Cocaine Trafficking in Asphalt Material: An Unusual Report of Cocaine in Seized Drugs

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Cocaine is an illicit drug commonly found by law enforcement in seizures around the world. This paper describes a rare case of cocaine trafficking in asphaltic material, possibly in the form of cocaine hydrochloride. The material was found and seized in barrels during an operation conducted by the Brazilian Federal Police. The sample was initially extracted and resulted negative for cocaine via Scott’s Test, but further screening by gas chromatography coupled with mass spectrometry (GC-MS) confirmed the presence of cocaine. Afterwards, samples were subjected to quantitative GC-MS analysis. The concentrations of cocaine ranged from 0.11 to 1.53 ng/10 mg in the extracts of precipitate material found in the barrels. Considering that extraction efficiency was around 57.44%, it is estimated that 1.07 – 15.34% of barrel’s sediment weight was constituted by cocaine.

Keywords: cocaine, seized drugs, drug trafficking, GC-MS, forensic chemistry

INTRODUCTION
Cocaine is an illicit drug with high potential to cause addiction, presenting several harmful effects on human health and well-being. Despite the danger it poses, it is estimated that 20 million people worldwide used cocaine in 2019.1 In 2019, global seizures of cocaine increased by 9.6% in comparison to 2018, with
a total of 1,436 tons of cocaine being seized worldwide.\textsuperscript{2} South America is the region where the majority of cocaine is seized, accounting for 755 tons of cocaine in 2019.\textsuperscript{2} Regarding its production, there is a tendency towards the stabilization of cocaine’s manufacture.\textsuperscript{2} Data on prevalence and trends concerning drug use, combined with information on trafficking modalities and routes, is useful to assess the global market and to develop actions to prevent and reprimand trafficking.

One of the main challenges of detecting cocaine trafficking in seized materials is when the drug is concealed in another medium or material. In the case of cocaine, it has been reported the occurrence of cocaine in dark materials, the so-called “black cocaine”.\textsuperscript{3,4} Drug smugglers combine cocaine in the form of freebase or salt with dark materials to hinder the detection of the drug during law enforcement inspections.\textsuperscript{3} Consequently, presumptive testing for cocaine using in these dark materials, using colorimetric tests such as Scott’s Test, often provide a false-negative result.\textsuperscript{3,4}

Cocaine has been found and reported in several types of dark powders such as in toner cartridges for printers, industrial dyes and plastic materials.\textsuperscript{3} However, it seems that this occurrence of “black cocaine” is more common in the form of dark powders, hidden in other materials, whereas the occurrence of cocaine in non-powder dark materials is not usually common. This work presents an unusual case report, describing the seizure of a material similar to asphalt in Brazil, which masked the presence of cocaine as hydrochloride – a non-predominant form of cocaine for trafficking across the South America borders. The use of asphalt-like materials to hide cocaine is very uncommon; asphalt has been only reported in Colombia (trafficked to the Netherlands)\textsuperscript{5} and Canada\textsuperscript{6}. However, in the literature, to the best of our knowledge, there are no published reports on the chemical analysis of cocaine in asphalt material and this is the first report of occurrence of cocaine in asphalt in Brazil.

CASE HISTORY

This case was the result of the Brazilian Federal Police operation called “Operação Betume”, which dismantled a criminal organization with connections in the Triple Border region between Brazil, Peru and Colombia and responsible for trafficking drugs to Europe, Asia, Africa and Oceania.

On October 13, 2016, in the city of Belém (PA, Brazil), Federal Criminal Experts investigated a rental shed dedicated to the storage of several products and goods (Figure 1). In this shed were found 232 metallic barrels with capacity of approximately 200 L each, labeled as “waterproofing material” (Figure 2). All the barrels found in the shed were sampled and 30 barrels were randomly opened and inspected. Inside the barrels, a viscous, dark color liquid was found (Figure 3). The material exhibited a diesel oil-like appearance and smell, consistent with the appearance of an asphalt-waterproofing agent. In six out of the 30 barrels examined, a precipitated material, in the form of a pasty and dark-color mass, similar to grease, and with a characteristic odor of cocaine base paste was found.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure1.jpg}
\caption{Figure 1. View of the shed: barrels at the bottom of the shed, woodwork in the center and wheat covered with black canvas on the left. Source: Brazilian Federal Police Report.}
\end{figure}
The samples were subjected to preliminary examinations at the Renato Chaves Scientific Expertise Center in Belém and sent for confirmatory and quantitative analyses at the Laboratory of Forensic Toxicological Analyses of the Department of Chemistry, in the Faculty of Philosophy, Sciences and Letters of Ribeirão Preto, at the University of São Paulo (FFCLRP-USP).

![Figure 2. Barrels found in the shed, where the asphalt material was collected. Source: Brazilian Federal Police Report.](image)

![Figure 3. Viscous, dark color liquid samples collected from the barrels. Source: Brazilian Federal Police Report.](image)

**MATERIALS AND METHODS**

**Materials**

Cocaine, and cocaine-d₃ were purchased from Cerilliant (Round Rock, TX, USA). Lidocaine, cotinine and HPLC grade ethyl acetate were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ammonium hydroxide was purchased from Mallinckrodt (Staines-Upon-Thames, Surrey, UK).

