

Chemical Profiling of Street Cocaine from Different Brazilian Regions

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This work describes results of chemical profiling by gas chromatography with flame ionization detector (GC-FID) of the main components (purity, oxidation level, and cutting agents) in 642 street cocaine samples seized in five different Brazilian States between 2011 and 2014. The analysis revealed the presence of cocaine with mean content of 49.8%. Freebase samples showed cocaine average content of 66.0%, whereas hydrochloride and not determined (n.d.) present cocaine content of 44.5% and 11.8%, respectively. Cocaine base samples show moderately (16%) to not oxidized (81%) levels, whereas cocaine hydrochloride samples exhibit moderate (37%) to high (22%) oxidation degrees. Approximately 34% of all the analyzed samples did not have any adulterant identified. Base cocaine samples are even less adulterated (42% uncut) with phenacetin being present in 53% (average content of 15%). Caffeine and lidocaine were mostly found in hydrochloride samples, while the n.d. samples show a combination of either phenacetin or a caffeine/lidocaine mixture. A mass balance approach is presented and seizures information can be combined to deliver intelligence and statistical analysis that might contribute to the understanding of street cocaine composition scenario. A total of 269 samples were characterized as crack cocaine showing phenacetin as the main adulterant and presenting an average cocaine content of 68.3%.

Keywords: cocaine, chemical profiling, crack cocaine, street drug, cutting agents

Introduction

The Brazilian Federal Police (BFP) has been implementing, since 2006, a profiling program for illicit drugs known as the PeQui project (acronym for Perfil Químico das Drogas in Portuguese, meaning drug chemical profiling in English), and it was designed to provide both accredited forensic reports and scientifically based police

intelligence/investigative information. It accomplishes that by means of detailed chemical analysis of cocaine seized in Brazil and was developed at the Central Laboratory of the National Institute of Criminalistics (NIC) in Brasília, Distrito Federal, Brazil, since 2010.^{1,2} One of the major PeQui project goals is to develop and validate analytical methodologies for the quantification of cocaine and *cis*- and *trans*-cinnamoylcocaine alkaloids, as well as the more frequent pharmaceutical used as cutting agents (i.e., benzocaine, phenacetin, caffeine, lidocaine, aminopyrine,

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levamisole, hydroxyzine, procaine and diltiazem) at NIC. Gas chromatography with flame ionization detection (GC-FID) was the analytical technique of choice due to its ruggedness, stability and low cost when compared to mass spectrometry techniques. It has been successfully associated with a high throughput sample preparation routine.

The BFP PeQui project mainly deals with interstate and international drug trafficking samples, usually involving high quantities and purity (low cut) seizures, where the analyte cocaine is the main component of the product cocaine. Two recent articles showed that the average cocaine content on samples seized in Brazil between 2009 and 2013 was about 70-71% (N = 369 samples).^{1,3} Yonamine *et al.*⁴ have analyzed by gas chromatography with nitrogen phosphorus detection (GC-NPD), the BFP cocaine seizures at the International Airport of São Paulo and also some intercepted at the Brazilian postal service during the year of 2011 (N = 54 samples, cocaine average content of 62%).

While PeQui project continues to focus on BFP apprehensions, it has become progressively important to establish scientifically sound information regarding street drugs seizures, which are usually performed outside BFP jurisdiction, e.g., by local law enforcement agencies and analyzed on Brazilian State forensic institutes. One such initiative has already been undertaken at NIC in 2011, when a comparison between BFP seized samples and local apprehensions made by the police in Acre State proved that a supposed new drug, called oxi, was actually a misclassification of the ordinary forms of presentation of street cocaine.⁵

Some articles reporting analyses of street cocaine apprehended in Brazil have been published since 2003. Bernardo *et al.*⁶ quantified 200 samples seized at Minas Gerais State (Southeast region of the country) by GC-FID with an average cocaine content of 28.1%. Carvalho *et al.*⁷ analyzed 389 white powder samples seized in São Paulo City (Southeast region), also by GC-FID with an average content of 37.5%.

