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Article

Chemical Profiling of Cocaine Seized by Brazilian Federal Police in 2009-2012: Major Components

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Perfis químicos de cocaína podem fornecer informações relevantes para autoridades da área de segurança pública. Desde 2006, a Polícia Federal tem trabalhado em seu próprio perfil químico de impurezas da cocaína (projeto PeQui). No esforço de estabelecer rotinas de perfil químico, este trabalho descreve os resultados obtidos para identificação de componentes majoritários (pureza da cocaína, grau de oxidação e fármacos utilizados como adulterantes), através da análise por cromatografia gasosa com detector de ionização de chama (GC-FID) de 210 amostras apreendidas em diferentes estados brasileiros entre 2009 e 2012. A pureza média observada para cocaína foi de 71% (expressa como base) e o grau de oxidação, determinado pela medida relativa entre *cis*/*trans*-cinamoilcocaína e cocaína, mostrou-se dependente do local de apreensão. A maioria das amostras não oxidadas foram apreendidas nos estados que fazem fronteira com os países produtores. A forma de base livre é a mais comumente encontrada (59%) e mais de 50% das amostras analisadas não apresentaram nenhum adulterante majoritário. Dentre os fármacos adulterantes identificados, fenacetina foi o mais abundante (30% das amostras). Levamisol, cafeína e lidocaína também foram identificados. O projeto PeQui tem sido utilizado regularmente para prover informações técnicas cientificamente embasadas para a análise de inteligência em segurança pública e de dados estatísticos que podem contribuir para um melhor entendimento do tráfico de cocaína.

Cocaine chemical profiling can provide relevant information for law enforcement authorities. Since 2006, Brazilian Federal Police has been working on its own cocaine impurity profiling program (PeQui project). In the effort to establish chemical profiling routines, this work describes major component results (cocaine purity, degree of oxidation and pharmaceutical products used as cutting agents), identified by gas chromatography with flame ionization detection (GC-FID) analysis of 210 samples seized in several Brazilian states between 2009 and 2012. The mean purity of cocaine was 71% (expressed as base) and the degree of oxidation, determined by the relative content between *cis*/*trans*-cinnamoylcocaine and cocaine, depends on the location where the seizures were performed. Most of the not oxidized samples were seized on traditional cocaine producer country border states. Cocaine is mainly present in free base form (59%) and more than 50% of the analyzed samples did not have any major adulterant. Among the identified cutting agents, phenacetin was the most abundant (30% of the total samples). Levamisole, caffeine and lidocaine were also identified. The PeQui project has been used on regular basis to provide technical and scientifically based information to law enforcement intelligence analysis and statistical data that might contribute to the better understanding of the cocaine trafficking.

Keywords: cocaine, chemical profiling, purity, refining, cutting agents, PeQui

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Introduction

Several scientific and law enforcement institutions around the world have been implementing their own profiling programs, always trying to establish drug chemical characterization studies and routines to provide useful data for law enforcement authorities involved with illicit drugs issues.[1-5] Brazil is a major player in the illicit drugs market, considering the population size (200 million inhabitants) and the consumption of cocaine and cannabis. The UNODC 2012 World Drug Report (WDR)[6] states that there is an increase in cocaine use in Brazil that pushed the federal government to launch a national program in 2010 focused in crack, cocaine and other drugs, aiming to promote public policies to reduce drugs supply and demand, as well as investing in education and health care.[7] The WDR also found an increased tendency in federal seizures, focused in international or interstate apprehensions, that have more than tripled since 2004, reaching 27 tons in 2010, and how it could also reflect the role of Brazil as a country of departure for cocaine smuggled across the Atlantic Ocean.

It is also important to point that Brazil, as one of the world's ten largest chemical manufacturers, has a regionally relevant chemical industry and is the only country that borders all the main coca leaf producing countries.[8] Therefore, chemicals control represents a particular challenge to Brazilian authorities, demanding reliable and scientific based information about the current trends on drugs manufacturing. It's also crucial to be aware of the methodologies that have been used by cocaine producers or dealers to extract, refine, dilute and adulterate (e.g., adding pharmaceutical products, as phenacetin, caffeine and lidocaine) the illicit drug that passes through the Brazilian territory or has been consumed by local users.[9]

Since 2006, the Brazilian Federal Police (BFP) has been developing and implementing its own illicit drug chemical profiling program. The PeQui project ("Perfil Químico de Drogas" in Portuguese) was designed to provide police intelligence information and forensic chemistry results, regarding both drug origin and seizure correlations throughout detailed chemical analysis. As BFP mainly deals with federal and interstate crimes and drug trafficking, it is also relevant to aggregate to PeQui project scientific based information about street drugs seizures, usually performed by local law enforcement institutions. Some initiatives have already been undertaken,[10] but further studies still depend on sponsorship.

