

# Comprehensive Screening for PAHs in Sugarcane Products after QuEChERS with Sweet Separations using an Rxi-17Sil MS column, GC-MS, and GCxGC-TOFMS

Julie Kowalski, Corby Hilliard, Jason Thomas, and Jack Cochran  
Restek Corporation, 110 Benner Circle, Bellefonte, PA 16823

## Background

The reason for screening sugarcane products is for the known amounts of toxins, called PAHs, which can be caused by burning the fields of sugarcane, during manual harvest.

### PAH- Polycyclic Aromatic Hydrocarbons

Formed during incomplete combustion and pyrolysis

- Some PAHs are genotoxic and carcinogenic
- Help with manual harvest
- Increases sugar weight by evaporating the water in the stalk
- Most human exposure is through food and inhaled air

Determining the exposure of PAHs in Sugarcane and Sugarcane products

Sugarcane and sugarcane products are targeted for PAHs, due to the 13 PAHs that were clearly carcinogenic and genotoxic, including the four selected for this study: benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(a)pyrene; due to burning of the raw stocks prior to the manual harvesting.



In this work, a combination of QuEChERS, GCxGC TOFMS, and GC-MS will be evaluated to determine a variety of PAHs found in Sugarcane Products.

QuEChERS sample preparation is "Quick Easy Cheap Effective Rugged and Safe" allowing high throughput.

Comprehensive two-dimensional GC (GCxGC): increase peak capacity by applying two independent separations.

Typically GCxGC involves a serial column configuration with different stationary phases.

Chromatography is performed on the first column, and then effluent from the first column is continually and quickly focused and injected by a modulator onto the second column.

Separation results are plotted as a retention plane (column 1 retention time x column 2 retention time).

