

Supplemental material for ...

Chemical characterization of marijuana blunt smoke by non-targeted chemical analysis

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Supplementary Table S1. GC×GC-TOFMS method parameters for collection of primary screening data.

GC×GC-TOFMS system	LECO Pegasus 4D
GC 1st-dimension column	100% dimethylpolysiloxane, 30 m, 0.25 mm i.d., 1 µm d _f
GC 2nd-dimension column	50% phenyl polysilphenylene-siloxane 1 m, 0.1 mm i.d., 0.1 µm d _f
GC carrier gas	Helium
GC carrier gas flow rate	Constant flow, 1.3 mL/min
GC inlet temperature	250 °C
GC injection volume	1 µL splitless
GC 1st-dimension column oven program	45 °C (1.5 min hold) 45 °C – 100 °C @ 20 °C/min 100 °C – 270 °C @ 3 °C/min; hold 1 min 270 °C – 320 °C @ 20 °C/min; hold 16 min
GC 2nd-dimension column oven program	80 °C (1.5 min hold) 80 °C – 275 °C @ 3 °C/min 275 °C – 330 °C @ 20 °C/min; hold 11 min
GC modulator temperature offset from first oven	+20 °C
GC modulation time	3 seconds
Transfer line temperature	290 °C
MS source temperature	200 °C
MS detector voltage	Tune voltage + 200 V
MS acquisition masses	35–600 amu
MS data acquisition rate	100 spectra per second
MS resolving power	Unit mass resolution

Supplementary Table S2. GC×GC-TOFMS method parameters for collection of mass spectral data with high resolving power and high mass accuracy.

GC×GC-TOFMS system	LECO GC-HRT4D
GC 1st-dimension column	100% dimethylpolysiloxane, 30 m, 0.25 mm i.d., 1 µm d _f
GC 2nd-dimension column	50% phenyl polysilphenylene-siloxane 1 m, 0.1 mm i.d., 0.1 µm d _f
GC carrier gas	Helium
GC carrier gas flow rate	Constant flow, 1.3 mL/min
GC inlet temperature	250 °C
GC injection volume	1 µL splitless
GC 1st-dimension column oven program	45 °C (1.5 min hold) 45 °C – 100 °C @ 20 °C/min 100 °C – 270°C @ 3 °C/min; hold 1 min 270 °C – 320°C @ 20 °C/min; hold 16 min
GC 2nd-dimension column oven program	80 °C (1.5 min hold) 80 °C – 275 °C @ 3 °C/min 275 °C – 330 °C @ 20 °C/min; hold 11 min
GC modulator temperature offset from first oven	+20 °C
GC modulation time	3 seconds
Transfer line temperature	320 °C
MS source temperature	250 °C
MS detector voltage	Tune voltage
MS acquisition masses	35–600 amu
MS data acquisition rate	Use recommended acquisition rate
MS resolving power	25,000, full width half maximum
MS mass accuracy	1 ppm

