

# Clinical, Forensic, & Toxicology Applications

## Identification of Cocaine Adulterants

### Using GC and HPLC

#### Abstract

Identification of cocaine adulterants plays a critical role in identifying sources, dealers, and routes of distribution. Both GC and LC methods can be used to “fingerprint” cocaine samples. Here we show the analysis of simulated cocaine samples by both techniques and give column and instrument conditions for successful analysis.

#### Introduction

Illicit cocaine commonly is diluted (“cut”) with adulterants or diluents that mimic the drug’s stimulant or local anesthetic effects. Incorporating these additives into cocaine increases the volume or weight of product available for sale, which increases profits for the drug dealer. Because the composition of an illicit cocaine mixture can be a unique “fingerprint”, linking the material to a specific dealer, identification of adulterants and diluents in seized cocaine is critical to determining possible routes of distribution and sales.

Either gas chromatography (GC) or high performance liquid chromatography (HPLC) can be used to analyze cocaine adulterants such as sugars (e.g., lactose), anesthetics, analgesics, and stimulants. GC most commonly is used for analyses of all cocaine adulterants, with the exception of sugars. Sugars are analyzed and detected more easily by HPLC, because they must be derivatized before they can be analyzed by GC.

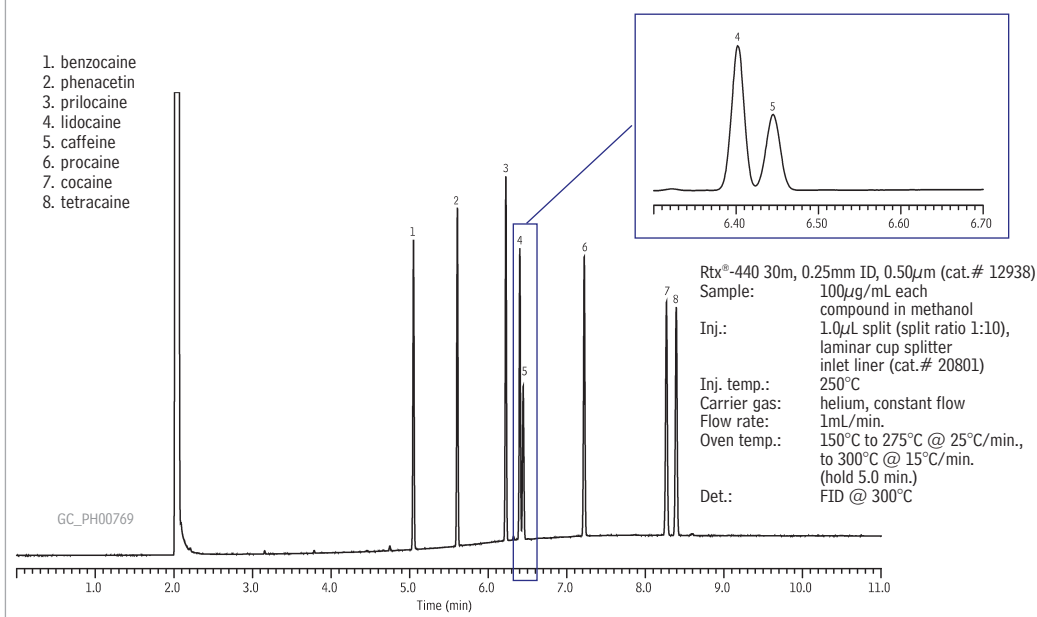
Cocaine adulterants separated by GC can be detected using flame ionization detection (FID), nitrogen-phosphorus detection (NPD), or mass spectrometry (MS). Although FID and NPD provide good sensitivity for identifying and quantifying cocaine adulterants (Figure 1), MS is the most widely accepted detection method. Not only is GC/MS very sensitive, the mass spectral data provide positive identification of the adulterants, and are accepted as confirming evidence in courts of law.

HPLC is used less commonly, but it provides reproducible retention times, reliable peak identification and reliable quantification. With HPLC, ultraviolet-visible detection (UV-Vis) at either fixed or variable UV wavelength is the most common detection mode for most adulterants. Sugars exhibit little or no UV absorbance, and must be evaluated with refractive index detection (RI) (Figure 2). HPLC/MS can provide confirming spectral data, but comprehensive methodology is still under development.