## Scope

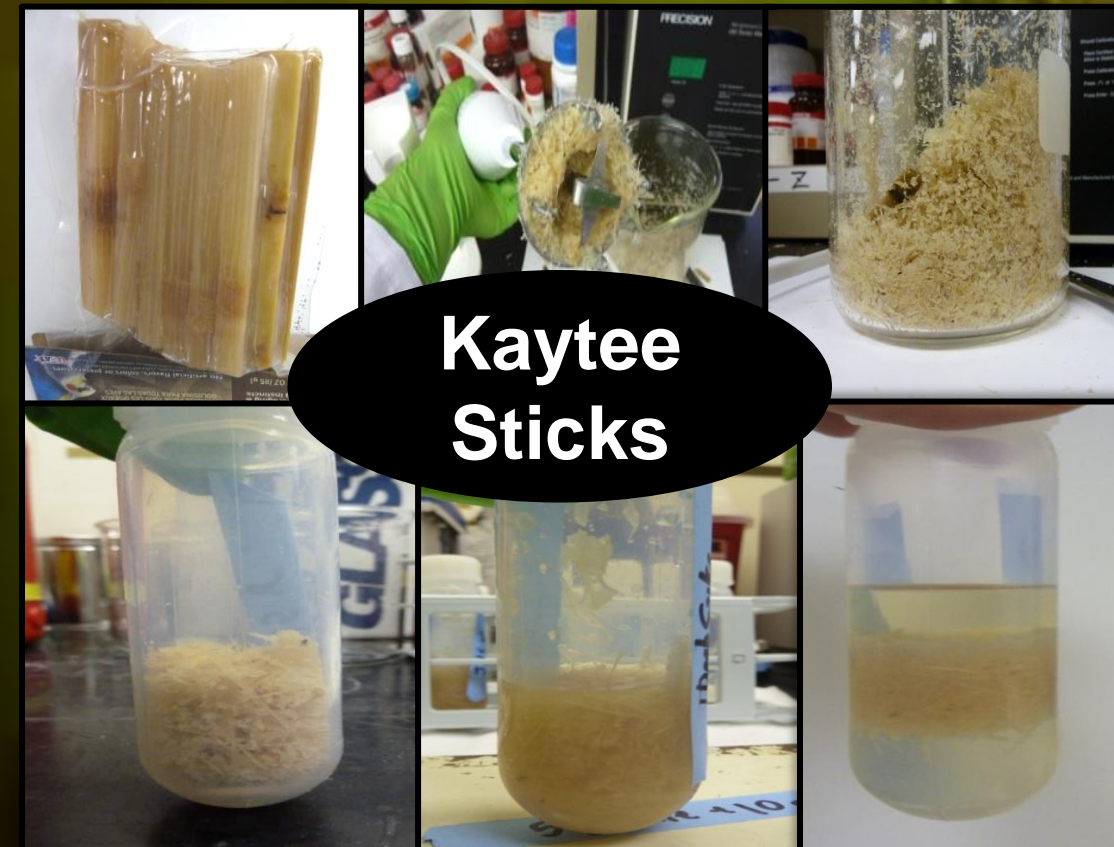
### Sample Preparation

Sugarcane Product

QuEChERS extraction

### Instrumental Analysis

GC-MS      GC x GC TOFMS



### Dry Sugarcane Root Wetting:

5 grams sugarcane root, Add 10 mL water and shake to wet, then extract

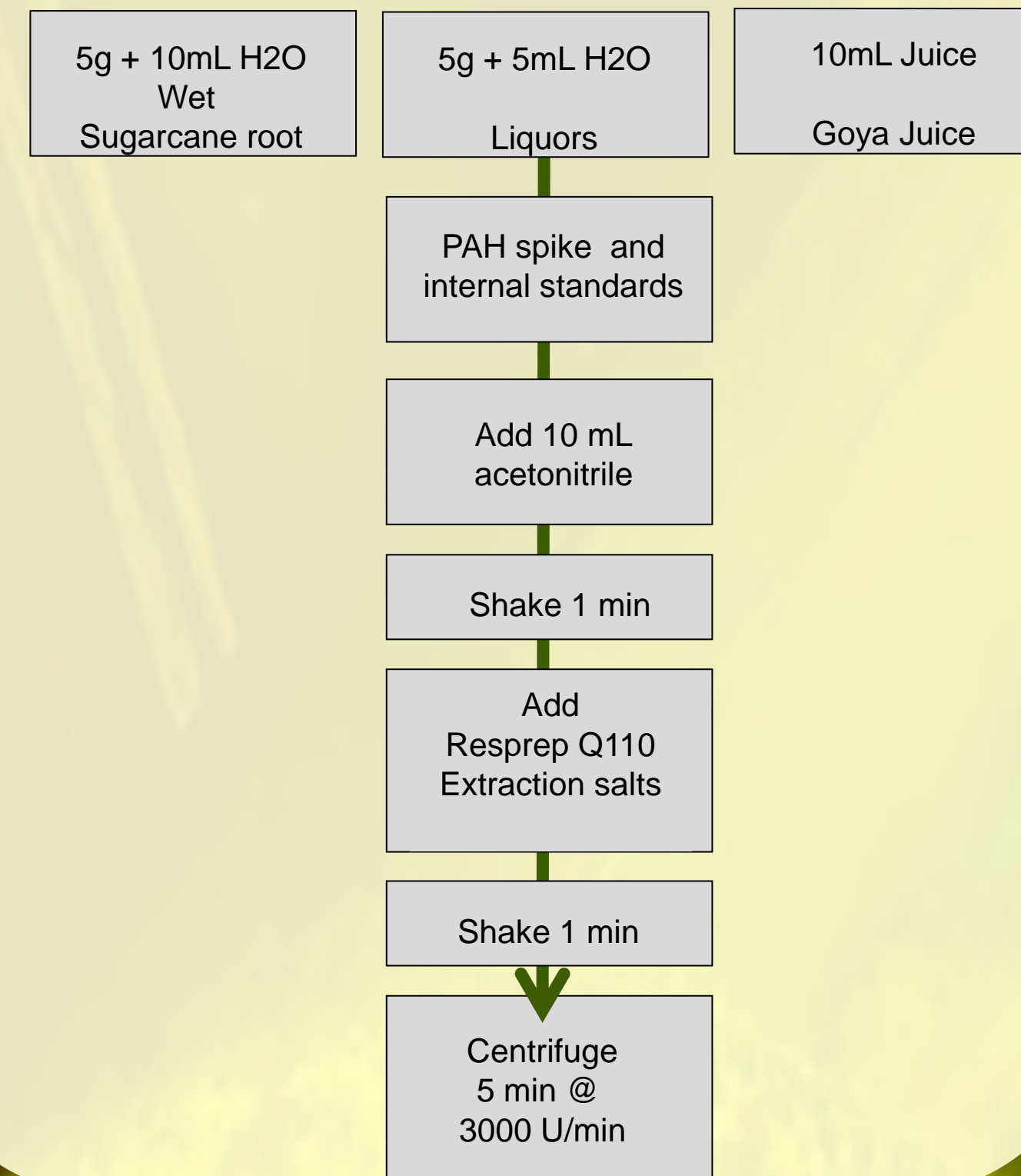
### Sugarcane Products:

