SHIMADZU
Excellence in Science

Application News

No. GCMS-1501

Gas Chromatograph Mass Spectrometer

Analysis and Quantitation of Cocaine on Currency Using GC-MS/MS

Shilpi Chopra, Ph.D., Laura Chambers

■ Introduction

Cocaine (CAS # 50-36-2), a white crystalline alkaloid derived from the *coca* plant, is a popular illegal drug of abuse in the United States and elsewhere. Cocaine is a stimulant that acts on the central nervous system (CNS) causing increased heart rate, tightness in the chest, heightened alertness, numbness, stroke, and even death.

Paper currencies around the world are usually made of a cellulose based paper which can adsorb cocaine onto the surface, and when a person handling cocaine subsequently touches paper money, or uses the bill as a tool to inhale cocaine, the currency easily becomes contaminated. When this contaminated paper money comes into contact with other bills, the cocaine is easily transferred from one bill to the next.

This application note describes a method for extraction, identification, and quantitation of cocaine on paper money from nine different geographical areas around the globe, including five samples from the United States, using the Shimadzu GCMS-TQ8040 triple quadrupole mass spectrometer and the Multiple Reaction Monitoring (MRM) monitoring mode (Figure 1).

Figure 1: Shimadzu GCMS-TQ8040 Triple Quadrupole Mass Spectrometer

■ Experimental

Sample Preparation

Fifteen individual paper notes from nine different countries were each extracted with 10 mL of methanol, and the final volume reduced to 1 mL prior to analysis. No other sample preparation was necessary.

Gas Chromatography Conditions

The capillary column had a 5% phenyl stationary phase, with dimensions of 15 meter x 0.25 mm I.D. x 0.25 µm film thickness. The inlet was maintained at an isothermal temperature of 250 °C, and operated in the splitless mode with a 2.0 minute splitless time. The GC oven was programmed starting at 150 °C (1 minute hold), and ramped to 290 °C at 10 °C per minute, with a final hold time of 1 minute. The GC-to-MS transfer line temperature was held constant at 280 °C. The solvent delay was 4.0 minutes, and cocaine eluted at 8.26 minutes (Figure 2).

MRM Conditions

The GCMS-TQ8040 was operated in the MRM mode to take full advantage of the enhanced selectivity for the target compound. There were two options for developing the MRM method: individual MRM transitions for cocaine can be selected from the Shimadzu Smart Forensics Database[1], or they can be optimized individually using the MRM Optimization Tool[2]. For cocaine, the Smart Forensic Database provides a suite of seven fully optimized MRM transitions with collision energies, empirically derived peak ratios for QA, and retention indices for predicting retention times. Any combination of the seven transitions can be selected for analysis depending on what types of matrix interferences may be present.