The BFP already has a network of 30 forensic chemistry labs, which includes all 27 Brazilian states and the National Institute of Criminalistics (NIC, in Brasília, Federal District). The NIC has the technical coordination attribution to develop and implement the PeQui project routines according to the different realities around the country (i.e., demand for drug analysis, availability of instrumentation, training and staff). As the majority of BFP state labs have at least one gas chromatograph coupled with both flame ionization detection (FID) and mass spectrometer (MS) detectors, the main developments were performed to be used by the GC-FID mode.

In the present study, the major components cocaine and *cis* and *trans*-cinnamoylcocaine were quantified by GC-FID, while the more common pharmaceutical cutting agents (adulterants) were qualitatively identified by retention times (benzocaine, phenacetin, caffeine, lidocaine, levamisole, hydroxyzine, procaine, diltiazem), considering previous works already published in Brazil[11,12] and elsewhere.[13-21] Currently is in development in NIC a method to lead to a more comprehensive quantification of major components in cocaine seized samples also by GC-FID.

The samples analyzed in the present study were seized during 2009-2012 in western Brazilian states [Amazonas (AM), Acre (AC), Rondônia (RO), Mato Grosso (MT), Mato Grosso do Sul (MS) and Paraná (PR)], which border with traditional coca leaf producing and cocaine processing countries (Colombia, Peru and Bolivia) and also in Brasília (FD) and São Paulo (SP), due to their economic and geographic relevance. In 2011, 72% of all 24 metric tons of cocaine apprehended by BFP were seized in those states.

This work's main goal is to establish a chemical profile of cocaine seizures in Brazil nowadays. The major components and levels of oxidation of the cocaine samples was determined and discussed.

Experimental

Chemicals

Cocaine·HCl standard (88.4% as base) were purchased from Lipomed AG and *trans*-cinnamoylcocaine (99.8%) was provided by the Drug Enforcement Administration (DEA) Special Testing and Research Laboratory (STRL) and stored at –20 °C. 2,2,2-triphenyl-acetophenone, dipentyl phthalate and caffeine (98.5%) were provided by Acros Organics; benzocaine (99.9%); lidocaine hydrochloride monohydrate, procaine hydrochloride (≥ 97%), tetramisole hydrochloride (levamisole), diltiazem hydrochloride (> 99%) and hydroxyzine dihydrochloride (≥ 98%) were purchased from Sigma and phenacetin (99.9%) was provided by TCI-EP. All working solutions

were prepared by dilution of reference materials with chloroform (HPLC Grade) provided by Tedia Brazil. 2,2,2-triphenyl-acetophenone and dipentyl phthalate were used as internal standards dissolved in a solution of chloroform and 3% (v/v) of diethylamine. Helium, synthetic air, nitrogen and hydrogen (> 99.995% of purity) were supplied by IBG.

Sampling

For cocaine seizures, the PeQui sampling strategy was established with a threshold seizure size (at least 5 kg) where profiling samples should be taken from. Samples from 2009-2012 seizures performed in 8 Brazilian states were sent to NIC and 210 samples were randomly selected to major components analysis. Table 1 shows the origin and sample numbers *per* state. Figure S1 (Supplementary Information) shows the Brazilian territory as well as the localization of the studied states.

Table 1. Origin of 210 analyzed samples

Brazilian state	Brazilian region	Number of samples analyzed (total = 210)
Acre (AC)	North	18
Amazonas (AM)	North	17
Rondônia (RO)	North	20
Federal District (FD)	Central-West	24
Mato Grosso do Sul (MS)	Central-West	16
Mato Grosso (MT)	Central-West	36
Paraná (PR)	South	39
São Paulo (SP)	Southeast	40

Sample preparation

All the samples were prepared following the PeQui Project methods, as described in the next sections.

