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Artigo

EVALUATION OF COCAINE SAMPLES SEIZED IN THE STREETS OF THE STATE OF RIO DE JANEIRO, BRAZIL

Luiza D. Sant'Ana[a,b,*], Valeria C. de Sousa[b], Frances R. dos Santos[b], Bruno D. Sabino[a,c], Amadeu Cardoso[c], Marco Edilson F. de Lima[b] and Rosane N. Castro[b]

[a]Departamento Geral de Polícia Técnico-Científica, Polícia Civil do Estado do Rio de Janeiro, 20231-014 Rio de Janeiro – RJ, Brasil

[b]Departamento de Química Orgânica, Instituto de Química, Universidade Federal Rural do Rio de Janeiro, 23890-000 Seropédica – RJ, Brasil

[c]Contraprova Análises, Ensino e Pesquisas Ltda, 24120-191 Niterói – RJ, Brasil

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Fifty-two samples of street cocaine seized in the state of Rio de Janeiro, from May 2016 to April 2017, were evaluated according to their purity, presence of inorganic and sugar diluents and concentration of pharmacologically active adulterants. Cocaine contents, as well as the adulterants caffeine, lidocaine and phenacetin, were evaluated by gas chromatography coupled with mass spectrometry. The samples were screened by Raman spectroscopy for the presence of inorganic diluents and carbohydrates. The main diluents were calcium carbonate and sodium bicarbonate, which were found in 93% and 71% of the cocaine hydrochloride samples, respectively. Caffeine was found in 91% of the cocaine hydrochloride samples, while phenacetin was found in all freebase cocaine samples. Freebase cocaine samples were majorly composed of pharmacological active compounds (adulterants), unlike cocaine hydrochloride samples, which were majorly composed of inorganic compounds (diluents). It could be observed, by Raman Spectroscopy associated to multivariate analysis, similarities on cocaine hydrochloride composition according to certain criminal gangs. The percentage of pharmacological active compounds varied significantly on the analyzed samples, showing that these adulterants are indiscriminately added to street cocaine, what may increase consumers' health risks.

Keywords: cocaine hydrochloride; freebase cocaine; cutting agents; chemical profiling; criminal gangs.

INTRODUCTION

Cocaine is one of the major alkaloid compounds found in leaves of plants from the Erythroxylum gender (family Erythroxylaceae), mostly from the varieties *Erythroxylum coca* var. coca and *Erythroxylum novogranatense* var. novogranatense and var. truxillense. Cocaine corresponds to 75% of the total alkaloids (0.5 to 1.5%) found in the leaves of these species. Cocaine is addictive and acts to inhibit the monoamine oxidase (MAO) enzyme, which is responsible for the degradation of monoamines, thereby affecting the reuptake of serotonin. It also stimulates the release of noradrenalin and dopamine, blocks sodium channels on peripheral nerves and is a potent anesthetic. Cocaine consumption also increases the strength and speed of cardiovascular contraction and provokes symptoms of euphoria and excitement.[1] These properties make it one of the most commercialized drugs on the illicit market worldwide.

Cocaine extraction is performed by acid-base extraction through immersion of coca leaves in acidic or alkaline solutions or by maceration with organic solvents. The refining process consists of oxidation, precipitation and successive dilutions for bleaching and purity increase.[2] During these steps, many adulterants and diluents can be added in order to increase product volume and consequently the profit. Furthermore, street cocaine is frequently adulterated by local merchants, so that the materials seized on streets are generally less pure than the materials seized in the international airports.[3]

Cocaine is more commonly consumed in two different forms: freebase cocaine (crack) and cocaine hydrochloride (cocaine HCl), though it can also be found in other forms, such as coca paste and merla. Crack is freebase cocaine, frequently found as little rocks, formed by the heating of cocaine hydrochloride with sodium bicarbonate in water. Street cocaine powder (cocaine hydrochloride) is water soluble, being usually snorted or injected. Otherwise, crack (cocaine freebase) is usually smoked once it vaporizes at around 98 °C. Cocaine hydrochloride has a higher melting point (near 195 °C) and it does not efficiently vaporizes as freebase cocaine does.[4,5]

Since 2006, Brazilian Federal Police, with aid from the United Nations Organization (UNO), implemented the PeQui Project, which aims to analyze the chemical profile of drugs seized in Brazil, seeking origin characteristics and correlations among the seized samples. Many works have been published as a result of the PeQui Project, which could help to elucidate the characteristics of drugs seized in many states and identify the trends on the illicit market in Brazil.[6-8]

Many of the studies published in the last years were concerning cocaine purity and the presence of pharmacological active adulterants. Bernardo *et al.*[9] analyzed 186 samples of street cocaine apprehended in Minas Gerais by GC-FID, finding cocaine in concentrations between 4.3 and 87.1%, caffeine ranging from 2.8 to 63.3%, lidocaine ranging from 0.5 to 92% and prilocaine ranging from 1.4 to 20.7%. The presence of lidocaine was verified in 68 of the 105 samples that were positive for caffeine. Diluents were identified by qualitative tests, in which carbonates and bicarbonates were identified in 41.2% of the samples, starch in 51.2% and glucose, sucrose, lactose and fructose were found in 11.5%, 14.8%, 6.2% and 3.3%, respectively. Maldaner *et al.*[6] analyzed 642 samples of cocaine seized in the states of Bahia, Acre, Distrito Federal, Goiás and São Paulo, observing that 58% of the cocaine hydrochloride was adulterated by addition of the CNS stimulant caffeine, while 54% of the freebase cocaine samples were adulterated by addition of different amounts of the analgesic phenacetin.