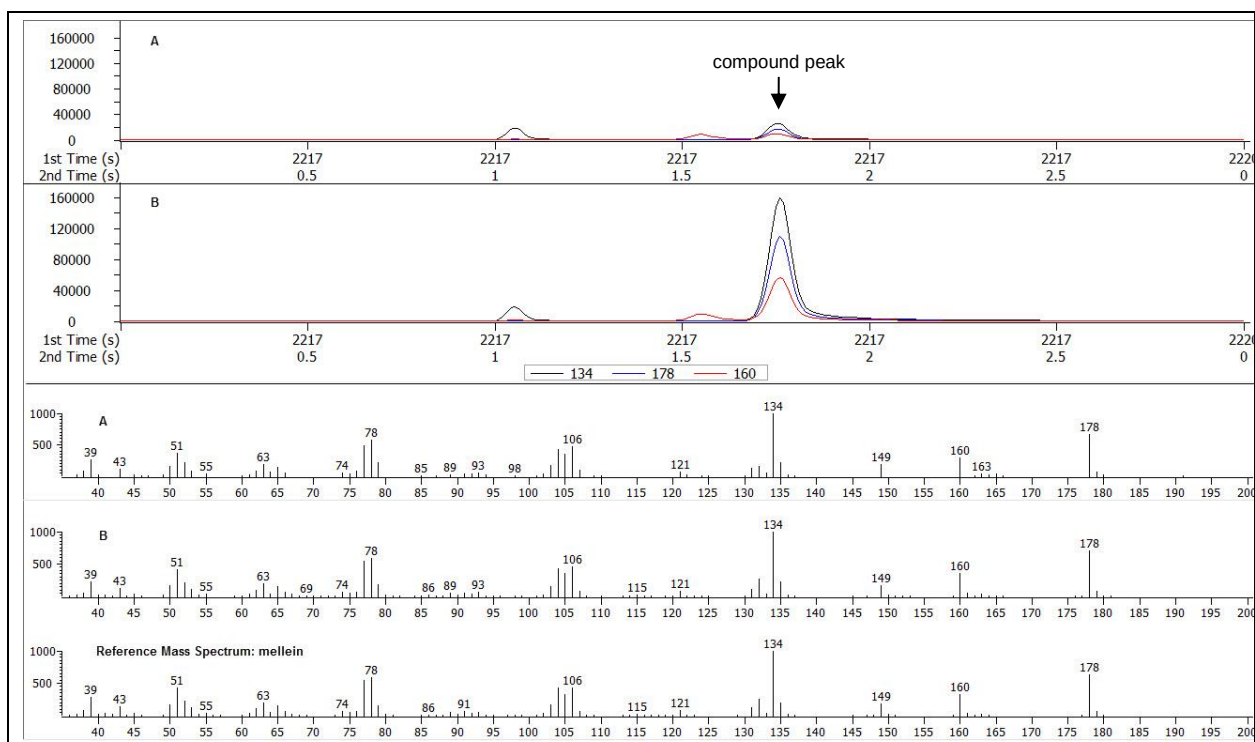
Supplementary Table S3. Operating parameters for GC-MS method with EIMS.