#### Procedure

We prepared simulated samples of illicit cocaine by adding equal concentrations of a variety of stimulants, including caffeine, local anesthetics (e.g., lidocaine), and over-the-counter analgesics (e.g., phenacetin) to cocaine hydrochloride. We developed GC and HPLC methods for identifying each adulterant focusing on

**Figure 1** An Rtx<sup>®</sup>-440 GC column resolves lidocaine/caffeine and other cocaine adulterants to baseline.



maximizing compound resolution while minimizing analysis time in order to increase sample throughput.

To compare the separation of caffeine and lidocaine by GC/MS at lower concentrations, we prepared and analyzed a sample containing 80% cocaine, 10% caffeine (1.0ng on column), 5% lidocaine (0.5ng on column) and 5% phenacetin.

For HPLC analysis, we began with equal amounts of adulterants in the cocaine mix; the on-column concentration for all compounds was 100ng. HPLC/UV-Vis conditions were optimized to give the maximum separation and the shortest analysis time. Then, we prepared and analyzed a sample containing 65% cocaine, 15% caffeine, 10% procaine, and 10% phenacetin (on-column concentrations of 133ng, 33ng, 20ng, and 20ng, respectively).

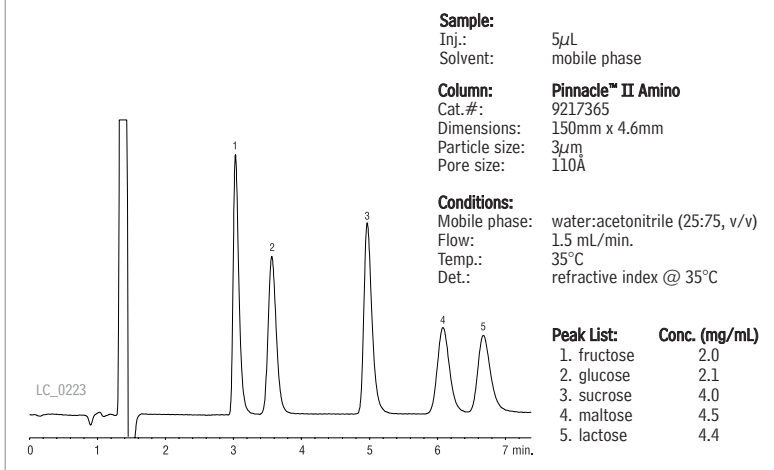
### Results

Under the best GC/MS conditions analysis time was 6.5 minutes (Figure 3). All compounds were resolved to baseline, with the exception of caffeine and lidocaine, which were resolved by approximately 40% (Figure 3), most likely due to MS vacuum effects on sample flow through the column. Caffeine and lidocaine have very different mass spectra, however, so extracted ion analysis provides positive identification of each compound (Figure 4). At the lower concentrations tested, only 10% resolution was obtained, but extracted ion analysis provided absolute identification and allowed proper integration (quantification) (Figure 5). Again, analysis time was 6.5 minutes.

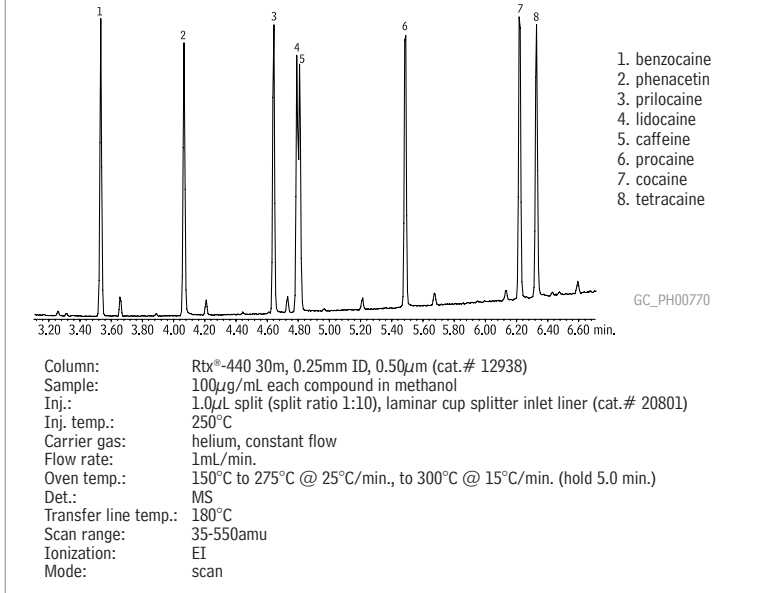
Using HPLC and an Ultra C18 column, all compounds were resolved to baseline with the exception of prilocaine and lidocaine, which were resolved by approximately 10% (Table 1). Analysis time was 8.0 minutes for both initial testing at 100ng on-column (data not shown) and subsequent testing at variable concentrations (Figure 6).

