



Anti-theft device staining on banknotes detected by mass spectrometry imaging



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ABSTRACT

We describe the identification and limits of detection of ink staining by mass spectrometry imaging (MSI), as used in anti-theft devices (ATDs). Such ink staining is applied to banknotes during automated teller machine (ATM) explosions. Desorption electrospray ionization (DESI) coupled with high-resolution and high-accuracy orbitrap mass spectrometry (MS) and a moving stage device were applied to obtain 2D molecular images of the major dyes used for staining, that is, 1-methylaminoanthraquinone (MAAQ), rhodamine B (RB) and rhodamine 6G (R6G). MAAQ could not be detected because of its inefficient desorption by DESI from the banknote cellulose surface. By contrast, ATD staining on banknotes is perceptible by the human naked eye only at concentrations higher than $0.2 \mu\text{g cm}^{-2}$, whereas both RB and R6G at concentrations 200 times lower (as low as $0.001 \mu\text{g cm}^{-2}$) could be easily detected and imaged by DESI-MSI, with selective and specific identification of each analyte and their spatial distribution on samples from suspects. This technique is non-destructive, and no sample preparation is required, which ensures sample preservation for further forensic investigations.

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1. Introduction

The much-accelerated growth of bank and automated teller machine (ATM) thefts in Brazil in recent years is worrying to Brazilian authorities [1,2]. Considering the negative consequences to society, all efforts aimed to demotivate and detect such crime are welcome. Anti-theft security inks and bank dye security packs are commonly used by anti-theft devices (ATDs) to deter ATM robberies [3,4]. ATDs are activated during the theft event and create a cloud of dye particles or soaking liquid; this cloud or liquid is intended to cause staining on the stolen banknotes and on clothes, shoes, and other objects belonging to the thieves.

Analytical methods can identify stolen banknotes if the dye is properly characterized. ATD stains on the stolen banknotes should make the banknotes nontransferable and therefore valueless [1]. Thieves therefore usually attempt to bleach – and often succeed in bleaching – the stained banknotes; hence, analytical methods that are able to detect such dyes at trace, non-visible amounts would be invaluable for their forensic detection.

The extraction and characterization of security dyes from washed USA banknotes has been performed using Fourier transform infrared spectroscopy [5]. Mass-spectrometry-based techniques, including gas chromatography–mass spectrometry (GC–MS) [6–8] and tandem mass spectrometry (MS/MS) [9], have also been applied to characterize 1-methylaminoanthraquinone (MAAQ), which is the most commonly used ATD security ink (Fig. 1C). Other chemicals used in anti-theft devices include pepper spray products such as capsaicin (Fig. 1D), dihydrocapsaicin (Fig. 1E) and nonivamide (Fig. 1F) [10], and tear gas variants such as

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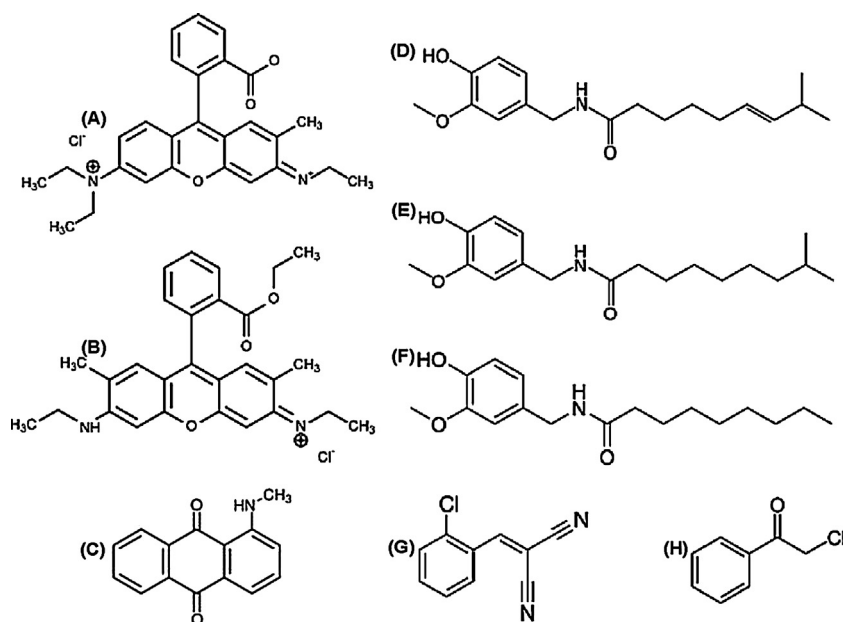