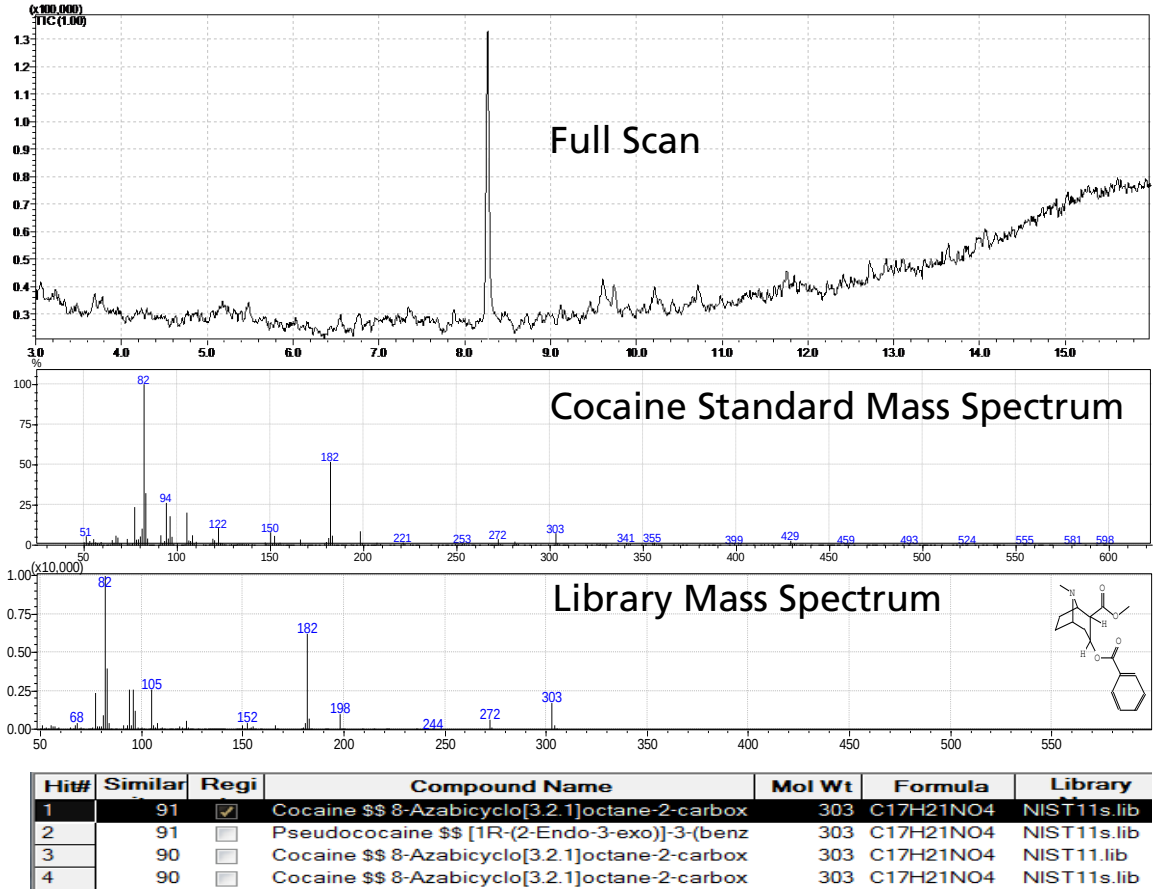

Figure 2: Full-scan TIC of Cocaine with Spectrum and Library Search Results

Because there was only one compound of interest for this study, the required MRM transitions were selected and optimized easily and quickly at the point-of-use. Three transitions were selected based on the sensitivity of their response, and using the *m/z* 182 dominant high mass ion fragment as the precursor in all cases. The three selected transitions are shown in Table 1.

Table 1: MRM Transitions Used for Identification and Quantitation of Cocaine

Transition	Precursor > Product	Collision Energy	Ratio
Primary Tx	182.0 > 82.0	15	100 %
Confirmation Tx #1	182.0 > 122.0	15	43 %
Confirmation Tx #2	182.0 > 93.0	15	37 %

■ Results and Discussion

Method Validation

Several statistical tests were run to validate the method, including establishing a linear calibration, repeatability, limit of detection, and percent recovery. A 9-point calibration curve was prepared (external standard method) from 0.005 to 100 µg/mL (part-per-million, ppm). The method was determined to be linear over this range with an R^2 value of 0.9966, as shown in Figure 3. Repeatability was tested by analyzing six aliquots of the mid-range, 1.0 µg/mL standard, and resulted in a relative standard deviation (RSD) of < 6% for the peak area counts using the primary MRM transition. Figure 4 shows chromatograms of the three overlaid MRM transitions from analysis of the 1.0 µg/mL cocaine standard.