Sample homogenization

Samples were manually crushed and homogenized. Only cocaine base samples were homogenized in the presence of liquid nitrogen. The cryogenic procedure is adequate to treat "sticky" cocaine base samples. In all cases, the final product was a homogeneous and finely divided solid, which was used in the following steps.

Sample preparation for quantification analysis

Amounts of 8.0 mg ± 0.5 mg of each previously crushed sample were mixed with 10.0 mL of internal standards solution [2,2,2-triphenylacetophenone (0.051 mg mL^{-1}) and dipentyl phthalate (0.490 mg mL^{-1}) in chloroform solution with 2% diethylamine] and carefully stirred until homogenization. Around 1 mL of fresh prepared solutions were transferred to glass vials, sealed and sent to chromatographic analysis.

Gas chromatography coupled to flame ionization detector (GC-FID)

Quantification analysis and identification of cutting agents were carried out in an Agilent Technologies 6890N gas chromatograph with a flame ionization detector, using an Agilent Technologies 7683B Series autosampler, according to the following conditions. Injection volume: 1.0 μL; split ratio = 50:1; chromatographic column: DB1-MS Methyl Siloxane, 35 m × 200 μm (i. d.) × 0.33 μm film thickness; oven temperature program: 150 °C for 2 min, 40 °C min^{-1} to 315 °C for 4 min; injection port temperature: 280 °C; FID temperature: 320 °C; carrier gas flow rate: 1.0 mL min^{-1} (helium).

Quantitative and qualitative determinations

Quantification of major components

Eight solutions of cocaine (from 0.014 to 1.441 mg mL^{-1}) and six solutions of *trans*-cinnamoylcocaine (from 0.002 to 0.222 mg mL^{-1}), all expressed as bases, were prepared in triplicate and used to obtain the analytical curves, with dipentyl phthalate (0.490 mg mL^{-1}) and 2,2,2-triphenyl-acetophenone (0.051 mg mL^{-1}) as internal standards, respectively. The *cis*-cinnamoylcocaine was determined with the *trans*-cinnamoylcocaine analytical curve.

Figures of merit, such as specificity, linearity, repeatability, accuracy and working range of the method were evaluated before analysis. The control samples results were all within acceptable limits.

Classification of oxidation levels was performed applying DEA/USA criteria: samples containing less than 2% of total cinnamoylcocaines (*cis*+*trans*-cinnamoylcocaine) relative to cocaine are classified as "highly oxidized"; between 2-6% are classified as "moderately oxidized"; more than 6% are classified as "minimally or not oxidized".[22]

Qualitative analysis of major components

Some typical cocaine cutting agents were identified by retention time comparison with available reference materials and mass spectrometry analysis, using the same conditions in the two injectors and two detectors (FID and MS) Agilent Technologies 6890N gas chromatograph.

Infrared (FTIR/ATR-Nicolet iS10 model, equipped with a SMART iTR accessory) and qualitative analyses were used to differentiate the cocaine form of samples (base or hydrochloride salt).

Results and Discussion

Qualitative analysis of major components

The GC-FID analysis showed that 51% of the samples did not have any significant adulteration with typical pharmaceutical products (Figure 1). That scenario can be justified considering that the samples seized by BFP are connected with international trafficking, i.e., before the adulteration steps to improve profit in street drugs level. It is interesting to note that SP state samples showed only 20% of non-adulterated samples.

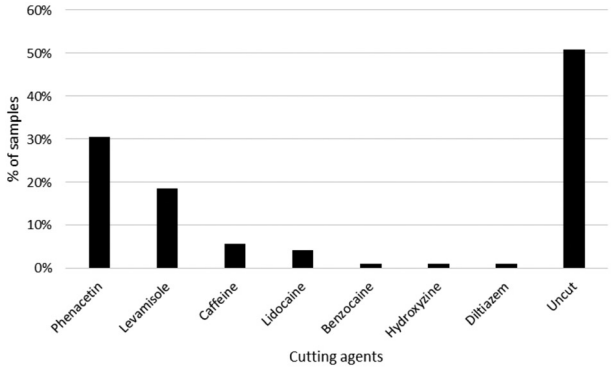


Figure 1. Presence of cutting agents in all analyzed samples.

The results show a predominance of phenacetin as the main adulterant (such as described in France by Evrard *et al.*[20]), being found in 30% of samples. Previous routine analysis of BFP used to identify phenacetin as typical adulterant found in cocaine seizures from north Brazil, but the results of this work showed that phenacetin is present as the main adulterant in all states studied. Levamisole (19%), caffeine (6%) and lidocaine (4%) were also found in a significant number of samples.

