



A green method for the determination of cocaine in illicit samples



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ARTICLE INFO

Article history:

Received 10 July 2013

Received in revised form 21 January 2014

Accepted 23 January 2014

Available online 7 February 2014

Keywords:

Cocaine
Illicit samples
Near infrared
Green analytical method
Partial least squares

ABSTRACT

Direct determination of cocaine in untreated seized samples has been made based on diffuse reflectance measurements of the near infrared (NIR) radiation through samples contained inside standard glass vials. The method used a series of previously analyzed samples, by the reference gas chromatography method, to build a partial least squares calibration model which was validated using an independent set of samples. The use of a general model for samples containing from 11.38% till 86.44% (w/w) cocaine was based on the use of spectral ranges from 12500.7 to 10128.6, 9339.8 to 6967.7 and 5388.3 to 4597.6 cm^{-1} with previous first derivative and vector normalization data pre-processing and provided a root mean square error of prediction (RMSEP) of 4.0% (w/w) with a residual prediction deviation (RPD) of 3.9% (w/w), based on the use of 8 latent variables, 34 samples for calibration and an independent set of 44 samples for validation. The aforementioned results could be improved on considering two separate models, one for high concentrated bulk samples and another for samples diluted with cutting agents. Additionally a new set of batch samples with cocaine concentrations from 60% till 84% was evaluated by using the developed method.

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1. Introduction

Cocaine, benzoylmethylecgonine or the systematic IUPAC name methyl (1R,2R,3S,5S)-3-(benzoyloxy)-8-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate, is nowadays the most common illicit drug subjected to the international control around the world and every year in Spain hundred of kilograms and thousands of street doses are seized by the police and it creates the need for the analytical control of both, pure cocaine distributed by the international drug cartels and doses seized in the streets [1].

Cocaine is a highly addictive drug which affects the human behaviour and can damage the brain [2]. It is consumed as pure white cocaine hydrochloride or mixed with other white powders, being phenacetin, lidocaine, procaine, caffeine, piracetam and levamisole some of the most frequently found cutting agents in seized samples [3,4].

Gas and liquid chromatography are the recommended methods commonly employed for cocaine determination in official laboratories, following the recommendations of the United Nations Office

on drugs and crime [5] and it is clear that the chromatographic methods are highly sensitive and selective for this purpose. However their use involves sample destruction, tedious and solvent consume sample preparation steps and requires the intensive operator handling. Because of that, there is and increasing interest on the use of vibrational spectroscopy based analytical methods like Raman [6,7], mid-infrared (MIR) [8–10] and near-infrared (NIR) [11,12] that can be applied for the direct determination of illicit drug components in untreated samples, thus offering green alternatives to be used in continue routine analysis [13,14].

MIR has been employed for the quantitative determination of cocaine using KBr pellets based on the integration of the carbonyl band [15] and Raman spectroscopy has been used for cocaine hydrochloride characterization in illicit drugs [16–19].

On the other hand NIR has been only used for the direct determination of heroin and codeine in drugs [20] and for the determination of heroin in seized street drugs [21]. So, the objective of the present study was the development of a non destructive and fast green alternative method for the determination of cocaine in seized illicit street drugs, based on the measurement of diffuse reflectance NIR spectra of samples introduced inside standard glass vials and the use of previously analyzed samples of the same type to build partial least squares (PLS) calibration models.

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2. Materials and methods

2.1. Apparatus and reagents

Diffuse reflectance measurements were obtained with a Fourier transform NIR instrument model Multipurpose Analyzer (MPA) from Bruker (Bremen, Germany). The system was equipped with a single detector in which the radiation was focused by means of an integrating sphere, used as measurement accessory. 2 mL standard glass chromatographic vials (12 mm × 32 mm) of 9.5 mm internal diameter were employed as measurement cells to contain untreated samples. For instrument control and data acquisition, also for spectra treatment and data manipulation OPUS program version 6.5, from Bruker GmbH, was employed.

A gas chromatographic system Agilent model 7890A (Palo Alto, CA, USA) equipped with a flame ionization detector and an Agilent HP-5 capillary column (30 m × 0.32 mm × 0.25 μm) was used to obtain reference data of samples employed through this study.

A certified cocaine chlorhydrate (99.89%) from Lipomed (Arllesheim, Switzerland), tetracosane analytical grade from Fluka (Sigma–Aldrich Co., St. Louis, MO, USA) and absolute ethanol (99.5%) from Panreac (Barcelona, Spain) were used for GC analysis.

2.2. Samples

78 cocaine samples seized between 2009 and 2010 were analyzed by the gas chromatography reference method, having obtained cocaine concentrations between 11.38% and 86.44% (w/w), expressed as cocaine base, thus including from seized individual doses to high purity batches.

2.3. Reference procedure for gas chromatography

The United Nations GC procedure for cocaine analysis was employed as reference method. An accurate sample weight of 10–20 mg of the homogenized sample was dissolved in 8 mL of a 0.02% (w/v) tetracosane solution in ethanol, being employed a 3 min sonication time in an ultrasound water bath and then was diluted to a final volume of 10 mL. 0.5 μL of the aforementioned solution were directly introduced in the gas chromatograph by means an automatic injector, in the split mode using a nitrogen carrier gas of 7.0 mL/min, and analyzed in the isothermal mode with an injector and detector temperature of 280 °C and an oven temperature of 220 °C.

