

Short communication

Validated, non-destructive and environmentally friendly determination of cocaine in euro bank notes

Francesc A. Esteve-Turrillas, Sergio Armenta, Javier Moros, Salvador Garrigues, Agustín Pastor, Miguel de la Guardia*

Department of Analytical Chemistry, Universitat de València, Edifici Jeroni Muñoz, 50th Dr. Moliner, 46100 Burjassot, Valencia, Spain

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Abstract

A non-destructive, fast and environmentally friendly procedure has been developed for cocaine determination in euro bank notes. Cocaine was extracted with 15 ml methanol by vortex agitation during 5 min. The extract was evaporated and reconstituted in 0.5 ml methanol. GC–MS–MS analysis was performed using as precursor ion m/z 182.2, with an excitation energy voltage of 1.60 eV, being the product ions measured m/z 150.2 and 82.0. A limit of detection of 0.15 ng per note and a repeatability of 6%, established from the relative standard deviation, of a 1 ng ml^{-1} level, were achieved. Recoveries of 101 ± 2 and $98 \pm 3\%$ were obtained for samples spiked with 100 and $10 \mu\text{g}$ respectively. Results show that all the euro bank notes measured (16 samples) were contaminated with cocaine in the range between 1.25 and $889 \mu\text{g}$. Two different contamination levels, high level ($150\text{--}889 \mu\text{g}$) and low one ($1.25\text{--}77 \mu\text{g}$) were found and it could be related with the direct or indirect contact with the drug.

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1. Introduction

Cocaine is one of the most widely extended illicit drugs in the world [1] and any note that was used to inhale a powder containing cocaine would contain small amounts of the drug retained by the paper fibers. Previous studies demonstrated that paper currency in general circulation is contaminated with cocaine [2,3].

There are precedents on the cocaine determination in paper currency by gas chromatography coupled to mass spectrometry in USA and UK bank notes. Table 1 summarizes the precedents found in the literature and the main features of methods employed and it can be seen that at least 15 min extraction time is required followed by a clean-up step and being obtained a limit of detection of the order of 1 ng ml^{-1} .

The aim of the present work has been to develop a non-destructive, fast, validate and environmentally friendly

methodology to determine cocaine in euro bank notes by GC–MS–MS.

2. Experimental

2.1. Apparatus and reagents

A Finnigan (Waltham, MS, USA) Trace gas chromatograph with a Teknokroma TRB-META.X5 column ($30 \text{ m} \times 0.32 \text{ mm i.d.}$, $0.25 \mu\text{m}$ film thickness) (Barcelona, Spain), equipped with a Finnigan ion trap mass spectrometer detector Polaris Q was used for cocaine determination.

A Velp Scientifica vortex shaker (Milan, Italy) and a Büchi Rotavapor R-205 (Flawil, Switzerland) coupled to a Büchi vacuum controller V-800 were used in sample preparation.

Cocaine hydrochloride standard was supplied by Sigma (Madrid, Spain). Methanol, acetonitrile and chloroform

* Corresponding author. Tel.: +34 96 354 4838; fax: +34 96 354 4838.
E-mail address: miguel.delaguardia@uv.es (M. de la Guardia).

Table 1
Previously reported procedures for the determination of cocaine in euro bank notes

Sample	Extraction solvent/ volume (ml)	Extraction time	Clean-up	Detection system	LOD	Recovery (%)	Reference
USA \$	Acetonitrile/5	2 h	SPE	GC–MS	1 ng ml ⁻¹	–	[2]
USA \$	CHCl ₃	30 min	Not	GC–PCI–MS	1 ng	91.7–93.0	[3]
USA \$	Methanol/10		SPE	GC–MS	–	–	[4]
USA \$	0.1 M HCl/5	15 min	SPE	GC–MS	1 ng	95.2	[5]
Canadian \$	Ethanol	–	CHCl ₃ /H ₂ SO ₄ / NaOH/CHCl ₃ / ethyl acetate	GC–NPD, GC–MS	–	–	[6]
Swiss francs	None	–	Not	IMS	0.25 ng	–	[7]
UK £	None	30 s	Not	MS	–	–	[8]
UK £							
Canadian \$	None	30 s	Not	MS	–	–	[9]
USA \$							

Note: references obtained from the analytical abstracts 1984–2003 and current contents 1997–2004.