Positive identification and accurate quantification of prilocaine and lidocaine are very difficult if both compounds are present in the sample. We evaluated

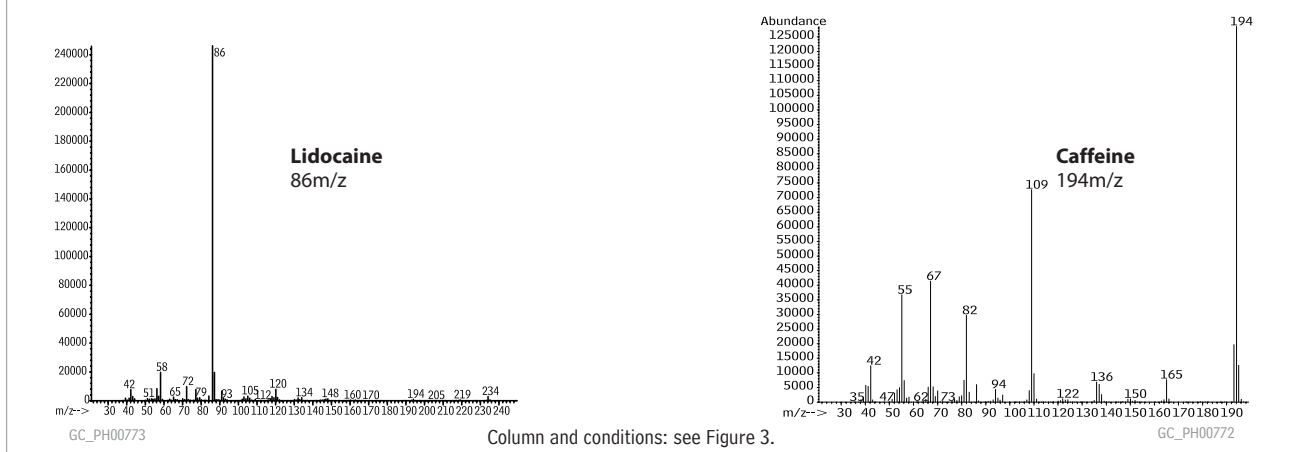
**Figure 2** Sugars are best analyzed by HPLC/RI. A Pinnacle™ II Amino column provides excellent resolution.



