Use of Carbon-13 Labeled Glycerol to Identify Potential Decomposition Products from E-liquids

John H. Lauterbach, Ph.D., DABT
Lauterbach &Associates, LLC
211 Old Club Court, Macon, GA 31210-4708 USA
Andrae Spencer, Ph.D.
Global Laboratory Services, Inc.
2107 Black Creek Rd SE, Wilson, NC 27893 USA

Introduction

- Presence of acetaldehyde and other low molecular-weight carbonyl compounds in mainstream e-cigarette aerosols has been one of key arguments against use of e-cigarettes
- Possible sources of carbonyl compounds
  - Pyrolysis of glycerol
  - Pyrolysis of other e-liquid constituents
  - Decomposition or outgassing of materials used to fabricate the e-cigarette
- Use of fully carbon-13 labeled glycerol should help resolve source of carbonyl compounds

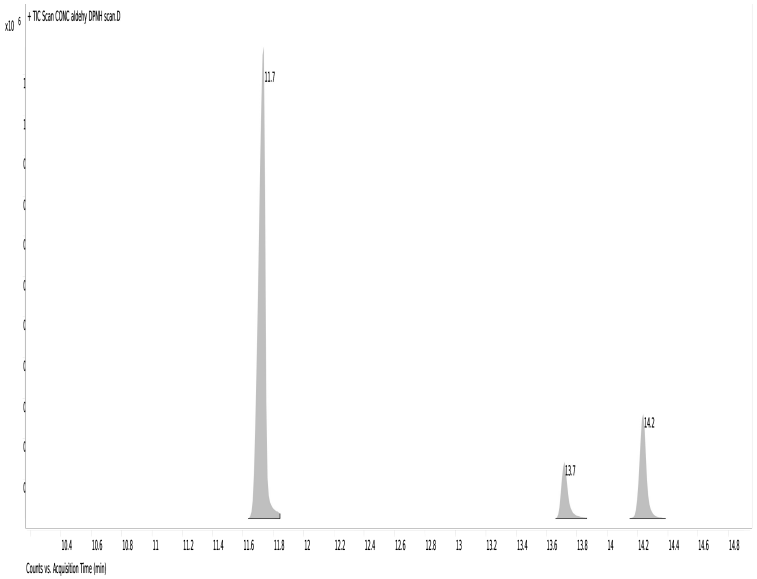
Experimental – Page 1

- V2 brand e-cigarettes with blank V2 cartomizers
- Borgwaldt-KC LX20 linear 20 port machine
  - Adapted for use with liquid traps
  - 55/30/3 square-wave, 230 – 250 puffs
- Standards and Reagents
  - Glycerol $^{13}C3$, 99 atom % ^{13}C, Aldrich
  - Spectrum Propylene Glycol USP
  - Supelco-DNPH Mix 1
  - Other reagents generally used with this method
- Cartridge preparation – First set
  - 0.1g total loaded on each cartridge
    - $C^{12}GLY/C^{12}PG$, 1:1
    - $C^{13}GLY/C^{12}PG$, 4:1