Fortunately, in the last two years, articles including street cocaine analysis have been more frequent in the literature, mainly due to the forensic chemists graduate studies and more effective collaborations between universities and forensic institutions. Floriani *et al.*⁸ validated a high-performance liquid chromatography with absorciometric detection using a diode array detector (HPLC-DAD) method to quantify cocaine, benzoylecgonine and adulterants (caffeine, lidocaine, phenacetin, benzocaine and diltiazem) and analyzed 115 cocaine samples (26 samples as hydrochloride and 89 samples as freebase chemical form)

seized between 2007-2012 at Paraná State (South region of the country). A high cocaine content was found, since 52 samples showed cocaine levels ranging from 80-97% and at least other 25 samples had cocaine content between 60-80%. In a study of Fukushima *et al.*⁹ focused in smoked cocaine (i.e., freebase), 404 samples seized in the streets of São Paulo City were analyzed by GC-FID and a high cocaine content drug (average of 71.3%) was also found. Magalhães *et al.*¹⁰ quantified by gas chromatograph coupled with mass spectrometry (GC-MS) 31 street cocaine samples seized in the Brazilian States of Minas Gerais (Southeast region) and Amazonas (North region). The majority of Minas Gerais State samples exhibited lower purity (average of 26%), while Amazonas State samples presented higher levels of cocaine (average of 40%).

Besides dealing with diverse sample origins (street drugs or interstate/international trafficking), different analytical schemes and specific goals, these studies have contributed to bring scientifically based information regarding the characteristics of cocaine based products by means of chemical analysis thus fulfilling a knowledge gap not provided by psychological, toxicological nor prevalence studies.

In the present study, a relevant number of street cocaine samples (N = 642) seized in five different Brazilian States (Distrito Federal and Goiás, Center-West region; São Paulo, Southeast region; Bahia, Northeast region and Acre, North region of the country) has been analyzed. The applied methodology quantifies major alkaloids (cocaine, *cis*- and *trans*-cinnamoylcocaine) and common pharmaceutical cutting agents (benzocaine, phenacetin, aminopyrine, caffeine, lidocaine, levamisole, hydroxyzine, procaine and diltiazem) in a single GC-FID run. This work also focuses on a mass balance approach, which takes into consideration sample content, as well as the total amount of drug seized by law enforcement agencies in Goiás State.³

The objective of this work is to bring further scientifically based results obtained from samples within the scope of PeQui project, concerning the analysis of street cocaine samples analyzed in NIC since 2010, when the Brazilian Federal Government launched a national program to promote public policies to reduce drug supplies and demand (including investment in education and health care of drug addicts).¹¹

Experimental

Chemicals and materials

Cocaine base (96.1%) and *trans*-cinnamoylcocaine base (98.2%) were purchased from NMI (Australia).

Dipentyl phthalate (97.0%) and caffeine (98.0%) were provided by Acros Organics (USA). Benzocaine (97.2%), lidocaine hydrochloride monohydrate (96.0%), procaine hydrochloride (98.7%), tetramisole hydrochloride (99.9%), diltiazem hydrochloride (98.7%), hydroxyzine dihydrochloride (98.1%) and aminopyrine (99.1%) were purchased from Sigma-Aldrich (USA). Phenacetin (99.3%) was provided by TCI-EP (Japan). All standard solutions were prepared by dilution of reference materials with chloroform (HPLC grade) provided by Tedia (Brazil). Dipentyl phthalate was used as internal standard dissolved in a solution of chloroform with 0.2% (v/v) of diethylamine (PA), purchased from Sigma-Aldrich (Belgium). The bottle-top 10.0 mL dispensers (Dispensette Organic) were supplied by BrandTech (Germany). Helium, synthetic air, nitrogen and hydrogen (>99.995% of purity) were supplied by IBG (Brazil).

Sampling

All 642 street cocaine samples were obtained from seizures performed in five Brazilian States between 2011–2014 and brought to NIC to be analyzed in the routine of PeQui project. Table 1 shows the origin and number of samples *per* State. Figure S1 (Supplementary Information) shows the Brazilian territory as well as the localization of the States/regions studied.

Table 1. Origin and numbers of samples *per* State

Brazilian State	Brazilian region	N (total = 642)
Acre (AC)	North	61
Bahia (BA)	Northeast	50
Distrito Federal (DF)	Central-West	34
Goiás (GO)	Central-West	206
São Paulo (SP)	Southeast	291

N: Number of samples.

In a similar approach of a previous work,³ detailed data were extracted from Goiás State apprehension (206 samples correspond to a total mass of 31 kg). The percentage of each analyte in a sample was multiplied by the correspondent mass of that specific seizure, providing a mass balance book keeping in terms of alkaloid and adulterant content.