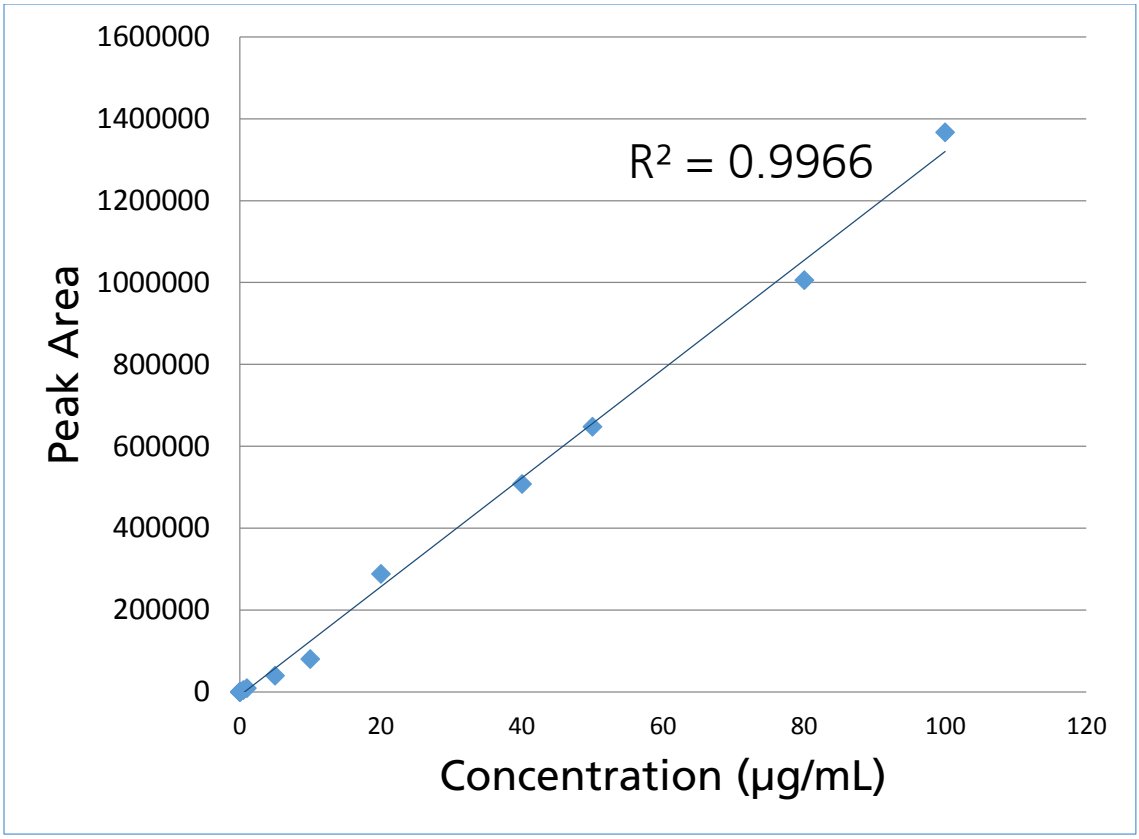

Figure 3: Linear Calibration Curve for Cocaine from 0.005 to 100 µg/mL

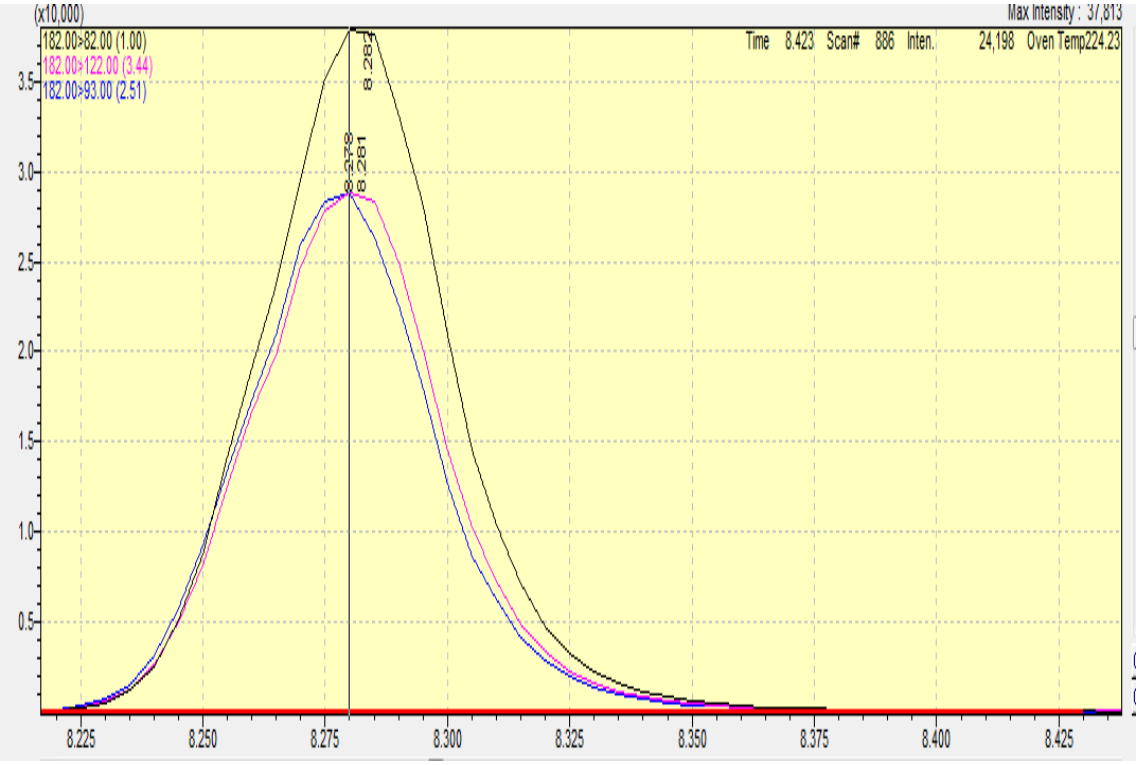

Figure 4: Three Overlaid Transitions for the mid-level, 1.0 µg/mL Cocaine Standard