Sugarcane Root, Goya Juice and Whiskey, which is produced from Sugarcane, Finished Products (4)



## Experimental

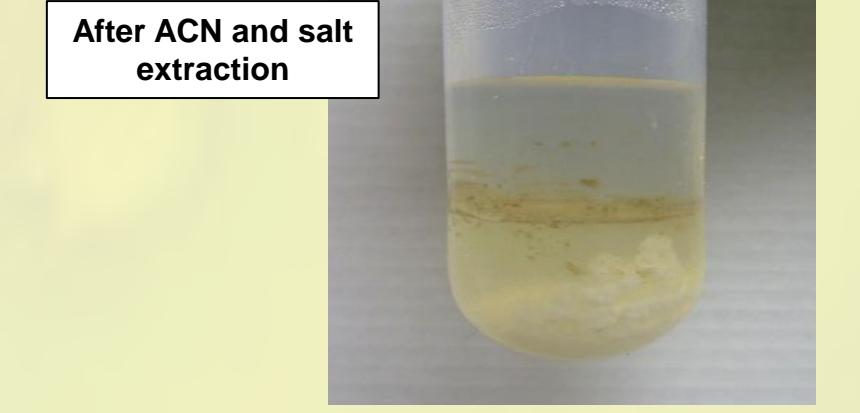
### QuEChERS Extraction



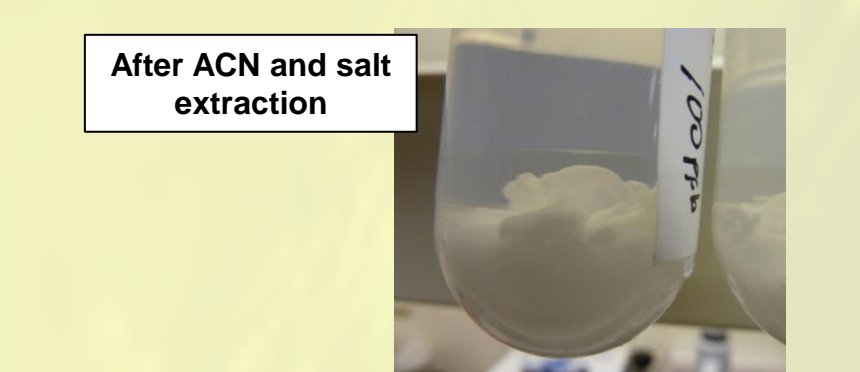
Comprehensive PAH List: US EPA 8310 (16 compounds), EU 15 + 1 list, and interferences (3 compounds) total of 29 compounds

Extractions:

### 10 mL Goya Juice



Sample: 10 Cane Rum  
10 mL liquor: no layer formation  
5mL liquor and 5mL water



Shimadzu QP 2010  
GC/MS-SIM

- Injection**
- Temp: 275 C
  - Injection: 1 µL fast, splitless (valve 1.0 min)
- Column**
- Rxi-17Sil MS 30m x 0.25mmID x 0.25µm
- Conditions**
- Oven: 65 C (0.5 min), 40 C/min to 270 C, 2.5 C/min to 330 C @ 6 C/min (hold 12min)
  - Carrier: He, constant flow 1.5 mL/min
  - Transfer Line: 300 C
- MS Conditions**
- Source temperature: 280 C
  - Electron ionization: 70 eV
  - Stored mass range: SIM

