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Purity and adulterant analysis of crack seizures in Brazil

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ABSTRACT

Cocaine represents a serious problem to society. Smoked cocaine is very addictive and it is frequently associated with violence and health issues. Knowledge of the purity and adulterants present in seized cocaine, as well as variations in drug characteristics are useful to identify drug source and estimate health impact. No data are available regarding smoked cocaine composition in most countries, and the smoked form is increasing in the Brazilian market. The purpose of the present study is to contribute to the current knowledge on the status of crack cocaine seized samples on the illicit market by the police of São Paulo. Thus, 404 samples obtained from street seizures conducted by the police were examined. The specimens were macroscopically characterized by color, form, odor, purity, and adulterant type, as well as smoke composition. Samples were screened for cocaine using modified Scott test and thin-layer chromatographic (TLC) technique. Analyses of purity and adulterants were performed with gas chromatography equipped with flame ionization detector (GC-FID). Additionally, smoke composition was analyzed by GC–mass spectrometry (MS), after samples burning. Samples showed different colors and forms, the majority of which is yellow (74.0%) or white (20.0%). Samples free of adulterants represented 76.3% of the total. Mean purity of the analyzed drug was 71.3%. Crack cocaine presented no correlations between macroscopic characteristics and purity. Smoke analysis showed compounds found also in the degradation of diesel and gasoline. Therefore, the drug marketed as crack cocaine in São Paulo has similar characteristics to coca paste. High purity can represent a greater risk of dependency and smoke compounds are possibly worsening drug health impact.

1. Introduction

Addiction to illegal drugs causes public health problems worldwide [1,2]. In 2009, an estimated 21.8 million Americans aged 12 or older had used an illicit drug. This estimate represents 8.7% of the population aged 12 or older. Illicit drugs include marijuana/hashish, cocaine (including crack), heroin, hallucinogens, inhalants, or prescription-type psychotherapeutics used nonmedically [3]. The world latest estimates indicate that 17 million people used cocaine at least once in the past year, equivalent to 0.37% of the global population aged 15–64 [4]. The last survey conducted in 2012 found that smoked cocaine is used by approximately 370,000 people in the capitals and DC of Brazil (total population around 200 million), while in Southeast where the most populated capital, São Paulo, is located, 115,000 users were estimated [5].

Brazil has a 16,000 km land border with ten neighboring countries and receives large quantities of cocaine from the main producing countries (Colombia, Peru, and Bolivia). Smoked cocaine has been increasing, which led the government to create a national program called 'Crack, é possível vencer!' or 'Crack: you can defeat it', which provides several strategic actions aimed at preventing consumption and promoting comprehensive care to crack cocaine users [6]. Knowledge of drug composition, such as purity percentage and adulterants, is an important data for hazard characterization and also explains the prevalence of acute cocaine toxicity, overdoses, and fatal reactions [7].

While in Brazil usage of the term 'crack' refers to all forms of smoked cocaine, its origin is from United States, as an onomatopoeia of the crackling sound when sodium chloride is burned. The

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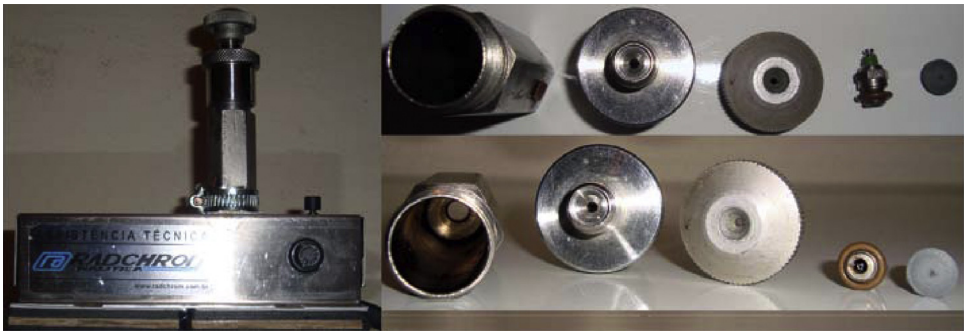

