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Development of forensic analytical chemistry method for examination of Merla by thermal analysis and high resolution gas chromatography

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Abstract The objective of this work is the TG and DSC analysis of "Merla" samples as well as the separation and identification of organic compounds by *Ultra Fast GC* method. The obtained results showed the grouping and the establishment of the degree of the sample's similarity based in the Euclidean Distance. The cluster was a useful tool to determine if the samples, confiscated from different users by police, were manufactured in the same or different laboratories. Consequently one can conclude if in any city operates one or more drug manufacturing laboratories.

Keywords Cocaine · Gas chromatography · Merla · Thermal analysis

Introduction

Cocaine (benzoylmethylecgonine) is an alkaloid obtained from the plants *Erytroxylum coca* and *Erytroxylum novogranetense* through a process where the leaves are macerated with an organic solvent and the resulting brownish suspension (with a 70–85% of cocaine concentratio) sent to a refining process [1]. The residual sediment, generated by this process has low cocaine concentration is called "Merla" (http://www.pcdf.df.gov.br/apcfolders.asp August, 08 2007). Nowadays Merla is a cocaine derivative drug which main constituent is cocaine mixed with organic and inorganic compounds as carbonate, bicarbonate, marble's powder, battery's solution, boric acid, sodium borate, anesthetics and other substances. The amount of cocaine used in each Merla manufacturing process is variable and there are cases where fake Merla drugs that use stimulants instead of cocaine are produced [2].

Analysis of cocaine samples was made by several analytical techniques and some disadvantages were observed. The UV–VIS spectroscopy showed low sensitivity and specificity [3]. The Infrared spectroscopy (FTIR) showed problems with compounds that have bonds similar to cocaine, e.g., other classes of alkaloids present in samples of forensic interest [2]. TLC is a technique that is frequently used in forensic laboratories for identification and separation of cocaine, but is not possible to quantify inorganic compounds with this technique [4]. The HRGC and HPLC techniques, after the extraction methods, allow the cocaine to be analyzed in qualitative and quantitative methods but the inorganic analysis of the compounds arrested, could not bring information about the manipulation process [5–8].

Merla is a complex mixture of compounds with different volatilities therefore thermogravimetry is a suitable technique that allows the brute sample fractionation by thermal decomposition and sequential volatilization of compounds, making possible the identification of chemical composition by HRGC-MS, after isolation and collection of desirable fraction [9].

Zamponi et al [2], developed a fast methodology using TG and DSC for direct analysis of mixtures containing cocaine, allowing the quantification with a good

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reproducibility and sensibility. But presence of adulterants influences of melting points of cocaine making difficult the sample identification.

In forensic laboratories, methods that allow the determination of the original material are important to establish the source of evidence [10]. Therefore, multivariance analysis techniques are used to correlate the data generated from thermal analysis and another analytical techniques with external factors (geographical origin, production process [11–15]) because they can explore a set of experimental results and group the samples.

The objective of this work is the determination of the thermal behavior of "Merla" samples using TG and DSC techniques and procedures of separation and the identification of organic compounds that constitute the sample using HRGC with FID and MS detectors. Chemometric treatment of results was made using Hierarchical Cluster Analysis (HCA) method for classification and grouping the samples.

Experimental

Sampling

Thirty different samples, provided by the "Instituto de Criminalística Leonardo Rodrigues" (Brazil) were analyzed. The sample Go-02 was from a powder narcotic and the other ones from "Merla". The samples and their respective arrest places are shown in Table 1.

Table 1 Specification of analyzed samples

Sample		City	Sample		City
1	AL-01	Águas Lindas	16	Go-02	Goiânia
2	An-01	Anápolis	17	Go-03	Goiânia
3	CO-01	Cidade Ocidental	18	Lu-01	Luziânia
4	CO-02	Cidade Ocidental	19	Lu-02	Luziânia
5	CO-03	Cidade Ocidental	20	Lu-03	Luziânia
6	Fo-01	Formosa	21	Lu-04	Luziânia
7	Fo-02	Formosa	22	NG-01	Novo Gama
8	Fo-03	Formosa	23	Pla-01	Planaltina
9	Fo-04	Formosa	24	Pla-02	Planaltina
10	Fo-05	Formosa	25	Pla-03	Planaltina
11	Fo-06	Formosa	26	Pla-04	Planaltina
12	Fo-07	Formosa	27	SA-01	Santo Antonio do Descoberto
13	Fo-08	Formosa	28	Va-01	Valparaíso
14	Fo-09	Formosa	29	Va-02	Valparaíso
15	Go-01	Goiânia	30	Va-03	Valparaíso