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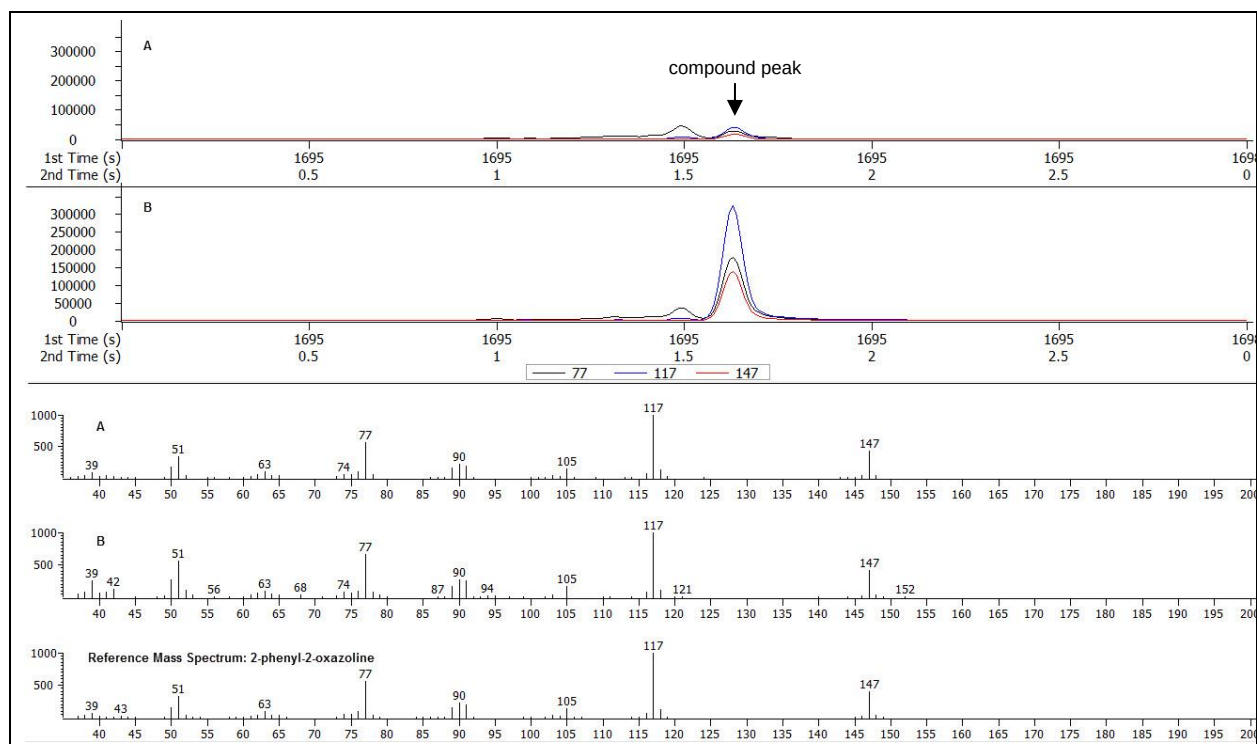
GC-MS system		Agilent 6890N/5973					
Mode		Electron ionization mass spectrometry (EIMS), selected ion monitoring (SIM)					
GC column		Rtx-1701: 14% cyanopropylphenyl/86% dimethyl polysiloxane, 30 m, 0.25 mm i.d., 1 μm d _f					
GC carrier gas		Helium					
GC carrier gas flow rate		Constant flow, 1.5 mL/min					
GC inlet temperature		250 °C					
GC injection volume		1 μL splitless					
GC column oven program		45 °C (2.0 min hold) 45 °C – 260 °C @ 10 °C/min; hold 10 min 260 °C post temp; hold 5 min					
Transfer line temperature		280 °C					
MS source temperature		230 °C					
MS quad temperature		150 °C					
SIM group #	Start time (min)	m/z	Dwell	m/z	Dwell	m/z	Dwell
1	5.0	77	50	107	50	122	50
2	16.5	77	50	117	50	147	50
3	18.5	80	50	162	50	164	50
4	20.0	134	50	160	50	178	50
Analytes (monitored ions)			Linear calibration equations				
			Calibration ranges in extract (μg/mL)		Calibration ranges per smoked item (μg/rod)		
mellein (m/z 178, 134, 160)			0.10–2.5		1.5–37.5		
2-ethylphenol (m/z 107, 77, 122)			0.20–5.0		3.0–75		
3-ethylphenol (m/z 107, 77, 122)			0.52–5.2		7.8–78		
4-ethylphenol (m/z 107, 77, 122)			1.0–25		15–375		
acenaphthene-d ₁₀ (m/z 162, 164, 80)			Not Applicable (internal standard)				

Supplementary Table S4. Operating parameters for GC-MS method with CIMS.