Sample preparation

All cocaine samples were manually crushed and homogenized using mortar and pestle. Cocaine freebase samples were homogenized in the presence of liquid nitrogen as described in a previous work.⁵ The cryogenic procedure is adequate to treat sticky cocaine base

samples and in most cases the final product resulted in a homogeneous and finely divided powder.

Amounts of 12.25 ± 0.25 mg of each crushed sample were weighted in 25 mL Erlenmeyer flasks, mixed with 10.0 mL of dispensed internal standard solution (dipentylphthalate at 0.490 mg mL^{-1} in $\text{CHCl}_3/0.2\%$ diethylamine) and carefully stirred until dissolution. Freshly prepared solutions were transferred to 2 mL glass vials and sealed for further gas chromatography injection.

Gas chromatography with flame ionization detector (GC-FID)

Quantification analysis is part of the scope of NIC ISO/IEC 17025 accredited methods and it was carried out in 6890N gas chromatograph with flame ionization detector (Agilent, USA), using a 7683B Series autosampler (Agilent, USA). Chromatographic conditions: injection volume: 1.0 μL ; split ratio: 50:1; column: RXi-1MS methyl siloxane, $25 \text{ m} \times 200 \mu\text{m}$ (i.d.) $\times 0.33 \mu\text{m}$ film thickness; oven temperature program: 150 °C for 2 min, rate of 40 °C min^{-1} to 315 °C, hold for 4.5 min; injection port temperature: 280 °C; FID temperature: 320 °C; carrier gas flow rate: 1.0 mL min^{-1} (helium). The GC-FID conditions were optimized in both method development and validation in order to assure adequate selectivity of all quantified analytes in a twelve-minute run. Eventual identification of analytes was carried out in a 6890N gas chromatograph coupled with a 5973 Inert (70 eV) mass spectrometer detector (Agilent, USA).

Major components like cocaine, *cis*- and *trans*-cinnamoylcocaine and pharmaceutical cutting agents/adulterants (benzocaine, phenacetin, caffeine, lidocaine, aminopyrine, levamisole, hydroxyzine, procaine and diltiazem) were quantified using the previous GC-FID method. The content of cocaine alkaloids and adulterants are expressed as base in freebase and “not determined” (n.d.) forms and as hydrochlorides when cocaine in salt form is detected. Analytical curves were constructed by regression of chromatographic peak areas *versus* concentration ($R^2 > 0.999$). Additional method validation figures of merit were evaluated (specificity, linearity, repeatability, accuracy, working range, limit of detection (LOD) and limit of quantification (LOQ)) and are presented as Supplementary Information (Table S1). Quality control sample results were all within acceptable limits. Cocaine oxidation levels were determined considering the total *cis* + *trans*-cinnamoylcocaine ratio relative to cocaine.¹²

Qualitative analysis of major components

Attenuated total reflection infrared spectroscopy

(ATR-FTIR, Nicolet iS10 model, equipped with a SMART iTR accessory, USA) and classical spot tests were used to establish the cocaine form, i.e., freebase (N = 411) or hydrochloride salt (N = 65).

PeQui analytical scheme has been designed to deal with typical BFP cocaine samples (high purity, low cut). Some other issues need to be addressed when dealing with street drug cocaine samples. For example, samples with both low cocaine content (e.g., < 5%) and high of adulterant content (> 50%, e.g., caffeine or lidocaine) can't be easily classified as freebase or hydrochloride cocaine neither using ATR-FTIR nor classical spot tests. Successful classification is further hindered by the presence of boric acid as a frequent diluent, hydrolysis degradation and even the occurrence of samples with no cocaine.² This type of sample has been grouped as not determined (n.d.) form of presentation (N = 166).

Results and Discussion

Qualitative analysis of adulterants

The GC-FID analysis of 642 street cocaine samples showed that 34% did not present any significant adulteration with typical pharmaceutical products (Figure 1). That overall adulteration scenario is quite different when compared to the one observed in uncut seizures performed by BFP (e.g., 40-45% uncut samples)³ which are related to international drug trafficking. Nevertheless, it is interesting to note that 43% of street freebase cocaine samples are uncut and therefore quite similar to BFP freebase samples (Figure 2).

