

Characterization of Complex Forensic Samples by Gas Chromatography–High Resolution Time-of-Flight Mass Spectrometry

John Rorabeck¹, David E. Alonso² and Joe Binkley² | ¹Berrien County Forensic Laboratory, Berrien Springs, MI; ²LECO Corporation, St. Joseph, MI

Introduction

Background

Controlled substances such as marijuana, cocaine, heroin, and methamphetamines are commonly seized by law enforcement officials and routinely analyzed by forensic laboratories. More recently, synthetic drugs such as bath salts, cannabinoids, naturally occurring herbal remedies, and hallucinogenic mushrooms have gained popularity as chemical stimulants and opiate substitutes. This study focused on the comprehensive profiling of complex botanicals obtained from drug seizures.



Botanicals



Bath Salts



Magic Mushrooms

Analytical Challenges

- Chemical Diversity of Compounds
- Novelty of Synthetic Compounds
- Concentration Range of Sample Constituents
- Complexity of Botanical Matrices
- Inappropriate Sample Preparation Methods
- Unsuitable Instrumental Analysis Protocol

The Solution

- Tailored Sample Preparation
- GC-HR TOFMS (Pegasus GC-HRT):
 - High-Quality Spectral Data
 - Comprehensive
 - Search Against Well-Established Databases (e.g., NIST, Wiley)
 - Excellent Mass Accuracy Values (<1 ppm) = Robust Formulas for Fragment, Molecular, and Adduct Ions
 - High Resolution Deconvolution™ (HRD™)
 - High Resolving Power (up to 50,000) = Increased Selectivity for:
 - Discovery
 - Confirmation
 - Comprehensive Profiling of Complex Samples



Pegasus® GC-HRT

L = 20m R = 25,000
L = 40m R = 50,000

Experimental

Sample Preparation Methods

Botanical samples were obtained from a forensic laboratory after they had been analyzed and pertinent cases were completed. General analysis for volatile materials was accomplished through head-space solid-phase microextraction (HS-SPME). Solvent extraction followed by derivatization was utilized for comprehensive profiling of samples.



HS-SPME (Volatiles)

Placed 0.05 g of crushed sample (mortar and pestle) in a 10 mL headspace vial. Added 0.5 g NaCl and 1 mL of either deionized water or 10% NaOH (aq). Extraction was carried out using a 50/30 μm DVb/CAR/PDMS Stableflex, 24 Ga SPME fiber. The procedure included fiber conditioning (1 hr at 270°C), incubation (3 min at 95°C), extraction (15 min at 95°C, 250 rpm interval agitation—5s on, 2s off), followed by desorption in the GC-injector (5 min at 250°C).

Solvent Extraction/Derivatization (Profiling)