Table 2 lists the frequency of each cutting agent used to adulterate the samples *per* Brazilian state.

Figure 2 showed the same results as Figure 1, but separating the samples by region of seizure. Results of the presence of cutting agents in all set of analyzed samples are described in the Supplementary Information (Table S1).

Quantitative analysis of major components

The GC-FID quantitative analysis showed wide variations on the content of cocaine (expressed as base), covering the range of 12.0% to 93.4% purity, while the overall average content was 71.2%. Despite the geo-economics differences between the Brazilian states studied, the average levels of cocaine were similar, ranging from 64% to 74% (Figure 3). It is important to mention that the minimum purity in some states (AC, FD and SP) were above 47%, showing high cocaine levels for all samples analyzed from those sites. On the other hand, some samples from AM, RO and PR had less than 20% of cocaine.

Figure 4 shows the distribution of cocaine purity in all analyzed samples (Figure 4a) and *per* state (Figure 4b-4i). It can be seen that most samples (51.9%) had levels between 70 and 80% of cocaine. It is also observed that the samples from PR (south) showed the highest levels of cocaine, with 46% of the samples with purity of 80-90%. More detailed quantitative results in the set of samples analyzed are described in the Supplementary Information (Table S1).

Table 2. Cutting agents identified in analyzed samples

Brazilian state	Cutting agents identified[a] (number of samples)[b]							
	Uncut	Phe	Lev	Caf	Lid	Ben	Hyd	Dil
Acre (AC)	10	8	0	1	0	0	0	0
Amazonas (AM)	9	5	1	4	0	0	0	1
Rondônia (RO)	15	5	0	1	0	0	0	0
Federal District (FD)	14	9	6	2	0	0	0	0
Mato Grosso do Sul (MS)	8	6	1	0	1	0	1	0
Mato Grosso (MT)	18	9	9	0	0	0	0	0
Paraná (PR)	23	11	4	2	1	2	0	0
São Paulo (SP)	10	11	18	2	7	0	1	1
Total[c]	107	64	38	12	9	2	2	1

[a]Phe = phenacetin, Lev = levamisole, Caf = caffeine, Lid = lidocaine, Ben = benzocaine, Hyd = hydroxyzine, Dil = diltiazem; [b]One or more adulterants can be present in each powder; [c]Procaine was not detected in any sample.

