8.j Analysis of cocaine on USD Banknotes by GC-FID

Marra Clay (Class of 2017) and Megan Rocha (Class of 2017)
Instrumental Methods of Analysis
December 2016

Introduction

Cocaine is a powerful stimulant drug that is derived from coca leaves. It is illegal in the United States, but is a common street drug. It typically takes the form of a fine white powder (National Institute on Drug Abuse, 2016). Cocaine is particularly dangerous because it has the capacity to cause significant damage to the heart and brain, and it can alter emotions (Carr, 2001). Cocaine is also a very addictive drug which can have long-term and life threatening consequences, and according to the 2006 National Survey on Drug Use, 35.3 million Americans ages 12 and above have used cocaine (Foundation for a Drug Free World). Users tend to consume cocaine intranasally by inhaling it through a rolled currency bill. When the bill is then put into circulation with other bills, the trace amounts of cocaine spread. It has been determined that the concentration of cocaine on bills is not influenced by external factors such as rural or urban location, and socioeconomic standing of local drug dealers does not impact whether or not cocaine will be found on that area's bills (Ebejer, 2007). Over 90% of bills in circulation in the United States contain detectable levels of cocaine, and there are several different techniques for measuring cocaine (Park, 2009). Analytical methods primarily include gas chromatography, liquid chromatography, capillary electrophoresis, immunoassay, thermal desorption-mass spectrometry, and ion-mobility spectrometry (Armenta, 2008).

Cocaine was first detected on banknotes by GC-MS in 1987 (Aaron, 1987). The drawback to GC-MS is sample preparation and analysis time. While CE is relatively effective, compared to MS, it lacks specificity. Immunoassay has the ability to produce false results, and current TD-MS methods do not fully extract cocaine from bills (Armenta). Because IMS is not cost effective for an undergraduate laboratory course, this investigation opted to use gas chromatography- flame ion detection (GC-FID). The purpose of this investigation is to design a project for instrumental analysis of dollar bills for trace cocaine concentrations by GC-FID. Data for the lab

experiment is provided so that this laboratory procedure can be used for wet or dry experiments.

Methods and Procedure

A solution of OmniSolv High Purity Solvent Methanol (CAS# 67-56-1) was prepared to contain 50 ppm caffeine (CAS# 58-08-2) and is used as the solvent throughout the experiment.

A set of 12 standards were prepared with the solvent at varying cocaine concentrations that range from 0.1 through 120 ppm. Thirty individual bills were collected as samples from two cities: Walla Walla, Washington, and Richland, Washington. Cocaine was extracted from the samples by gently mixing them at 12 rpm for no less than 24 hours in 10 mL of solvent. The samples were then filtered through a 0.2 micrometer filter. Samples were then analyzed on an Agilent Technologies GC-FID. The Agilent Technologies 6890N network GC system used an Agilent 7683 series injector and a J&W 122-5032 DB-5, 30.0M x 250μm x 0.25μm nominal capillary column. The linear velocity of the mobile phase was 50 cm/sec. The method used for both of the instruments began with an oven temperature of 80°C for 2 minutes, then increased at a rate of 10°C /min until 130°C was reached and sustained for 1 minute. It then continued at a rate of 2°C/min until 210°C was reached and sustained for 1 minute, ending with a rate of 10°C/min until 250°C was reached and sustained for 1 minute.

Results and Discussion

Several filtered sample extracts were discolored, some red and others yellow, likely due to other contaminants on the banknotes. Fifteen of the samples were collected from Walla Walla and contained an average cocaine mass of 0.04 ± 0.02 mg. Fifteen additional banknotes were collected from Richland and had an average cocaine mass of 0.054 ± 0.008 mg. Of the 30 samples analyzed, 28 of them had a detectable concentration of cocaine, with one sample from each city failing to produce a peak. It is to be expected that a few of the samples would not have a cocaine peak, as many studies have shown that around 90% of bills have cocaine on them. This investigation found 93% of samples to have detectable amounts of cocaine.

Figure 8.j-1 depicts the calibration curve created using the standards on the GC-FID. The calibration curve does not include the 0.1 and 0.5 ppm cocaine standards because they fell below the GC-FID detection limit of 1 ppm and therefore, the number of standards was reduced to ten. The generated line is very linear, with an R-squared value of 0.99881. Because of its linearity, this calibration curve was determined to be effective in predicting unknown cocaine concentrations in the extract and then converted to mass of cocaine on each banknote. Figure 2 is the chromatogram for the 120 ppm standard for example. Figure 3 is a sample chromatogram from a 1 USD banknote from Richland, Washington. The determined cocaine masses are noted in Table 8.j-1, which identifies the bills with their location and their USD value.