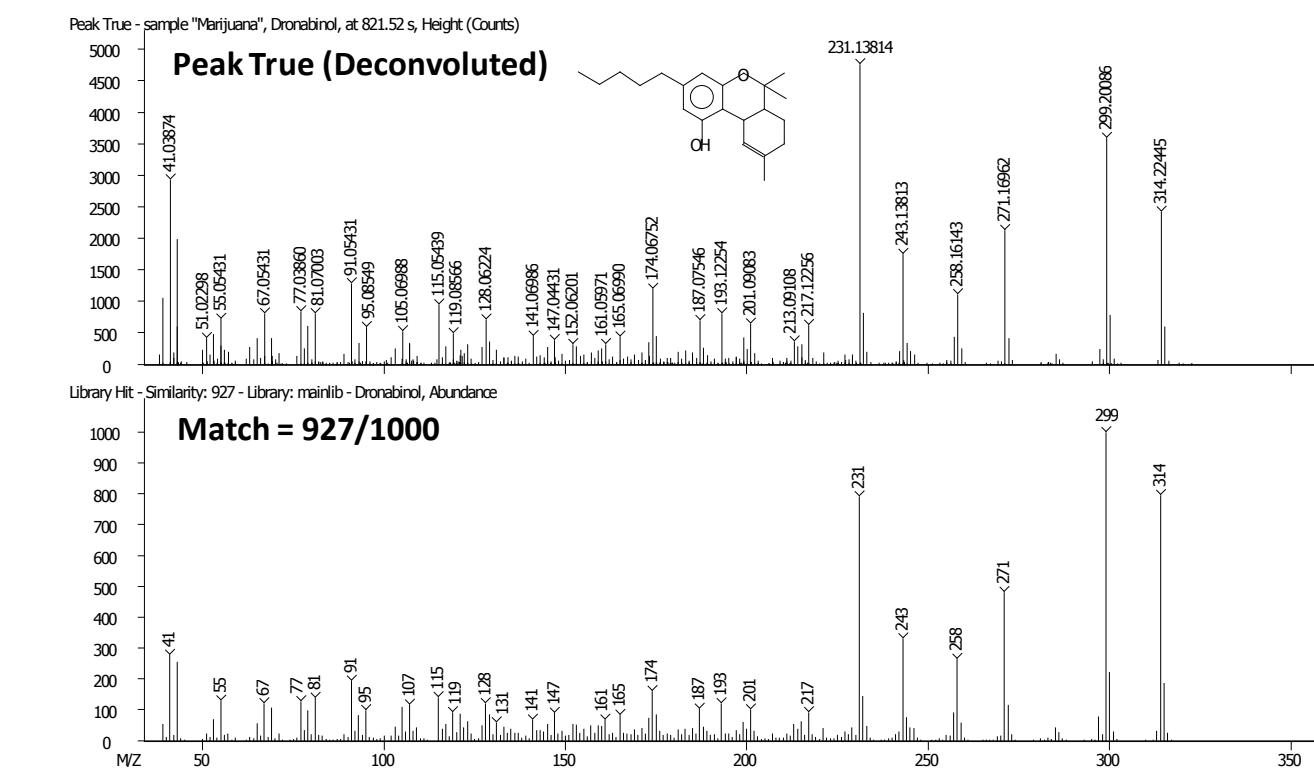
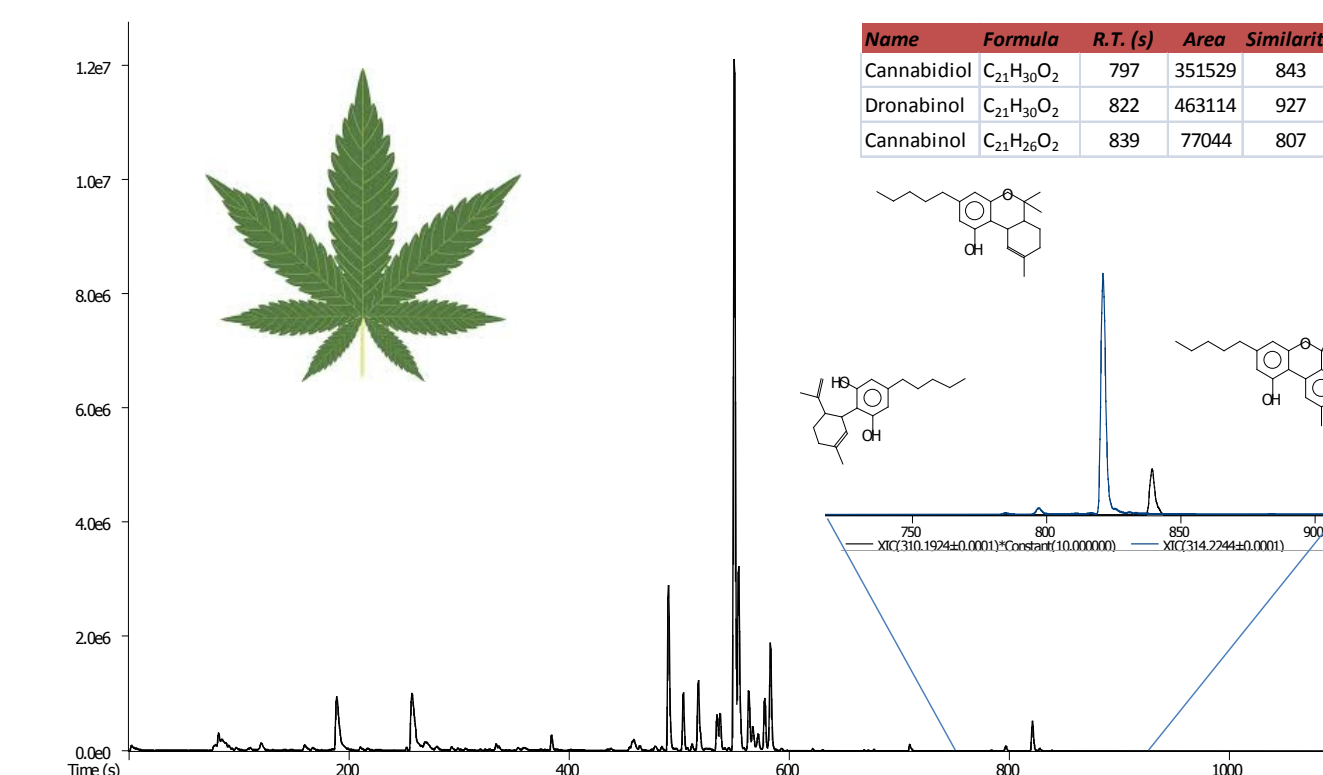
Samples (0.025 g) were mixed with methanol (2 mL) and sonicated for 25 minutes. The heterogeneous mixtures were filtered and dried with N₂ gas. The samples were then treated with MEOX (25 μL, 60°C, 1 hr), MSTFA (50 μL, 60°C, 1 hr), and transferred to 2 mL GC vials for analysis.