Cocaine commercialized in Brazil is usually originated from

*e-mail: luizadoliveira@gmail.com

Bolivia, Peru or Colombia. In turn, cocaine also leaves Brazil for international trafficking, mainly to Africa, Europe and Asia.[10] The degree of adulteration may vary according to geographical origin or availability of clandestine labs. Magalhães *et al.*[11] observed higher purity in cocaine seized in Amazonas State (15.4 to 97.8%) compared to cocaine seized in Minas Gerais state (6.4 to 75.3%). These findings could be related to the proximity of the Amazonas State with Colombia, one of the main cocaine producers.

The presence of cocaine adulterants may vary according to place and time. Lidocaine and sugars were the two main cutting agents used in the 1980s, while in the beginning of the 1990s lidocaine was not detected in cocaine commercialized in Spain anymore. By the end of the 1990s, lidocaine, caffeine and phenacetin were the main adulterants in cocaine commercialized in Italy. Diltiazem, hydroxyzine and levamisole were first reported from 2004 to 2006 in the United States and Europe. Nowadays, the main adulterants found in Europe are phenacetin, levamisole, caffeine, diltiazem, hydroxyzine and lidocaine, similar to what is found in Brazil. These spatiotemporal differences might be related to availability and price of the adulterants in certain areas.[12]

Souza *et al.*[13] analyzed 512 cocaine samples seized in Espírito Santo from the year 2008 to 2012. The presence of phenacetin was observed only in the samples seized in 2012, showing that this is a more recently used cutting agent. A higher degree of adulteration was observed in samples seized in the metropolitan region, suggesting a traffic route directed from the countryside to the capital.

The Scientific Working Group for the Analysis of Seized Drugs (SWGDRUG) establishes minimum recommendations for the forensic identification of seized drugs based on the techniques, efficiency and reliability. Raman spectroscopy and mass spectrometry are classified as category A (most reliable), while spot tests are classified as category C (least reliable).[14]

In this work, gas chromatography coupled with mass spectrometry was used for identification and quantification of pharmacological constituents, while Raman spectroscopy was used for identification of inorganic and sugar constituents. Screening the constituents on street cocaine is important for public health, as many of the substances added to cocaine can be harmful to users according to its dose and may interact both with cocaine and other drugs as well. Lidocaine, for instance, significantly potentiates cocaine-induced toxicity, increasing the convulsant potency of cocaine when consumed simultaneously.[15] Caffeine also has synergic effects with cocaine, increasing the intensity and duration of cocaine symptoms, toxicity, convulsion rates and aggravation of cardiovascular problems.[16-18]

This study aims to evaluate the purity, the content of pharmacological active adulterants and the presence of inorganic and sugar diluents of fifty-two samples of cocaine in their two most consumed forms (cocaine hydrochloride and freebase cocaine), seized in three different regions of Rio de Janeiro State (City of Rio de Janeiro, Baixada Fluminense and Costa Verde) and classified according to the labels of the three main criminal gangs found on the state.

EXPERIMENTAL

Reagents and samples

This work analyzed fifty-two samples of cocaine (forty-four of cocaine powder and eight of freebase cocaine) seized by PCERJ (Polícia Civil do Estado do Rio de Janeiro) in the State of Rio de Janeiro, Brazil, from May 2016 to April 2017. Thirty-three samples were seized in the city of Rio de Janeiro, five samples were seized in Baixada Fluminense, eleven samples were seized in Costa Verde and three samples were seized from unknown areas. The samples were also classified according to the criminal organizations indicated on their label, which in this work were referred as "A", "B" and "C". The samples were kept in the dark and stored at room temperature until analysis. Methanol (HPLC grade) used and the analytical reagents sodium carbonate, aluminum sulphate, sodium bicarbonate calcium carbonate, starch, sucrose, D-glucose, lactose and mannitol were acquired from VETEC (Rio de Janeiro, Brazil). Cocaine standard was obtained by successive purification steps and had its purity of 98% confirmed by GC and HPLC. All standards were of analytical grade: caffeine, lidocaine and phenacetin standards were acquired from Sigma-Aldrich Chemie (St. Louis, MO, USA).

Presumptive tests

The spot tests (Scott test, Wagner test and silver nitrate test), as well as the esterification tests, were performed on each sample in order to verify the presence of cocaine. The tests were also performed for each standard to indicate possible false-positive results. The samples and the standards were analyzed according to the method described by the United Nations Office on Drugs and Crimes Manual,[19,20] with minor modifications.