Fig. 1. Chemical structures of the main dyes used as ATDs: (A) rhodamine B (RB), (B) rhodamine 6G (R6G), (C) 1-methylaminoanthraquinone (MAAQ), (D) capsaicin, (E) dihydrocapsaicin, (F) nonivamide, (G) orthochlorobenzalmalononitrile and (H) 2-chloroacetophenone.

ortho-chlorobenzalmalononitrile (Fig. 1G) and 2-chloroacetophenone (Fig. 1H) [11]. Red dyes from the rhodamine family (Fig. 1A and B, rhodamine B and rhodamine 6G, respectively) are also used [12] as ATDs, and laser desorption mass spectrometry (LDMS) has been used to detect Basic Red 1:1 (m/z 429) and Basic Violet 11:1 (m/z 457) [13].

The forensic techniques used to inspect the banknote surface should ideally be non-destructive, rapid and simple. Over the last decade, a new class of desorption/ionization techniques for ambient mass spectrometry has been developed, and these techniques enable the desorption, ionization, and mass spectrometry characterization of analytes directly from surfaces in an open atmosphere with little or no sample preparation [14–16]. These techniques, such as desorption electrospray ionization (DESI) [17] and direct analysis in real time (DART) [18], followed by related techniques such as ELDI [19], EESI [20], DAPPI [21] and EASI [22], and others [23], have been demonstrated to serve as attractive tools for the direct forensic characterization of chemicals on surfaces, thereby ensuring forensic evidence preservation and allowing rapid, accurate and minimally destructive chemical profile screening [24].

For ATD analysis, DART-MS has already been applied and was able to identify MAAQ, orthochlorobenzalmalononitrile and capsaicin [25], and EASI-MS has been shown to function as a suitable technique for the surface inspection of suspect banknotes from ATM explosions that were contaminated by the ATD dye rhodamine B [12]. Mass spectrometry imaging (MSI) using DESI, that is, DESI-MSI, has also offered a breakthrough approach in chemical analysis [17], providing spatially specific chemical composition information on surfaces. MSI has also been applied to forensic chemistry because of its high chemical specificity and relative ease of use [26,27]. For instance, DESI-MSI has been used to inspect ink tracings in questioned documents [28] and to image latent fingerprints with forensic exogenous contaminants, i.e., explosives and illegal drugs [29,30].

In this work, we investigated the ability of DESI-MSI as a method to identify non-visible ATD residues directly from the surface of Brazilian banknotes.

2. Experimental

2.1. Materials and samples

HPLC-grade methanol was purchased from Burdick & Jackson (Muskegon, MI, USA). MAAQ, R6G and RB were purchased from Sigma-Aldrich, Brazil Ltd., at purities of 98%, 95% and 95%, respectively. A banknote of nominal value of R\$50 was obtained from a local bank and used in the experiment that examined homemade ATD banknote contamination to evaluate the DESI-MSI method.

2.2. DESI-MSI

The analysis was performed using a Q-Exactive (Thermo Fisher Scientific – Germany) mass spectrometer coupled to an Omni Spray 2-D Ion Source (Prosolia – USA) for data acquisition. The FireflyTM v.1.3.0.0 data conversion was used to generate the images, which were treated in BioMap3804. For the homemade ATD banknote contamination and the real forensic case, the MSI analysis was run by applying 50 runs with a step size of 0.2 μm , flow rate of 5.0 $\mu\text{L min}^{-1}$ and velocity of 700 $\mu\text{m s}^{-1}$.

2.3. Results and discussion

Fig. 2 summarizes the procedures used to test the ability of DESI-MSI to detect ATDs directly from the surface of a Brazilian banknote. The sample was placed on a 2D platform, which was automatically moved under a spray nozzle to expose selected areas of interest. Specific m/z images of the sampled area showing the spatial distribution of the abundance of the selected ion were created. The banknote was contaminated with 2 μL of three commonly used ATD dyes (MAAQ, RB and R6G) at four different concentrations (Fig. 2). The application of each 2 μL of dye solutions produced a round spot of approximately 0.5 cm in diameter (0.25 cm^2), which resulted in concentrations of approximately $C_1 = 0.001$, $C_2 = 0.05$, $C_3 = 0.2$ and $C_4 = 1.0 \mu\text{g cm}^{-2}$, respectively.

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