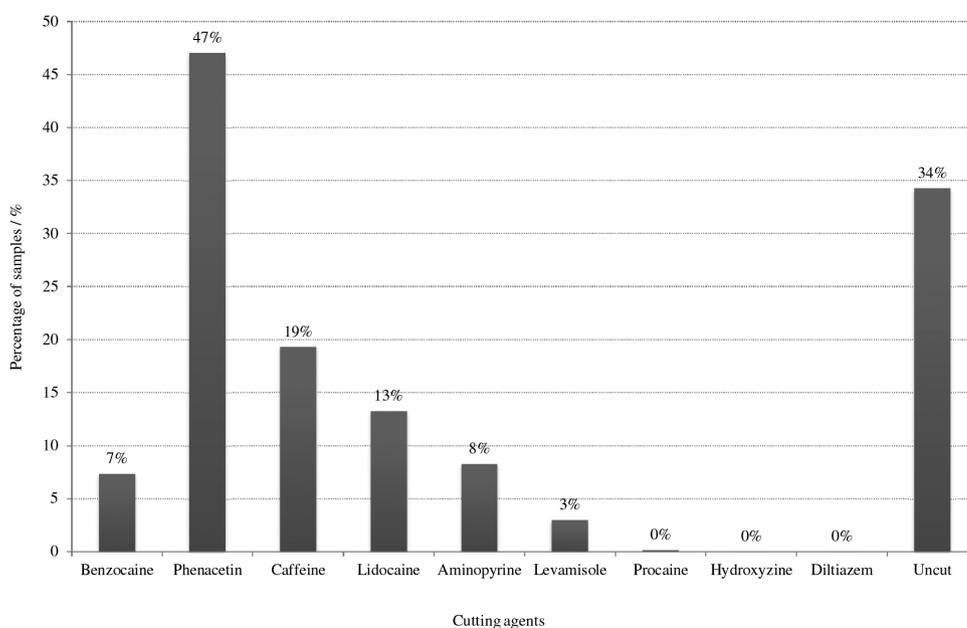


Figure 1. Presence of cutting agents in all samples.

Results also show a predominance of phenacetin as the main adulterant in street drug cocaine, being found in 47% of samples. Previous works¹⁻³ and BFP routine analysis identified phenacetin as typical adulterant found in trafficking cocaine seizures in all Brazilian States studied. The adulterants caffeine and lidocaine (19-13%) have a higher incidence than aminopyrine, benzocaine and levamisole (8-3%). Procaine was quantified in just one sample and hydroxyzine and diltiazem were not detected.

The prevalence and mean content of each cutting agent used to adulterate the samples (all samples separated according to cocaine form of presentation) are listed in Table 2. The highlighted data indicate that phenacetin is present in relatively high content (15.2%) in freebase cocaine samples, while caffeine and lidocaine are used to cut hydrochloride samples (30.3 and 10.4% of mean content, respectively). The n.d. samples show a combination of those two scenarios. Detailed quantitative results *per* State are described in Supplementary Information (Table S2 and Figures S2-S11).

Quantitative analysis of cocaine alkaloids

The overall GC-FID quantitative analysis of cocaine alkaloids showed a wide variation on the content of cocaine, covering the range of 0 to 97.7%, with an average content of 49.8% (standard deviation: 29.5) (Figure 3). The ratio between *cis* + *trans*-cinnamoylcocaine and cocaine (oxidation level indicator) revealed that only a minority of samples (5%) underwent high oxidation, while moderate or low/not oxidized samples composed about 77% of the samples (Figure 3).