For the Scott test, a small amount of each sample or standard (less than one milligram) was added to a Petri dish, followed by the addition of two drops of an aqueous solution of 10% cobalt chloride and two drops of an aqueous solution of 10% ammonium thiocyanate. The formation of a blue precipitate indicates the presence of cocaine (either salt or freebase). For the Wagner test, the same mass of the sample or standard was added to a Petri dish, followed by the addition of two drops of an aqueous solution of 10% iodine. A brown precipitate indicates the presence of salt cocaine. Precipitation with silver nitrate was performed by adding the same mass of the sample or standard to a Petri dish followed by two drops of a 10% silver nitrate aqueous solution. The formation of a white or yellow precipitate indicates the presence of salt cocaine.

Esterification test was performed in water bath, using a porcelain crucible for reacting a small quantity of the sample with five drops of concentrated sulfuric acid and the same volume of ethanol. The characteristic odor of ethyl benzoate, observed after around ten minutes of heat, is indicative of the presence of cocaine.

Gas chromatography

The identification and quantification of adulterants present in each sample was carried out by the method proposed by Lapachinske *et al.*,[3] with minor modifications. An aliquot of 5 mg of each sample was dissolved in methanol, followed by ultrasonic bath for 10 minutes and centrifugation for 3 minutes at 3000 rpm. An aliquot of the upper layer was collected and injected in a gas chromatographer coupled with mass spectrometry.

Each standard was diluted in methanol to concentrations ranging from 50 to 600 μg mL^{-1} and injected in GC-MS, obtaining standard curves with equations $y = 222.38x - 3239.5$ ($R^2 = 0.9987$) for cocaine, $y = 136.87x + 1695.6$ ($R^2 = 0.9993$) for caffeine, $y = 324.33x - 658.22$ ($R^2 = 0.9964$) for lidocaine and $y = 280.07x - 6170.4$ ($R^2 = 0.9998$) for phenacetin.

Gas chromatographer coupled with a mass selective detector model QP2010 Plus (Shimadzu, Japan) was operated in the electron impact mode (70 eV) and full scan acquisition in the range of 40–500 *m/z*. Chromatographic separation was achieved on a VF-5ms fused-silica capillary column (30 m x 0.25 mm x 0.25 μm, Varian). The carrier gas was helium and was used at a flow rate of 1.0 mL min^{-1}. The oven temperature program was as follows: 148 °C for 1

min, followed by heating to 200 ºC at a rate 10 °C min^{-1}, heated at a rate of 20 °C min^{-1} to 270° and finally, held for 15 min at isothermal conditions. The injector and interface temperatures were set at 240 °C. Identification of substances was done by comparing experimental spectra with the spectra from NIST08 Mass Spec Library (library match > 80%), as well as by comparing the compounds with mass spectra and retention times of standards (RT ± 2%).

Raman spectroscopy

Each sample and the analytical reagents sodium carbonate, aluminum sulphate, sodium bicarbonate calcium carbonate, starch, sucrose, D-glucose, lactose and mannitol were individually inserted in a vial and directly analyzed by Raman spectroscopy. The analysis was performed using a FT Raman Bruker MultiRAM with laser source in 1064 nm (near infrared), germanium detector cooled with liquid nitrogen, potency adjusted to 150 mW, spectral range from 200 to 4000 cm^{-1}, resolution of 4 cm^{-1}, performing 32 scans for cocaine samples and 16 scans for the standards. The samples were processed in ACD Labs software (Toronto, Canada) in order to compare them with the spectra obtained for each standard and to identify possible diluents.

Statistical analysis

Due to its several processing steps, botanical characteristics and adulteration possibilities, cocaine composition can vary considerably according to its origin or manufacturer. Multivariate analysis plays an important role in characterizing the cocaine profile and establishes possible similarities among cocaine samples. Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) were performed with the statistical software The Unscrambler X 10.3 (Oslo, Norway), while the correlation matrix was conducted using BioEstat 5.0 (Amazonia, Brazil).

RESULTS AND DISCUSSION

Presumptive tests

All the samples analyzed in this work showed positive results on all presumptive tests. As expected, both cocaine powder and freebase cocaine showed positive results on Scott test, while only cocaine powder showed positive results on silver nitrate test, as shown in Figure 1. That is due to the chlorine atom present on cocaine hydrochloride, which combines to the silver ion to form silver chloride precipitate. Wagner test showed a deeper brown color for cocaine powder samples.

Caffeine and phenacetin showed negative results in all spot tests. Lidocaine showed negative results on Wagner test, silver nitrate test and esterification test, however, it showed a positive result on the Scott test. Sodium carbonate showed a deep violet color and sodium bicarbonate showed a light violet color on Scott test and false-positive results on silver nitrate test. Carbonates can react with silver compounds, leading to silver carbonate, a yellowish salt [$2Ag^+ + HCO_3^- + H_2O \rightarrow Ag_2CO_3 + H_3O^+$]. Sodium carbonate did not show as deep a yellow color as sodium bicarbonate did due to its low solubility in water. Starch showed a deep blue color in Wagner test due to interactions of the amylase helix with iodine ions (Figure 2).

