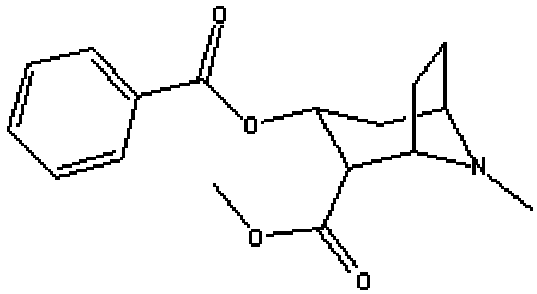
Fingerprint Identification of Cocaine Adulterants by GC and LC

Tim Herring, Kristi Sellers and Rick Morehead

Restek Corporation, 110 Benner Circle, Bellefonte, PA 16823

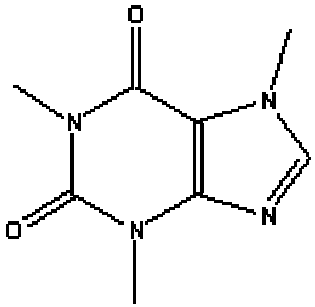
Introduction

Cocaine



Illicit cocaine is commonly “cut” with adulterants or diluents that mimic the stimulant or local anesthetic effects of cocaine. Incorporating these additives into cocaine increases the volume or weight of product available for sale, which results in increased profits for drug dealers. Because illicit cocaine composition can be specific to a dealer, adulterant and diluent identification of seized cocaine is critical in determining the possible routes of distribution and sales.

Caffeine



Both Gas Chromatography (GC) and High Performance Liquid Chromatography (HPLC) can be used to identify cocaine adulterants such as sugars, anesthetics, analgesics and stimulants. Several different detection systems can be used to obtain identification and quantitative information.

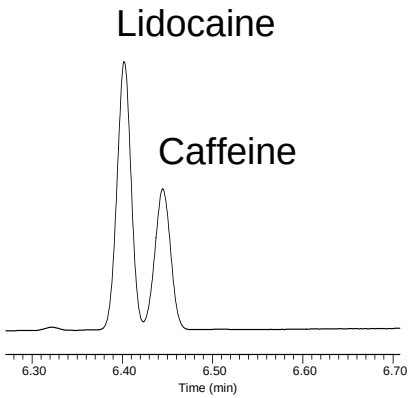
Gas chromatography is the most common analytical technique used for the analysis of all of the adulterants found in cocaine with exception of sugars. Although sugars can be derivatized for analysis by GC, they are more easily detected using HPLC.

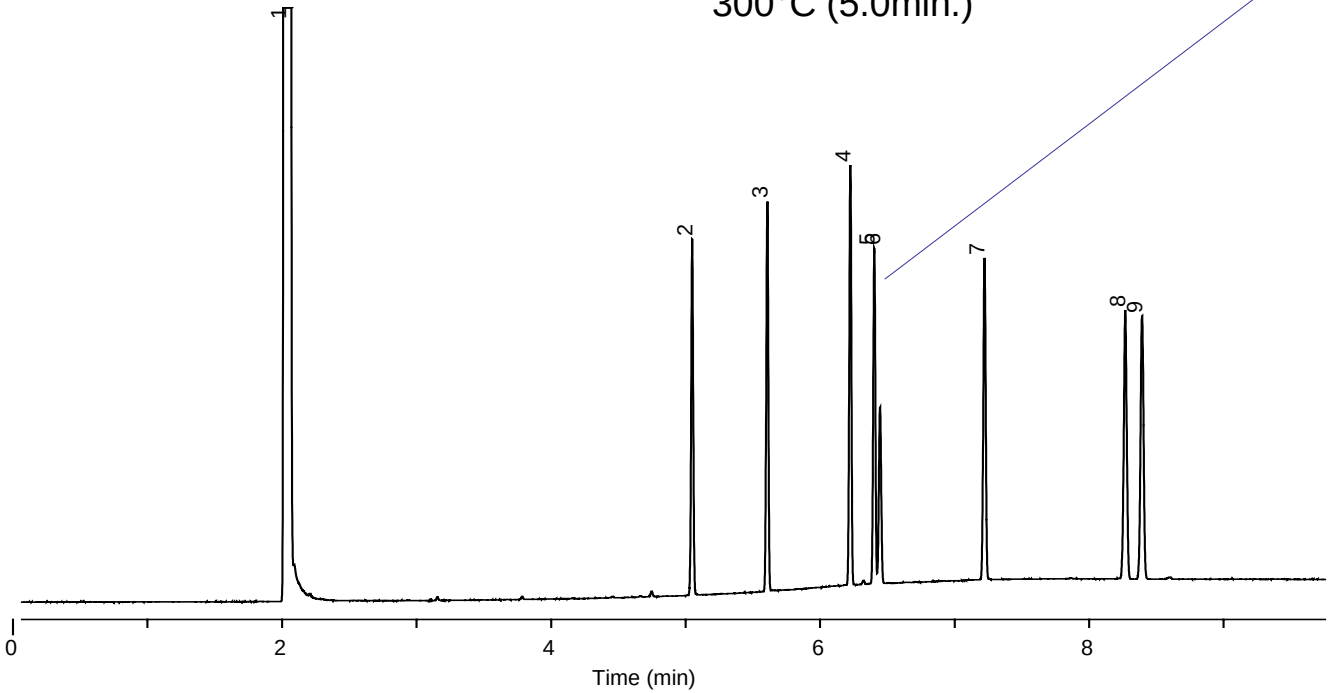
Detection of adulterants found in cocaine after separation by GC can be performed using FID (Flame Ionization Detection), NPD (Nitrogen Phosphorus Detection) and MS (Mass Spectrometry) detectors. Although FID and NPD provide good sensitivity for identifying and quantitating adulterants found in cocaine (see Chromatogram #1), GC/MS is the most widely accepted detection method. GC/MS data is not only very sensitive, but also provides positive identification of the adulterants based on mass spectral information. MS data can be used as confirming evidence in a court of law.