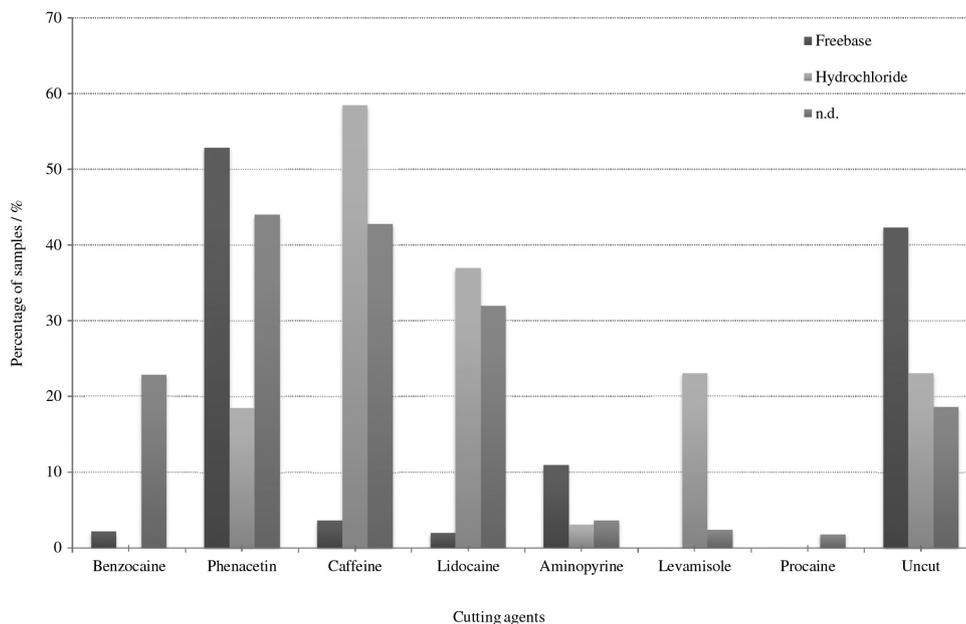


Figure 2. Presence of cutting agents in different cocaine forms of presentation.

Table 2. Cutting agents identified in all samples and cocaine forms of presentation

		Cutting agents identified ^a							
		Uncut	Ben	Phe	Caf	Lid	Ami	Lev	Pro
All samples (N = 642)	Prevalence ^b / %	34	7	47	19	13	8	3	0
	Mean content ^c / %	–	13.7	12.2	21.9	9.7	4.4	10.8	2.5
Freebase (N = 411)	Prevalence / %	43	2	54	4	2	11	0	0
	Mean content / %	–	14.6	15.2	16.9	2.8	4.1	0	0
Hydrochloride (N = 65)	Prevalence / %	23	0	18	58	37	3	23	0
	Mean content / %	–	0	2.4	30.3	10.4	16.6	13.2	0
n.d. (N = 166)	Prevalence / %	9	23	44	43	32	4	2	2
	Mean content / %	11	13.5	4.8	18.5	3.0	0.0	1.5	2.5

^aBen = benzocaine; Phe = phenacetin; Caf = caffeine; Lid = lidocaine; Ami = aminopyrine; Lev = levamisole; Pro = procaine; ^bone or more adulterants can be present in each sample; ^cmean content on samples that contain the adulterant.

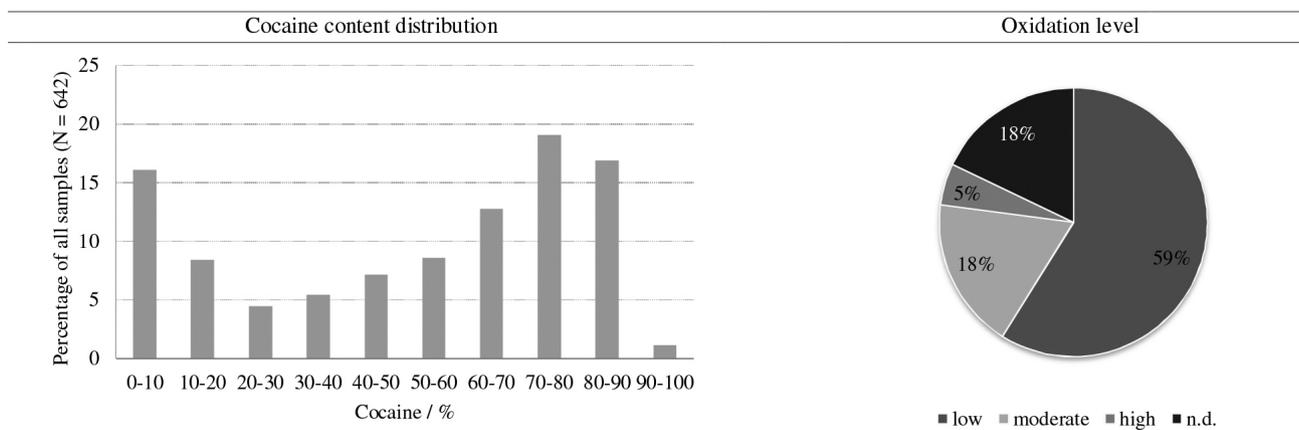


Figure 3. (a) Histogram of cocaine content distribution and (b) oxidation levels (all samples).