The false positive result of lidocaine on the Scott test might be related to its structural similarities to cocaine. Both compounds have a tertiary amine that may interact with the cobalt ion from thiocyanate complex.[2,21] This complex was prepared and its X-ray structure was recently described by Tabrizi and co-authors.[21] The formation of a colored complex with Co(II) is not observed for caffeine or phenacetin.

Besides lidocaine, some other drugs or medicines can show false-positive results on the Scott test, such as promethazine (antihistamine), diltiazem (which is used to treat high blood pressure) and 5-methoxy-*N,N*-diisopropyltryptamine HCl (an hallucinogenic drug commonly

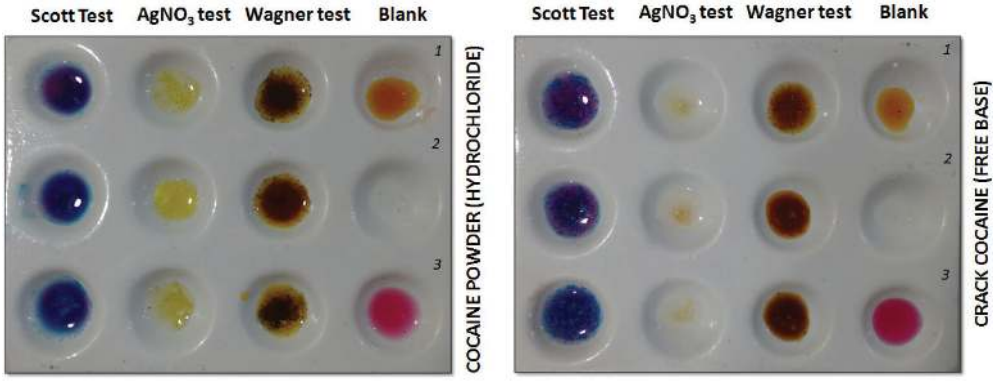

Figure 1. *Spot tests (Scott test, silver nitrate test and Wagner test) for three cocaine HCl samples and for three freebase cocaine samples. Blank: 1 for Wagner test, 2 for silver nitrate test and 3 for Scott test*

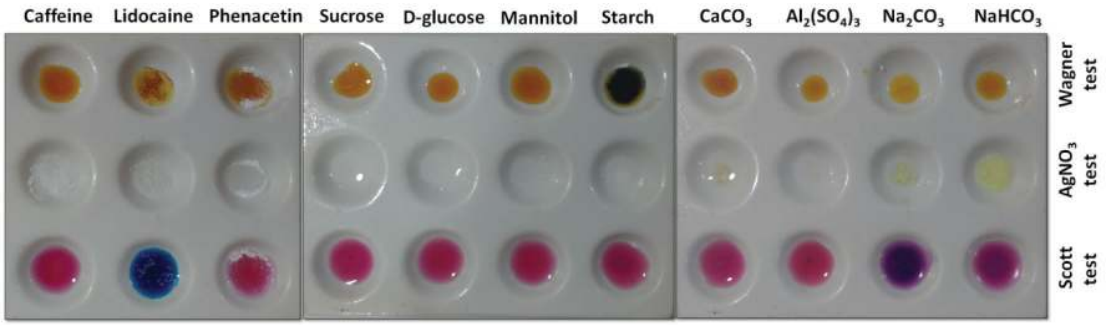

Figure 2. *Spot tests (Scott test, silver nitrate test and Wagner test) for the standards*

known as "foxy").[22,23] Also, the exceeding amount of sample used on the Scott test may lead to false-positive results. It was described by Tsumura and co-authors[22] that an amount of 2 mg of dibucaine HCl or heroin HCl and 4 mg of ketamine HCl produces a blue color similar to cocaine on the Scott test. Therefore, the maximum sample weight should be up to 1 mg for a more precise result.

All samples showed positive results for the esterification test. This is an important test to distinguish possible false-positive results, as common adulterants such as caffeine, lidocaine and phenacetin do not hydrolyze to ethyl benzoate.

Though some presumptive tests can show false-positive results, they were able to detect the presence of cocaine in all the analyzed samples on this work (minimum cocaine content of 1.90%).

Gas Chromatography

Retention times obtained by the conditions used in this work, as well as the main peaks observed for each adulterant, are listed in Table 1.

