



Thin layer chromatography coupled to paper spray ionization mass spectrometry for cocaine and its adulterants analysis



Thays C. De Carvalho^a, Flavia Tosato^b, Lindamara M. Souza^b, Heloia Santos^b, Bianca B. Merlo^c, Rafael S. Ortiz^d, Rayza R.T. Rodrigues^b, Paulo R. Filgueiras^b, Hildegarde S. França^e, Rodinei Augusti^f, Wanderson Romão^{b,e,*}, Boniek G. Vaz^{a,b,**}

^a Instituto de Química, Universidade Federal de Goiás, 74001-970 Goiânia, GO, Brazil

^b Laboratório de Petroléomica e Química Forense, Departamento de Química, Universidade Federal do Espírito Santo, 29075-910 Vitória, ES, Brazil

^c Laboratório de Química Legal, Superintendência de Polícia Técnico-Científica da Polícia Civil do Estado do Espírito Santo, 29045-300 Vitória, ES, Brazil

^d Superintendência de Polícia Federal no Estado do Rio Grande do Sul, 90160-093 Porto Alegre, RS, Brazil

^e Instituto Federal do Espírito Santo, 29106-010 Vila Velha, ES, Brazil

^f Departamento de Química, Universidade Federal de Minas Gerais, 31270-901 Belo Horizonte, MG, Brazil

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ABSTRACT

Thin layer chromatography (TLC) is a simple and inexpensive type of chromatography that is extensively used in forensic laboratories for drugs of abuse analysis. In this work, TLC is optimized to analyze cocaine and its adulterants (caffeine, benzocaine, lidocaine and phenacetin) in which the sensitivity (visual determination of LOD from 0.5 to 14 mg mL⁻¹) and the selectivity (from the study of three different eluents: CHCl₃:CH₃OH:HCOOH_{glacial} (75:20:5 v%), (C₂H₅)₂O:CHCl₃ (50:50 v%) and CH₃OH:NH₄OH (100:1.5 v%)) were evaluated. Aiming to improve these figures of merit, the TLC spots were identified and quantified (linearity with R² > 0.98) by the paper spray ionization mass spectrometry (PS-MS), reaching now lower LOD values (> 1.0 μg mL⁻¹). The method developed in this work open up perspective of enhancing the reliability of traditional and routine TLC analysis employed in the criminal expertise units. Higher sensitivity, selectivity and rapidity can be provided in forensic reports, besides the possibility of quantitative analysis. Due to the great simplicity, the PS(+)-MS technique can also be coupled directly to other separation techniques such as the paper chromatography and can still be used in analyses of LSD blotter, documents and synthetic drugs.

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1. Introduction

Cocaine is mainly consumed as a salt (cocaine hydrochloride) or in a freebase form (crack). Cocaine hydrochloride is a water-soluble salt obtained as a powder, and it can be administered via aspiration or intravenously. Crack, however, appears as a rock and is slightly soluble, but it is easily volatilized when heated because of its low melting point (approximately 95 °C) and can be administered via smoke [1]. According to the International Union

of Pure and Applied Chemistry (IUPAC), cocaine is a [1R-(exo,exo)-3-(benzoyloxy)-8-methyl-8-azabicyclo[3.2.1]octane-2-carboxylic acid methyl ester. Its molecular formula is C₁₇H₂₁NO₄, and its molar mass is 303.4 g mol⁻¹. Cocaine's melting point range is 96–98 °C, and its pK_b = 5.4 [2,3].

In the last few years, the purity of “commercial” cocaine has been decreasing. To increase drug volume and therefore drug trafficking profits, chemical additives are blended to the alkaloid as adulterants and/or diluents. Among the chemical additives, psychoactive substances, commonly anesthetics, are used to mimic or increase the drug effect for users [4,5]. Fig. 1a–d shows the chemical structures of some adulterants found in cocaine samples seized in the Brazilian illicit market. They are: benzocaine, phenacetin, caffeine and lidocaine [3].

Expert methodologies for cocaine analysis are mostly qualitative. At least two examinations are performed: a preliminary test using wet chemistry and an analytical test with higher selectivity.

* Corresponding author at: Instituto Federal do Espírito Santo, 29106-010 Vila Velha, ES, Brazil. Tel.: +55 27 3149 0833.

** Corresponding author at: Instituto de Química, Universidade Federal de Goiás, 74001-970 Goiânia, GO, Brazil. Tel.: +55 62 3521 1016x261.

E-mail addresses: wandersonromao@gmail.com (W. Romão), bonigontijo@yahoo.com.br (B.G. Vaz).