Pegasus 4D TOF MS  
GCxGC-TOFMS

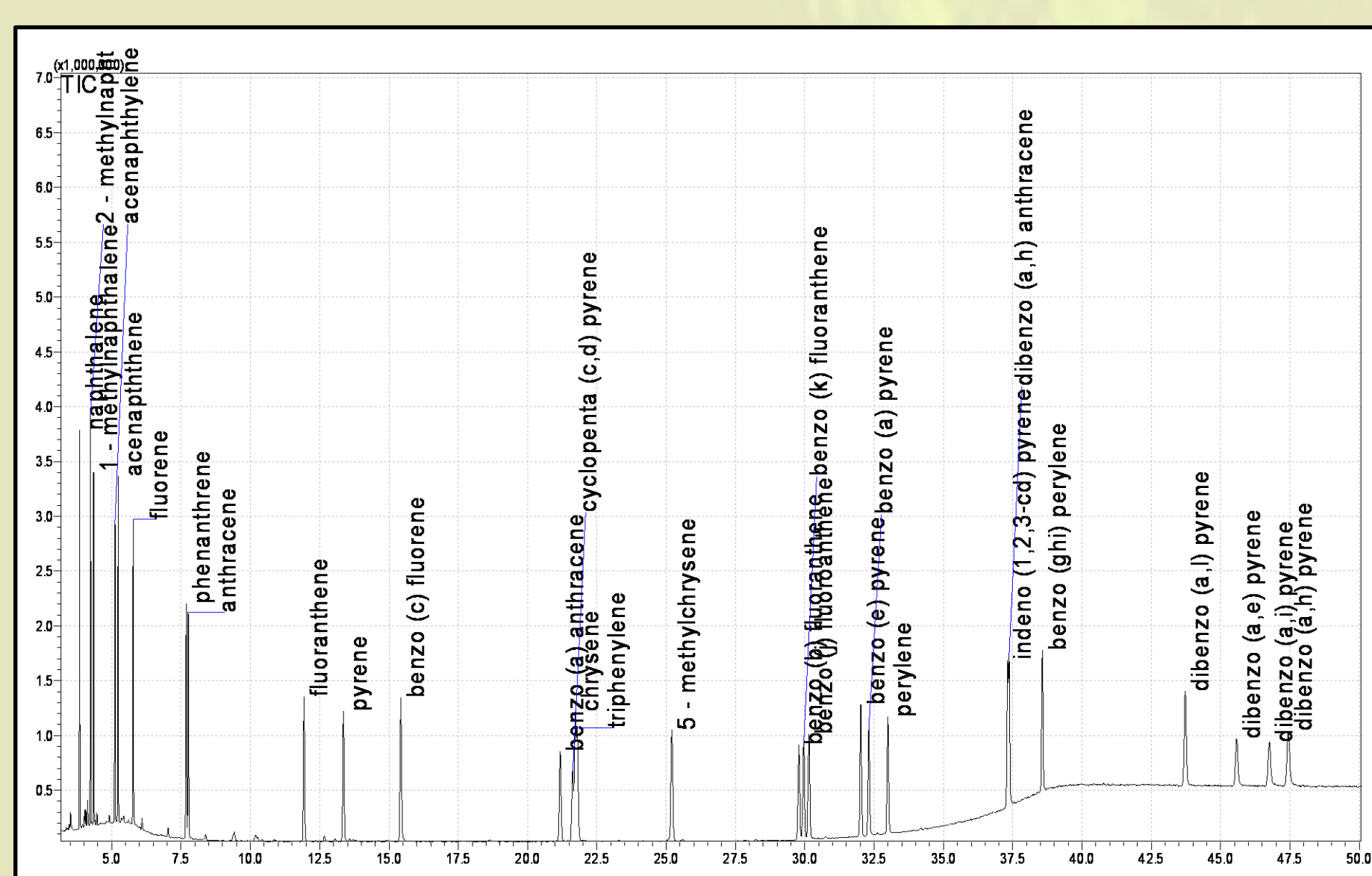
- Injection**
- Temp: 250 C
  - Injection: 1 µL fast, splitless (valve 1.0 min)
- Columns**
- Rxi-5Sil MS 30m x 0.25mmID x 0.25µm
  - Rtx-200 1.3 m x 0.25 mm x 0.25 µm
- Conditions**
- 1<sup>st</sup> Oven: 70 C (1 min), 5 C/min to 310 C
  - 2<sup>nd</sup> Oven: 75 C (1 min), 5 C/min to 310 C
  - Carrier: He, constant 2.0 mL/min
  - Modulation time: 3 sec
  - Transfer line: 300 C
- LECO Pegasus® TOFMS Conditions**
- Source temperature: 250 C
  - Electron ionization: 70 eV
  - Stored mass range: 40 to 550 u
  - Acquisition rate: 100 spectra/sec