Table 1. Retention times (RT) and main peaks observed for the standards

Compounds	RT (min)	Base, P1, P2, ions M^+ (*m/z*)
Cocaine	12.5	82, 182, 94, 303 M^+
Caffeine	9.5	109, 55, 67, 194 M^+
Lidocaine	9.7	86, 58, 234 M^+
Phenacetin	8.1	108, 109, 179 M^+

While freebase cocaine samples showed an average of 66% (± 19%) of pharmacological active compounds, cocaine powder samples showed only 24% (± 9%), showing that it is majorly composed of non-active compounds. Freebase cocaine samples showed superior purity, with an average cocaine content of 27.6% (± 7.8%) compared to the average content of 7.9% (± 3.3%) observed for cocaine hydrochloride samples. Most of the freebase cocaine samples showed purity above 20%, while most cocaine hydrochloride samples showed purity between 5 and 10%, as shown on the histograms below (Figure 3). The average contents of cocaine and each pharmacological constituent, as well as their range, is described in Table 2.

The percentage of the pharmacological compounds observed for each sample is shown in Figure 4. The most frequent adulterant found in cocaine hydrochloride was caffeine, which was present in 91% of the samples (n = 40), corresponding to around 61% of the pharmacological constituents. Phenacetin was found in all freebase cocaine samples, corresponding to around 48% of the pharmacological constituents. Phenacetin is a Non-Steroidal Anti-Inflammatory Drug (NSAID) with prohibited commercial use in many countries, such as USA, Czech Republic, Denmark, Germany, Belgium and Australia, due its carcinogenic and kidney-damaging properties.[24-26] In Brazil, phenacetin has its commercial use controlled by Federal Police[27] and its presence in drugs is heading out of use due to its side effects.

Maldaner *et al.*[6] analyzed cocaine hydrochloride and freebase cocaine in five Brazilian states (Acre, Bahia, Distrito Federal, Goiás and São Paulo), finding caffeine in most of the powdered samples (58%) and phenacetin in most of the freebase cocaine samples (54%). Lapachinske *et al.*[3] analyzed 54 cocaine samples seized by Brazilian Federal Police in São Paulo International Airport in the year 2011, showing a percentage of 29.6% of uncut samples and a purity ranging from 16.5% to 91.4%, which was much superior to that observed in this work (1.9 to 17%). All samples analyzed by Lapachinske *et al.* were related to international traffic and were seized on the moment before they would leave country. That may explain their higher purity compared to the samples analyzed in this work, as street cocaine is often successively adulterated and diluted in order to increase profits.

Researches indicate a high pharmacological interaction between cocaine and caffeine. When these compounds are associated, cocaine

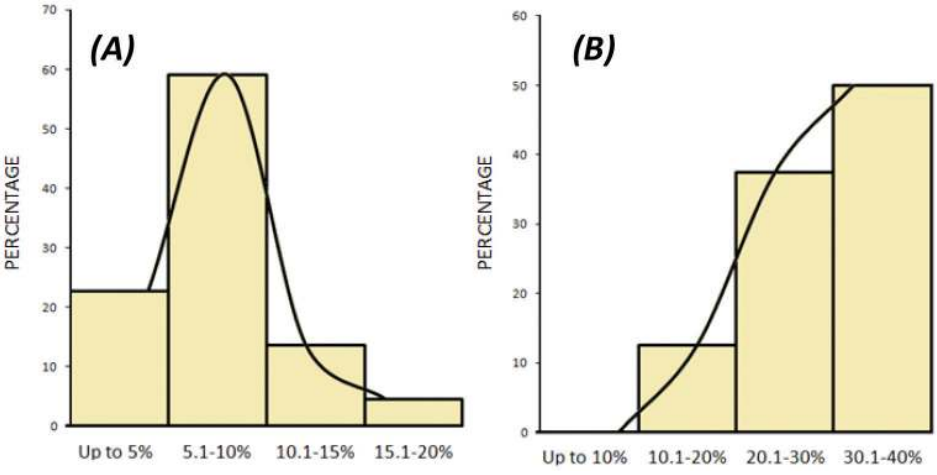

Figure 3. *Histograms showing cocaine hydrochloride (A) and freebase cocaine (B) purity range*

Table 2. Average content, standard deviation (S.D.) and percentage range of cocaine and each adulterant on cocaine HCl and freebase cocaine

	Average contents ± S.D.		Range (min and max values)		Pharmacological property
	Cocaine HCl	Freebase cocaine	Cocaine HCl	Freebase cocaine	
Cocaine	7.86 ± 3.32	27.60 ± 7.83	1.90 – 17.04	13.09 – 36.31	Psychoactive stimulant
Caffeine	14.73 ± 7.83	6.52 ± 9.74	0.00 – 29.13	0.00 – 25.26	Psychoactive stimulant
Lidocaine	1.13 ± 3.14	-------	0.00 – 17.57	-------	Local anesthetic
Phenacetin	0.22 ± 1.01	31.93 ± 18.15	0.00 – 5.45	9.95 – 57.51	Analgesic