Instrument Parameters

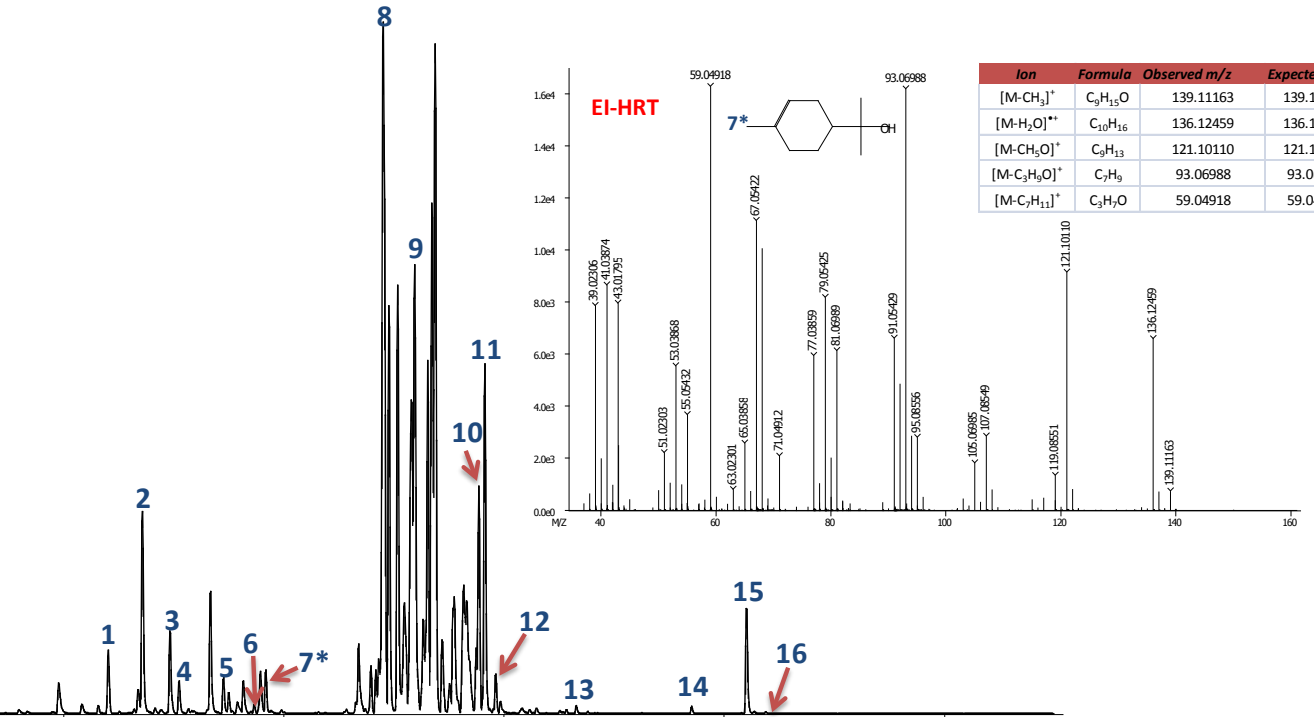
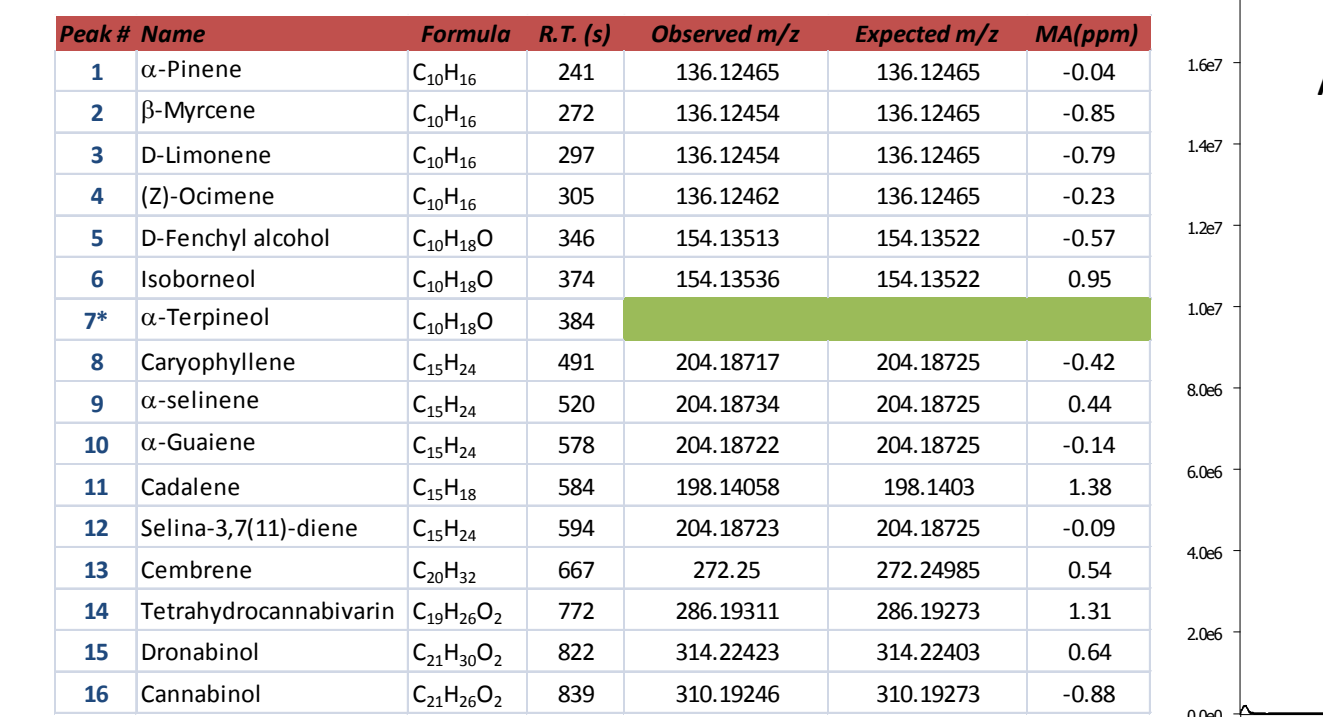
GC		Agilent 7890 with Gerstel MPS Auto Sampler	
Column	Restek Rxi-5 MS (30 m x 0.25 mm x 0.25 μm)	Carrier Gas, Flow	He, 1.0 mL/min Constant Flow
Injection	1 μL, Split 5:1, SPME	Inlet Temperature	270°C
Temp. Program	70°C (2 min) to 280°C at 20°C/min (3 min)		
MS		LECO Pegasus® GC-HRT	
Transfer Line Temp.	300°C	Ion Source Temp.	EI 250°C; CI 200°C
Ionization	EI (70 eV); CI (140 eV)	Mass Range	EI 35–510; CI 60–510
Acquisition Rate	6 spectra/second	Calibration (Internal)	PFTBA
Reagent Gas	5% Ammonia in Methane		