Benefits of GC x GC analysis

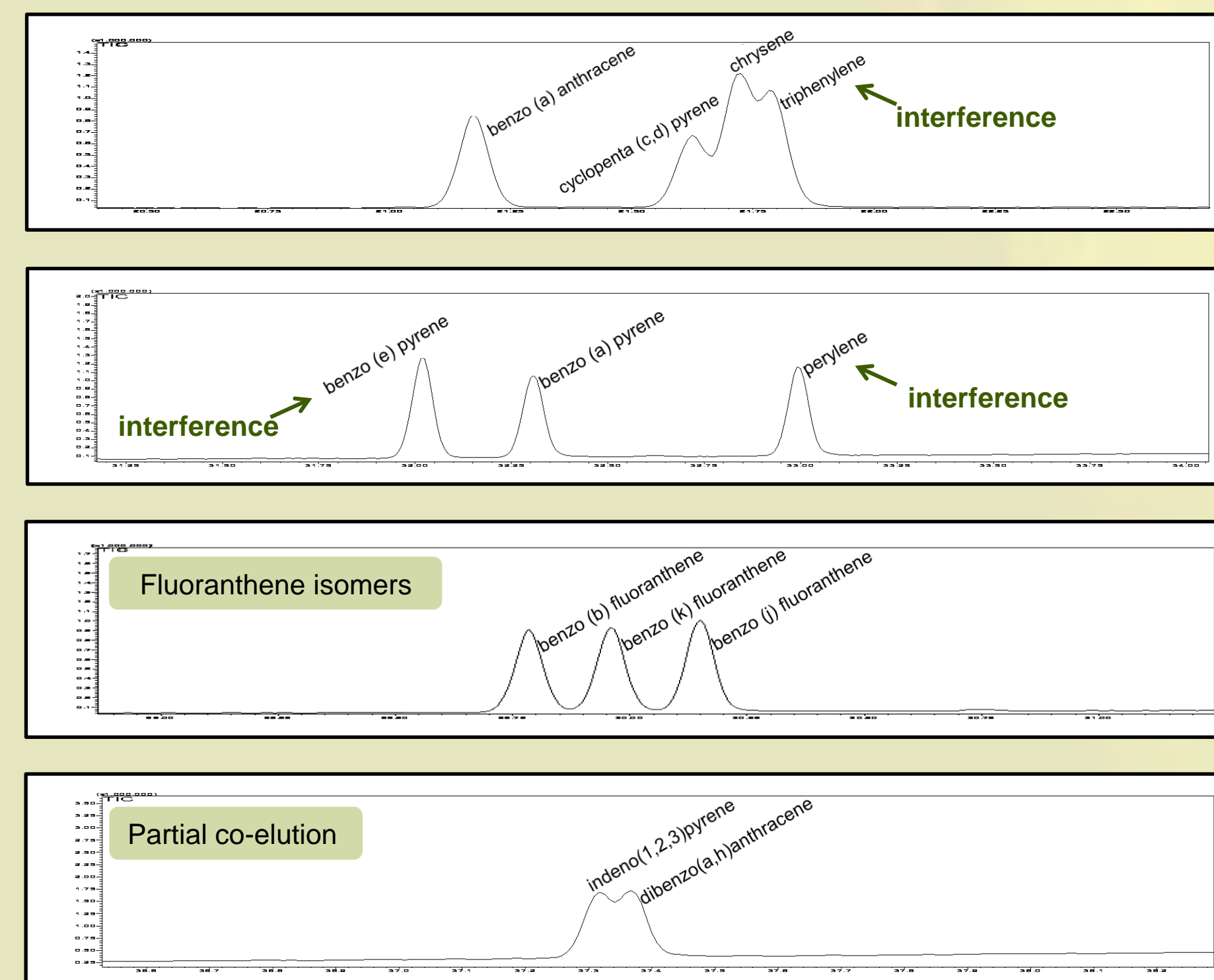
- Two independent separation mechanisms provides better resolution
- Improved resolving power by increasing peak capacity
- Sensitivity enhancement by focusing through modulation
- Grouping by chemical class simplifies complex sample characterization