2.4. PLS-NIR procedure

Homogenized powdered samples were placed inside glass chromatography vials of 9.5 mm internal diameter and 2 mL volume (50–75 mg are enough quantity to create a layer of 2 mm height inside the vial) and NIR spectra recorded between 13,500 and 3500 cm⁻¹ at a nominal resolution of 4 cm⁻¹ and using 50 cumulated scans per spectrum. Final spectra were obtained in Kubelka Munk units, the background being established from the closed integrating sphere of the spectrometer. Three spectra of each sample, made in the same vial but varying its position by rotation, were obtained in order to increase the variability of spectra and to increase sample representativity. Spectral data corresponding to the three replicates of each sample were processed separately/independently. Sample spectra were classified by means hierarchical cluster analysis and divided in two independent sets, one used for calibration and the second one for validation purpose. Using the selected calibration set, the appropriate PLS models were built using the best pre-processing method, wavenumber range, and number of factors (latent variables) for cocaine quantization in illicit drugs. The PLS model

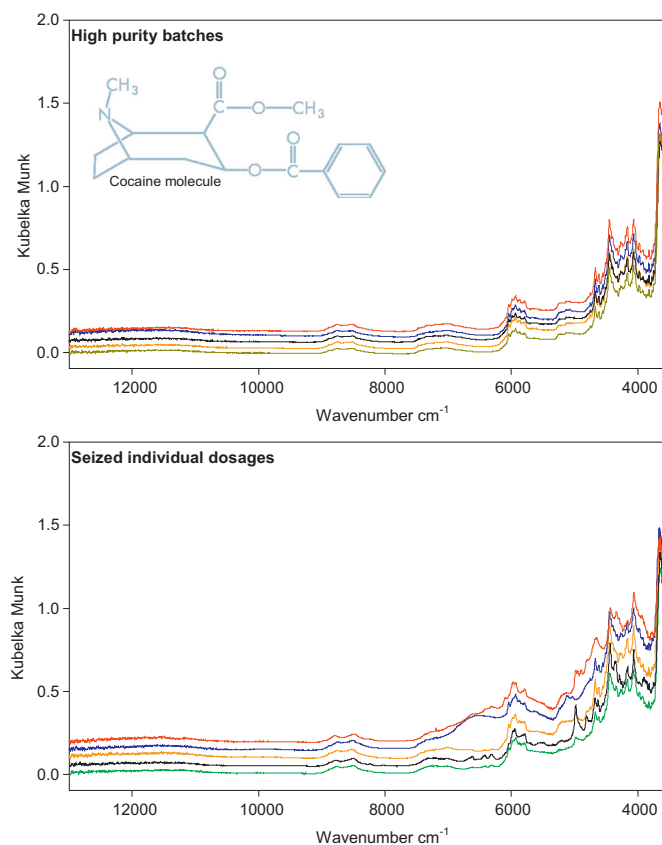


Fig. 1. FT-NIR spectra of street seized and bulk samples containing cocaine.

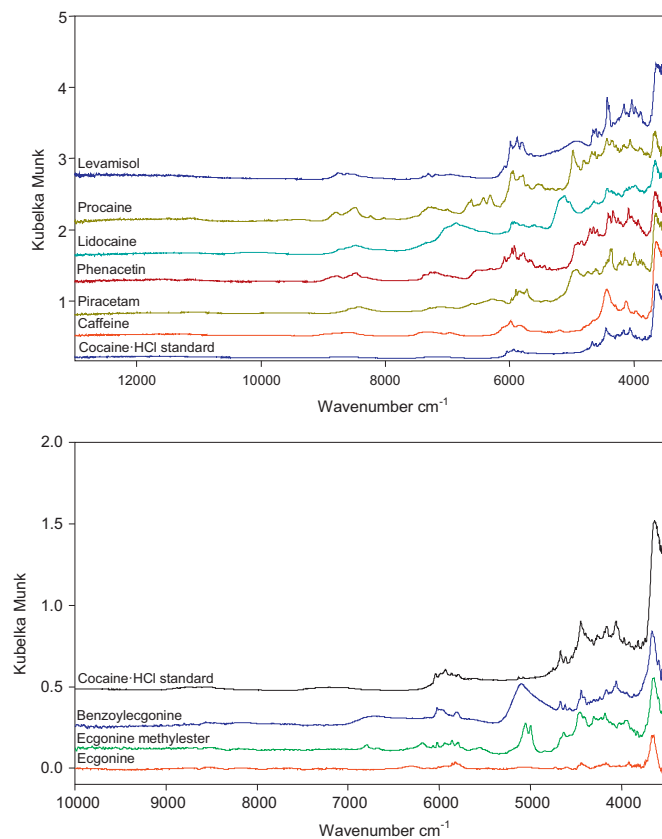


Fig. 2. FT-NIR spectra of cocaine chlorhydrate standard, cocaine related compounds and cutting substances.

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