HS-SPME Results

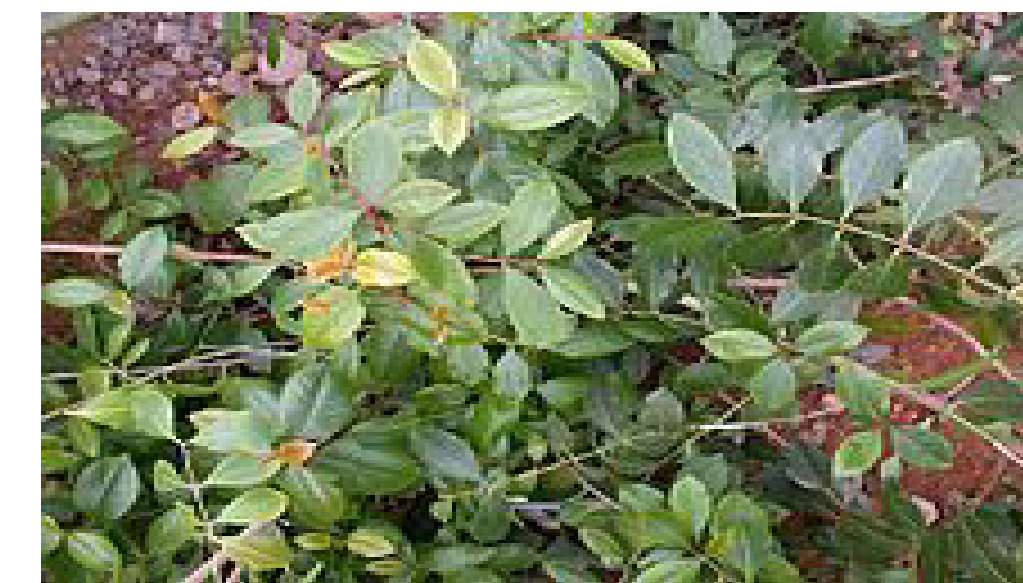
A) Marijuana (High-Quality Spectral Data)



