterfeit currency, the 2nd generation of Real banknotes has already been falsified, mainly those of the nominal values R\$100 and R\$50. Official statistics show that an average of 450,000 counterfeit notes have been seized per year recently, and the rate is increasing [1]. This crime also leads to great worldwide financial damage, and new security items are

normally rapidly imitated, since the counterfeiters are using increasingly advanced technologies of printing and copying, applying mainly computational reproduction methods, which include image-capturing in electronic media (scanners), processing (software) and printing (laserjet, inkjet, off-set) or direct photocopying. These methods can lead to the production of 'high-quality counterfeit banknotes', which may be difficult to differentiate from genuine notes by visual inspection, microscopy analysis or even spectroscopic analysis.

Owing to the diversity of counterfeiting methods, their increasing dissemination and sophistication and the counterfeiter's knowledge of the security items employed, it has become crucial to develop and implement rapid, minimally destructive and unequivocal methods for counterfeit screening at the molecular level. In forensic science and in the specific field of questioned documents, banknote counterfeiting analyses for many different bills from several countries have been performed, applying diverse analytic methodologies. Mossbauer and X-ray fluorescence [2], ATR-infrared spectroscopy [3] and Raman spectroscopy [4,5] have constituted a set of interesting non-destructive

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forensic analyses; however, processing the amount of data acquired with similar spectroscopic methods for counterfeit and genuine banknotes requires the use of chemometrics tools [6]. The use of gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/mass spectrometry (LC/MS) to characterize the ink composition of banknotes has been reported [7–11], but the pretreatment procedures required for GC/MS and LC/MS are usually time-consuming and may result in irreparable damage to the banknotes, which is not useful for forensic sample preservation [12]. Laser-based mass spectrometric ionization methods, such as matrix-assisted laser desorption/ionization (MALDI) and nanoparticle-assisted laser desorption/ionization (NALDI), minimize banknote destruction due to the high spatial resolutions of the pulsed laser beam used in both techniques [13], but these techniques are operated in a vacuum suitable only for the detection of nonvolatile compounds, and the spatial limitations of the ion sources can require the banknotes to be cut or folded to fit in the source.

Recently, a new class of ionization techniques for ambient mass spectrometry has been developed [14–17]. These techniques enable the desorption, ionization, and mass spectrometry characterization of volatile and nonvolatile analytes directly from their natural surfaces and matrixes in an open atmosphere with little or no prior sample work up. Therefore, these techniques are attractive for the direct characterization of questioned documents and may possibly serve as a rapid, minimally destructive and unequivocal method for document identification and tracking [18]. A set of these ambient ionization techniques, namely 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 been used to study chemical compounds on the surfaces of manuscripts and banknotes. When DART is used, the surface of the banknote is impacted by a plasma generated from a heated helium gas stream to desorb and ionize volatile compounds [23]. Recently, ELDI-MS was used to rapidly distinguish authentic from counterfeit United States dollar and New Taiwan dollar banknotes, using a high-energy pulsed laser beam to desorb nonvolatile compounds and compounds that stayed underneath the surface in an electrospray plume [24]. EASI and DESI [25] ambient ionization sources were applied to analyze 1st-generation Brazilian Real, US\$ dollars and Euro bills and successfully functioned as an instantaneous, reproducible, and non-destructive method for chemical analysis.

In this work, rapid and non-destructive EASI-MS analysis at the molecular level was applied to the investigation and molecular information acquisition of 2nd-generation Brazilian Real (R\$) banknotes and seized suspect banknotes. Here, EASI is reported to be an efficient, simple and versatile ionization for questioned document analysis in the forensic field and might be coupled with a simple and accessible single quadrupole mass spectrometer for routine molecular fingerprint acquisition or with an ultrahigh-resolution and ultrahigh-accuracy Fourier transform ion cyclotron resonance mass spectrometer for deeper identification and characterization.

## 2. Experimental

### 2.1. Methods and materials

HPLC-grade methanol and formic acid were purchased from Burdick & Jackson (Muskegon, MI). Four sets of samples in triplicate were obtained from a local bank. Each set had nominal values of R\$100, R\$50, R\$20 and R\$10 and were satisfactorily analyzed by applying the EASI source to obtain the genuine banknote MS fingerprint. Two sets of counterfeited homemade samples in triplicate, each with nominal values of R\$100 and R\$50 (the nominal values most commonly seized), were prepared by scanning authentic bills and printing copies using available laserjet and inkjet printers on white alkaline paper. Seven seized suspect counterfeited banknotes (four with a nominal value of R\$100 and three with a nominal value of R\$50) were provided by the

Technical-Scientific Police Superintendency, Criminalistic Institute Dr. Octávio Eduardo de Brito Alvarenga from São Paulo State (IC-SPTC-SP), Brazil, and analyzed as outlined below.