The percent recovery from each sample was determined by first analyzing a 0.004 µg/mL sample and using that response and the calibration curve to estimate the expected response of a 0.006 µg/mL sample. This was then compared to the response of an actual 0.006 µg/mL sample, and the ratio expressed as a percentage. The recovery was estimated to be 98% at 0.006 µg/mL.

LOQ and LOD was determined using the IUPAC method, using the equation shown below:

$$LOD = ks_B / m$$

Where:

- *k* is the S/N threshold required to define a peak, using 3 for the LOD and 10 for the LOQ
- s_B is the standard deviation of the blank, which was determined taking the standard deviation of the noise readings from 10 data points adjacent to the peak at S/N between 2 and 3
- *m* is the slope of calibration curve

The Limit of Quantitation (LOQ) and Limit of Detection (LOD) were found to be 0.01 µg/mL and 0.005 µg/mL respectively.

Real-World Samples

Fifteen individual paper currency notes were extracted using the procedure described above, analyzed using the MRM method, and quantified against the calibration curve. Calculated concentrations were converted to nanograms (ng) of cocaine per paper note, to illustrate how much of the illegal drug was found on the currencies from different countries. Results are shown in Table 2.

Table 2: Amount of Cocaine Detected on Currency from Different Countries

Origin of Currency Tested	Denomination	Amount of Cocaine Found
USA, Florida	20 Dollars ($20)	1.76 ng
USA, Florida	20 Dollars ($20)	8.25 ng
USA, New Jersey	1 Dollar ($1)	2.85 ng
USA, New Jersey	1 Dollar ($1)	19.6 ng
USA, New Jersey	1 Dollar ($1)	1.1 ng
China	10 Yuan	0.84 ng
Indonesia	1 Rupiah	0.68 ng
France	10 Euro	ND
Brazil	1 Real	ND
Mexico	1 Peso	ND
Mexico	10 Peso	ND
Canada	1 Canadian Dollar	ND
Britain	5 Pounds	ND
India	100 Rupee	ND
India	500 Rupee	0.69 ng
ND = Not Detected		

■ Conclusion

The MRM analysis method for cocaine was quickly and easily developed at point-of-use, and was used to detect and quantify the amount of cocaine found on different currencies from around the world. The $1 and $20 bills from the United States easily had the highest amount of cocaine, and in at least one case it was 20-times higher than the amount found on the paper currency from the next highest country, China.

■ Acknowledgement

The authors wish to acknowledge Professor Nicholas H. Snow and Ramkumar Dhandapani at Seton Hall University, NJ where these analyses were conducted.

■ References

1. The Smart Forensic Database, Shimadzu Corporation (Japan), is part of the Smart Database Series. It is registered with 201 forensic toxicological substances such as poisons, drugs of abuse, psychotropic drugs, pharmaceuticals, and pesticides. It includes over 1200 fully optimized MRM transitions with collision energies, with ion ratios and retention indices, and full GC-MS/MS operating conditions. The Smart Forensic Database is used to create fully optimized MRM methods automatically for analysis of forensic toxicological substances.

2. The MRM Optimization Tool, Shimadzu Corporation (Japan), works with Shimadzu's unique Smart MRM function to automatically find and optimize up to 10 transitions for each compound in a list. The process is fully automated so that even a TQ novice can be successful the first time, and comes standard with all Shimadzu triple quadrupole instruments.

3. Chopra, Shilpi, "Extending the Limits of Solid Phase Microextraction" (2014). Seton Hall University Dissertations and Theses (ETDs). Paper 1990.

First Edition: May 2015

SHIMADZU Corporation
www.shimadzu.com/an/

SHIMADZU SCIENTIFIC INSTRUMENTS
7102 Riverwood Drive, Columbia, MD 21046, USA
Phone: 800-477-1227/410-381-1227, Fax: 410-381-1222
URL: www.ssi.shimadzu.com