Thermal analysis

The thermogravimetric curves

The thermogravimetric curves of Merla samples were obtained using a Mettler Toledo TGA/SDTA 851[e]. The purge gas was nitrogen with at a flow rate of 50 mL min^{-1}. The heating rate was 50 °C min^{-1}, in the range of 25–1,400 °C. The initial sample masses were about 7 mg. Alumina crucibles were used for the TG-DTA experiments.

DSC analysis

The DSC curves were recorded using a Mettler Toledo DSC 822[e]. The purge gas was nitrogen with a flow rate of 50 mL min^{-1}. The heating rate was 10 °C min^{-1}, in the range of 25–600 °C. The initial sample masses were about 5 mg. Aluminum crucibles, with perforated cover were used for the DSC experiments.

Chromatographic analysis

Basic organic compounds extraction

One milliliter of barium hydroxide (pH 10) and 1 mL of Ethyl acetate (HPLC grade) were added to 100 mg of "Merla" sample. The solution was stirred in a Vortex Shaker for 1 min and the sample was centrifuged to 1,500 rpm for 1 min. Two liquid phases and a solid precipitate were obtained. The solution was cooled to temperatures below −5 °C until the solidification of aqueous phase and removal of organic phase.

Ultra fast GC analysis

For organic phase analysis, a Gas chromatrograph GC 6890 Agilent, with a FID detector, Ultra fast GC LM-05 column with dimensions of 3.0 m × 0.05 mm × 0.25 μm and H_2 from 5.0 a 60 cm/s as purge gas, were used. The injector temperature was 280 °C in "split" mode, using 1:100 rate. The oven operated in the 170–260 °C temperature range with a heating rate of 20 °C min^{-1}, held for 0.5 min, with time total of 5 min.

HRGC-MS-EI cocaine identification

A gas chromatograph GC17A coupled to a Shimadzu mass spectrometer QP-5050, with an electronic impact (EI) and a LM-05 column with dimensions of 30.0 m × 0.25 mm × 0.35 μm and He with flow of 5.0 as purge gas, was used. The interface and the injector operated at temperature of 280 °C, with injection in split mode at 1:50 rate. The furnace was operated at isothermal of 270 °C for 22.0 min.