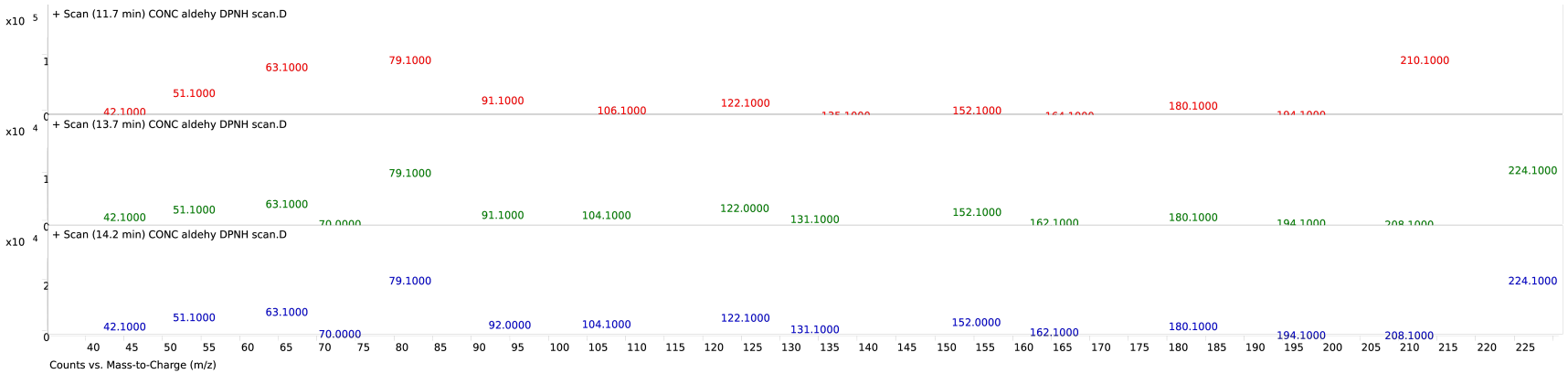
Experimental – Page 2

- GC/MS Experimental
  - Agilent 7890S GC with 5977A MSD & 7690 auto-sampler
  - Column: Perkin Elmer Elite-5ms, 30m, 0.25 mm ID, 0.24µm df
  - Temperature program: initial: 125 °C to 230 °C at 5 °C per minute, then hold for 9 minutes
- Additional standards
  - Supelco 47340-U, Acetaldehyde-2,4-DNPH
  - Supelco 44-2597, Formaldehyde-2,4-DNPH
  - Supelco 44-2441, Acrolein-2,4-DNPH
  - Aldrich 1,2-Propanediol-1,2-13C2, 99 atom % 13C

Results - standards



rt	Compound
11.7	Formaldehyde-2,4-DNPH
13.7, 14.2	Acetaldehyde-2,4-DNPH



DNPH Standards

Supelco-DNPH Mix 1 -- Note RT and spectra of formaldehyde-DPNH (210 m/z), and two acetaldehyde-DPNH peaks (224 m/z), averaged spectra and background subtracted

Compound	rt	Abundance (m/z)	Ratio to base peak
Formaldehyde-DNPH	11.7	49661 (210) 4578 (211)	11:1
Acetaldehyde-DNPH	13.7	6671 (224) 664 (225) 50 (226)	10:1 152:1
Acetaldehyde-DNPH	14.2	14416 (224) 1535 (225) 150 (226)	9:1 96:1

DNPH V2 Reagent Blank

Blank V2 cartridge puffed – Note RT and spectra of formaldehyde-DPNH (210 m/z), and two acetaldehyde-DPNH peaks (224 m/z), averaged spectra and background subtracted

Compound	rt	Abundance (m/z)	Ratio to base peak
Formaldehyde-DNPH	11.7	3926 (210) 348 (211)	11:1
Acetaldehyde-DNPH	13.77	34 (224) nd (226)	---
Acetaldehyde-DNPH	nd	---	---

C^{12}GLY/C^{12}PG, 1:1, Vapor

Table from baseline averaged spectra and background subtracted.

Compound	rt	Abundance (m/z)	Ratio to base peak
Formaldehyde-DNPH	11.7	9973 (210) 870 (211)	--- 11:1
Acetaldehyde-DNPH	13.7	568 (224) nd (225) nd (226)	--- --- ---
Acetaldehyde-DNPH	14.2	1002(224) nd (226)	--- ---

$C^{13}GLY/C^{12}PG$, 4:1, Vapor

Table from baseline averaged spectra and background subtracted. Possible interfering peak co-eluting with the 13.7 acetaldehyde peak (248 m/z), second acetaldehyde peak is clean.

Compound	rt	Abundance (m/z)	Ratio to base peak
Formaldehyde-DNPH	11.7	3606 (210) 1617 (211)	--- 2:1
Acetaldehyde-DNPH	13.7	60 (224) 93(226)	--- 0.6:1
Acetaldehyde-DNPH	14.2	176(224) nd(225) 306(226)	--- --- 0.6:1

Summary of Initial Test

The changing ratio of the C^{12} base peak (224 m/z) and the C^{13} base peak (226 m/z) of aldehyde chromatographic peaks indicates that we are forming the acetaldehyde from the C^{13} GLY.