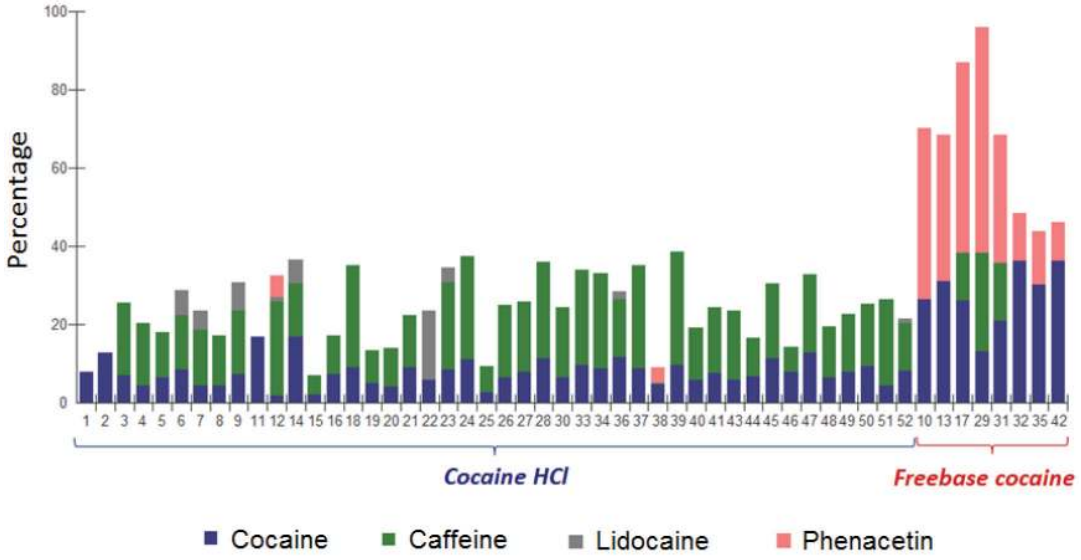

Figure 4. *Cocaine and adulterant contents for each sample*

effects increase in intensity and duration.[16] That may explain the presence of caffeine in most of the analyzed samples. Studies in rats showed that the combination of cocaine with caffeine also promotes an increase in toxicity, seizures and death rate.[17]

It could be observed by PCA (Figure 5) scores graph a grouping of the freebase cocaine samples from criminal gang B (samples C32, C35 and C42). These samples did not show caffeine in composition, showed less phenacetin content (11.9% ± 1.9) and higher cocaine purity (34.3% ± 3,5) compared to other freebase cocaine samples, which showed an average phenacetin content of 43.9% (± 9.7) and an average purity of 23.6% (± 6.9). The loadings graph showed that cocaine and phenacetin contents were the most important variables for the grouping of freebase cocaine samples, while caffeine and lidocaine contents were responsible the grouping of cocaine hydrochloride samples.

Raman spectroscopy

Peak positions of the main Raman bands of the standards, found in this work, and their tentative vibrational assignments, based on literature data, are listed in Table 3. The most common diluents found in cocaine hydrochloride were calcium carbonate, present in 93% of the samples, and sodium bicarbonate, present in 70.5% of the samples. Aluminum sulphate, sodium carbonate, starch, lactose and mannitol were present in 4.5 to 6.8% of cocaine hydrochloride samples. It was only detected the presence of sodium bicarbonate in one of the eight freebase cocaine samples and it was not observed the presence of the other diluents in any other sample. Sucrose and D-glucose were not present in any cocaine hydrochloride or freebase cocaine sample.

Calcium carbonate and sodium bicarbonate were mainly found associated in cocaine hydrochloride, corresponding to 71.4% of the samples that showed at least one of these cutting agents. Samples showing calcium carbonate and sodium bicarbonate in a non-associated form corresponded to 26.2 and 2.4%, respectively, as shown in Figure 6.

Calcium carbonate and sodium bicarbonate are easily found in Brazilian local markets and are usually added to cocaine after it comes to Brazil, by local drug dealers. Calcium carbonate is a white, insoluble salt, used as a calcium supplement against osteoporosis, as a soil acidity regulator and in the manufacturing of mortar and cement. It is also commonly found in markets as chalk. Sodium bicarbonate is a white and soluble salt, easily found in drugstores due to its antacid property.