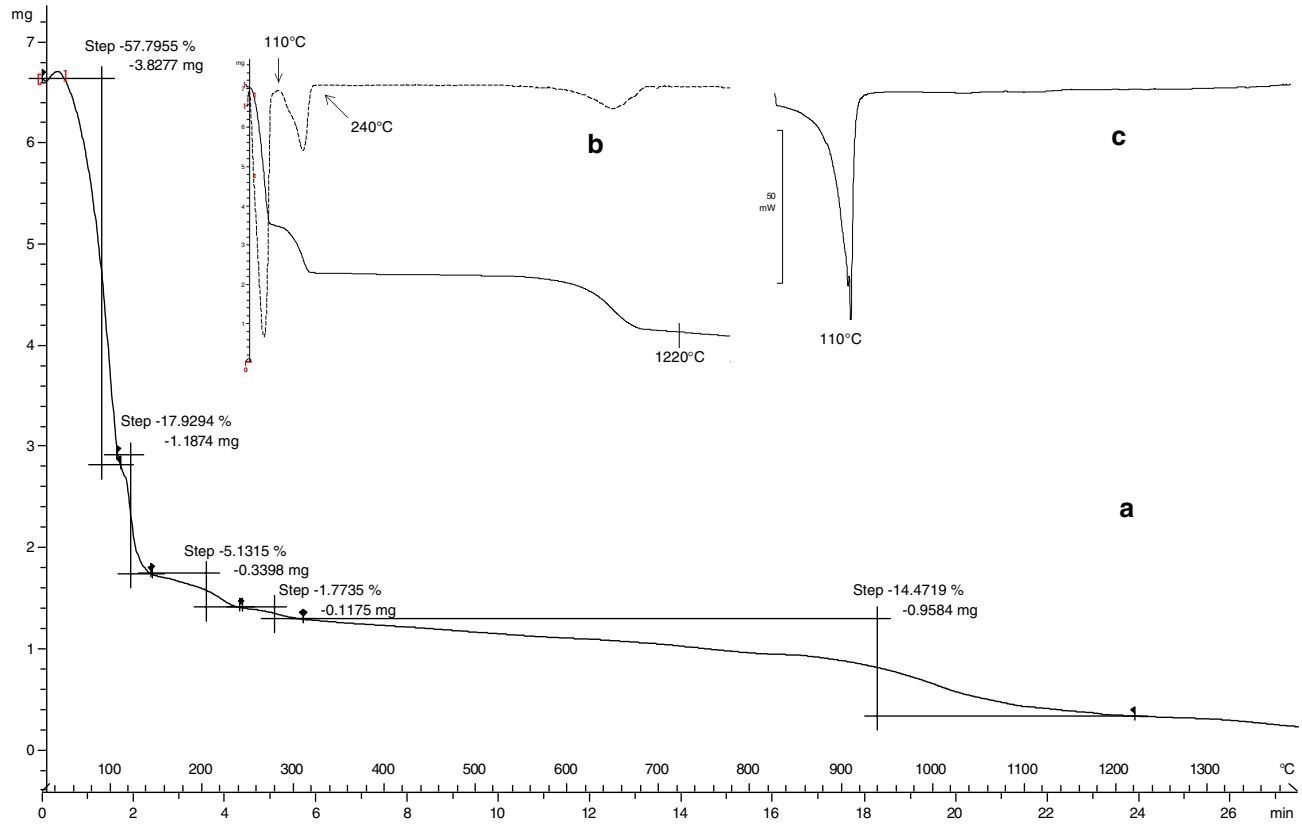

Fig. 1 TG and DSC curves of Merla sample AL-01. **a** TG curve obtained from Merla samples; **b** TG and DTG curves obtained from a mixture $NaHCO_3$ and H_2O 1:1; **c** DSC curves obtained from Merla samples

Results and discussion

The TG and DSC curves of the Merla sample AL-01 are shown in Fig. 1. The first mass loss at 110 °C was attributed to dehydration. The second mass loss at 145 °C is due to dehydration and volatilization of organic compounds that were identified by chromatographic analysis. For the third mass loss, a comparison between several TG curves obtained from TG analysis from a binary mixture between the $NaHCO_3$ and H_2O with Merla samples and inorganic salts used in Merla manufacture [2] (Na_2CO_3, $NaHCO_3$, $B(OH)_3$, NaOH, Na_2SO_4) with Merla samples were made. The TG curve from the mixture of $NaHCO_3$ and water (Fig. 1b) showed a great similarity in the third and fifth steps in TG curve obtained from Merla samples (Fig. 1a) and it was attributed to thermal decomposition of $NaHCO_3$ to Na_2CO_3 with formation of CO_2 and H_2O. The forth mass loss at 315 °C is probably due to the presence of adulterants and the fifth mass loss at 1,220 °C is attributed to the thermal decomposition of Na_2CO_3 to Na_2O and CO_2.

The mass loss results obtained from TG and the endothermic event integration with a peak at 110 °C (Fig. 1c) for Merla samples are shown in Table 2.

The Liquid–liquid extraction process was necessary for elimination of non volatile compounds in the chromatographic system. Inorganic salts presents in Merla were precipitated as barium salts, while basic character substances, as cocaine, were converted in free bases, insoluble in aqueous phase and soluble in non-polar organic solvents.

For the organic phase analysis, a developed method of Ultras Fast GC, using an extremely short chromatographic column for HRGC with a small diameter was used. This method showed an efficient separation with time of analysis inferior than traditional methods, as observed in Figs. 2 and 3. It was observed that the extraction process realized a clean up in the sample, eliminating the chromatographic peaks of minor elution time (inferior polarity), that weren't soluble in organic phase with ethyl acetate and should be retained in aqueous phase. The chromatographic peaks numbered in Figs. 2 and 3 were identified by mass spectrometry. Comparisons among the peaks and the equipment's spectrometric database were made, and the peaks were identified as: 2 (cocaine), 3 (*trans*-cinnamoylcocaine) and 4 (*cis*-cinnamoylcocaine). The Peak 1 was not detected by HRGC-MS analysis.