SPE: solid-phase extraction. GC–MS: gas chromatography–mass spectrometry. GC–PCI–MS: gas chromatography–positive chemical ionization mass spectrometry. GC–NPD: gas chromatography with nitrogen-phosphorous detection. IMS: ion mobility spectrometry.

for pesticide residue analysis were provided by Scharlau (Barcelona, Spain). Euro bank notes were obtained randomly from different Spanish cities. The money was in general circulation at the time. Upon collection, the bills were placed in independent storage plastic bags to avoid the cross-contamination and stored at room temperature until the cocaine determination. Non-circulated euro bank notes were obtained directly from a Spanish bank.

2.2. Cocaine extraction

Euro bank notes were placed inside a 30 ml glass centrifuge tube and 15 ml methanol were added. Each tube was capped and shaken by vortex during 5 min. After that, bank notes were cleaned with 5 ml methanol which were mixed with the previous extract. To improve the limit of detection of the method the final extract could be evaporated in a rotary evaporator and reconstituted in 0.5 ml methanol before sample injection.

2.3. GC–MS–MS cocaine analysis

One microlitre of the methanol extract, after appropriate dilution if required, was injected in the splitless mode at 250 °C, employing helium as carrier gas in constant flow mode at 1 ml min⁻¹. Oven temperature program was 150 °C, held for 1 min, increased at a rate of 10 °C/min up to 250 °C and finally held 5 min. The transfer line temperature was 300 °C.

Helium was used as damping gas with a flow of 1.5 ml min⁻¹. Transfer line and ion source temperatures were 300 and 250 °C, respectively and an electron voltage of 70 eV was employed for electron impact ionization.

MS–MS acquisition was performed using as precursor ion *m/z* 182.2, with an excitation energy voltage of 1.60 eV and product ions measured were *m/z* 150.0 and 82.0. Ion

trap tests and mass calibration were weekly performed with perfluorotributylamine (PFTBA).

3. Results and discussion

3.1. Extraction conditions

Several solvents such as acetonitrile, chloroform and methanol were checked in order to improve cocaine extraction and to avoid the note destruction. Although the high solubility of cocaine in chlorinated solvents [3], its use causes the damage of the security band and holographic marks of the euro notes making them useless. On the other hand, a partial destruction and a massive amount of solid co-extracted compounds occur when acetonitrile was used as suggested before [2]. Taking into account all these considerations, methanol was used to obtain a non-destructive extraction procedure.

A recovery study was made by addition of 100 µl cocaine standard solution of 100 µg ml⁻¹ on non-circulated bank notes in order to select the most appropriate solvent volume and the number of extraction steps being found a mean recovery of 98 ± 3% for a single extraction with 15 ml methanol.

In order to test the effect of fat and matrix substances present in used euro bank notes two independent and consecutive extractions were made on the same sample for a series of bank notes. Between 0.9 and 2.1% recovery, respect to the first extraction, was obtained in the second one. So, we can conclude that there is no matrix effect on the cocaine extraction and only one step is necessary.

3.2. GC–MS–MS parameters selection

To improve the sensitivity of cocaine determination a GC–MS–MS procedure was developed. The effect of

instrumental conditions, such as precursor ion selected, damping gas flow, excitation voltage energy and ions measured were evaluated.

The most intense characteristic ions found in the cocaine MS spectrum were m/z 182.2 and 82.0. A precursor ion of m/z 182.2 was selected for the collision-induced dissociation, because it provides fragmentation ions with high m/z values for a right measurement.

Previous studies demonstrate that high damping gas flows enhanced the trapping efficiency but it may decrease the repeatability [10], thus damping gas flow was increased from 0.3 to 2.0 ml min^{-1} . Fig. 1a shows that the m/z 182.2 area, increases till to reach a plateau for damping gas flow equal or higher than 1 ml min^{-1} . So, a value of 1.5 ml min^{-1} was selected.

