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EA-IRMS: Tracing the geographical origin of cocaine

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Goal

Illustrate how isotope fingerprints can help trace cocaine production regions through analysis of coca leaves and cocaine samples.

Introduction

Cocaine is one of the world's most widely used narcotics and this widespread use and abuse has resulted in more investigations aimed at tracing the coca cultivation regions and identifying exportation routes of the illicitly isolated cocaine. Tracing the origin of cocaine has previously been achieved at the regional scale[1], however, as a result of a significant expansion of coca cultivation and movement for processing and distribution, the identification of cocaine origin at the sub-regional scale has become increasingly difficult. Despite the complexities evident, it has been shown that isotope fingerprints in seized cocaine provide an enhanced insight that allows the coca cultivation region to be identified when combined with trace alkaloids.

This application note is a summary of the work by Mallette et al (2016)[1] and focusses on the isotope fingerprint data from coca leaves and seized cocaine samples. Further data on trace compounds, statistical data analysis and the analytical procedures used are presented by the authors in detail in their publication[1] and the interested reader is directed there for full details.

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Isotope fingerprints of coca plants and cocaine

The carbon and nitrogen isotope fingerprints ($\delta^{13}C$ and $\delta^{15}N$ values) in coca plants follow the predicted pattern as they relate to environmental factors. The carbon fingerprints generally follow changes in elevation associated with temperature and partial pressure of CO_2 along the altitudinal transect, whilst nitrogen fingerprints vary according to changes in local precipitation and soil type, and conditions therein, that directly affect local nitrogen cycling.

The hydrogen and oxygen isotope fingerprints ($\delta^{2}H$ and $\delta^{18}O$ values) of seized cocaine can be utilized to help trace geographical origin. The coca plants, from which cocaine is illicitly produced, carry a local-regional fingerprint primarily derived from the hydrological cycle, which is associated with local-regional rainfall[2,3], but can also be influenced by cultivation practices, soil processes and geological characteristics of the local area, altitude and proximity to the shoreline[3]. The oxygen and hydrogen isotope fingerprints change in rainfall as you move further inland from the shoreline and with increasing altitude because the heavier isotopes are the first to be released from the clouds[3,4]. This effect can be tracked in the oxygen and hydrogen isotopic fingerprints of leaves of the coca plants. Importantly, the isotope fingerprint does not change during the isolation of cocaine from the coca leave itself, meaning that the isotope fingerprint of the isolated cocaine reflects the environment from which the coca cultivation occurred. This, therefore, provides a framework for tracing the seized cocaine back to it's origin.

Analytical configuration

For simultaneous $\delta^{13}C$ and $\delta^{15}N$, around 0.9–1.2 mg of cocaine was weighed into tin capsules and introduced into the EA-IRMS System and processed through combustion/reduction reactors in the presence of oxygen. Samples were bracketed by an internally calibrated atropine secondary standard, which was calibrated to primary standards relative to Vienna Pee Dee Belemnite (VPDB) for carbon and AIR for nitrogen.

The analysis of $\delta^{2}H$ and $\delta^{18}O$ was carried out by weighing around 0.20–0.25 mg of cocaine into silver capsules and introducing them to the pyrolysis reactor of the EA-IRMS System, held at 1400 ˚C, to produce H_2 and CO. Samples were bracketed by an internally calibrated C-28, C-34 and atropine secondary standards as well as benzoic acid primary standard (IAEA-601), which were calibrated to primary standards relative to Vienna Standard Mean Ocean Water (VSMOW) for hydrogen and AIR for oxygen.

Tracing the origin of seized cocaine: a journey from South America to USA

Mallete et al (2016)[1] collected 572 coca leaf samples from 19 known growing regions throughout Bolivia (*n* = 58), Colombia (*n* = 361), and Peru (*n* = 153). These samples served as a true reference point to compare the seized cocaine with. Figure 1 shows isoscapes for carbon (Figure 1a), nitrogen (Figure 1b) and hydrogen (Figure 1c) isotope fingerprints of coca leaves across Colombia, which were used to identify and understand general differences observed with the direct analysis of cocaine samples. The isotope fingerprint data complemented the trace alkaloid data, which is indicative of the coca variety used in production and varies across South America, and chemometrics based multivariate statistics, which was designed to simultaneously evaluate all collected data and visualize their trends relative to the known growing regions in South America. Collectively, these data improved the regional and, importantly, sub-regional origin classifications for seized cocaine, allowing accurate identifications on cocaine origin to be made within Colombia.

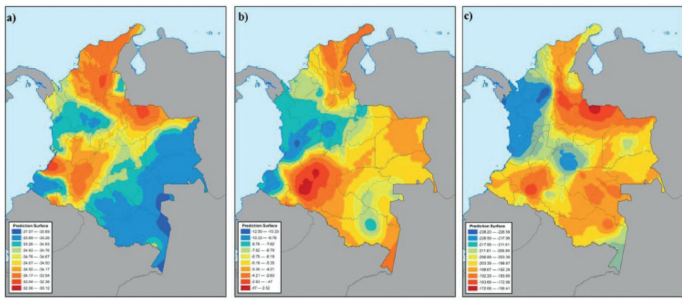

Figure 1. Example of cocaine isoscapes from Colombia showing carbon (a), nitrogen (b) and hydrogen (c) isotope fingerprints.

Aircraft drop seized in Uruguay identifies new coca growing region in Bolivia

Analysis of cocaine seized from an "aircraft drop" in Uruguay led to the discovery of a previously unknown coca growing region in northern Bolivia. Alkaloid and isotope fingerprint data indicated the cocaine may have originated from Bolivia. At the time of seizure, the only known coca growing region to in Bolivia was the Chapare Valley. However, the isotope fingerprints of the seized cocaine were unlike any other coca or cocaine samples previously analyzed from the Chapare Valley. The $\delta^{13}C$ values suggested the coca grew in a region of lower altitude and the $\delta^{15}N$ values suggested a more tropical, wet environment with increased nitrogen availability in the soil, indicating a region closer to the equator and in a more northern location than the Chapare Valley. Additionally, the $\delta^{2}H$ and $\delta^{18}O$ values suggested a much wetter, low-lying environment than the Chapare Valley. The combination of the four isotope fingerprints indicated the cocaine was processed from coca leaf originating north of the Chapare Valley, in a much wetter, low-lying region of Bolivia. The isotope fingerprint data were combined with intelligence reports from the pilot responsible for carrying the cocaine, who stated that the plane originated from Beni, Bolivia. Prior to this seizure, there had been no evidence of coca cultivation in the Beni region of Bolivia, which lies north of the Chapare Valley. However, isotope fingerprints successfully identified the differences between these coca growing regions and thus a new coca growing region in Bolivia.

Summary

The origin classification of cocaine to one of 19 known coca-growing regions in Colombia, Peru, or Bolivia is now possible. In addition, comparing unknown cocaine samples to a database of authentic geographically referenced cocaine samples and utilizing the framework described by Mallete et al (2016)[1] allows for the discovery of new coca growing regions within South America. This was best exemplified in the example of identifying Beni, Bolivia as a coca growing region previously unknown to the enforcement and law authorities.

This study has shown the powerful contribution that isotope fingerprints of coca leaves and cocaine make to identifying the origin of seized cocaine. Moreover, these data are based on bulk measurements of carbon, nitrogen, hydrogen and oxygen using Elemental Analysis Isotope Ratio Mass Spectrometry, such as the Thermo Scientific™ EA IsoLInk™ IRMS System (not used in this study).

References

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