Table 2 Analytical results of TG, DSC and HRGC

Sample	Variable									
	% Mass loss (TG)								DSC	HRGC
	110 °C[a]	145 °C	240 °C	315 °C	380 °C	520 °C	810 °C	1,220 °C	Energy (mJ)	% Cocaine area
AL-01	57.8	17.9	5.1	1.8	–	–	–	14.5	−8,485.89	85.8
An-01	46.8	26.8	–	11.2	–	–	–	14.7	−7,026.72	40.1
CO-01	42.8	21.7	–	20.4	–	–	–	16.1	−6,189.12	34.2
CO-02	71.2	12.4	–	–	4.1	–	–	11.6	−7,730.06	0
CO-03	–	78.4	–	3.9	–	–	–	13.9	−7,047.44	0.04
Fo-01	63.5	21.3	–	5.4	–	–	7.0	3.6	−7,702.51	0
Fo-02	–	82.1	–	5.3	–	–	7.0	3.7	−7,470.15	0.02
Fo-03	–	86.2	–	2.7	–	–	–	8.1	−6,604.86	0.7
Fo-04	–	87.8	–	2.5	–	–	–	6.9	−9,018.67	0.3
Fo-05	–	88.8	–	2.2	–	–	–	7.0	−10,015.00	0.6
Fo-06	–	86.0	–	2.8	–	–	–	7.9	−9,977.88	4.5
Fo-07	–	81.2	–	4.2	–	–	–	11.2	−11,820.00	2.11
Fo-08	–	89.0	–	4.8	–	–	–	7.4	−10,140.00	0.05
Fo-09	45.4	36.4	–	7.3	–	–	11.6	26.0	−9,816.72	0.8
Go-01	45.9	30.2	–	8.5	–	–	–	11.1	−4,791.83	34.4
Go-02	–	–	–	–	–	79.0	–	20.5	−227.16	15.9
Go-03	46.6	18.6	–	14.1	–	–	4.7	9.9	−7,280.31	11.6
Lu-01	–	78.8	–	7.6	–	–	–	9.6	−7,658.28	0
Lu-02	–	83.3	–	2.6	–	–	–	9.6	−5,105.16	0.08
Lu-03	–	78.2	–	9.5	–	–	–	9.6	−7,126.12	0.4
Lu-04	67.5	15.4	5.3	2.4	–	–	–	8.3	−4,721.48	0.6
NG-01	–	–	83.5	2.9	–	–	–	10.5	−10,000.01	0.01
Pla-01	39.1	35.8	–	12.7	–	–	4.4	6.3	−6,731.64	3
Pla-02	21.2	39.4	–	18.0	–	–	–	18	−5,359.87	26.8
Pla-03	–	76.3	7.3	–	–	–	–	13.7	−7,854.64	21.2
Pla-04	–	76.2	7.4	–	–	–	–	12.8	−5,653.97	20.8
SA-01	–	75.2	–	4.2	–	–	–	15.3	−8,069.94	0
Va-01	43.9	23.3	–	12.5	–	–	–	14.9	−5,869.68	100
Va-02	–	72.4	–	9.7	–	–	–	12.7	−5,498.53	16.4
Va-03	39.0	27.8	–	16.7	–	–	–	16.8	−6,637.51	20.7

[a] Final temperature of mass loss

The cocaine was quantified by the chromatographic peak area normalization of each sample in comparison with the larger cocaine area obtained in the chromatograms.

The relative quantification of cocaine by normalization is shown in Table 2. It was observed a great variation of the percent of cocaine in Merla sample and wasn't detected cocaine presence in four samples. (Lu-01, CO-02, Fo-01 and SA-02). This samples did not presented in viscous of white color, but they liquefied generating a viscous fluid of light brownish color.

To realize the statistical treatment of the data (Table 2), were used the HCA, through the software "Statistica" version 5.1, for classification and group of samples.

With chemometric treatment realized by HCA, a dendogram shown in Fig. 4 was obtained. This dendogram shows the classification in two distinct groups (I and II) far away by 22 units of Euclidian distance, attributed to the differences in manipulation techniques and Merla preparation, resulting in distinct compositions.