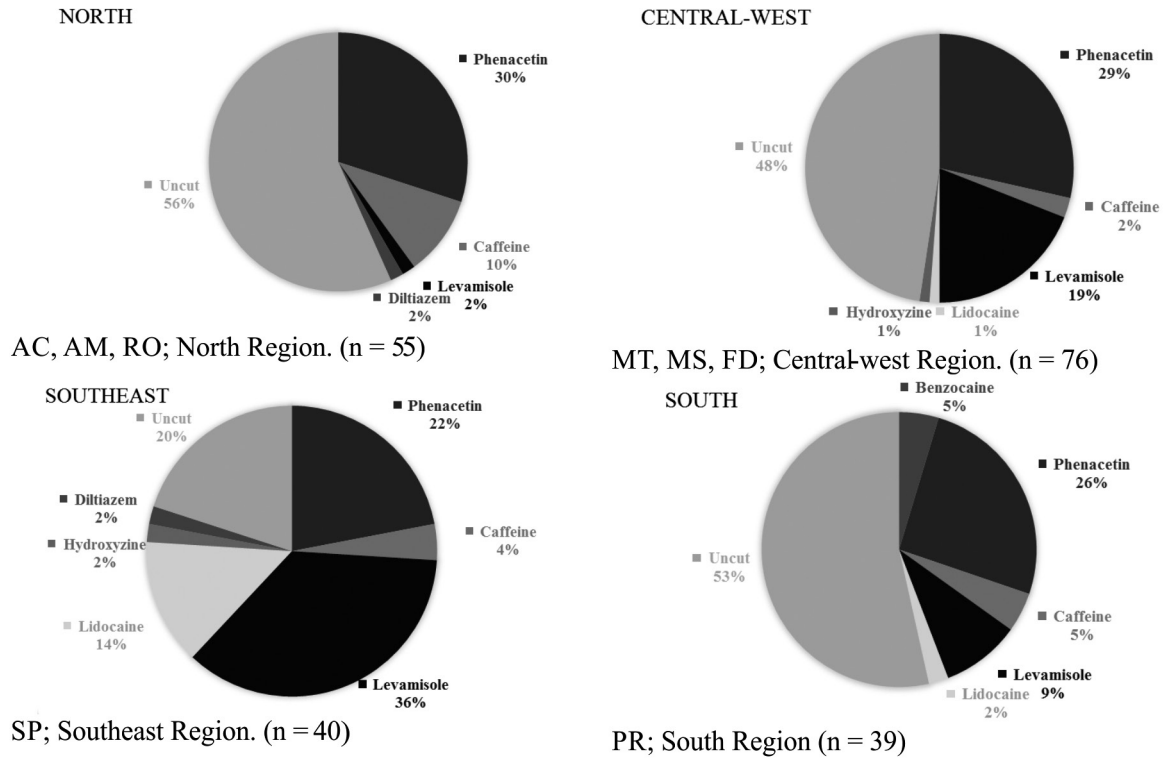


Figure 2. Presence of cutting agents in samples from different regions of Brazil.

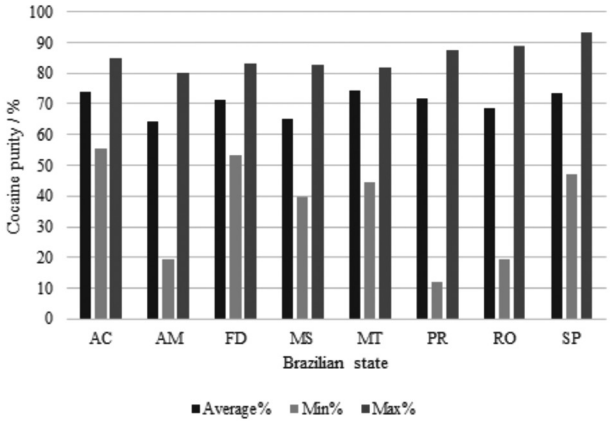


Figure 3. Cocaine purity (average, minimum and maximum), *per* state.

The ratio among *cis*+*trans*-cinnamoylcocaine and cocaine (oxidation levels) revealed that only a minority of samples (20%) underwent high oxidation, while minimally or not oxidized samples were responsible for 42% of the total (Figure 5a).[22] Figure 5b shows the scenario *per* state. Detailed results and classification are also described in the Supplementary Information (Table S1).

Most samples of free base cocaine (e.g., coca paste, coke base or *crack* cocaine)[9] suffered only moderate oxidation (21%) processes or were neither oxidized (72%) (Figure 6a). On the other hand, most cocaine hydrochloride samples undergone moderate (61%) or high (38%) oxidation (Figure 6b).

Conclusions

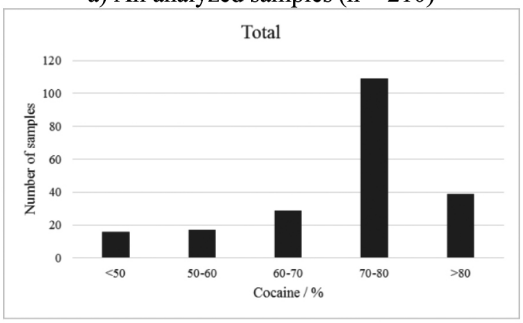
From a set of 210 samples seized by Brazilian Federal Police between 2009-2012, the chemical profiling routines of PeQui project to major components revealed that the illicit drug cocaine is mainly present in free base form (59%), with purity (expressed as base) in the range of 12 to 93% (mean 71%).

The oxidation levels, determined by the relative content between *cis*+*trans*-cinnamoylcocaine and cocaine determined in GC-FID analysis showed that most samples were composed of moderately (38%) and not oxidized (42%) cocaine. A tendency to high oxidation degree occurred mainly on cocaine hydrochloride samples.