It is observed that freebase cocaine samples showed the highest levels of cocaine content (average of 66.0%, Figure 4). Hydrochloride and n.d. present lower average cocaine content (44.5 and 11.8%, respectively), reflecting the significant cutting process already discussed.

The *cis*- + *trans*-cinnamoylcocaine to cocaine ratio revealed that most cocaine freebase samples either underwent moderate oxidation processes (16%) or no oxidation at all (81%). On the other hand, most cocaine hydrochloride samples experienced moderate (37%) to high (22%) oxidation processes. Due to the low content of cocaine alkaloids in n.d. samples, below LOQ in many cases, the oxidation level classification cannot be fully applied. More detailed quantitative classification and analysis *per* State are described in Supplementary Information (Table S2 and Figures S12-S16).

Forensic intelligence analysis can be performed in many ways using the same dataset of chemical profiling results. Such a dataset can be expanded anytime as more information become available. The total amount, date and place of seizure in conjunction with quantitative results, presentation forms and oxidation levels add value to PeQui reports and contribute to re-direct law enforcement efforts.

In a first example, a mass balance³ can be used to estimate, using a population of 206 street cocaine samples from Goiás State (31 kg seizure total amount), that the alkaloids correspond to 59% on a mass basis (i.e., 18 kg) and cutting agents correspond to 26% (i.e., 8 kg). This picture can be put into perspective in a broader scenario, where comparison with international trafficking samples analyzed using the same method show the relevance of the