**Preliminary analyses**

Assuming that the cocaine present in the samples collected from the barrels was in the form of freebase, hydrochloric acid and methanol were added to the black paste precipitate obtained after filtration of the asphalt material. After this procedure, the Scott’s Test was performed on this precipitate. Then, qualitative analysis of the material was carried out using gas chromatography coupled with mass spectrometry (GC-MS).
Sample preparation

For quantitative analysis of cocaine in the seized material, five samples of the sediment material were collected from the content of different barrels and subjected to extraction and analysis. In preliminary tests, it was found that the cocaine present in the seized material was predominantly in the salt form and not as freebase. Thus, the extraction method consisted of extracting cocaine in two steps. In the first step, 10 mg of the sample were weighed and inserted into a microcentrifuge tube. Then, 1 mL of deionized water was added to the content. Next, the sample was subjected to agitation in vortex for 30 s and sonicated for 20 min. Subsequently, 10 µL of the aqueous phase were collected and transferred to a glass tube, followed by the addition of 90 µL of 30% ammonium hydroxide solution and 1 mL of ethyl acetate. The tubes were subjected to agitation for 15 min at 210 rpm and subsequently centrifuged for 5 min at 2000 rpm. After centrifugation, an aliquot of 10 µL of the supernatant was transferred to a clean glass tube, containing 100 ng of isotope labeled cocaine-d₃ (internal standard, ISTD) in methanolic solution. The content of the tubes was subjected to evaporation under nitrogen flow at 40 °C. After evaporation, the extract was reconstituted with 100 µL of ethyl acetate and subjected to GC-MS analysis. The remaining supernatant was collected and subjected to Scott’s Test, to evaluate the possible presence of cocaine in this aliquot. On the contrary to the first test approach, this latter gave a positive result.

GC-MS analysis

Confirmatory analyses were performed using an Agilent 7890A gas chromatograph coupled to an Agilent 5975C single quadrupole mass spectrometer (Agilent Technologies®, Santa Clara, CA, USA), operating in electron ionization mode. The chromatographic separation was performed in a HP-5MS (30 m x 250 µm; 0.25 µm) capillary chromatographic column (Agilent Technologies®, Santa Clara, CA, USA). The injector temperature was 280 °C. The initial oven temperature was 90 °C (held 1 min), ramped to 300 °C at a 15 °C/min rate, remaining at this temperature for 5 min. Helium 6.0 was used as the carrier gas, at a flow rate of 1 mL/min. Temperatures of transfer line, source and quadrupole were kept at 280, 230 and 150 °C, respectively. MS analysis operated in single ion monitoring (SIM) mode. The following ions were monitored for cocaine: m/z 82 (quantifier), 182 and 303. For the ISTD (cocaine-d₃), m/z 85 (quantifier), 185 and 306 were evaluated.

Quantitative analyses

In order to calculate the concentration of cocaine in the samples, an analytical curve was constructed using a surrogate (blank) sample: Neutrol asphalt paint (Vedacit®, São Paulo, SP, Brazil), a product similar to the real samples, also used as a waterproofing material. Method’s limit of quantitation (LLOQ) was defined as the lowest concentration of analyte which could be determined with an accuracy and precision of at least 20%. The following cocaine concentration levels were aimed: 10, 100, 150, 500, 750 and 1000 ng/10 mg of raw sample. Whereas, ISTD was consistently spiked at concentration of 100 ng/10 mg. The calibrators were prepared in triplicate, by spiking aliquots of the standard solutions to the asphalt paint only after it was submitted to the extraction, this because spiking prior extraction would imply in the addition of a large quantity of reference materials (which are only available as 1 mg mL⁻¹ certified standards). For this reason, the efficiency of the extraction method should be estimated and considered for the determination of cocaine concentrations in raw samples. At this stage, lidocaine was used as a surrogate for cocaine, due to their similar physicochemical properties, and once solid standard of lidocaine salt is commercially available in larger quantities. Blank samples were fortified before and after the extraction procedure with lidocaine in amount equivalent to the dilution factor (100 times) used in the procedure for extraction of cocaine from the samples. The fortification with an internal standard (in this stage, cotinine) occurred before extraction in both cases. The assays for determination of extraction recovery were performed in triplicate. The area ratios obtained in the two procedures were compared (pre- and post-extraction fortification) in order to calculate, in terms of percentage, the recovery of the used extraction method. The calculation considered the fortification in the final stage as equivalent to an extraction with recovery of 100%. Thus, the value obtained by the analytical curve was corrected by the extraction efficiency and the dilution factor (100 times).
RESULTS AND DISCUSSIONS