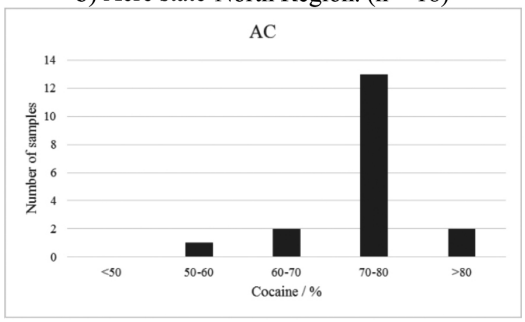
More than 50% of the samples analyzed did not have any adulterant, which is coherent with the cocaine international trafficking seizures performed by Brazilian Federal Police in a relative high purity scenario. Among the pharmaceuticals products identified as cutting agents, phenacetin was the most abundant (30% of the total samples) and was found in seizures all over the country. Levamisole (18%), caffeine (6%) and lidocaine (4%) were also identified, but with some regional bias.

The PeQui project has been used on regular basis to provide technical and scientifically based information to law enforcement intelligence analysis and statistical

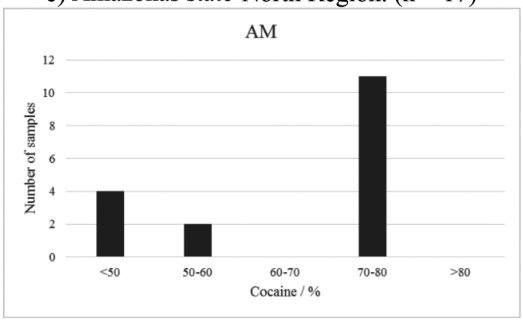
a) All analyzed samples (n = 210)



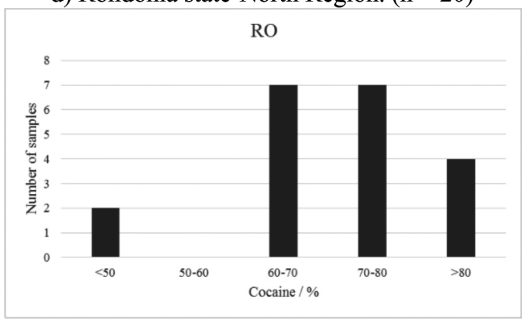
b) Acre state-North Region. (n = 18)



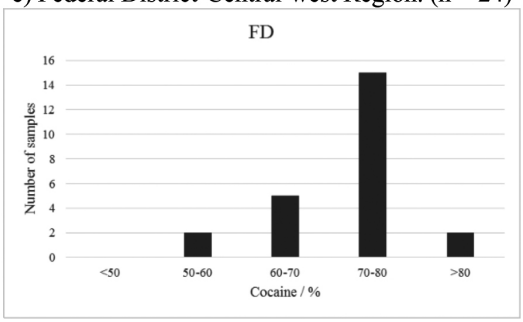
c) Amazonas state-North Region. (n = 17)



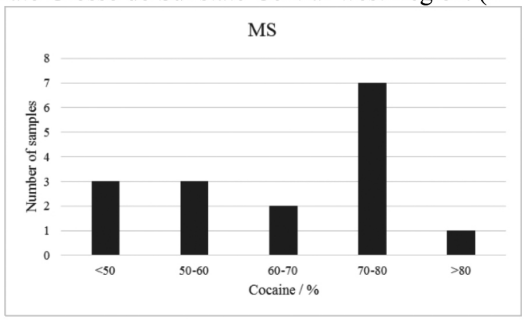
d) Rondônia state-North Region. (n = 20)



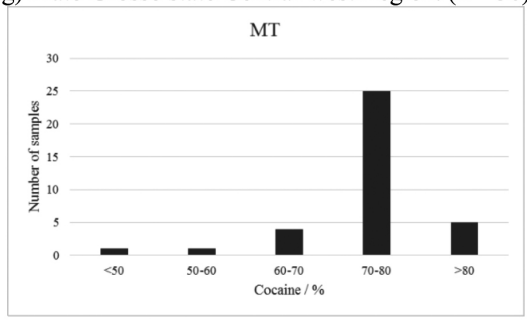
e) Federal District-Central-west Region. (n = 24)



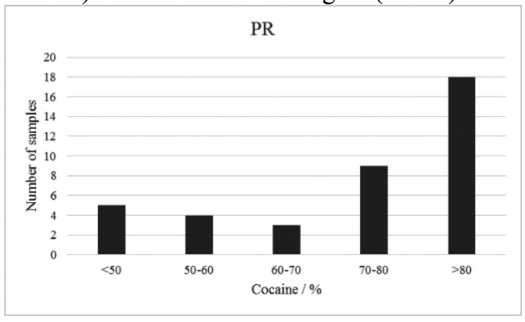
f) Mato Grosso do Sul state-Central-west Region. (n = 16)



g) Mato Grosso state-Central-west Region. (n = 36)



h) Paraná state-South Region (n = 39)



i) São Paulo state-Southeast Region. (n = 40)