B) Compressed Hash (Excellent Mass Accuracy)

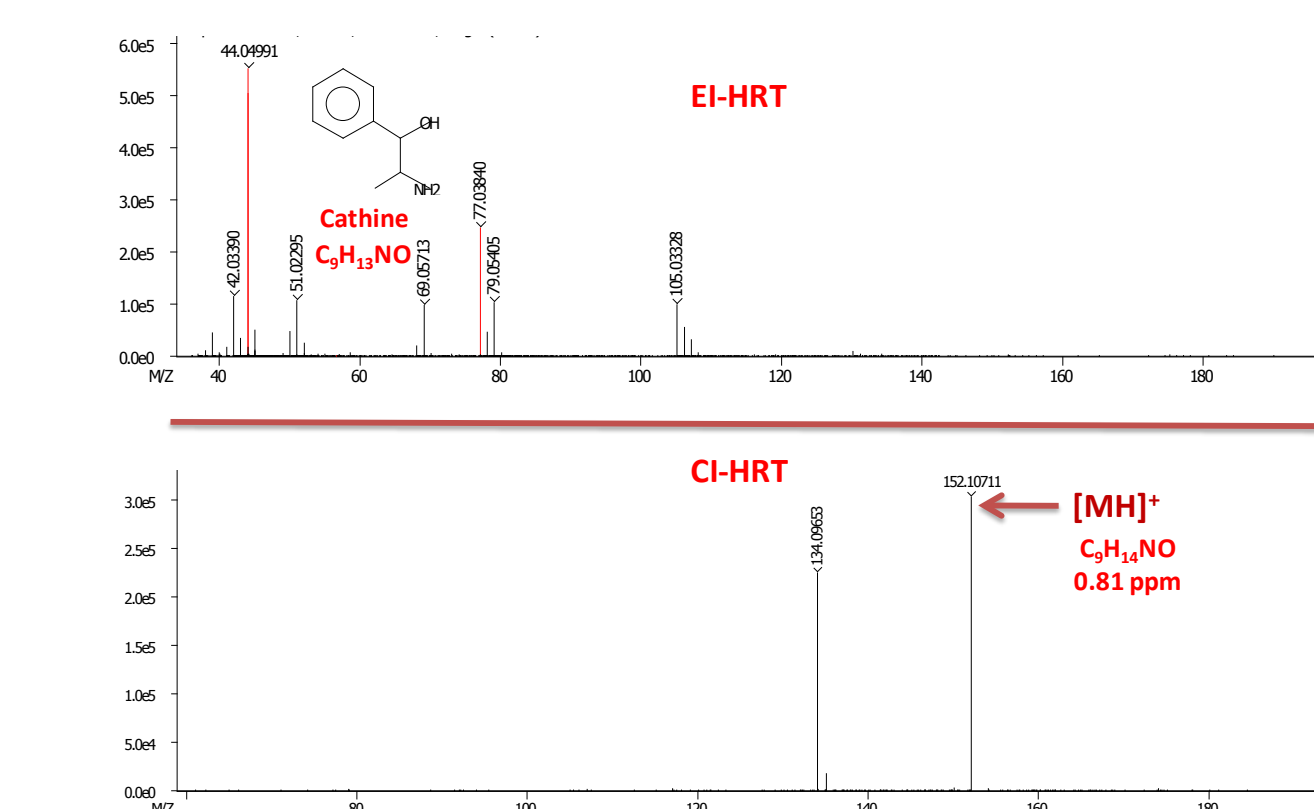
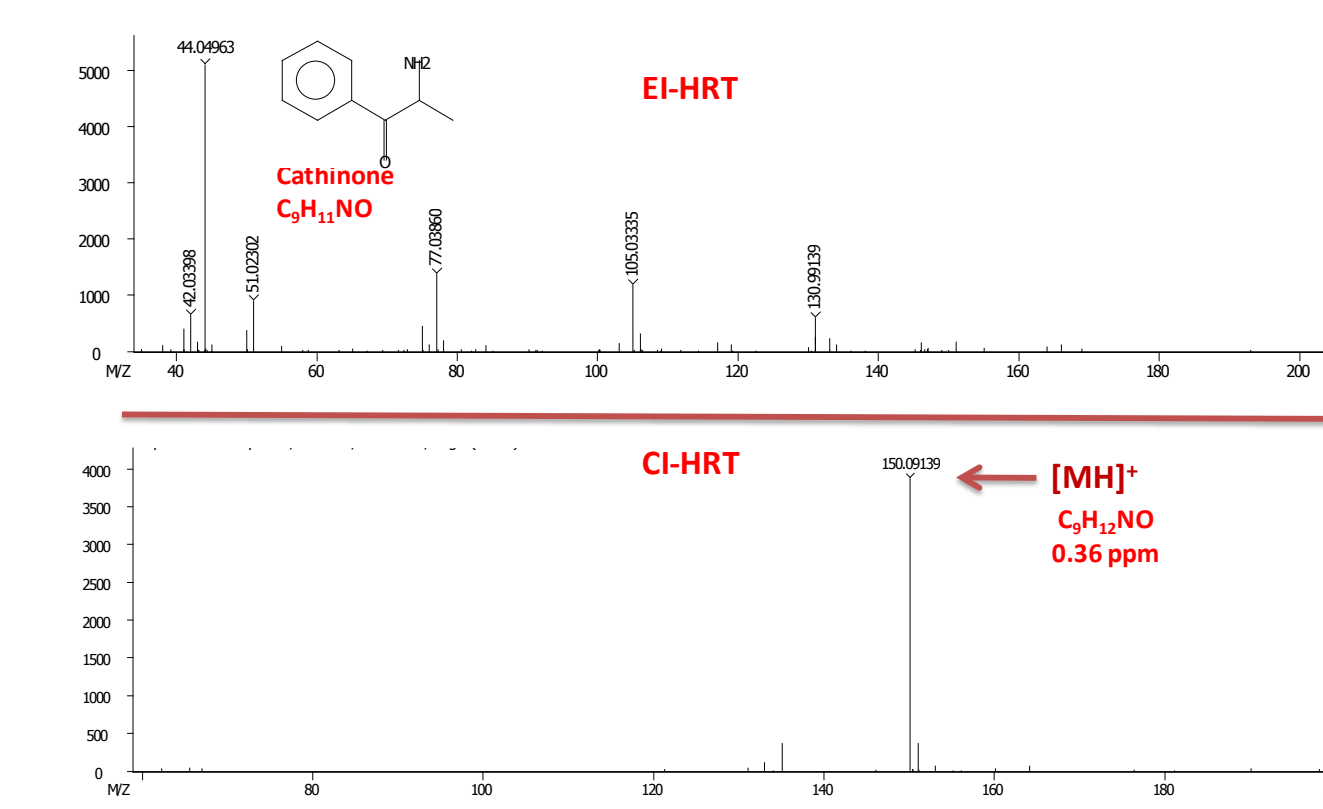