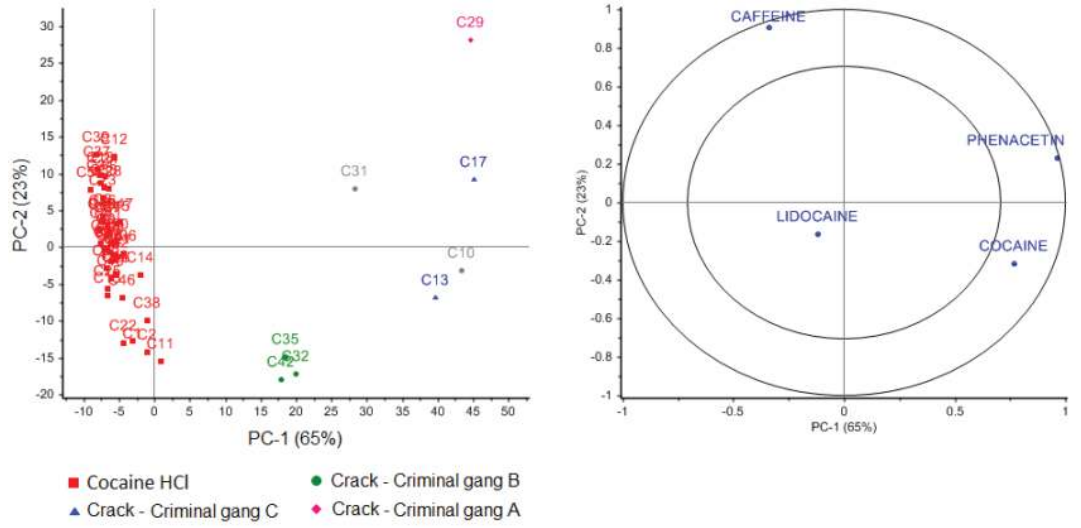

Figure 5. *At left, scores graph showing cocaine powder samples grouping (GC-MS results). At right, loadings graph showing the influence of each variable*

Table 3. Peak positions of the main Raman bands of the standards and their tentative vibrational assignments

Diluents	Wavelength (cm^{-1})	Assignments[28-34]
Starch	854.7	C-C stretching
	941.5	C-C stretching (carbohydrates)
	1126.7	C-C stretching (carbohydrates or proteins)
	1261.6	In-plane deformation =C-H (carbohydrates)
	1342.6	CH_2 / CH_3 angular deformation (carbohydrates)
	1383.1	CH_3 angular deformation (carbohydrates)
	1458.4	CH_2 angular deformation (carbohydrates or proteins)
	2852.6 to 2989.6	C-H symmetric and asymmetric stretchings
Sodium bicarbonate	1045.7	C-O stretching
	1267.4	O-C-O symmetric stretching
Sucrose	200 to 700	C-C-C, C-C-O e O-C-O e C-O-C deformations
	850.9	C-C stretching
	922.2	C-OH deformations
	1126.6	C-C stretching (carbohydrates or proteins)
	1238.5	C-O stretching
	1348.4	CH_2 / CH_3 angular deformation (carbohydrates)
	1462.2	CH_2 angular deformation (carbohydrates or proteins)
	2897 to 2995.3	C-H symmetric and asymmetric stretchings
Calcium carbonate	773.7	CO_3 angular deformation
	1086.2	CO_3 stretching
Sodium carbonate	1070.7	C-O stretching
	1080.4	C-O stretching
Glucose	542.3	C–C–O deformation
	843.2 and 914.5	C-C stretching and C-H angular deformation
	1074.6	C-H stretching
	1150	C-O-C stretching
	1346.5	C-C-H stretching
	1460.3	CH_2 vibration
	2877.7 to 2945.2	C-H symmetric and asymmetric stretchings
Aluminum sulphate	993.6	SO_4 vibrations
Lactose	200 to 600	C–C–C, C–C–O, C– C, and C–O deformations
	350	C-O-C vibrations
	1000 to 1100 and 1300 to 1400	C-O stretching, C-OH deformations and C-O-C stretching
	1469.9	CH_2 deformation
	2887.4 to 2978.0	C-H symmetric and asymmetric stretchings
Mannitol	875.9	C-O-C stretching
	1037.9	C-C-O stretching
	2902 to 2985	C-H symmetric and asymmetric stretchings

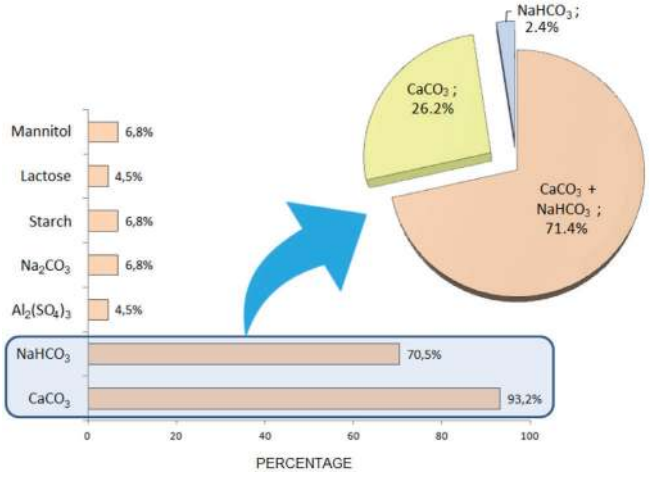

Figure 6. *Frequency of each diluent in cocaine hydrochloride samples*

For multivariate analysis, Raman peaks were classified by intensity and peaks below 10% of height were discarded. Peaks between 10 and 30% height were classified as intensity 1, peaks between 30 and 60% height were classified as intensity 2, peaks between 60 and 90% height were classified as intensity 3 and peaks between 90 and 100% were classified as intensity 4.

As expected, it could be observed by PCA a clear discrimination of the cocaine hydrochloride samples and the freebase cocaine samples (Figure 7), indicating considerable differences on the profiles of cocaine HCl and freebase cocaine.