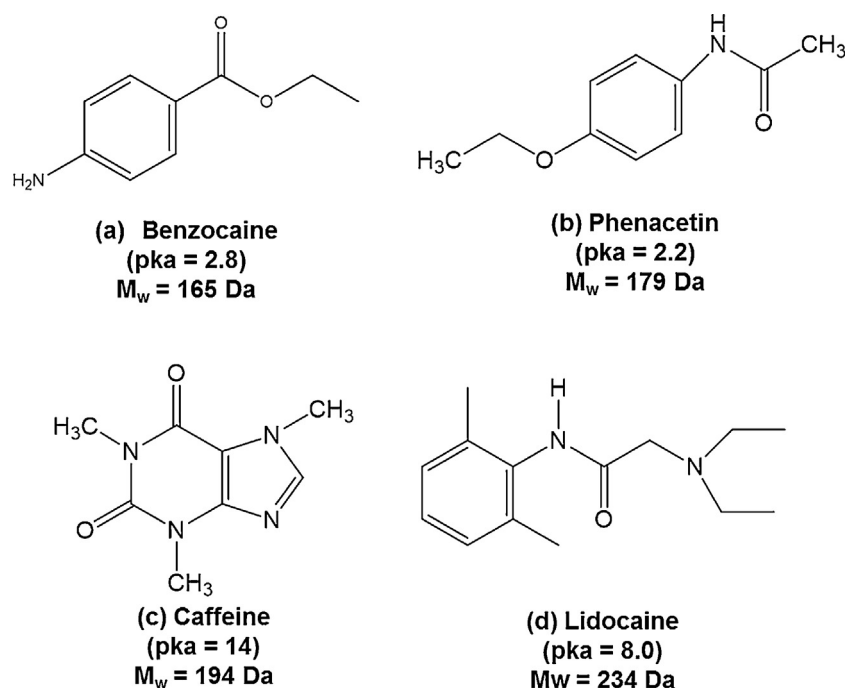


Fig. 1. Main adulterants seized in Brazilian illicit cocaine market.

Colorimetric tests or pre-tests have the advantages of rapidity, low cost and ease of execution and interpretation. However, they feature low specificity. Among the colorimetric tests used to determine the presence of alkaloids, is usually employed the test using a solution of cobalt thiocyanate [5,6]. Nevertheless, positive results can be found when some adulterants or diluents are present, such as lidocaine, powdered milk and promethazine.

Other analytical methodologies are routinely applied for cocaine analysis, including thin layer chromatography (TLC) [7–10], gas chromatography coupled with mass spectrometry (GC–MS) [11] and gas chromatography coupled with flame ionization detector (GC–FID) [12,13]. Among them, TLC is a more simple and cheap separation technique, being extensively used in the most Brazilian forensic laboratories for drugs of abuse analysis (cocaine, crack, marijuana, and ecstasy tablets) [5,14]. TLC is based on the differences of affinities of analyte between the stationary and mobile phases. TLC has also been explored for cocaine detection in urine and other biological matrixes [15].

The compounds separated on the TLC plate form spots which are usually detected with UV light, iodine vapor, or other visualization reagents. However, some spots may be missed in visualization. In addition, the visualization methods are not capable of identifying the nature of the separated compounds. To overcome this limitation, mass spectrometric methods have been developed for identifying the compounds separated on the TLC plates [16].

Recently, the use of new techniques of ambient mass spectrometry, that allow desorption, ionization and characterization of analytes via mass spectrometry directly from their natural matrixes, becomes an attractive alternative in forensic problems. These ionization/desorption techniques require no sample preparation or pre-separation [1,7,17,18].

Paper spray ionization (PS), introduced in 2010 by Wang et al., [19] is a new ambient mass spectrometry technique for qualitative and quantitative analysis of complex mixtures. PS–MS involves directly loading the sample onto a triangular-shaped paper, which is wetted with a solvent and placed in front of the mass spectrometer inlet. The spray of the charged micro-droplets is formed by application (usually 3–5 kV) in the opposite side of the

paper tip and the desolvation occurs without any sheath gas [20]. The PS–MS mechanism of ions formations in the gaseous phase is similar to ESI process.

The PS–MS has been explored in various applications, mainly to analyze directly complex samples such as illicit substances in raw urine, pharmaceuticals in whole blood [21], biological tissue [22], contaminants in foodstuffs [23], and other applications [24]. Herein, the TLC system is optimized and has its figures of merit improved (detection limit, sensitivity and selectivity) from coupling to PSI–MS method. This analytical methodology has been employed to detection and quantification of cocaine and its adulterants (benzocaine, phenacetin, caffeine and lidocaine).

2. Experimental

2.1. Reagents and solutions

A reference standard sample of cocaine provided by PC–ES (Civil Police of Espírito Santo State, Brazil) and standards of phenacetin, benzocaine (both provided by Sigma–Aldrich, Sao Paulo), lidocaine and anhydrous caffeine (Vetec Química Fina Ltda, Rio de Janeiro and Bandeirante Brazmo Industria e Comercio Ltda, Sao Paulo, respectively) were used to prepare stock solutions of 12, 14 and 20 mg mL⁻¹.

The reagents used in the TLC and PS–MS analysis were methanol HPLC grade (J.T.Baker), formic acid 99% RPE ACS PA (Carlo Erba reagentes), ammonium hydroxide (Sigma Aldrich), Milli-Q water, chloroform, glacial acetic acid and ethyl ether (Vetec Química Fina Ltda, Rio de Janeiro).

2.2. TLC

Initially, an optimization of the TLC system was performed by varying the application volume (5, 10, 15, 20 and 25 μL), the form of application (micropipette, silica capillary and microsyringe) and the analyte concentration (4, 6, 8, 10, 14 and 16 mg mL⁻¹). In this step, cocaine was used as analyte, silica gel as stationary phase with support of aluminum and the methanol:NH₄OH mixture in

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