## Results

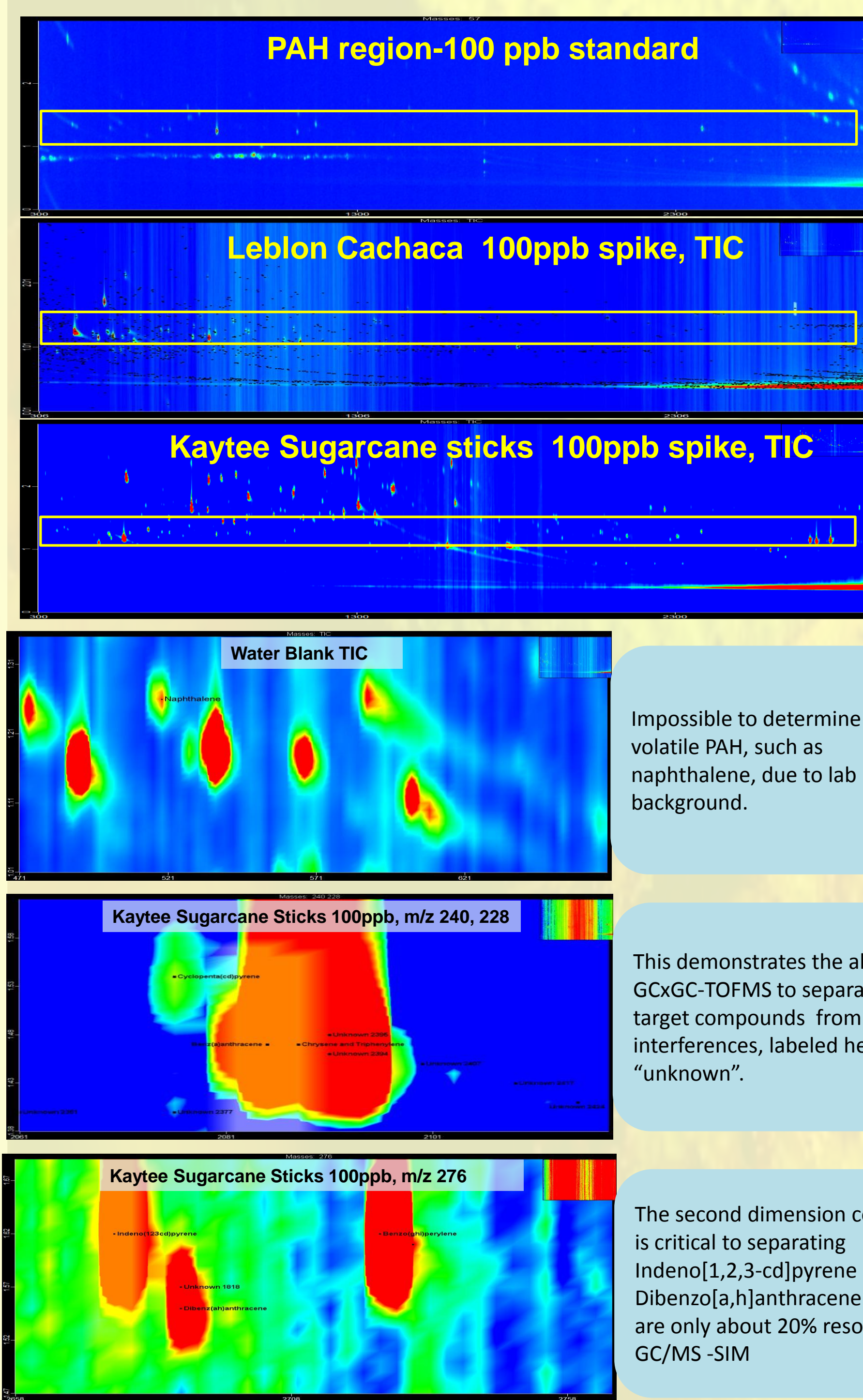
### GC-MS TIC 1ppm standard of 29PAHs



### Key Separations



### GCxGC-TOFMS Chromatograms



Impossible to determine most volatile PAH, such as naphthalene, due to lab background.