Fig. 1. Burner apparatus used to mimic the burning of stones.

salt is a residue produced when hydrochloride salt cocaine is mixed with sodium hydroxide under heating to form cocaine in base form [8]. Crack consumed in Brazil is possibly produced by cocaine salts or coca paste obtained from the first extraction of coca leaves. Considering that drug composition depends on the preparation process, a correct classification and knowledge of the drug composition is essential to assess effects on health and changes in traffic profiles [9].

The nomenclature of smoked cocaine is based on production; the name coca paste is given to the product of the first extraction step. Dried coca leaves are moistened with an alkaline solution to solubilize cocaine in kerosene or other organic solvent. The kerosene solution is then mixed with dilute sulfuric acid to convert soluble alkaloids in an aqueous acid solution. Ammonia water is added to the sulfuric acid solution and cocaine sulfate is converted to cocaine base (water insoluble) that is filtered and termed coca paste. In the second extraction step, the coca paste is diluted with diluted sulfuric acid and an oxidizing agent is added to remove cinnamoylcocaine. The product is mixed with an alkaline solution to obtain the base form that is named cocaine base, which is purer than coca paste [10]. Technical reports of the Brazilian Federal Police use the DEA's criteria based on oxidation levels determined by percentage of cinnamoylcocaine (CICOC) to determine if the smoked cocaine is crack (highly oxidized or less than 2% of CICOC), freebase (moderately oxidized or 2–6% of CICOC) or coca paste (unoxidized or >6% of CICOC) [11]. Other names for crack, such as merla and oxy, are used by drug users or drug dealers, but have not a scientific basis.

Drug purity and composition varies according to the region, availability and their presentation. Previous French reports analyzed 373 samples of cocaine salts obtained in 2006. Median purity was 23% and average purity was 29%. The most frequent adulterants were phenacetin (54%), caffeine (17%), paracetamol (14%), diltiazem (11%), lidocaine (11%), and levamizol (6%) [12]. In Luxembourg the purity of 471 cocaine salt samples varied according to year and samples were very heterogeneous. Cocaine mean concentration was lowest in 2009 (43.2%) and highest in 2005 (54.7%), the adulterants phenacetin, caffeine, diltiazem, lidocaine, levamisole and hydroxyzine were frequently detected, whereas procaine, paracetamol, methylephedrine, diclofenac, benzocaine, ephedrine and atropine were detected in much fewer samples [13]. Although many studies analyzed cocaine salts, smoked cocaine is a rising problem in many regions and few studies are available. In Brazil, a recent study of cocaine base ($N = 43$) seized in Acre (northern Brazil, bordering with Bolivia and Peru) shows samples with similar macroscopically characteristics (stones with colors ranging from white, pale yellow to light brown) and high purity, ranging from 50% to 85% (mean 73%), most of samples (57%) was 'not oxidized' cocaine, which means coca paste [11].

The present study was to contribute to the current knowledge of the composition of 404 cocaine samples in base form and to analyze the smoke of cocaine samples seized as crack by the police of São Paulo between March 2008 and November 2009.

2. Materials and methods

Samples were taken randomly from seizures in the metropolitan region of São Paulo, State of São Paulo, Brazil, and suspected to be crack cocaine by the Drug Analysis Laboratory of the Institute of Criminology of São Paulo. Sample collection ($N = 404$) was performed between March 2008 and November 2009. They were classified by macroscopic characteristics, such as color, form, odor, purity, and adulterant type, as well as smoke composition.

The samples were screened for cocaine using the modified Scott test that consists in colorimetric reactions. Initially, a solution of cobalt thiocyanate is added and a blue precipitate is observed. In a second step, hydrochloric acid 1 M is added and the blue

Fig. 2. Samples identified as crack cocaine by police authority (São Paulo, SP, Brazil).

