

Contents lists available at ScienceDirect

Forensic Science International



journal homepage: www.elsevier.com/locate/forsciint

The isotopic fractionation of carbon, nitrogen, hydrogen, and oxygen during illicit production of cocaine base in South America



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ARTICLE INFO

ABSTRACT

Article history: Received 25 April 2016 Received in revised form 13 September 2016 Accepted 18 October 2016 Available online 25 October 2016

Keywords: Cocaine Isotope ratio mass spectrometry Stable isotopes Fractionation Geosourcing Stable isotope measurements have become a key component in sourcing the origin of illicit cocaine seized within the United States. Therefore, it is imperative to understand the process by which isotopes may be fractionated during illicit cocaine processing. In a controlled observational study, there was apparent isotopic fractionation of carbon, nitrogen, hydrogen, and oxygen. To investigate the potential source of the fractionation, cocaine base was fractionally precipitated from a dilute sulfuric acid solution with dilute ammonium hydroxide. The values of δ^{13} C, δ^{15} N, δ^{2} H, and δ^{18} O for each fraction were measured by isotope ratio mass spectrometry (IRMS). There was an equilibrium fractionation observed in all measured stable isotopes. Early fractions were depleted, and later fractions were enriched, with ¹⁵N and ²H being the most affected. The described trend is opposite of the Rayleigh distillation observed for cocaine hydrochloride precipitation.

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1. Introduction

Isotope ratio mass spectrometry (IRMS) is a popular instrumental technique utilized in many areas of research, including plant biosynthesis, climate reconstruction, and geosourcing of natural products such as emeralds and coffee [1,2]. In forensic science, isotope measurements are routinely utilized for murder investigations, tracing the manufacturers of explosives, and determining the geographical origin of illicit drugs [3–5]. Recently, stable isotopic analyses were implemented to aid in the characterization and sourcing of illicit cocaine as belonging to one of 19 known coca growing regions in South America [6].

Cocaine is a natural alkaloid found in coca leaf. The stable isotopes present in cocaine (¹³C, ¹⁵N, ²H, and ¹⁸O) are incorporated through biosynthesis and are indicative of the environment in which the coca plant was grown. Cocaine is isotopically lighter than the coca leaf itself due to fractionation mechanisms during biosynthesis [7–11]. Additionally, the processing and purification of cocaine fractionates the stable isotopes incorporated into the cocaine molecule. The degree of fractionation of carbon and nitrogen isotopes during production of cocaine hydrochloride

from cocaine base was previously explored by Casale et al. [12]. That study showed the precipitation of cocaine hydrochloride follows the classic description of a Rayleigh fractionation. Isotopes were continually depleted as cocaine hydrochloride was precipitated from a solution containing cocaine base. Rayleigh fractionations most commonly refer to open chemical systems in which isotopes partition between two reservoirs as one reservoir decreases in size. Ideally, the system is in isotopic and thermodynamic equilibrium. It is suspected an equilibrium fractionation of this manner also occurs during the extraction and purification of cocaine base from coca leaf; to date, however, this has not been fully investigated.

The process by which illicit cocaine base is extracted from coca leaf varies across South America, but the basic methodology has changed very little over the past twenty years [13]. The consistency and continuity in illicit coca leaf processing has allowed for the full characterization of alkaloid content and isotopic incorporation in cocaine [6,11,14–16]. The information obtained through years of study is extremely valuable to determining the origin of illicit cocaine samples. Any significant changes in processing techniques are apparent upon analysis with these techniques, and continued observational studies keep track of any active processing changes. In the most recent controlled study, isotopic differences were noted in comparison to previous and expected results. The presented work was intended to address these differences and fully investigate the observed isotopic fractionation.

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2. Materials and methods

2.1. Materials

Authentic cocaine base was obtained from Peru. Atropine, C-28, and C-34 (TCI America, St. Louis, MO) were utilized as secondary isotopic internal standards during isotope ratio analyses. All chemicals and solvents used for the controlled laboratory study were reagent grade or better and did not require further purification. Coca leaf was obtained from Colombia for the controlled observational study.

2.2. Illicit production of cocaine base from coca leaf

Twelve cocaine processors with varying degrees of experience/ expertise were given approximately 100 kg of fresh coca leaf to extract cocaine base in a controlled setting. The processors produced individual batches of cocaine base of varying weights. Percent recoveries are listed in Table 1. Representative samples of coca leaf and cocaine base were obtained for purification and subsequent IRMS analyses.

In general, cocaine base throughout the Andean Ridge is processed from coca leaf by the same method. Approximately 100 kg of fresh coca leaf are shredded to a fine powder and then covered with a mixture of basic chemicals such as concrete. lime. or urea. A small amount of water is usually added, and the leaf is mixed thoroughly. The leaf is then soaked in approximately 100 L of gasoline in 55-gallon metal drums for at least one hour. After sufficient time for extraction is allowed, the gasoline is drained and mixed with a solution of dilute H₂SO₄. After the layers have separated, the acid solution is then removed from the gasoline. Cocaine base is then precipitated from the acidic solution with basic chemicals such as sodium carbonate or NH₄OH. At this stage, clandestine processors may choose to discard the initial cocaine precipitate, as it is brown and gummy in texture, before precipitating the remainder of the cocaine base. After precipitation is complete, the cocaine base is captured by gravity filtration and dried.