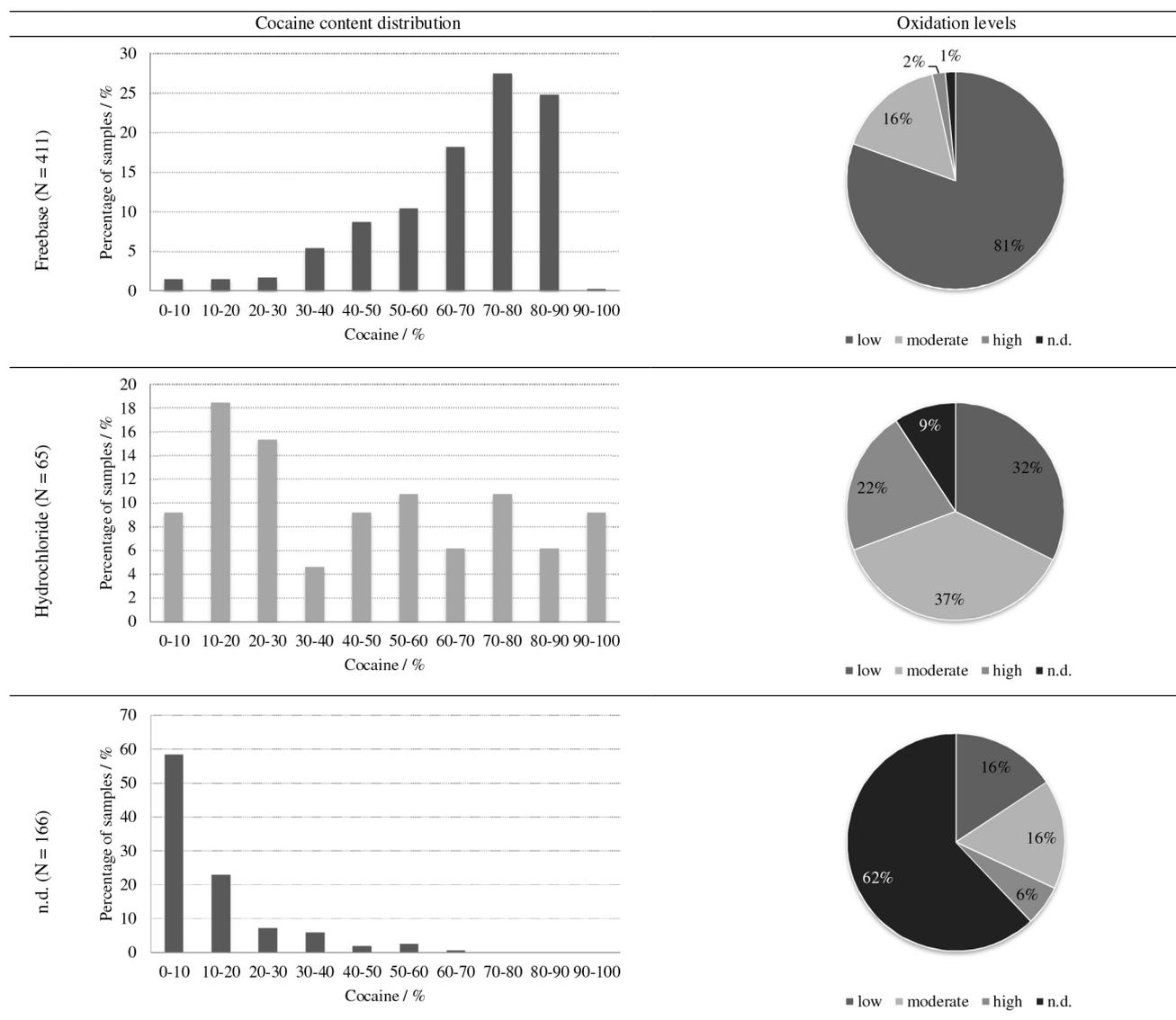


Figure 4. Histogram of cocaine content distribution and oxidation levels - forms of presentation.

local cutting process. Such information is useful to adjust law enforcement actions.

Finally, it has been possible to classify part of freebase cocaine samples from four Brazilian States as crack cocaine, i.e., rocks of melted cocaine in freebase form of presentation² (Bahia, N = 23; Distrito Federal, N = 26; Goiás, N = 98; and São Paulo, N = 122). The 269 crack cocaine samples had phenacetin as the main adulterant (mean content of 15% and prevalence in 51% of the samples). The seized crack presented low oxidation (84% of the samples) and high cocaine content (average of 68.3%). This picture is quite similar to the high purity international trafficking drug profile found by BFP in previous works with material routinely apprehended.¹⁻⁴ The results indicates that crack cocaine has not been significantly adulterated before reaching the street market and that consumers are smoking a high content cocaine product not only in São Paulo region (as described by Fukushima *et al.*)⁹ but also in all other Brazilian regions studied.

Conclusions

From a set of 642 street cocaine samples seized in five different States, in four regions of Brazil, the major component chemical profiling routine analysis of the PeQui project revealed the presence of a high cocaine content (up to 70%, with average value of 49.8%).

The majority of cocaine samples were classified as freebase (N = 411) or hydrochloride (N = 65). The 166 samples classified as not determined (n.d.) presented low cocaine alkaloid content and boric acid used as a cutting agent.

Freebase cocaine samples presented an average content of 66.0%, while hydrochloride and n.d. presented a cocaine content of 44.5 and 11.8%, respectively, reflecting the relevant cutting process in the last two groups. Most cocaine freebase samples presented moderately (16%) and not oxidized (81%) levels, whereas cocaine hydrochloride samples exhibited moderate (37%) to high (22%) oxidation degrees.

Approximately 34% of all the analyzed samples did not have any adulterant identified. Freebase cocaine samples are even less adulterated (42% uncut). Among the pharmaceuticals identified as cutting agents, phenacetin was shown to be the most abundant in freebase cocaine samples (53% of the samples with 15% average content), while caffeine and lidocaine were mainly found in hydrochloride samples (58 and 37% of the samples, respectively). The n.d. samples showed a combination of those two scenarios.

The freebase cocaine samples classified also as crack cocaine presented a high cocaine content (average of

68.3%), similar with the international trafficking profile found in BFP routine seizures. These results indicate that crack cocaine has not been significantly adulterated before reaching the street market and that consumers are smoking a high content cocaine product all over the Brazilian regions studied. Definitely, crack cocaine street samples cannot be classified as a mere byproduct of cocaine production. This information is crucial to professionals working with medical, psychological and toxicological aspects of crack cocaine addiction.

In conclusion, besides providing technical and scientifically based information to law enforcement, it has been shown how a mass balance approach and specific seizure information can be combined to PeQui project quantitative results in order to provide intelligence analysis and statistical data that might contribute to understand street cocaine composition ever-changing scenario.

Supplementary Information

Supplementary data (localization of the Brazilian States studied; additional method validation figures of merit; table and figures with detailed quantitative results and classification *per* State) are available free of charge at <http://jbcns.sbj.org.br> as PDF file.

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