Compound	rt	Blank	Standard	C12GLY & C12PG	C13GLY & C12PG
		Abundance Ratio			
Formaldehyde-DNPH m/z ratio (210:211)	11.7	11:1	11:1	11:1	2:1
Acetaldehyde-DNPH m/z ratio (224:226)	13.7	----	152:1	----	0.6:1
Acetaldehyde-DNPH m/z ratio (224:226)	14.2	----	96:1	----	0.6:1

Second experiment

- Cartridge Preparation
  - Second set
    - 0.1g loaded on each cartridge
    - C13GLY/H20, 2:1
    - C13PG/H20, 2:1
    - V2 Blank
    - C12GLY/H20/C12PG, 1:1:1
    - C13GLY/H20/C13PG, 1:1:1
  - Derivatization of starting materials with DNPH
    - C13GLY (0.1g)
    - C13PG (0.1g)
    - C12GLY (0.1g

C12GLY/H20/C12PG, 1:1:1

- Results with modified GC conditions

Compound	rt	Abundance (m/z)	Ratio to base peak
Formaldehyde-DNPH	7.1	2740 (210) 284 (211)	10 : 1
Acetaldehyde-DNPH	8.2	54 (224) 3 (226)	18 : 1
Acetaldehyde-DNPH	8.4	23 (224) 1 (226)	23 : 1
Acrolein-DNPH	9.3	50 (236) 8 (239)	6 : 1

C13GLY/H20/C13PG, 1:1:1

- Results with modified GC conditions

Compound	rt	Abundance (m/z)	Ratio to base peak
Formaldehyde-DNPH	7.1	12057(210) 3672(211)	3 : 1
Acetaldehyde-DNPH	8.2	109 (224) 72 (226)	2 : 1
Acetaldehyde-DNPH	8.4	60 (224) 37 (226)	2 : 1
Acrolein-DNPH	9.3	152 (236) 101 (239)	2 : 1

C13GLY liquid derivatized (0.1g)

- Results with modified GC conditions; liquid only, not from aerosol

Compound	rt	Abundance (m/z)	Ratio to base peak
Formaldehyde-DNPH	7.1	8924(210) 931(211)	10 : 1
Acetaldehyde-DNPH	8.2	84 (224) 9 (226)	9 : 1
Acetaldehyde-DNPH	8.4	36 (224) 3 (226)	12 : 1
Acrolein-DNPH	9.3	148 (236) 145 (239)	1 : 1

C13PG liquid derivatized (0.1g)

- Results with modified GC conditions; liquid only, not from aerosol

Compound	rt	Abundance (m/z)	Ratio to base peak
Formaldehyde-DNPH	7.1	31050(210) 3173 (211)	10 : 1
Acetaldehyde-DNPH	8.2	191 (224) 25 (226)	8 : 1
Acetaldehyde-DNPH	8.4	103 (224) 1 (226)	100 : 1
Acrolein-DNPH	9.3	128(236) 121(239)	1 : 1

C12GLY liquid derivatized (0.1g)

- Results with modified GC conditions; liquid only, not from aerosol

Compound	rt	Abundance (m/z)	Ratio to base peak
Formaldehyde-DNPH	7.1	10847(210) 1143 (211)	9 : 1
Acetaldehyde-DNPH	8.2	104 (224) 10 (226)	10: 1
Acetaldehyde-DNPH	8.4	40 (224) 4 (226)	10 : 1
Acrolein-DNPH	9.3	148(236) 145(239)	1 : 1

Conclusions

- These are preliminary results
- C13 glycerol does yield C13 acetaldehyde
- One deficiency of these results was that cartomizer was not fully loaded
- C13PG does not seem to produce as much acetaldehyde or acrolein, if any
- Adding PG and water is lessening the effect on acetaldehyde or acrolein
- It is not clear if we are forming formaldehyde
- 239 m/z representing (C13 acrolein) seems high versus derivatized starting materials