A 95% t-test analysis (see Table 8.j-2.) confirmed that these average values are not statistically significantly different between the two cities, however; it is important to note that the samples from Walla Walla also contained one fewer significant digit. This is due to higher variation in cocaine amounts between banknotes from Richland.

This experimental procedure could be improved in the future by including more banknotes of different USD values, and include cities outside of Washington state. By doing this, one could better predict the similarities in cocaine banknote concentrations across the nation as a whole, rather than be isolated to only southeastern Washington. They could also see if there is a significant difference in the amount of cocaine on higher denomination bills. Additionally, this experimental procedure may benefit from using nicotine as an internal standard instead of caffeine. Cocaine and caffeine boiling points are relatively close, while nicotine's boiling point is sixty degrees Celsius higher than that of cocaine. This may create better peak distinction.

This experiment could be expanded by analyzing the samples with either LC-MS or other methods listed in the introduction of this report. The chromatograms for the individual banknotes included many unknown chemicals, and it could be beneficial to analyze the samples on a GC-MS to identify them.

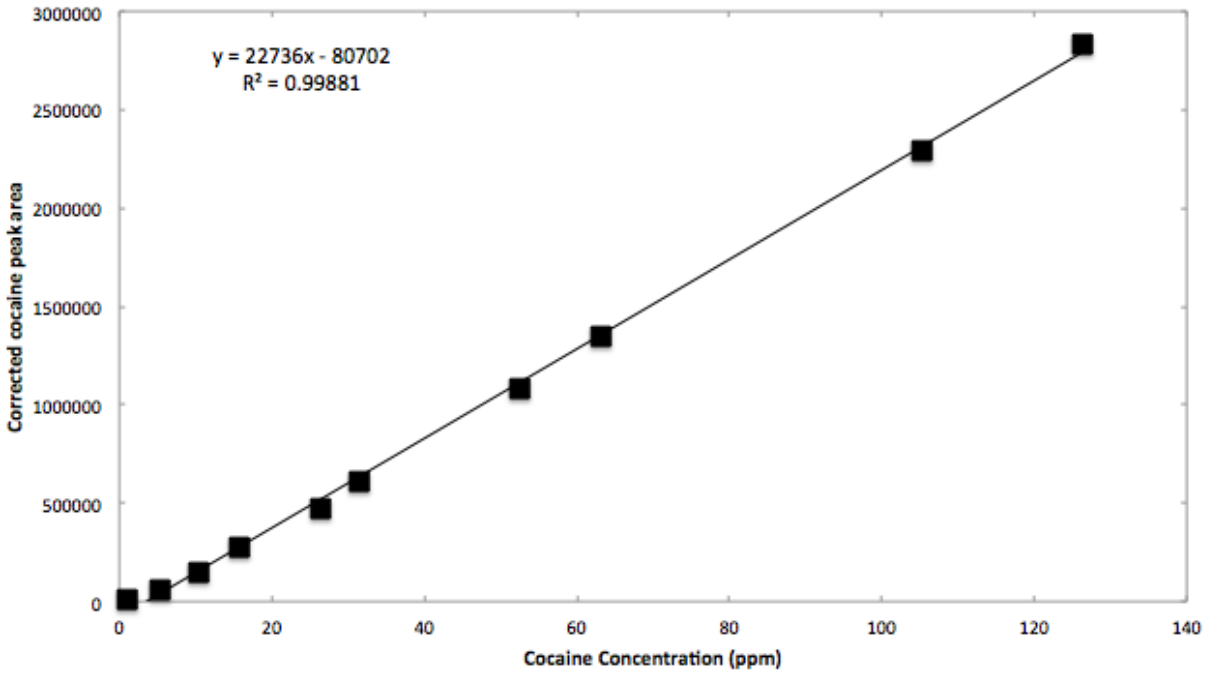

Figure 8.j-1. Calibration curve of cocaine concentration and the peak area, adjusted using the peak area of the internal standard.

