



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



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ABSTRACT

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 $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^2\text{H}$, and $\delta^{18}\text{O}$ 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 ^{15}N 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 (^{13}C , ^{15}N , ^2H , and ^{18}O) 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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