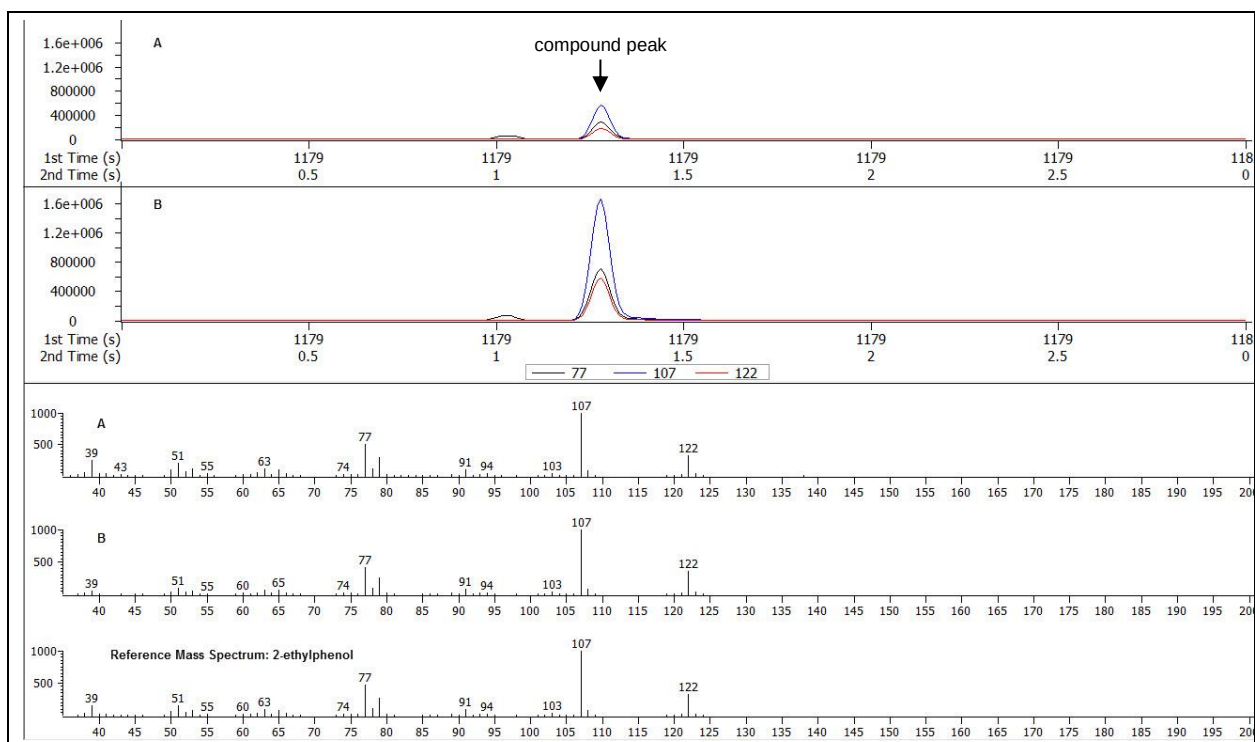
GC-MS system		Agilent 6890N/5973			
Mode		Chemical ionization mass spectrometry (CIMS), selected ion monitoring (SIM)			
Reagent gas		Methane			
GC column		ZB-35: 35% phenyl 65% dimethylpolysiloxane, 30 m, 0.25 mm i.d., 0.25 μm d _f			
GC carrier gas		Helium			
GC carrier gas flow rate		Constant flow, 1.5 mL/min			
GC inlet temperature		250 °C			
GC injection volume		1 μL splitless			
GC column oven program		45 °C (2.0 min hold) 45 °C – 290 °C @ 5 °C/min; hold 10 min 310 °C post temp; hold 5 min			
Transfer line temperature		280 °C			
MS source temperature		250 °C			
MS quad temperature		150 °C			
SIM group #	Start time (min)	<i>m/z</i>	Dwell	<i>m/z</i>	Dwell
1	5.0	148	100	176	100
2	22.0	165	100	193	100
Analytes (monitored ions)		Quadratic calibration equation, forced through origin Calibration range in extract ($\mu\text{g/mL}$) Calibration range per smoked item ($\mu\text{g/rod}$)			
2-phenyl-2-oxazoline (<i>m/z</i> 148, 176)		0.50–5.0		7.5–75	
acenaphthene- <i>d</i> ₁₀ (<i>m/z</i> 165, 193)		Not Applicable (internal standard)			



Supplementary Figure S1. Examples of extracted ion chromatograms for m/z 134, 178, and 160 (top) and mass spectra from compound peaks (bottom) illustrating the confirmed detection of mellein by GC $\times$ GC-TOFMS. **A:** Large blunt MSS sample. **B:** Large blunt MSS sample spiked with authentic standard of mellein. A reference mass spectrum from the NIST 17 Mass Spectral Library (NIST 2017) is shown below the two collected mass spectra.



Supplementary Figure S2. Examples of extracted ion chromatograms for m/z 77, 117, and 147 (top) and mass spectra from compound peaks (bottom) illustrating the confirmed detection of 2-phenyl-2-oxazoline by GC $\times$ GC-TOFMS. **A:** Large blunt MSS sample. **B:** Large blunt MSS sample spiked with authentic standard of 2-phenyl-2-oxazoline. A reference mass spectrum from the NIST 17 Mass Spectral Library (NIST 2017) is shown below the two collected mass spectra.



Supplementary Figure S3. Examples of extracted ion chromatograms for m/z 77, 107, and 122 (top) and mass spectra from compound peaks (bottom) illustrating the confirmed detection of 2-ethylphenol by GC $\times$ GC-TOFMS. **A:** Large blunt MSS sample. **B:** Large blunt MSS sample spiked with authentic standard of 2-ethylphenol. A reference mass spectrum from the NIST 17 Mass Spectral Library (NIST 2017) is shown below the two collected mass spectra.