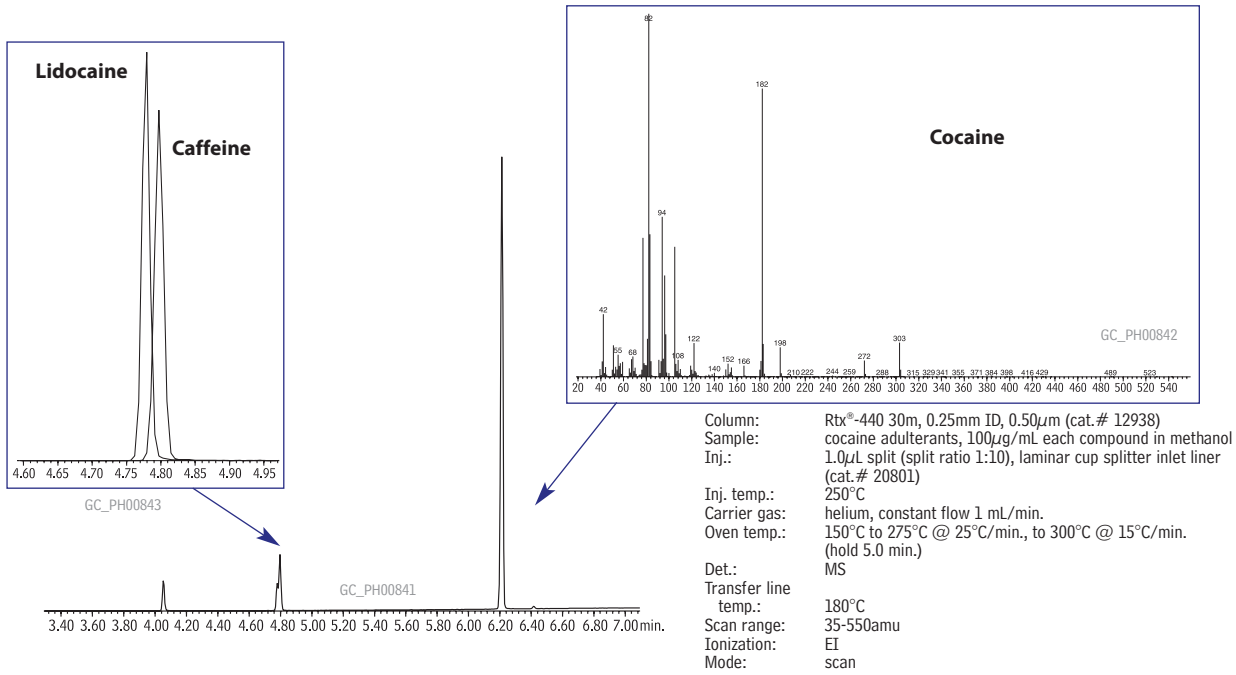
**Figure 3** Cocaine and adulterants separated on an Rtx®-440 GC column and detected by MS.



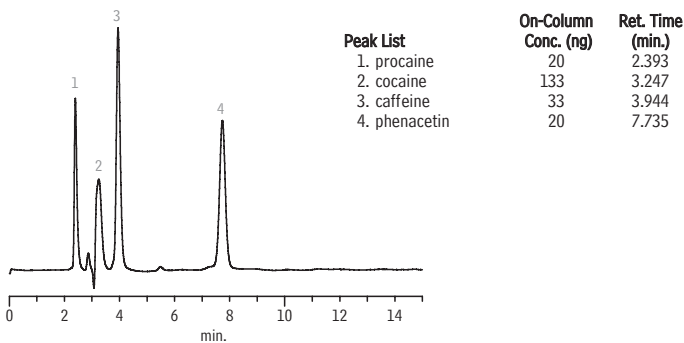
**Figure 4** Lidocaine and caffeine can be differentiated by their distinctive ions.



**Figure 5** Using GC/MS, lidocaine and caffeine can be quantified at 0.5ng and 1.0ng on column, respectively.



**Figure 6** An Ultra C18 HPLC column provided the best retention and greatest resolution of cocaine adulterants.



**Sample:**  
 Inj.: 20µL  
 Conc.: see peak list  
 Sample diluent: methanol

**Conditions:**  
 Mobile phase: 0.1% formic acid in water: methanol, 49:51 (v/v)  
 Flow: 0.50mL/min.  
 Temp.: 40°C  
 Det.: UV @ 234nm

**Column:**  
 Ultra C18  
 Cat.#: 9174565  
 Dimensions: 150mm x 4.6mm  
 Particle size: 5µm  
 Pore size: 100Å

several alternative HPLC stationary phases, including Allure® Basix, Allure® C18, Allure® PFP Propyl, Ultra Cyano, Ultra IBD, Ultra Amino, and Pinnacle™ II Amino, for improving the separation of prilocaine and lidocaine. These phases either did not retain all eight compounds or did not separate prilocaine and lidocaine. In comparison, the Ultra C18 column provided the best retention and the greatest resolution of all compounds in the study.