Table 1
Frequency distribution according to color and oiliness from the collection of samples.

Color	Oiliness					
	N°		Yes		Total	
	n	%	*n*	%	*n*	%
Yellow	220	73.6	79	26.4	299	74.0
White	68	84.0	13	16.0	81	20.0
Brown	10	47.6	11	52.4	21	5.2
Orange	1	100.0	0	0.0	1	0.2
Purple	1	100.0	0	0.0	1	0.2
Red	1	100.0	0	0.0	1	0.2
Total	301	74.5	103	25.5	404	100.0

precipitate persistence indicates positivity for cocaine [14]. Screening also included thin-layer chromatographic (TLC) with silica gel 60 plates (Merck) and toluene:acetone:ethanol:25% ammonia as mobile phase and platinum iodine reagent as chromogenic reagent [15–17]. Identification and quantification of cocaine and adulterants were performed with gas chromatography (Shimadzu gas chromatograph GC-2010 model), equipped with 6-port gas sampling valve and a flame ionization detector (GC-FID), a 60 m × 250 μm i.d. DB-1 capillary column with a film thickness of 0.25 μm, hydrogen as carrier gas with a flow rate of 2 mL/min, split injection 1:50 at 250 °C, and a 1 μL injection volume. The temperature program was 180 °C for 3 min, then 10 °C/min to 280 °C, then hold 5 min. The FID temperature was 300 °C. After weighing, samples were pulverized and diluted with ethanol to 0.5 mg/mL and analyzed with GC-FID. Smoke composition was analyzed by burning 10 mg of samples ($N = 6$). Choice of samples occurred in function of three characteristics: color, odor, and purity level. Two samples of each color (white, yellow and brown) were chosen. The criteria to choose odor was one sample of each color that possessed organic solvent smell or not. In regards to purity one of the samples present high purity level and other low purity, and finally one sample containing adulterants (caffeine and lidocaine) and other not. Samples were placed in an adapted burner (Fig. 1). The smoke was homogenized with a gas-tight syringe and injected (100 μL) in a GC–MS system that consisted of a Shimadzu gas chromatography 17-A model and quadrupole mass-selective detector QP5050 model, full scan mode. The survey was conducted by tracking the chromatograms peaks. These peaks were compared to the NIST library, an analysis directed to the search of possible contaminants and burning of product samples. The chromatographic conditions were the same of GC-FID analysis.

Table 2
Frequency distribution according to color and odor.

Color	Odor							
	Odorless		Solvent		Solvent and ammonia		Total	
	n	%	*n*	%	n	%	*n*	%
Yellow	11	3.7	282	94.3	6	2.0	299	74.0
White	3	3.7	73	90.1	5	6.2	81	20.0
Brown	0	0.0	17	81.0	4	19.0	21	5.2
Orange	1	100.0	0	0.0	0	0.0	1	0.2
Purple	0	0.0	1	100.0	0	0.0	1	0.2
Red	0	0.0	1	100.0	0	0.0	1	0.2
Total	15	3.7	374	92.6	15	3.7	404	100.0

3. Results

Samples showed different colors and forms (rock, paste, and crumbs) (Fig. 2). Most samples were yellow (74.0%) or white (20.0%) (Table 1), while 92.6% of the samples presented organic solvents' odor (Table 2). Odor criteria for the differentiation of each sample was carried through common sensorial analysis. Most samples (76.3%) were free of adulterants. Cocaine mean purity was 71.3% (SD ± 21.4), and adulterants as benzocaine, lidocaine, caffeine and procaine were found, while many samples (14.6%) contained adulterants not identified by our analytical method (Table 3). It was not observed correlation between colors and drug purity.