It could also be observed by PCA and HCA, a grouping tendency according to the criminal gangs A and B, either for cocaine hydrochloride and freebase cocaine (Figure 8). No grouping tendencies were observed according to geographical origin (samples seized in the city of Rio de Janeiro, Baixada Fluminense and Costa Verde), which may be related to the proximity of this areas. The three areas share borders and the samples were seized at approximately

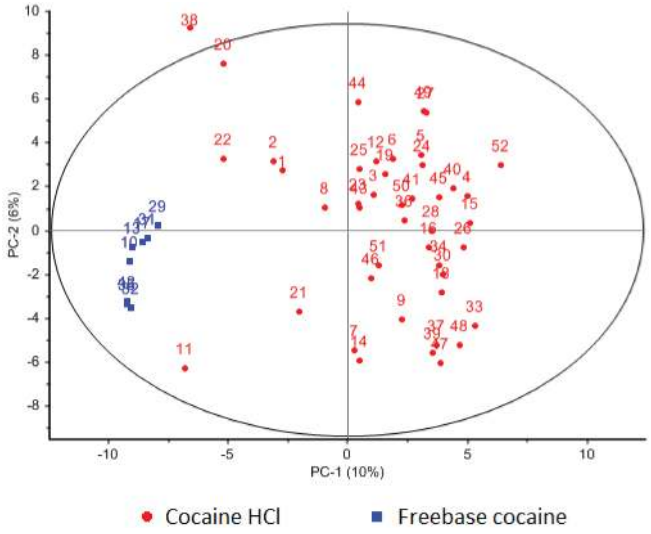

Figure 7. *Scores graph using intensity results obtained by Raman*

2948 km^2 of maximum distance.[35] It was not possible to verify grouping tendency for samples from the criminal gang C, possibly due to the low number of samples analyzed from this criminal gang.

Besides the fact that drugs from different criminal gangs can come from different providers, the isolation of areas dominated by different criminal gangs can result in particular practices in drug processing and adulteration.

CONCLUSIONS

Spot tests are useful for detecting the presence of cocaine in seized samples, even at low concentrations of cocaine (from 1.90%). Though lidocaine showed false-positive results on the Scott test, the association with other spot tests (silver nitrate and Wagner tests), especially with esterification test, allowed for unambiguous identification of the presence of cocaine in the analyzed samples. Freebase cocaine showed considerably higher purity compared to cocaine hydrochloride, as well as different adulteration profile. Caffeine was the most frequent adulterant in cocaine hydrochloride samples, while phenacetin was found in all freebase cocaine samples. As many cutting agents found in street cocaine have pharmacological properties, their usage may increase consumers' health risks once they are indiscriminately added to cocaine.

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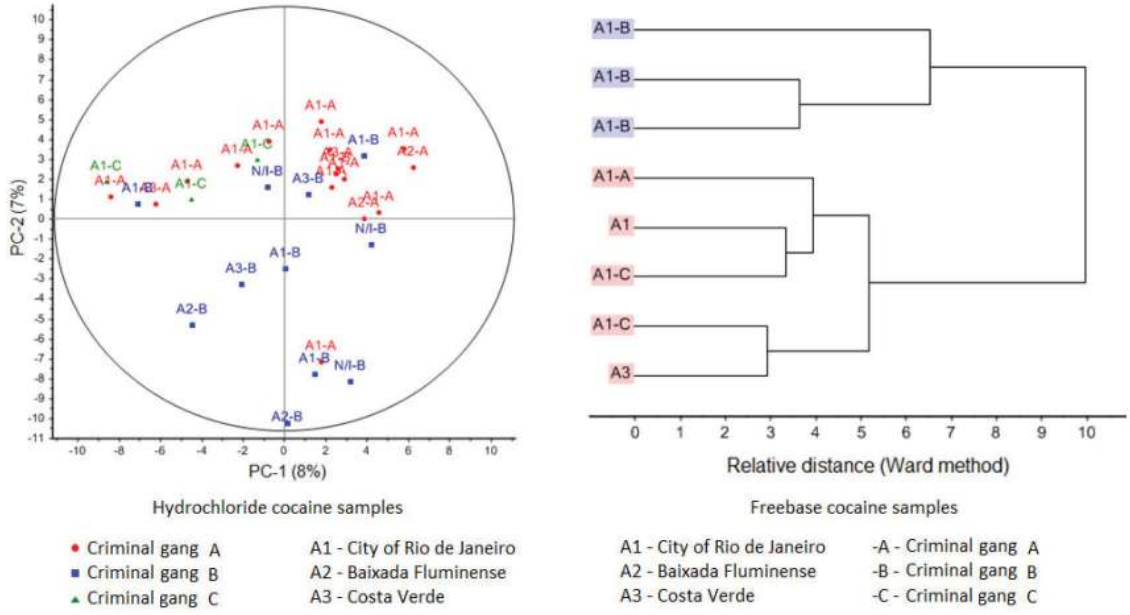

Figure 8. *At left, PCA scores graph showing cocaine HCl samples. At right, HCA showing the grouping of freebase cocaine samples from criminal gang B*

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