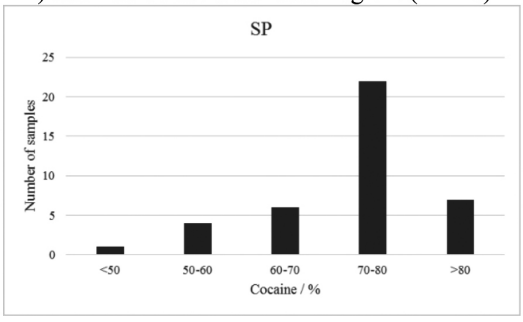


Figure 4. Distribution of cocaine purity in all analyzed samples (a) and *per* state (b-i).

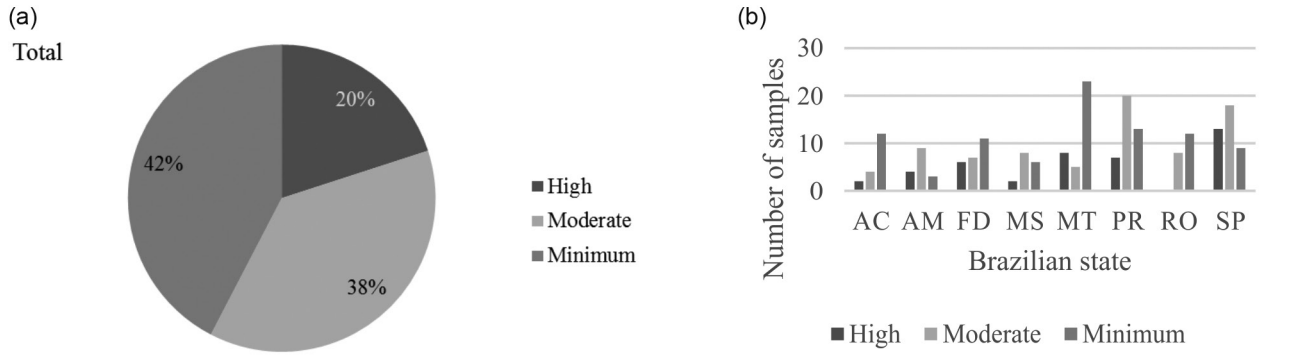


Figure 5. Oxidation levels of (a) all analyzed samples and (b) *per* state.

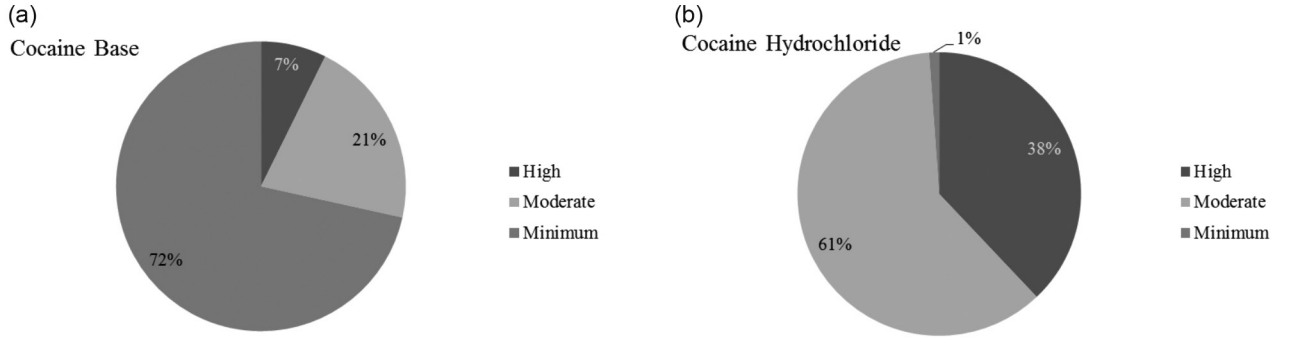


Figure 6. Oxidation levels of (a) free base cocaine (n = 123) and (b) cocaine hydrochloride (n = 87).

data that might contribute to a better understanding of the scenario of the cocaine international trafficking.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgements

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