Smoke analysis evidenced the presence of cocaine, lidocaine, caffeine, butadienylacetylene, 1,5-hexadiyne, naphthalene, biphenyl, pyridine, 1,3,5,7-cyclooctatetraene, benzonitrila, benzene, and ammonium benzoate.

4. Discussion

Macroscopic characterization was performed for all samples and showed the predominance of yellow samples with organic solvent odor. Samples color was not associated with drug purity, as regarded by addicts, who usually link drug color with its purity [8]. Odor has not been described by previous reports on crack cocaine, which could be justified as a remaining solvent from the extraction process.

The determination of cocaine content, adulterants and diluents in seizure samples is not only of clinical value, but also important for judicial and police authorities to know traffic dynamics [18]. The results show high cocaine content (mean = 71.3%, SD = 21,3%) and most samples (76.3%) were free of adulterants, in contrast to the results of several authors [19–22]. The most likely explanation for this discrepancy is that samples analyzed in this study do not fit the classical definition of crack cocaine (obtained by cocaine salts), but can be characterized as a cocaine base or coca paste with no adulterants and with traces of organic solvents as showed by Silva Junior et al. (2012), in a study made with cocaine denominated 'oxy', in Acre State, Brazil, Peruvian and Bolivian border [11]. The few adulterated samples showed composition similar to cocaine salts seized ($N = 389$) in São Paulo in 1997, in which mean purity was 37.5% [23]. Table 4 shows the comparison of our samples with other studies. Our data suggest that samples are not obtained from cocaine salts. Crack seized in São Paulo most likely enters the country in the form of coca paste. The presence of pyrolisis products from diesel and gasoline, such as naphthalene, benzene, and some alkanes support our inference, thus gasoline and diesel products are used in the very early extraction process during pasta base production in source countries.

In conclusion, the drug marketed as crack cocaine in São Paulo City has similar characteristics to coca paste. The high purity presents a greater risk of dependency and contaminants from

Table 3
Composition of samples seized between 2008 and 2009 in São Paulo.

	n	Mean conc. (%)	SD	Min. conc. (%)	Max. conc. (%)
Cocaine	403	71.3	21.4	0.1	99.7
Lidocaine	25	0.7	2.5	0.6	32.6
Benzocaine	19	0.6	3.7	2.8	47.5
Caffeine	22	0.4	4.4	0.9	45.5
Procaine	9	0.02	0.1	0.6	1.8

n: number of samples in which the substance has been detected; mean conc.: mean concentration; SD: standard deviation; min conc.: minimum concentration; max conc: maximum concentration.

Table 4
Comparison of seized drug composition with previous studies (mean of percents).

Contend	Crack (N = 404)		Silva Junior et al. (2012) Crack/Oxy (N = 23)		Carvalho and Midio (2008) Cocaine salt (N = 389)		Evrard et al. (2010) Cocaine salt (N = 343)		Schneider and Meys (2011) Cocaine salt (N = 471)	
	F	Mean ± SD	F	Mean ± SD	F	Mean	F	Mean	F	Mean ± SD
Cocaine	403	71.3 ± 21.4	23	72.74 ± 9.17	389	70	343	22	471	50.6 ± 20.6
Lidocaine	25	0.7 ± 2.5	–	–	12	3.2	36	11	128	1.9 ± 4.4
Benzocaine	19	0.6 ± 3.7	–	–	–	–	–	–	2	7.5 ± 0.8
Caffeine	22	0.4 ± 4.4	–	–	2	0.53	62	17	81	5.1 ± 11.1
Procaine	9	0.02 ± 0.1	–	–	20	4.9	–	–	22	3.1 ± 2.9
Phenacetin	–	–	5	3.8 ± 3.94	–	–	184	54	293	24.4 ± 19.6
Levamizole	–	–	–		–	–	–	–	246	3.3 ± 3.3

SD: standard deviation ; F: frequency.

solvents and other chemicals in smoke compounds are possibly worsening health impact.

Conflict of interest

The authors declare no conflicting interests in this research and its publication.

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