2.3. High performance liquid chromatography (HPLC)

Cocaine base samples prepared by the clandestine processors were purified by HPLC prior to isotopic analyses as previously described [17]. The collected fractions were dried at 75 °C under a stream of air and transferred to a 4 mL glass vial using a minimal amount of diethyl ether, which was then evaporated to obtain cocaine base powder.

2.4. Isolation of cocaine from bulk coca leaf used in observational study

Although this process was completed in a controlled laboratory setting, the chemical extraction is identical to that utilized by the 12 processors during their cocaine processing. The isolation of cocaine and trace alkaloids was accomplished using modified trap column methodology originally utilized by Moore et al. [18]. The entire procedure was recently described for the characterization of various coca cultigens from Colombia [15].

The extracted cocaine was diluted with dichloromethane and utilized to prepare a sample suitable for isotopic analyses. Approximately 8 mL (or 50 mg equivalents of cocaine) of the cocaine solution were dried down in a centrifuge tube. The remaining oil was reconstituted in approximately 1 mL of chloroform. The cocaine extract was then purified with a chromatographic column prepared with 10.0 g of basic aluminum oxide containing 4.0% water. Additional chloroform was added to the column, and the first 10 mL of the eluate were collected. The eluate was dried under nitrogen and then quantitatively transferred to a 4 mL vial with ether. The ether was evaporated at 75 °C leaving a white powder. The resulting cocaine base powder was accurately weighed in preparation for isotopic analyses.

2.5. Fractional precipitation of cocaine base (control)

Approximately 300 g of cocaine base was dissolved completely in 3.3L of water containing 35 mL of concentrated H₂SO₄ The solution was stirred for one hour, after which 170 mL of the solution was removed. This portion was designated as "t0," and cocaine base was fully precipitated from this solution with a 6.25 M solution of NH₄OH. The cocaine base was filtered via suction filtration and allowed to dry. The remaining 3.1 L of cocaine sulfate solution was used for the fractional precipitation of cocaine base. Approximately 30 mL of 6.25 M NH₄OH was initially added until the pH was approximately 6. Twenty milliliters of 6.25 M NH₄OH were then added, and a small amount of cocaine base precipitated immediately. The solution was allowed to sit for five minutes to complete crystallization. The precipitate was vacuum filtered, and the filtrate was collected. The process of adding 20 mL of NH₄OH, allowing the precipitate to settle, and filtering was repeated until no precipitate was formed upon addition of a final aliquot of NH₄OH. Each collected fraction of cocaine base was dried overnight in an oven at 40°C. Once dry, the fractions were ground to a fine powder and weighed separately. The entire procedure was completed in triplicate starting with approximately 300g of cocaine base. Ten to 13 fractions were collected for each 300 g portion of cocaine base.

Table 1

Stable isotope values of cocaine obtained from a controlled observational study, a controlled laboratory study, and the difference between those measurements. All isotope measurements are expressed in per mil (%).

Processor	% recovery	Observational study results				Controlled laboratory results				Difference $(\delta - \delta)$			
		$\delta^{13}C$	δ^{15} N	$\delta^2 H$	δ^{18} O	$\delta^{13}C$	δ^{15} N	$\delta^2 H$	δ^{18} O	Δ^{13} C	Δ^{15} N	$\Delta^2 {\rm H}$	Δ^{18} O
1	64.8	-32.8	-7.4	-217.1	19.0	-32.9	-10.0	-217.3	20.1	0.1	2.6	0.2	-1.1
2	46.3	-32.7	-4.7	-216.4	19.4	-32.9	-10.4	-221.2	17.8	0.2	5.7	4.8	-1.6
3	18.4	-32.6	-1.2	-213.5	19.2	-32.9	-10.1	-220.2	17.2	0.3	8.9	6.7	2.0
4	69.8	-33.6	-8.5	-224.4	19.9	-33.2	-8.7	-218.1	19.0	-0.4	0.2	-6.3	0.9
5	19.3	-32.7	-1.4	-213.9	21.9	-33.3	-8.5	-218.1	19.1	0.6	7.1	4.2	2.8
6	46.5	-33.2	-5.7	-219.8	20.8	-33.2	-9.0	-217.9	19.2	0.0	3.3	-1.9	1.6
7	85.5	-34.1	-9.7	-227.6	18.6	-33.9	-9.6	-224.4	17.9	-0.2	-0.1	-3.2	0.7
9	65.4	-33.3	-9.5	-218.8	19.5	-33.5	-10.6	-222.4	18.2	0.2	1.1	3.6	1.3
10	77.7	-33.7	-7.2	-215.8	21.1	-33.8	-7.5	-217.5	18.8	0.1	0.3	1.7	2.3
11	49.5	-34.0	-2.3	-210.8	20.4	-33.8	-7.4	-217.6	18.7	-0.2	5.1	6.8	1.7
12	50.8	-33.6	-4.6	-210.5	21.3	-33.8	-7.3	-218.2	18.7	0.2	2.7	7.7	2.6
Average of 1, 4, 7, 9, and 10	72.6	-33.5	-8.4	-220.7	19.6								

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