Cocaine Adulterants by GC/FID

Chromatogram #1

GC Column:	Rtx-440 30m, 0.25mmID, 0.50um (Part# 12938)
GC:	Agilent 6890
Injector:	Split, 10:1, 250°C
Injection Amt.:	1.0ul, sample 100ppm each in Methanol
Inlet Liner:	Laminar Cup Splitter
Flow Rate:	1.0 ml/min
Carrier Gas:	Helium
Detector Temp.:	300°C
Temp. Program:	150°C (0 min.), 25°C/min. to 300°C (5.0min.)





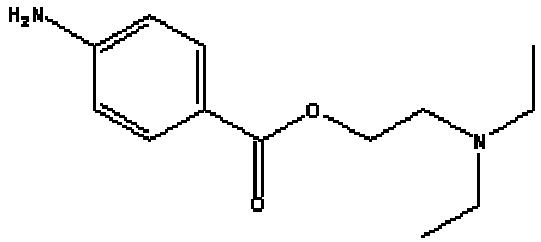
Peak List:

2. Benzocaine
3. Phenacetin
4. Prilocaine
5. Lidocaine
6. Caffeine
7. Procaine
8. Cocaine
9. Tetracaine

A second, less common, chromatographic method for identification of the adulterants and diluents in cocaine is High Performance Liquid Chromatography (HPLC). UV detection, either fixed or variable wavelength, is the most common detection mode. If sugars, such as lactose, are present, Refractive Index (RI) detection must be used since sugars have little or no UV absorbance(see Chromatogram #2).