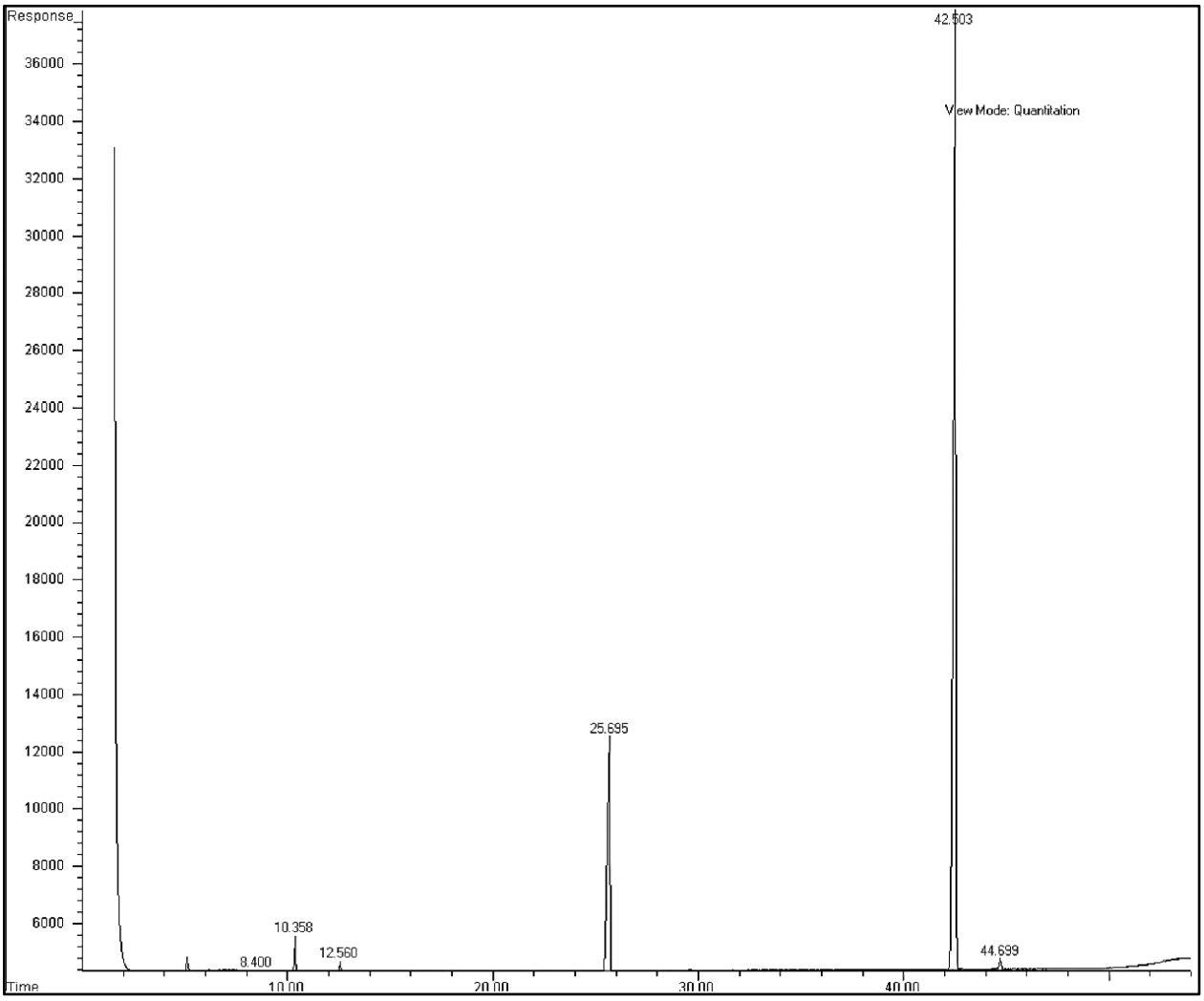

Figure 8.j-2. Chromatogram for 120 ppm cocaine standard for calibration curve generation, with cocaine peak at 42.503 minutes and caffeine internal standard peak at 25.695 minutes.