### 2.2. EASI-MS

Experiments were performed on a single quadrupole mass spectrometer (LCMS-2010EV; Shimadzu Corp., Kyoto, Japan) equipped with a homemade easy ambient sonic-spray ionization (EASI) source. Acidified methanol (0.1% by volume in formic acid) at a flow rate of 20  $\mu\text{L}/\text{min}$  and  $\text{N}_2$  at 100 psi were used to form the sonic spray used in the positive ion mode, EASI(+)-MS. The entrance angle of the capillary relative to the sample surface was ca. 45°. Each banknote sample (genuine set, homemade set and seized set) was directly analyzed by EASI(+)-MS without any sample treatment at the same three points on the sample surfaces. To confirm the molecular formula of the compounds detected at the surface of the seized suspect counterfeited banknotes and verify the versatility of the ambient ionization source, an EASI source operated in the positive ion mode was coupled to an ultrahigh resolution and ultrahigh accuracy Fourier transform-ion cyclotron resonance mass spectrometer (FT-ICR MS, ThermoScientific, Bremen, Germany). Mass spectra were accumulated over 100 microscans, centered and aligned using the Xcalibur 2.0 software (ThermoScientific). The elemental compositions of the compounds were attributed based on the measured  $m/z$  values. The conditions for EASI when coupled to the FT-ICR MS system followed the same specifications previously used in single quadrupole mass spectrometry; i.e., methanol (0.1% by volume in formic acid) at a flow rate of 20  $\mu\text{L}/\text{min}$  and  $\text{N}_2$  at 100 psi were used to form the sonic spray, EASI(+)-FT-ICR MS, and the entrance angle of the capillary relative to the sample surface was ca. 45°. More details of the EASI source and its operation (Fig. 1) are provided elsewhere [20,26].

## 3. Results and discussion

### 3.1. EASI(+)-MS

Initially, the chemical profiles of authentic 2nd-generation Brazilian Real (R\$) banknotes of different nominal values (R\$100, R\$50, R\$20 and R\$10) were obtained by EASI(+)-MS (Fig. 2) using a simple monoquadrupole MS instrument. Three different spots on the surface of the banknotes were analyzed. At all spots on all banknotes, similar chemical profiles were obtained throughout the whole printed surface. Therefore, regardless of the banknote nominal value, contrasting artistic and color patterns, or area analyzed, EASI(+)-MS shows distinctive and characteristic spectra indicating the presence of specific molecules, providing and establishing a chemical signature or chemical fingerprint for authentic 2nd-generation Brazilian Real (R\$) banknotes.

Note that, as reported for the 1st generation of Real banknotes [25], the 2nd-generation samples also display EASI(+)-MS profiles that are mostly dominated by background ions with a few less abundant ions that can be directly related to surface chemicals. This feature is characteristic of authentic Real banknotes, showing that most dyes and other chemicals used in the processing are deeply and/or strongly adsorbed in the authentic banknote paper. The EASI charged droplets are therefore inefficient at desorbing such chemicals, and little ion current is produced. The ions detected are likely from banknote plasticizers such as bis(2-ethylhexyl)phthalate, detected as protonated  $[\text{M} + \text{H}]^+$  and sodiated  $[\text{M} + \text{Na}]^+$  molecules of  $m/z$  391 and  $m/z$  413, and the ion of  $m/z$  284 due to an aliphatic amine of molecular formula  $\text{C}_{19}\text{H}_{41}\text{N}$  already observed in the first generation of Brazilian banknotes [25]. The ions of  $m/z$  494 have been attributed to the dihexadecyl dimethyl quaternary ammonium salt  $(\text{C}_{16}\text{H}_{31})_2\text{N}^+(\text{CH}_3)_2$ , whereas the ions of  $m/z$  522 and 550 are blank ions detected in the solvent due to common lab detergents [27]. Note that the ions of  $m/z$  304 and  $m/z$  235, which were randomly observed in the R\$20 and R\$50 genuine banknote samples, illustrated by the spectra in Fig. 2b and 2c, correspond to protonated cocaine and lidocaine,

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