The statistical treatment of data, allowed to observe in the dendogram, with a major confiability index, (Euclidian distance equals 22) the fact of existence of distinct laboratories in a same city, as for example the groups A and F,

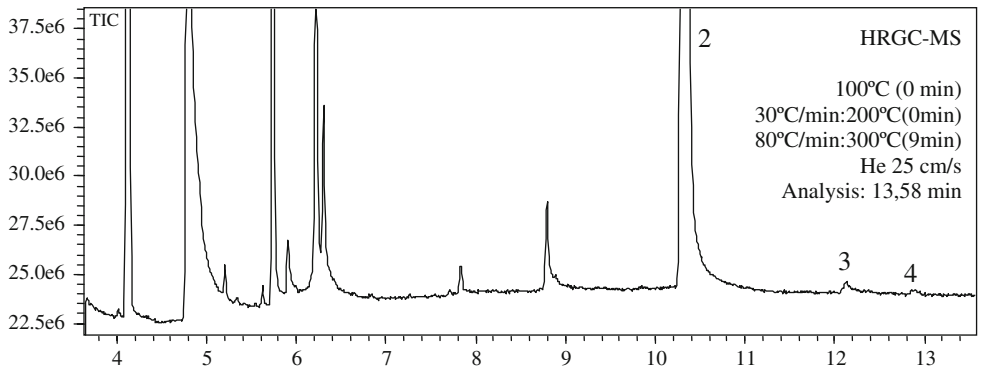

Fig. 2 Traditional method chromatogram for the sample AL-01

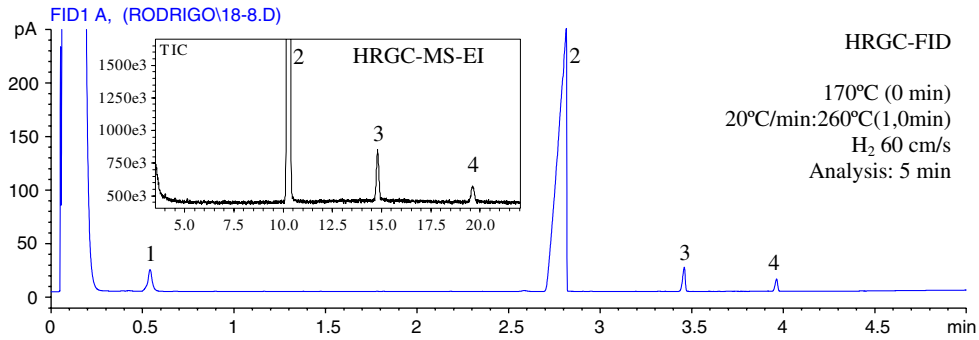

Fig. 3 Ultra Fast GC chromatogram for the sample AL-01

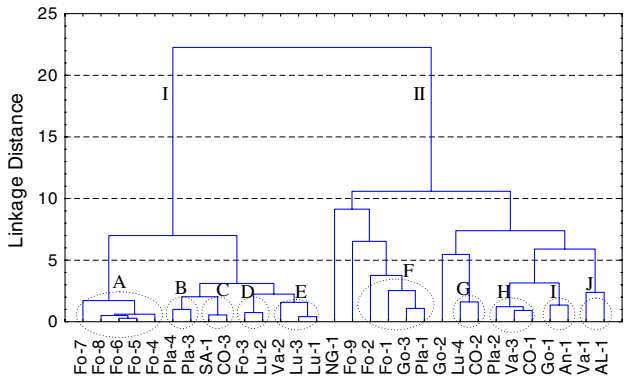

Fig. 4 Dendogram of classification and grouping of 30 Merla samples

with samples of same origin that were separated in groups I and II. It was confirmed that the samples of subgroup A, were manipulated in the same laboratory, because they have the same arrest origin and was grouped with a short Euclidian distance.

Conclusions

The TG and DSC analysis provided the analytical results related to the Merla composition. The developments of the Ultra Fast GC method, allowed shortening the analysis time from 13.58 to 5 min. The chromatographic analysis allowed the determination of the cocaine presence and its relative quantity in the samples. The chemometric treatment concluded that the samples from group I had different preparation origins from the samples of group II. The results suggest the occurrence of characteristics laboratories in a same city, as for example, the subgroups A and F, separated by a high Euclidian distance. The Ward's method allowed an evaluation and creation of a database bank of the analyzed samples that could establish the origin by the similarity grade, observing the fact that the samples with same arrest origin were grouped in the same subgroup, concluding that they were prepared in the same toxic-narcotic laboratory. This could lead directly the police force authorities in the investigation of the origin laboratories that distributes and prepare the drugs.

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