This demonstrates the ability of GCxGC-TOFMS to separate target compounds from matrix interferences, labeled here as "unknown".

The second dimension column is critical to separating Indeno[1,2,3-cd]pyrene and Dibenzo[a,h]anthracene that are only about 20% resolved by GC/MS-SIM

### Leblon Cachaca % Recoveries

compound	100 ppb		10 ppb		1 ppb	
	GC (SIM)	GCxGC	GC (SIM)	GCxGC	GC (SIM)	GCxGC
Naphthalene-d8	IS	IS	IS	IS	IS	IS
Naphthalene	110	80	99	76	98	96
Naphthalene, 2-methyl-	82	81	76	73	INT	107
Naphthalene, 1-methyl-	83	81	78	73	55	84
Acenaphthylene	80	80	77	82	90	90
Acenaphthene-d10	IS	IS	IS	IS	IS	IS
Acenaphthene	78	81	78	84	84	77
Fluorene	81	80	75	84	INT	84
Phenanthrene-d10	IS	IS	IS	IS	IS	IS
Phenanthrene	80	78	74	86	65	149
Anthracene	84	79	69	84	90	167
Fluoranthene	81	79	78	81	91	82
Pyrene	81	79	75	84	117	130
Benzo[c]fluorene	78	77	92	72	98	97
Benzo[a]anthracene	76	79	69	72	INT	79
Chrysene-d12	IS	IS	IS	IS	IS	IS
Cyclopenta(c,d)pyrene	82	78	83	60	ND	ND
Chrysene	63	142.93 C+T	113	152	INT	173
Triphenylene	89	C+T	86	C+T	INT	C+T
5-Methylchrysene	78	75	72	67	INT	58
Benzo[b]fluoranthene	67	141.73 b+j	72	142	3	166
Benzo[k]fluoranthene	64	98	76	91	121	56
Benzo[j]fluoranthene	66	b+j	75	b+j	179	b+j
Benzo[e]pyrene	63	75	78	76	65	112
Benzo[a]pyrene	66	73	89	65	78	60
Perylene-d12	IS	IS	IS	IS	IS	IS
Perylene	67	83	83	86	78	137
Indeno[1,2,3-cd]pyrene	71	74	77	55	ND	ND
Dibenzo[a,h]anthracene	69	95	88	89	ND	INT
Benzo(g,h,i)perylene	62	82	85	53	ND	157
Dibenzo[a,i]pyrene	59	NA	67	NA	ND	NA
Dibenzo[a,e]pyrene	108	NA	85	NA	ND	NA
Dibenzo[a,j]pyrene	79	NA	57	NA	ND	NA
Dibenzo[a,h]pyrene	77	NA	106	NA	ND	NA

GCxGC-TOFMS: combine chrysene and triphenylene

GCxGC-TOFMS: combine benzo[b]fluoranthene and benzo[j]fluoranthene

Matrix-matched standards  
GC/MS-SIM: 1 quant ion and 2 qual ions  
GCxGC-TOFMS: 1 quant ion and full spectral match

## Conclusions

- QuEChERS extraction seems to be a viable approach to extracting PAHs
- Cleanup was performed for comparison but data analysis not complete
- 1D GC-SIM MS
  - PAH selective column allows determination of interfering PAHs
  - Difficulty at low levels (sub ppb) – ion ratios
- GCxGC-TOFMS
  - Powerful tool but limited in analyte resolution with orthogonal BUT non-selective columns
  - Minimizes matrix interferences for quant data

## Acknowledgments

Joe Binkley, and Robert J Warren