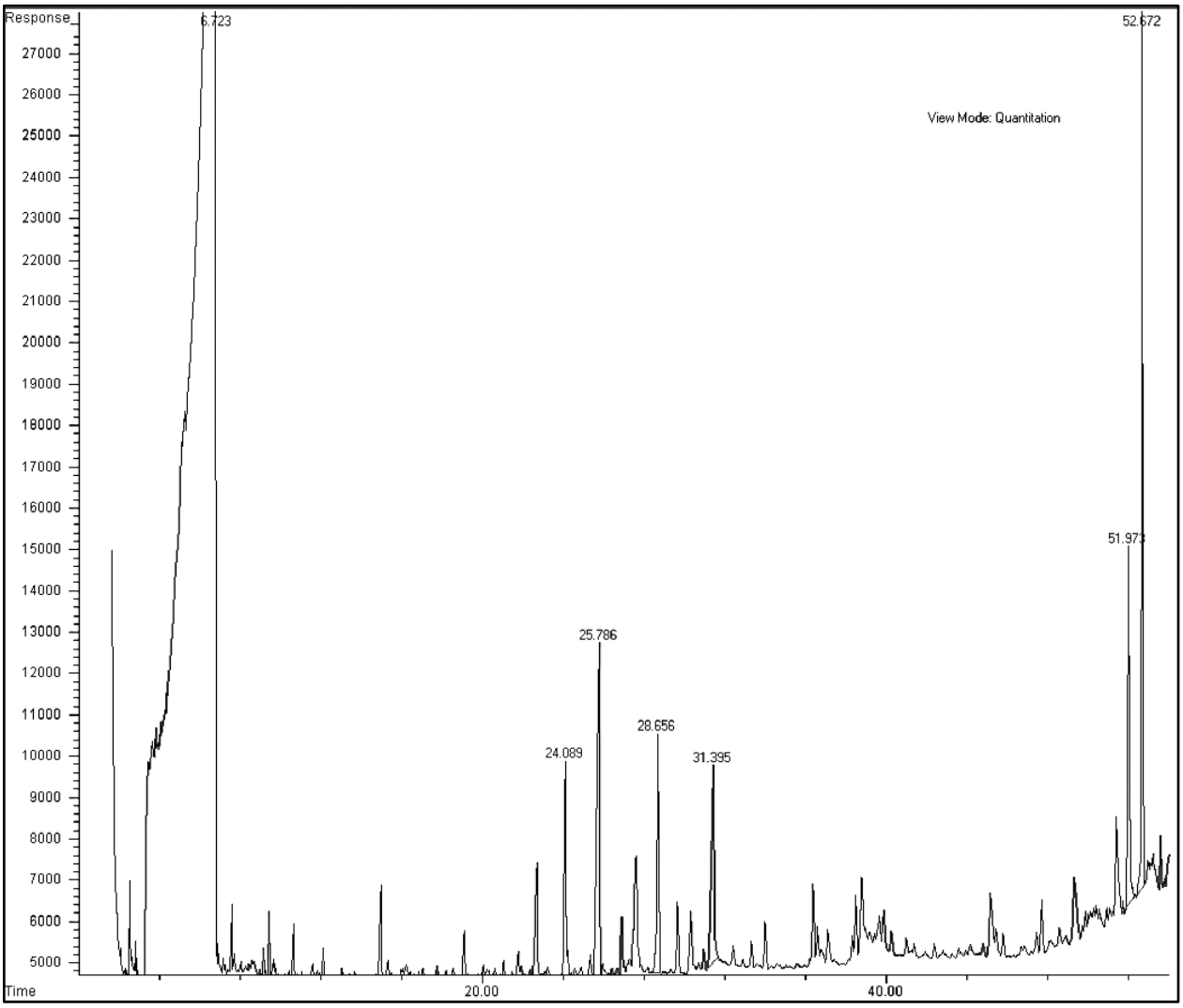

Figure 8.j-3. Chromatogram for 1 USD bill from Richland, Washington

Location	Bill Amount (USD)	Cocaine Mass (mg)
Walla Walla, Washington	1	0.0429
	1	0.0550
	1	0.0654
	1	0.0427
	1	0.0607
	1	0.0555
	1	0.0487
	1	0.0541
	1	0.0412
	1	0.0403
	5	0.0454
	5	0.0398
	10	0.0400
	20	0.0456
Richland, Washington	1	0.0513
	1	0.0398
	1	0.0413
	1	0.0549
	1	0.0394
	1	0.0399
	1	0.0412
	1	0.0551
	1	0.0414
	5	0.0560
	5	0.1388
	5	0.0557
	10	0.0574
	20	0.0509

Table 8.j-1. Mass of cocaine on individual bills from two different cities as determined by GC-FID.

	Richland, Washington	Walla Walla, Washington
Average cocaine (mg)	0.0545	0.0484
Standard deviation (mg)	0.0253	0.00842
Sample size	14	14

Table 8.j-3. Comparison of Richland and Walla Walla banknote cocaine levels for 95% confidence t-test analysis.

Works Cited

Aaron, R., Lewis, P. *Crime Lab* 1987, 14, 1.

Armenta, S., de laGuardia, M. *Trends in Analytical Chemistry* 2008, 27(4), 344-351.

Carr, A. F. *Health Care on the Internet* 2001, *5* (4), 75–78.

Ebejer, K. A.; Lloyd, G. R.; Brereton, R. G.; Carter, J. F.; Sleeman, R. *Forensic Science International* 2007, *171* (2-3), 165–170.

Foundation for a Drug Free World. *Get The Facts About Painkillers, Marijuana, Cocaine, Meth & Other Illegal Drugs.* http://www.drugfreeworld.org/drugfacts/cocaine/international-statistics.html (accessed Dec 6, 2016).

National Institute on Drug Abuse. *Cocaine* https://www.drugabuse.gov/publications/drugfacts/cocaine (accessed Dec 6, 2016).

Park, M. *CNN*. Turner Broadcasting System August 17, 2009.