C) Khat (High Resolution Deconvolution™)



Catha edulis

- Slow-growing shrub (warm climates)
- Chewed (fresh) or consumed as tea (dry)
- Wide variety of components: Amines, terpenes, sugar alcohols, amino acids, etc.
- Active compounds: Cathinone and Cathine



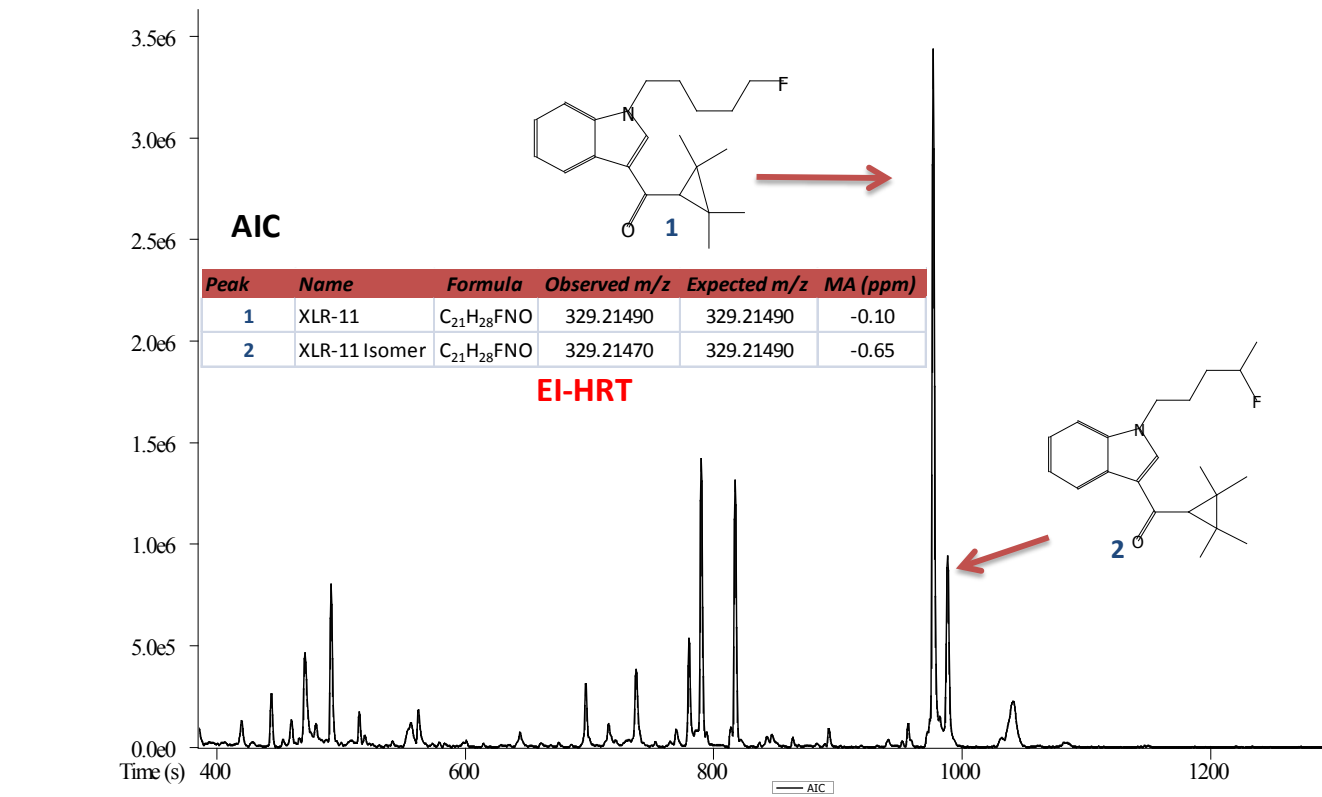
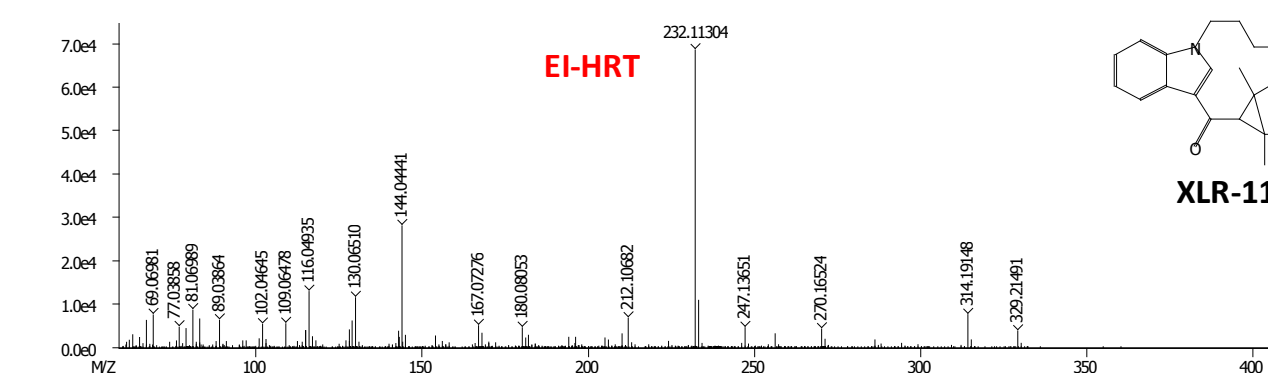
Liquid Extraction/Derivatization Results

D) Pokeweed (Discovery & Confirmation)

