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Changes in illicit cocaine hydrochloride processing identified and revealed through multivariate analysis of cocaine signature data

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ABSTRACT

For nearly 30 years, the methods utilized in illicit cocaine hydrochloride production have remained relatively consistent. Cocaine hydrochloride is typically produced one kilogram at a time. As a result, each individual kilogram is unique and distinct from other kilograms in any particular seizure based on the total alkaloid profile, occluded solvent profile, and isotopic signature. Additionally, multi-kilogram cocaine seizures are often comprised of cocaine from several different coca growing regions. There has been a documented shift in this type of processing based on the recent analysis of a large cocaine seizure in the Eastern Pacific. Signature analyses of samples from 21 kg randomly selected from a 517 kg seizure were virtually identical. Triplicate analyses of each sample via gas chromatography with flame ionization detection, static headspace gas chromatography mass spectrometry, and isotope ratio mass spectrometry were completed. An initial outlier evaluation of the data and an in-depth univariate analysis indicated there was no statistically significant difference among the 21 samples at the 95% confidence interval. Principal components analysis did reveal consistent minor deviations between the samples and known authentic data from the Nariño coca growing region of Colombia. These deviations were only observed on the latter principal components and could be explained by differences in solvent selection during cocaine hydrochloride processing. Chemical analyses in addition to a thorough statistical evaluation suggest a shift in the traditional small-batch method of cocaine processing to a multi-kilogram, high throughput approach.

1. Introduction

Illicit cocaine hydrochloride has maintained a presence in the United States drug market for decades [1–3]. The manner in which cocaine is produced has remained fairly consistent. Modifications have been made at times to make the process more efficient; however, the general methodology has always been the same. Cocaine base is extracted from coca leaf through several steps relying on acid/base chemistry. The cocaine base is then often oxidized with potassium permanganate to remove alkaloids that are co-extracted with cocaine, i.e., the cinnamoylcocaines. Cocaine base is then converted to cocaine hydrochloride via the use of hydrochloric acid and a variety of carrier solvents. From start to finish, each step has traditionally occurred on the kilogram scale [4].

The United States Drug Enforcement Administration's (DEA) Cocaine Signature Program (CSP) has monitored the state of illicit cocaine processing for over twenty years. The development of the program and its methods has been well documented in the scientific literature through dozens of publications. The program identifies and tracks processing trends and changes, as well as the origin of the cocaine base utilized to produce cocaine hydrochloride. The CSP's data has always been in agreement with the single kilogram processing scheme. Each kilogram has a unique signature that is comprised of the purity of cocaine, the presence or absence of adulterants/diluents, total coca alkaloid content, level of oxidation, cocaine hydrochloride conversion profile, as well as the cocaine base origin [5–6]. It is rare to identify two kilograms that are exactly the same; there are typically differences in at least one part of the entire cocaine signature. The CSP routinely analyzes cocaine hydrochloride that was part of what are often very large seizures, i.e., multi-tons. Samples from these seizures further illustrate the variety of kilograms that comprise large trafficking shipments destined for the United States. Seizures of this scale rarely contain cocaine hydrochloride produced from cocaine base originating from only one coca growing region in South America. Rather, the shipments often contain cocaine originating from several regions that are often not geographically close to one another; this is due to cocaine base trafficking routes throughout South America.

Recently, and for the first time, the CSP received samples from a

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large seizure that were virtually identical in all aspects of the cocaine signature. This particular sample set was re-analyzed in triplicate, and one additional analytical method was introduced that has never previously been implemented by the CSP. The use of a static headspace gas chromatograph coupled to an isotope ratio mass spectrometer (HS-GCC-IRMS) provided even further evidence of large scale processing. All of the data were subjected to several statistical outlier evaluations to validate the findings and conclusions.

2. Materials and methods

2.1. Materials

All chemicals and solvents used were reagent grade or better and were obtained from Sigma-Aldrich (St. Louis, MO). Internal standards for quantitation and trace alkaloid analyses were prepared in-house and stored at 7 °C prior to use. Internal standard solutions required for headspace analysis were stored at − 10 °C prior to use. All solutions were allowed to warm to room temperature prior to use. Cocaine base used for isotope calibrations was obtained from this laboratory's reference collection.

2.2. Illicit cocaine seizure

The cocaine hydrochloride analyzed was seized by the United States Coast Guard (USCG). In June 2015, a maritime vessel was detected in the Eastern Pacific traveling at high speeds. Subsequently, the vessel was intercepted, and 517 kg of cocaine hydrochloride was recovered. Twenty one, one gram samples from separate randomly selected kilogram bricks were submitted to this laboratory for full signature analysis. The samples were stored under ambient conditions prior to analyses.

2.3. Cocaine signature analyses

2.3.1. Cocaine quantitation

Each of the 21 samples were analyzed in triplicate (N = 63). The samples were quantitated before completing any further alkaloid analyses or isotopic analyses. Samples were quantitated via gas chromatography with flame ionization detection (GC/FID) with an Agilent (Palo Alto, CA) 7890A chromatograph fitted with a 30 m × 0.25 mm ID fused-silica capillary column coated with 0.25 μm DB-1 (Agilent). The instrument was operated in split mode (25:1). Samples were prepared by diluting with 5 mL of 0.9 mg/mL solution of isopropylcocaine in chloroform followed by 25 mL of chloroform with diethylamine [7]. The cocaine concentration was approximately 0.8 mg/mL for each sample.