Area of the m/z 82.0 and 150.0 ions, formed by dissociation of the m/z 182.2 precursor ion, were measured using different excitation voltage energies from 0 to 3 eV. As can be seen in Fig. 1b, an excitation voltage of 1.60 eV provided the highest signals.

3.3. Analytical features

Chromatograms of cocaine standard solutions and samples, obtained by the proposed GC–MS–MS procedure are shown in Fig. 2. As can be seen in the inset of the figure the most intense ions formed, by dissociation of the m/z 182.2 precursor, are m/z 82.0 and 150.0, as it has been indicated previously. These ions plus those at m/z 108.0 and 122.1 provide an excellent cocaine identification.

The calibration line obtained by peak area measurements at 11.34 min in the selected masses chromatogram in full scan and MS–MS acquisition modes, employing six standards ranging from 10 to 800 ng ml^{-1} , are shown in Table 2. The full scan mode provides a higher sensitivity than the MS–MS mode but also 10 times higher intercept values and a 2.2 ng note^{-1} limit of detection (LOD) instead of the 0.15 ng note^{-1} limit of detection found by MS–MS.

Repeatability, as the relative standard deviation of 5 independent measurements of a cocaine standard of 1 ng ml^{-1}

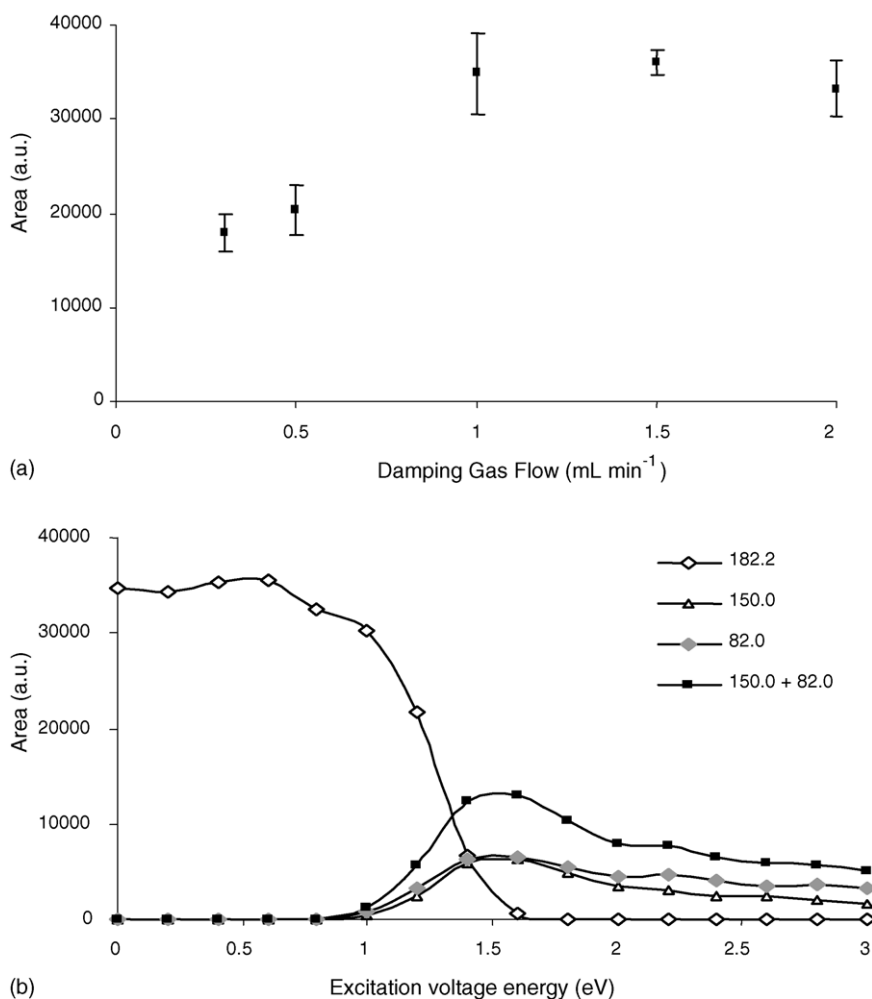


Fig. 1. Effect on experimental conditions on the area of the m/z 182.2 ion of a 250 ng ml^{-1} cocaine standard solution ($n = 3$). (a) Effect of the damping gas flow and (b) effect of the excitation voltage energy.