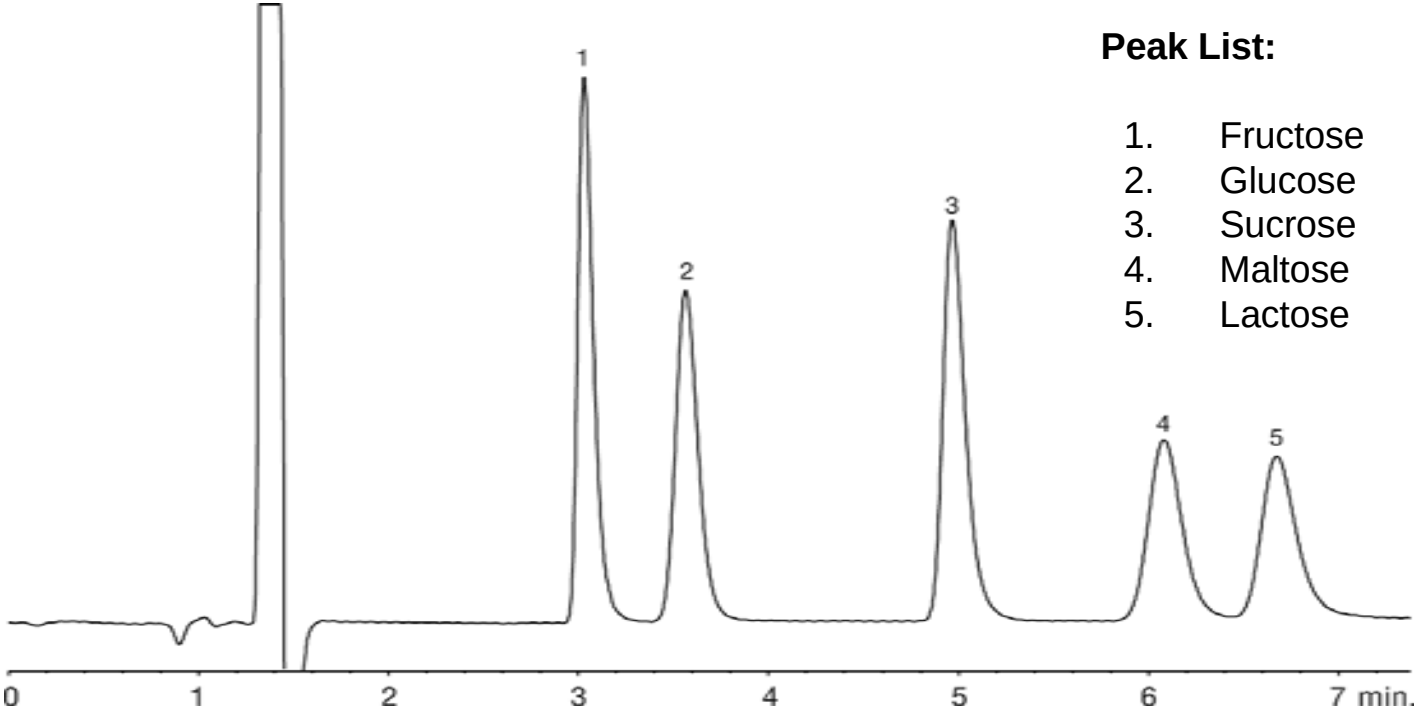
Both types of detection methodology provide reproducible retention times, adequate peak identification and good quantitation. HPLC/MS is an alternative technique for analyzing adulterants in cocaine. HPLC/MS can also give confirming spectral data similar to GC/MS. However, reliable HPLC/MS methodology is still under development.

Procaine



Sugars by HPLC/RI
Chromatogram #2

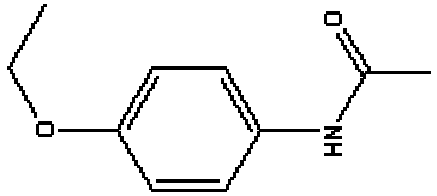
Column: Pinnacle II Amino, 3um, 150 X 4.6mm (Part# 9217365)
Mobile Phase: Water:Acetonitrile, 25:75
Flow Rate: 1.5ml/min.
Column Temp.: 35°C
Detector: RI @ 35°C
Injection Amt.: 5ul



Peak List:		Conc. (ug/ml)
1.	Fructose	2.0
2.	Glucose	2.1
3.	Sucrose	4.0
4.	Maltose	4.5
5.	Lactose	4.4

Experimental

Phenacetin



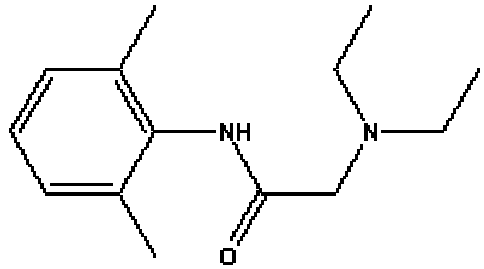
For the purposes of this study, GC/MS, and HPLC/UV-Vis data was obtained and analyzed. Mock samples of illicit cocaine were prepared using a variety of adulterants and diluents. Stimulants including caffeine, local anesthetics such as lidocaine, and over the counter analgesics like phenacetin, were added to cocaine hydrochloride in varying concentrations. A simple “dilute and shoot” sample preparation scheme was used to dissolve the samples before analysis. High Performance Liquid Chromatography (HPLC) and Gas Chromatography (GC) methods were developed for identifying each adulterant or diluent added to cocaine. Method development focused on maximizing the resolution of all of the compounds in the study while minimizing the total analysis time in order to increase sample throughput.

Cocaine Adulterants by GC/MS

Run Conditions #1

GC Column:	Rtx-440 30m, 0.25mmID, 0.25um fused silica capillary column (Part# 12923)
GC/MS:	Agilent 6890 w/5973 MS & 7683 Autosampler
Injector:	Split, 10:1, 250°C
Injection Amt.:	1.0ul, Sample in Methanol
Inlet Liner:	Laminar Cup Splitter
Flow Rate:	1.0 ml/min
Carrier Gas:	Helium
Transfer Line:	180°C
Solvent Delay:	5 min.
Scan Range:	35-550
Tune:	PFTBA
Temperature Program:	150°C (0 min.), 25°C/min. to 275°C (0 min.), 15°C/min. to 300°C (5.0 min.)