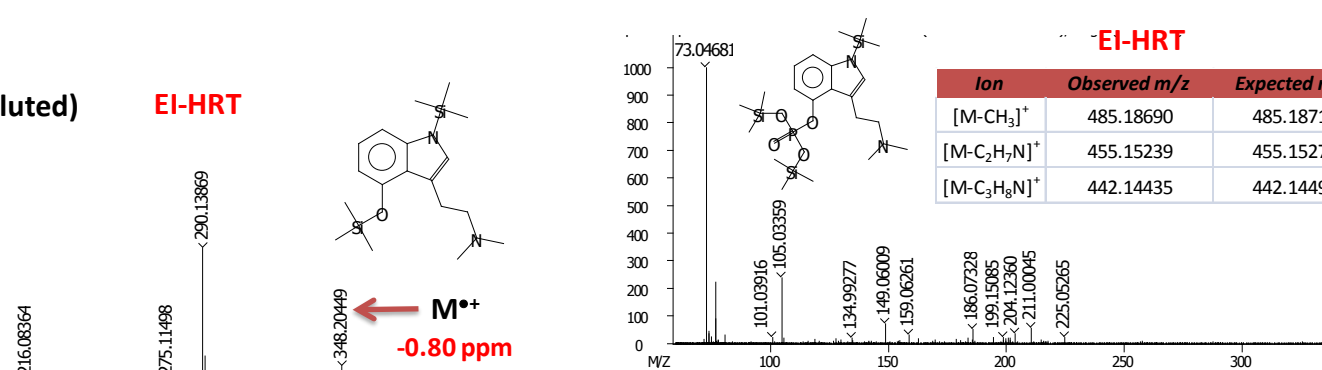
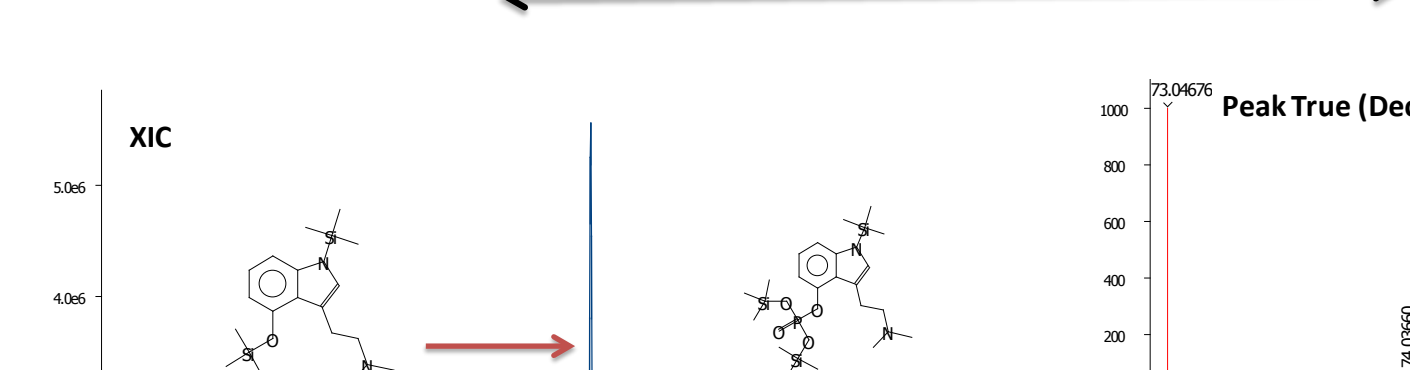
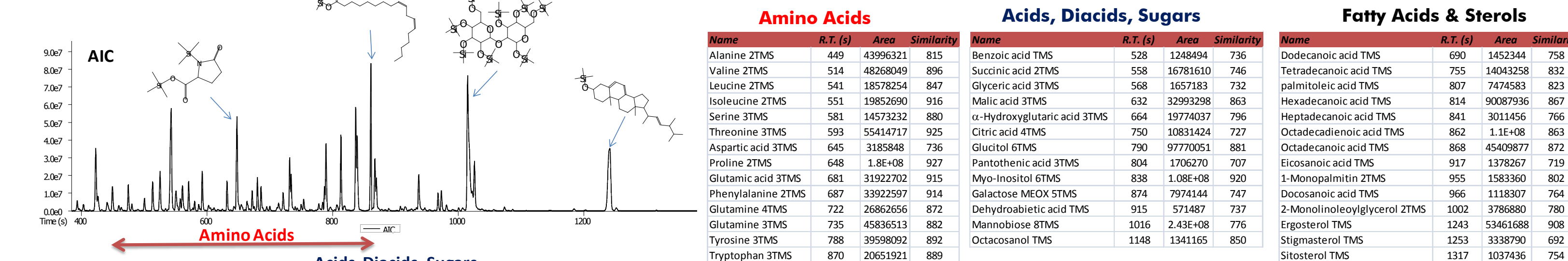


Phytolacca americana

- Perennial herbaceous plant
- Native to North America
- Has been used as medicine and food
- Can be dried and then laced with synthetic drugs



E) Magic Mushrooms (Comprehensive Profiling)



Summary

Proper sample preparation is critical for the analysis of complex samples. GC-HRT provides high quality, accurate mass data for:

- Spectral similarity searches (NIST, Wiley, etc.)
- Formula determination (fragment, molecular, and adduct ions)