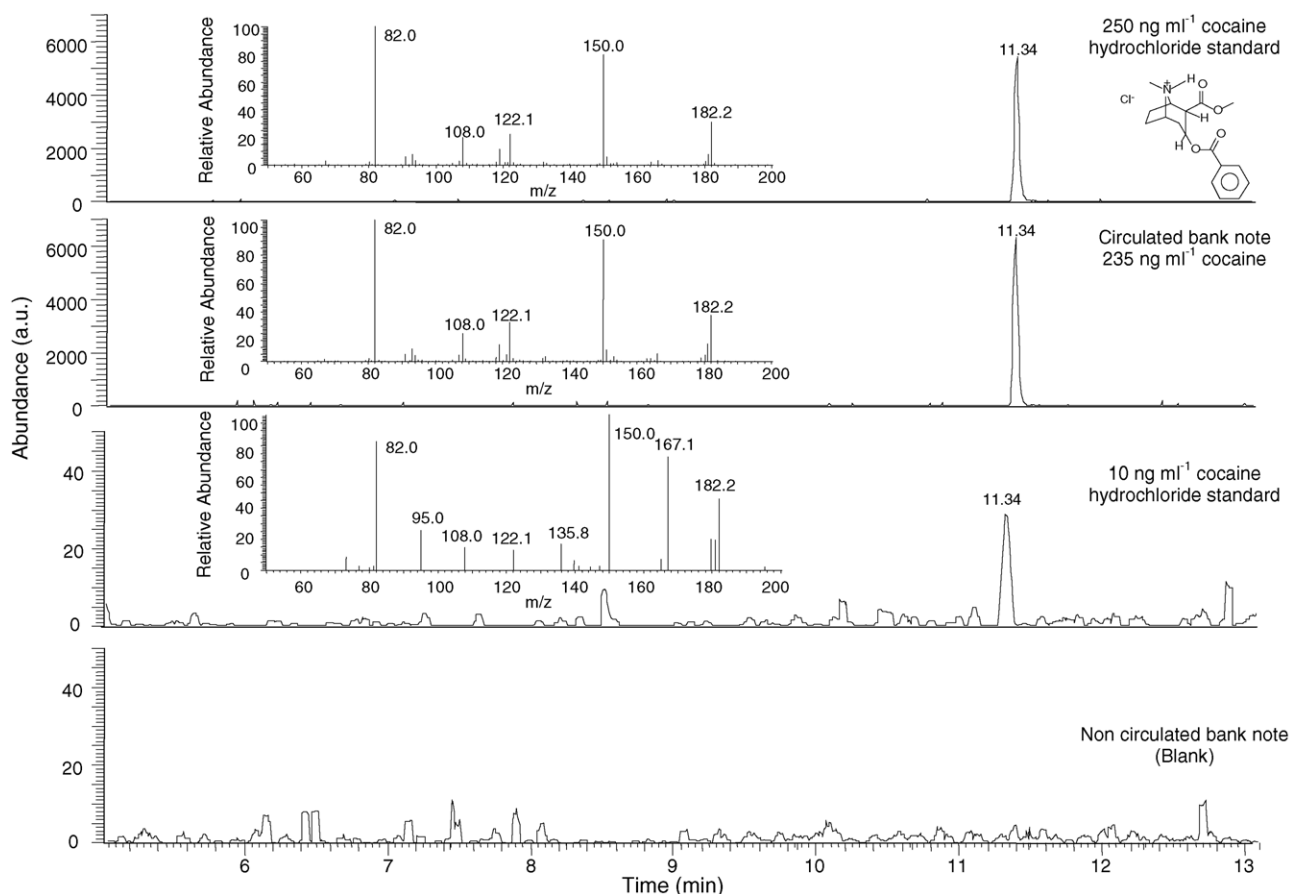


Fig. 2. Chromatograms of a 250 and 1 ng ml⁻¹ cocaine standard solutions, and from the extracts of an used bank note with a cocaine concentration of 235 ng ml⁻¹, which corresponds to $47.0 \pm 0.3 \mu\text{g note}^{-1}$, and a non-circulated bank note, obtained in the MS–MS mode using as precursor ion *m/z* 182.2. Insets: MRM spectra of the peak obtained at a retention time of 11.34 min.