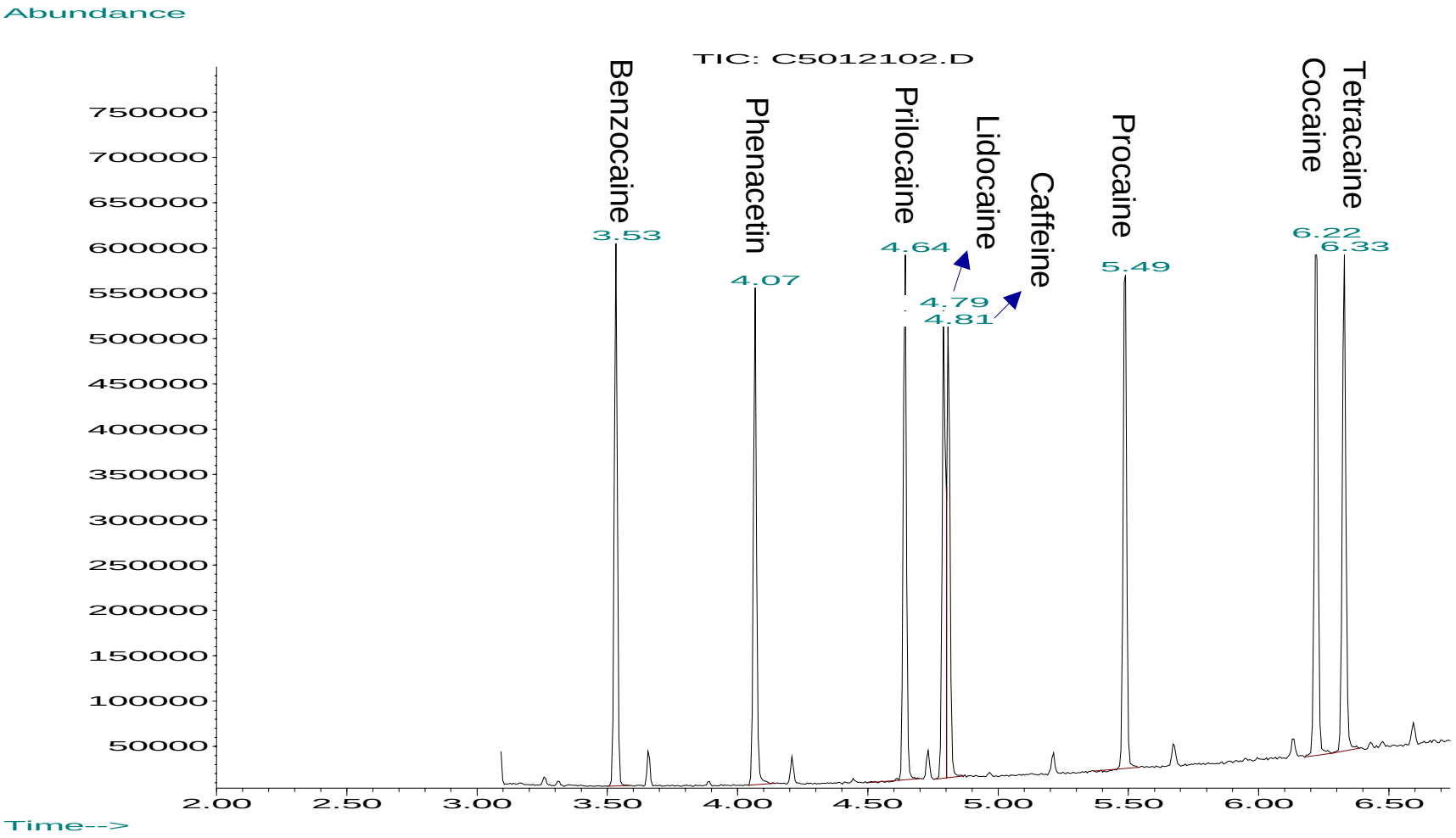
Lidocaine



Several different adulterants were added to cocaine in equal amounts. The on-column concentrations of all of the compounds were 10ng each. GC/MS run conditions were optimized to give the maximum separation and the shortest analysis time. (See Run Conditions #1). Total analysis time was 6.5 minutes. All compounds were baseline resolved with the exception of caffeine and lidocaine; They were resolved by approximately 25% (see TIC #1). However, since they have very different mass spectra, extracted ion analysis could be performed resulting in positive identification of each compound. Lidocaine has a distinctive mass fragment of 86m/z and caffeine has a distinctive mass fragment of 194m/z (see MS #1 & MS #2).