As result from preliminary analysis, after treating the black precipitate with HCl and methanol, a light-colored crust was formed on the borders of the glass beaker, which contained the precipitate. Subsequently, Scott’s Test was performed and indicated negative results. The mentioned precipitate was subjected to a simple extraction with methanol, followed by a qualitative GC-MS analysis. This confirmatory analytical exam indicated the presence of cocaine. Following these preliminary analyses, quantitative determinations were performed using Vedacit®. The blank chromatogram from the Vedacit® analysis and a sample of Vedacit® spiked with 10 ng of cocaine and 100 ng of ISTD are presented in Figure 4. The built analytical curve ranged from 10 to 1000 ng of cocaine per 10 mg of sample. Linear regression was used to obtain the intercept, slope and determination coefficient (R²), equal to -0.0127, 0.0103 and 0.995, respectively. The statistical analysis of the analytical curve was performed to assess the suitability of calibration equations for this dataset (ANOVA, F = 5934.08, p = 3.80×10⁻³⁴). This range is lower than the concentration found in the sample; however, it must be considered that the extract obtained from the samples exhibits a reduced concentration when compared with the original sample, due to the dilution factor and the extraction efficiency lower than 100%. The average extraction efficiency of the method was determined as 57.44%. The intraday precision and accuracy for the LLOQ for cocaine were 12.5% and 13.2%, respectively.

![Figure 4](image-url)

**Figure 4.** Aligned chromatograms obtained for the analysis of (A) a blank sample of Vedacit® and (B) a sample of Vedacit® spiked with 10 ng of cocaine and 100 ng of ISTD. The arrow indicates the analyte peak.

Without considering the correction factors, the concentration of cocaine in sediment ranged from 0.11 to 1.53 mg per 10 mg of sample, resulting in a cocaine percentage of 1.07% to 15.34% in the sample. The results of cocaine quantitation in the asphalt material are described in Table I.
Table I. Amount of cocaine present in the sediment samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Amount of cocaine in 10 mg of the sample</th>
<th>ng*</th>
<th>mg**</th>
<th>% in sample**</th>
<th>SD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment #1</td>
<td>221.73</td>
<td>1.27</td>
<td>12.74</td>
<td>5.51</td>
<td></td>
</tr>
<tr>
<td>Sediment #2</td>
<td>198.19</td>
<td>1.14</td>
<td>11.38</td>
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</tr>
<tr>
<td>Sediment #3</td>
<td>267.11</td>
<td>1.53</td>
<td>15.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sediment #4</td>
<td>213.60</td>
<td>1.23</td>
<td>12.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sediment #5</td>
<td>18.67</td>
<td>0.11</td>
<td>1.07</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Without correction *: value obtained by the analytical curve.
With correction **: value based on the analytical curve applying the extraction efficiency (57.44%) and the dilution factor (100 times).

Extracted ion chromatograms (EICs) and mass spectrum of a sediment sample at 13.79 min (cocaine retention time) are presented in Figures 5 and 6, respectively. It can be noticed the presence of all ions which characterize cocaine mass spectrum.

Figure 5. EICs for m/z 82, 182 and 303, from the analysis of sediment sample #1.
The quantification results suggested that cocaine is present in its salt form in the asphalt material, since cocaine hydrochloride tends to form a precipitate in a non-aqueous medium. In addition, this trafficking product was likely intended to be distributed to countries of final destination (in Europe, Asia, Africa and Oceania), which may have laboratories designed for a secondary extraction of cocaine incorporated in other substances for trafficking. It is also important to highlight that although the occurrence of cocaine in asphalitic material is very uncommon, a recent report from Canada was released in 2015, one year before the occurrence of this case in Brazil, which could suggest potential trends of cocaine trafficking in organized crime networks.

Regarding the Scott’s Test, preliminary tests resulted negative for cocaine when the sample was subjected to acidification and extraction with methanol. However, further tests yielded positive when subjecting the sample to alkaline pH and subsequent extraction in ethyl acetate. This result suggests that the recovery of cocaine in organic solvent, as described after the alkaline pH and agitation procedure, prevents the action of interfering agents that must act in the kinetics of the Scott Test reaction.

CONCLUSIONS
This study reports an unusual case of cocaine trafficking, using asphalitic material as a vehicle to hinder the detection of cocaine. In contrast to other seized materials (such as powders or capsules), this matrix is very difficult to analyze and its chemical composition appears to present a major source of interferers, responsible for hampering the results of preliminary tests. This case reiterates the importance of performing proper sample preparation prior to the analysis, especially when dealing with complex samples. Additionally, this case highlights the role of thorough investigation on a potential crime scene, considering that some materials might not be easily identified as sources or concealments of illicit drugs. After a suitable sample preparation, GC-MS analysis allowed us to identify and to quantify cocaine in asphalitic material. The results revealed that up to 15% of barrels’ sediment weight was composed by cocaine in the form of hydrochloride salt. Furthermore, this work is the first known report of the occurrence of cocaine in asphalitic materials in Brazil. Considering that many routes of cocaine trafficking are linked to South America, this report provides important information on an alternative way of cocaine trafficking in asphalt, which can be useful for national and international investigations.
Conflicts of interest
The authors declare no conflicts of interest.

REFERENCES