for MS–MS measurements and 10 ng ml⁻¹ for full scan ones provides values of 6 and 13% respectively.

Recovery studies made at 100 and 10 μg per note levels provided recoveries of $101 \pm 2\%$ and $98 \pm 3\%$ ($n = 3$), respectively. In short, the general features of the developed proce-

cedure are better than those of previously established methods [3,5].

3.4. Sample analysis

Results obtained in the analysis of 16 euro notes of different nominal values show that all the euro bank notes measured were contaminated with cocaine in the range between 1.25 and 889 μg . As it can be seen in Table 3, we can distinguish two different contamination levels, a high level (150–889 μg) probably due to a direct contact of the note with cocaine and a low one (1.25–77 μg) related with a cross-contamination through the paper currency circulation. The comparison of the average of both data populations, 422 ± 304 and 34 ± 23 , provided a t_{exp} value of 3.34, higher than the theoretical value of 2.14 for 14 freedom degrees and 95% probability level.

However our results differ from those reported by Sleeman et al. [9] who found that directly contaminated samples contain between 50 and 1000 times the concentration of unpolluted samples in the case of Canadian dollars.

Table 2

Analytical features of the cocaine determination by gas chromatography–mass spectrometry

Analytical parameters	Full scan	MS–MS
Intercept (a.u.) ^a	2000 ± 3000	170 ± 190
Slope (a.u. ng ⁻¹ note) ^a	166 ± 2	60.9 ± 0.6
R^2	0.999	0.9995
LOD (ng note ⁻¹)	2.2 (c)	0.15 (d)
LOQ (ng note ⁻¹)	7.4 (c)	0.5 (d)
RSD (%) ^b	13 (c)	6 (d)

LOD: limit of detection established from the expression $3s/b$, being s the standard deviation of five measurements of (c) 10 ng ml⁻¹ or (d) 1 ng ml⁻¹ cocaine standard and b the slope of the calibration curve.

LOQ: limit of quantification established from the expression $10s/b$.

^a Calibration curve obtained for six standards of cocaine at concentration levels from 10 to 800 ng ml⁻¹.

^b Relative standard deviation obtained from five independent measurements of (c) 10 ng ml⁻¹ or (d) 1 ng ml⁻¹ cocaine standard.

Table 3
Cocaine determination in euro bank notes by GC–MS–MS

Bank note	Sample	Cocaine ($\mu\text{g note}^{-1}$) ^a
5 €	1	11.3 \pm 0.8
	2	234 \pm 17
	3	1.25 \pm 0.04
10 €	4	273 \pm 3
	5	566 \pm 8
	6	150 \pm 2
	7	26.8 \pm 0.2
	8	39.0 \pm 0.2
	9	29.4 \pm 0.3
	10	889 \pm 12
20 €	11	27.2 \pm 0.5
	12	33.4 \pm 1.1
	13	10.1 \pm 0.4
	14	76.7 \pm 1.2
50 €	15	67.8 \pm 0.8
	16	47.0 \pm 0.3

^a Concentration values are the average \pm the standard deviation of three injections.

4. Conclusions

A non-destructive and environmentally friendly procedure has been developed for cocaine determination in euro bank notes. Problems related with the partial destruction of euro bank notes found on using previously proposed procedures [2,3] were avoided by using methanol as extraction solvent, providing quantitative recoveries without the need of a

previous clean-up of the extracts as it was noticed before [4,5].

An analysis frequency of 4 h⁻¹ using only 20.5 ml of methanol per sample was achieved.

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