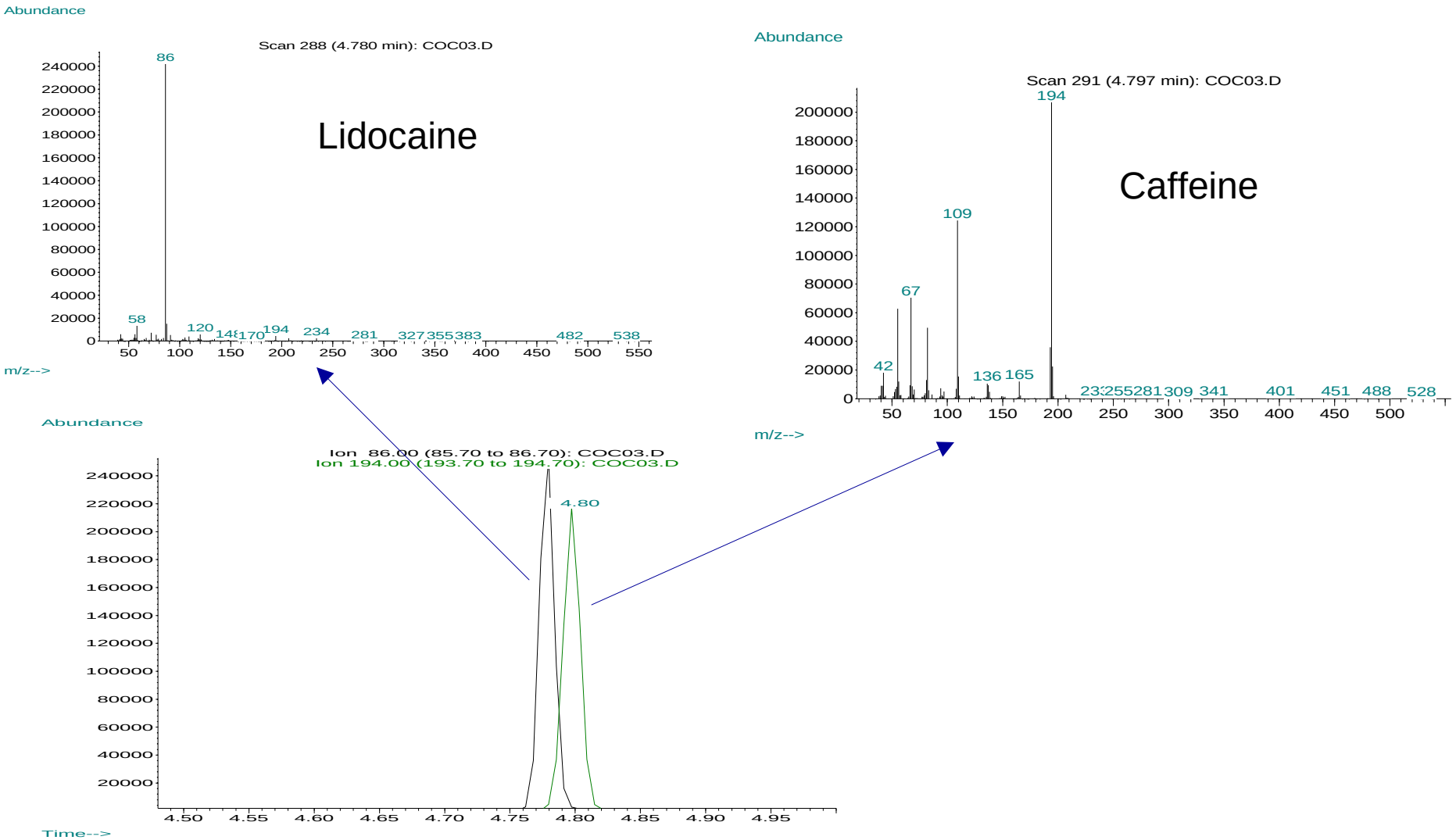
Cocaine & Adulterants by GC/MS

TIC #1



Cocaine & Adulterants by GC/MS

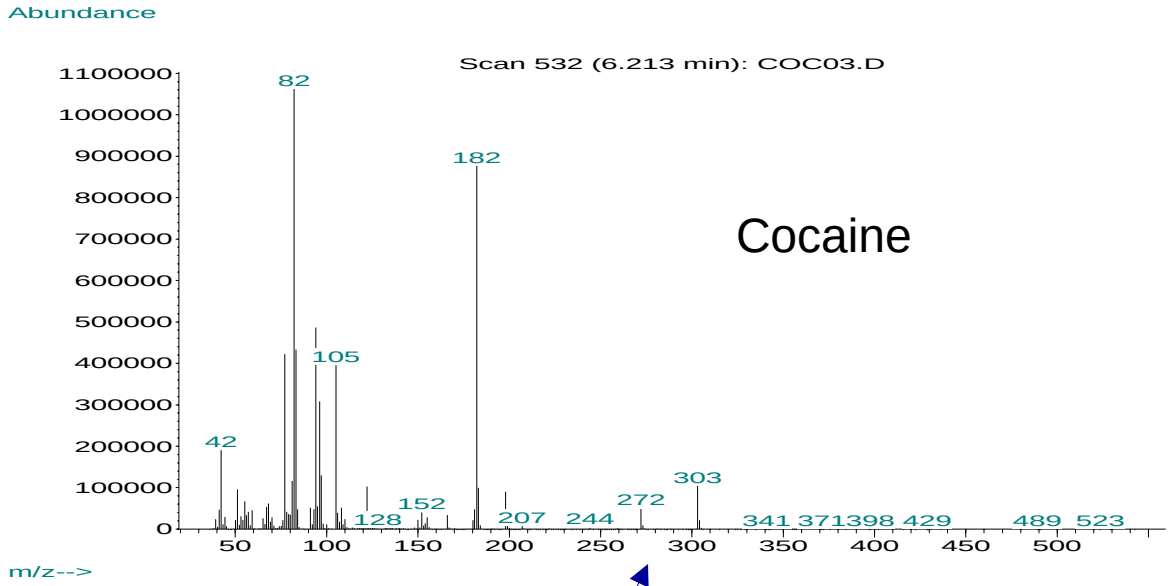
TIC, EI & Mass Spectrum of Caffeine & Lidocaine, MS #1 & MS #2



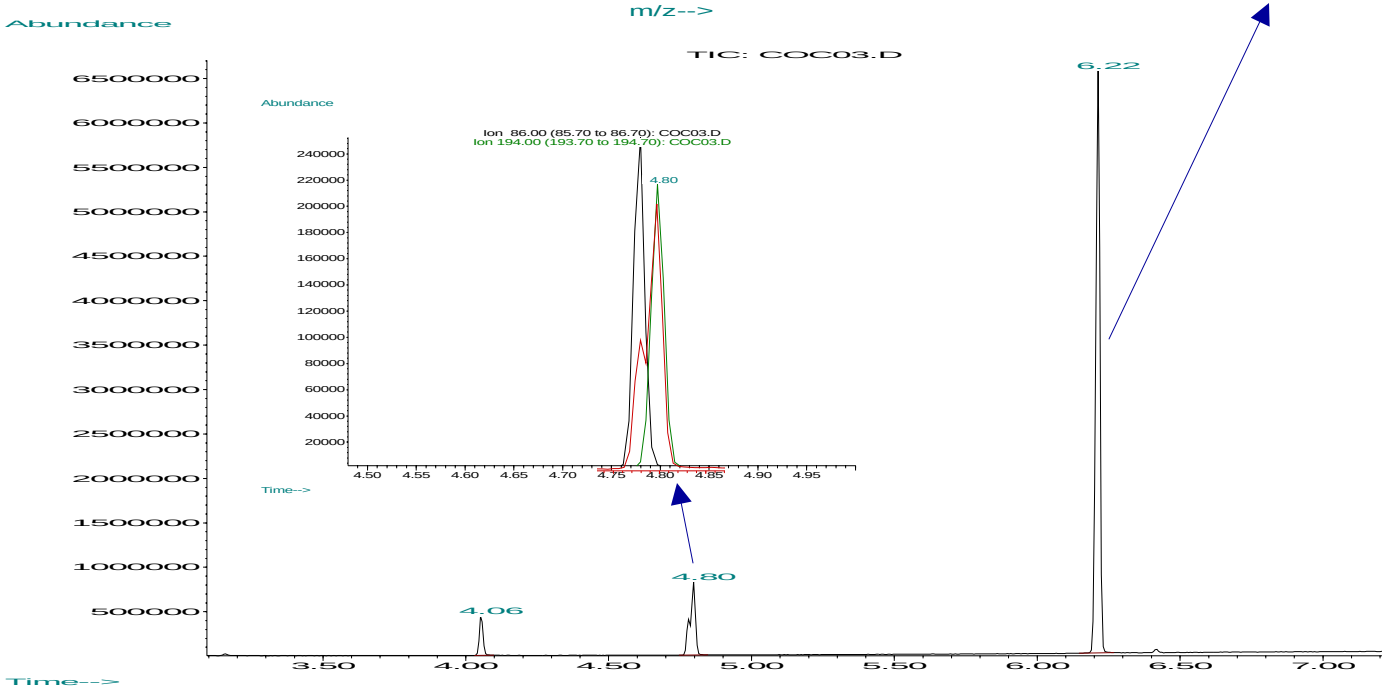
A mock sample containing 80% cocaine, 10% caffeine, 5% lidocaine and 5% phenacetin was prepared and analyzed to compare the separation of caffeine and lidocaine at lower concentrations. The on-column concentrations of the caffeine and lidocaine were 1.0 & 0.5 ng, respectively. At lower concentrations, only 10% resolution was obtained. Extracted ion analysis not only provided absolute identification, but also allowed for proper integration (quantitation) of each compound. (See TIC #2). Total analysis time was again 6.5 minutes.