### Conclusions

Simulated cocaine mixtures were “fingerprinted” by identifying and quantifying the adulterants they contained. GC/MS provides adequate semiquantitative information regarding the concentration of each additive relative to the concentration of cocaine, and the most reliable identification of each substance (through both retention time and mass spectrum data), and so is the preferred chromatographic method for analyzing cocaine and most cocaine adulterants. Sugars must be analyzed by HPLC/RI.

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

**Table 1** Prilocaine and lidocaine coelute by HPLC.

Compound	Ret. Time (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

### for more info

Smith, F.P., *Handbook of Forensic Drug Analysis* pp. 235-275, Elsevier, 2005. (Restek cat.# 23055)  
 Telepchak, M.F., T.F. August, and G. Chaney, *Forensic and Clinical Applications of Solid Phase Extraction* pp. 204-213, Humana Press, 2004.

## HPLC Columns

### Ultra C18 HPLC Columns (USP L1)

#### Physical Characteristics:

particle size: 5µm, spherical endcap: fully endcapped  
pore size: 100Å pH range: 2.5 to 7.5  
carbon load: 20% temperature limit: 80°C

5µm Column, 4.6mm		cat. #
150mm		9174565
150mm with Trident Inlet Fitting		9174565-700
Ultra C18 Guard Cartridges	qty.	cat. #
10 x 2.1mm	3-pk.	917450212
10 x 4.0mm	3-pk.	917450210
20 x 2.1mm	2-pk.	917450222
20 x 4.0mm	2-pk.	917450220

### Pinnacle™ II Amino HPLC Columns (USP L8)

#### Physical Characteristics:

particle size: 3µm, spherical pH range: 2.5 to 7.5  
pore size: 110Å temperature limit: 80°C  
carbon load: 2%

3µm Column, 4.6mm		cat. #
150mm		9217365
150mm with Trident Inlet Fitting		9217365-700
Pinnacle™ II Amino Guard Cartridges	qty.	cat. #
10 x 2.1mm	3-pk.	921750212
10 x 4.0mm	3-pk.	921750210
20 x 2.1mm	2-pk.	921750222
20 x 4.0mm	2-pk.	921750220

## GC Accessories



### Split Liners for Agilent GCs

ID* x OD & Length (mm)	qty.	cat. #
Laminar Cup Splitter		
4.0 ID x 6.3 OD x 78.5	ea.	20801
4.0 ID x 6.3 OD x 78.5	5-pk.	20802

\*\*Nominal ID at syringe needle expulsion point.

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Allure, Crossbond, Pinnacle,  
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## GC Columns

### Rtx®-440 Capillary GC Columns

(intermediate-polarity proprietary Crossbond® phase)

ID	df (µm)	temp. limits	length	cat. #
0.25mm	0.25	20°C to 320/340°C	30-Meter	12923
0.25mm	0.50	20°C to 320/340°C	30-Meter	12938

## Analytical Reference Materials

### Carbohydrate HPLC Performance Check Mix

glucose	2.0mg	maltose	4.5
fructose	2.1	sucrose	4.0
lactose	4.4		

Dry components in 4mL screw-cap vial. Reconstitute in 1mL acetonitrile:water (75:25) to 2.0, 2.1, 4.4, 4.5, 4.0 mg/mL, respectively.

cat. # 31809

No data pack available.

### Exempted Drug of Abuse Reference Materials

Concentration is µg/mL. Volume is 1mL/ampul.

Compound	CAS#	Solvent		cat. #
		Code	Conc.	
<b>Cocaine &amp; Metabolites</b>				
cocaethylene	529-38-4	ACN	1,000	34066
cocaine	53-21-4	PTM	1,000	34015
benzoylecgonine	519-09-5	PTM	1,000	34016
ecgonine	5796-31-6	PTM	1,000	34017
ecgonine methyl ester	38969-40-3	PTM	1,000	34018

ACN=acetonitrile, PTM=purge & trap grade methanol

## also available

### Exempted Drugs of Abuse

We also sell many other exempted drugs of abuse. See our general catalog or visit [www.restek.com](http://www.restek.com).

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