2.3.2. Trace alkaloid determinations

Trace alkaloid determinations were performed on an Agilent 7890A GC/FID fitted with a 30 m × 0.25 mm ID fused-silica capillary column coated with 0.25 μm DB-1701 (Agilent). The instrument was operated in split mode (50:1) for tropacocaine, trimethoxycocaine, and cinnamoylcocaine analyses, while the truxilline analyses were completed in splitless mode. Samples were prepared for determination of the relative amounts of tropacocaine, trimethoxycocaine, and cinnamoylcocaines by dilution with *para*-fluorococaine in chloroform (0.2 mg/mL) and derivatized with *N*-methyl-*N*-(trimethysilyl)-trifluoroacetamide (MSTFA). Hydrolysis products were also determined utilizing this method. The cocaine concentration was approximately 10 mg/mL for each sample [8].

Samples were prepared for truxilline analyses after a complex extraction and derivatization procedure. The entire procedure has been previously reported [9]. The internal standard used for the quantitation of truxillines was 4′-4″-dimethyl-α-truxillic acid dimethyl ester. During the procedure, cocaine is reduced and completely removed from the sample matrix (prior to derivatization with heptafluorobutyric anhydride (HFBA)) via acid extraction and solvent evaporation.

2.3.3. Occluded solvent analysis via HS-GC–MS

The amounts of occluded solvents were measured on an Agilent G1888 Network Headspace Sampler. The headspace was attached to an Agilent 5975C gas chromatograph fitted with a 60 m × 0.25 mm ID fused silica capillary column coated with 0.25 μm DB-1 (Agilent). All of the operating conditions have been previously described [10–11]. Each sample was prepared by adding 5 mL of sodium sulfate solution containing internal standard.

2.3.4. Purification of cocaine samples for isotope analyses

Prior to isotope analyses, each sample was purified via high performance liquid chromatography (HPLC) on an Agilent 1200 Series Preparative Liquid Chromatograph with a 1000 μL loop, preparative pump, thermostatted column compartment, and fraction collector. The HPLC was fitted with a silica column, Agilent Zorbax RX-SIL 4.6 mm ID × 100 mm with a 1.8 μm particle size. The elution gradient conditions have been previously described [12]. The collected pure cocaine fractions were dried at 75 °C under a stream of air and transferred to a 4 mL glass vial using diethyl ether. The diethyl ether was then evaporated to obtain pure cocaine base powder.

2.3.5. Isotope Ratio Mass Spectometry (IRMS) of cocaine and occluded solvents in cocaine

Carbon and nitrogen isotope ratio analyses of cocaine were determined using an elemental analyzer (EA) (Costech Analytical Technologies Inc., Valencia, CA) interfaced with a Delta Plus XP isotope ratio mass spectrometer (Thermo Fisher Scientific Inc., Bremen, Germany). Typically, 0.9–1.2 mg of cocaine was weighed into a tin capsule (Costech Analytical Technologies Inc.) and introduced into the EA using a Costech Zero-Blank autosampler. The EA reactor tubes were comprised of two quartz glass tubes filled with chromium (III) oxide/silvered cobaltous oxide and reduced copper, held at 1040 °C and 640 °C for combustion and reduction, respectively. A trap filled with magnesium perchlorate was used to remove water from generated combustion gases, and a post-reactor GC column was maintained at 65 °C for separation of evolved N_2 and CO_2. Helium was used as the carrier gas, and the system head pressure was adjusted to achieve a measured flow of 90 mL/min. Data was acquired and processed using ISODAT 3.0 software for all isotope analyses.

EA normalization and quality control materials consisted of internally calibrated atropine (TCI, St. Louis, Missouri) and cocaine base. Sample sequences were bracketed by an internally calibrated atropine secondary standard, typically at intervals of one standard every seven samples. The atropine and cocaine secondary standards were calibrated to primary isotopic standard materials IAEA-N-1, IAEA-N-2, LSVEC and NBS-19 and corresponding scale normalized isotope values are expressed as $\delta^{13}C_{VPDB\text{-}LSVEC}$ for carbon and $\delta^{15}N_{AIR}$ for nitrogen. System reproducibility was consistently 0.1‰ and 0.2‰ or better for all EA-IRMS $\delta^{13}C$ and $\delta^{15}N$ measurements, respectively.

Hydrogen and oxygen isotope ratio analyses of cocaine were determined using a thermo-chemical elemental analyzer (TCEA) interfaced with a Delta V isotope ratio mass spectrometer (Thermo Fisher Scientific Inc.). For TCEA-IRMS analyses, approximately 0.20 to 0.25 mg of purified cocaine was accurately weighed into silver capsules and introduced into the TCEA using a Costech Zero-Blank isolated autosampler. The capsules were pyrolyzed in the TCEA-IRMS system into H_2, CO, and C by passing through a ceramic reactor filled with a glassy