Cocaine & Adulterants by GC/MS

TIC #2 of Mock Sample, EI & Mass Spectrum of Cocaine



Cocaine

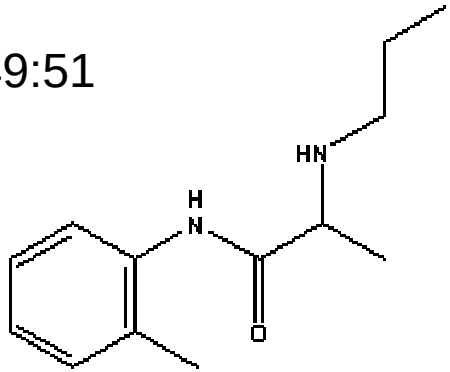


Cocaine & Adulterants by HPLC/UV-Vis

Run conditions #2

HPLC Column:	Ultra C18 5um, 150 X 4.6mm LC column (Part #9174565)
HPLC/UV-Vis:	Dionex HPLC with Gena 50 Autosampler
Column Temperature:	40°C
Flow Rate:	0.50ml/min
Sample Solvent:	Mobile Phase
Injection Amt.:	20ul
UV-Vis Wavelength:	234nm
Mobile Phase:	0.1% Formic Acid: Methanol, 49:51
Program:	Isocratic

Prilocaine



For HPLC analysis, several different adulterants were also added to the cocaine standard in equal amounts. The on-column concentrations of all of the compounds were 100ng each. HPLC/UV-Vis run conditions were optimized to give the maximum separation and the shortest analysis time. (See Run Conditions #2). Total analysis time was 8.0 minutes. All compounds were baseline resolved with the exception of prilocaine and lidocaine; They were resolved by approximately 10% (see Table #1). Since they have almost identical retention times, positive identification of each compound becomes very difficult as does accurate quantitation if both compounds are present in the sample.

Table #1. Cocaine & Adulterant Retention Times.

Ultra C18

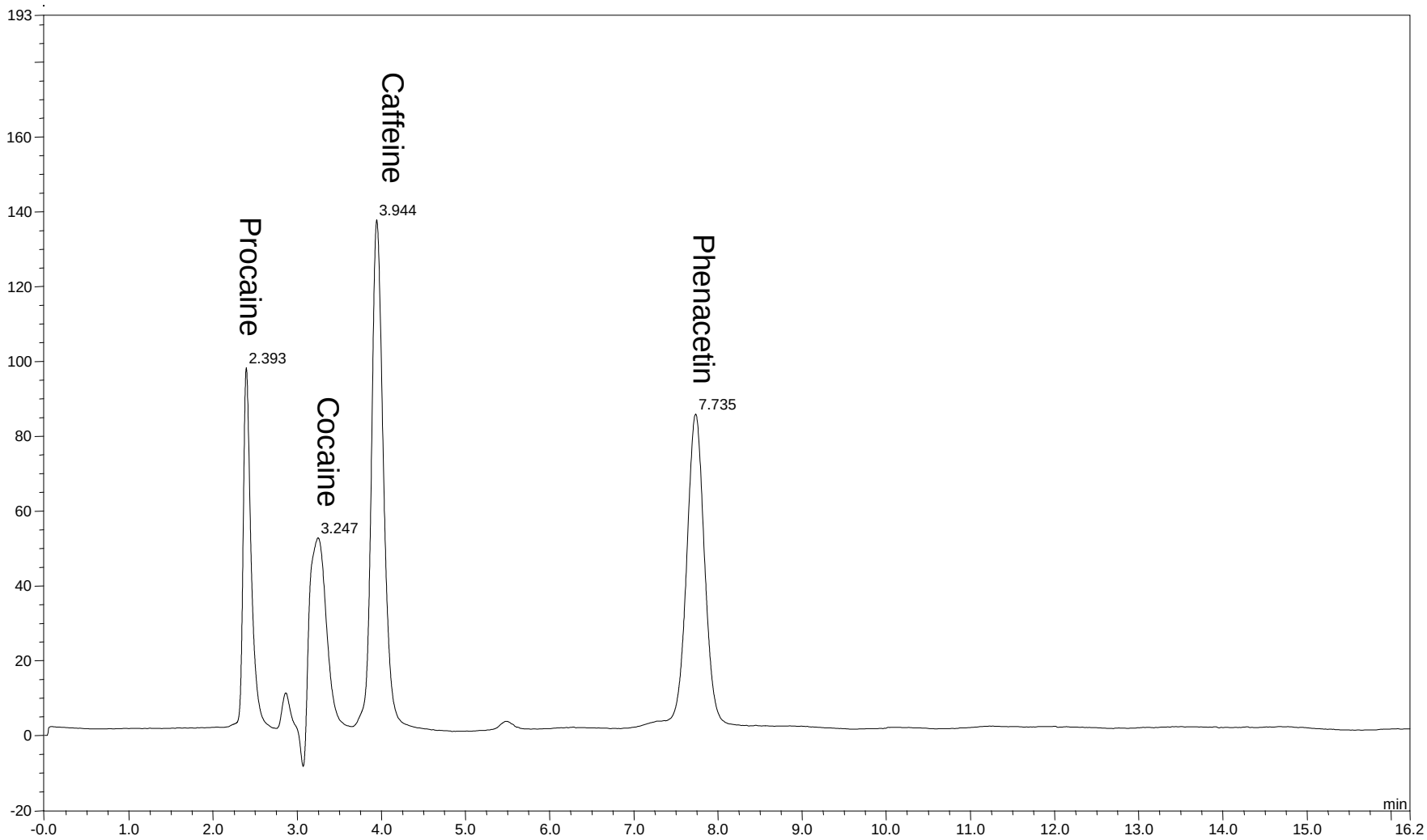
Compound	RT (min.)
Procaine	2.39
Prilocaine	2.75
Lidocaine	2.78
Cocaine	3.25
Caffeine	3.94
Tetracaine	4.63
Phenacetin	7.74
Benzocaine	8.01

Several different HPLC Stationary phases were evaluated to check for improved separation of the prilocaine and lidocaine. Phases such as Allure Basix, Allure C18, Allure PFP, Ultra Cyano, Ultra IBD, Ultra Amino and Pinnacle II Amino showed either no retention of all eight compounds (cocaine and the adulterants) or no separation of the prilocaine and lidocaine.

A mock sample containing 65% cocaine, 16% caffeine, 10% procaine and 10% phenacetin was prepared and analyzed on the Ultra C18 column. The on-column concentrations of the cocaine, caffeine, procaine and phenacetin were 133, 33, 20 and 20ng, respectively. The Ultra C18 stationary phase gave the best retention and the greatest resolution of all of the compounds considered in this study. (See Table #1 and Chromatogram #3). Total analysis time was again 8.0 minutes.

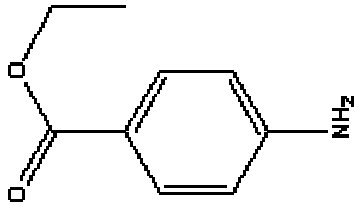
Cocaine & Adulterants by HPLC/UV-Vis

Chromatogram #3; Mock Sample at 234nm



Conclusions

Benzocaine



“Fingerprint” identification of mock cocaine samples could be achieved through the identification of the type and number of additives. Since GC/MS provides adequate semiquantitative information regarding the concentration of each additive relative to the cocaine concentration and the most undisputable identification of a substance (both retention time and mass spectrum data), it is the preferred chromatographic method for analyzing cocaine and cocaine adulterants. Sugars, of course, must be analyzed by HPLC using an RI detector.

Future method development work should be conducted in HPLC/MS to allow analysts the flexibility of using either GC/MS or HPLC/MS as their method of choice. Mobile phase and column choice will be critical parameters to optimize for this method.

References

1. Handbook of Forensic Drug Analysis, Frederick P. Smith, 2005
2. Forensic and Clinical Applications of Solid Phase Extraction, Telepchak, August and Chaney, 2004
3. Determination of Cocaine and Metabolites in Urine Using Electrospray LC/MS by Slawson, Shaw and Hughes, 2000

Tetracaine