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ONLINE AEROSOL ANALYSIS USING FTIR: ASSESSING CARBONYL YIELDS IN E-CIGARETTE AEROSOL

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(Part of Philip Morris International group companies)

Outline

- Introduction
  - Background
  - Motivation & Target
- Equipment & Method Concept
- Method Verification
- Carbonyls in e-cig Aerosols
  - Route of Generation
  - FTIR Identification & Quantification
  - Examples
- Summary

Background

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- Electronic cigarettes (e-cig) are emerging with numerous variations in designs and performance parameters within and across brands
  - Disposable or rechargeable, replaceable cartridges
  - Tank systems with larger batteries
  - Large capacity batteries, integrated circuits allowing heating power and flow adjustment (=> variation of nicotine delivery/puff)

- E-cigarette emissions need to be measured
  - Existing recommendations as to what needs to be tested (e.g. BSI, AFNOR)
  - Various groups working on the topic (e.g. CEN/TC 437/WG 4)
  - Carbonyls may be emitted by e-cigarettes, depending on the design and operations of the device

Motivation for Online e-cig Screening Method

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- Standard chemical characterization is time consuming
  - Multiple process steps required (trap aerosol/extract/measure/evaluate)
  - Accumulation of 10 to 50 puffs required
- Short product development cycles facilitated by rapid screening tools
  - Assess and optimize product performance
  - Monitor product quality and reliability

Target

- Primary: Quantify key e-cig aerosol constituents on a puff-by-puff basis

Done => Method presented at TSRC, Sep 2017, Palm Beach Gardens, Fl, USA (1) ☑

- Secondary: Quantify carbonyls during critical End of Battery/Liquid (EoB/EoL) e-cig operation

(1) PMI Science: https://www.pmiscience.com/library/ftir-method-e-cigarette-aerosol-characterization

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Online E-Cig Aerosol Analysis Concept

Key Constituents	Liquid Composition Range (% w/w)		Boiling Point
Water	6	20	100°C
Nicotine	0.45	7	247°C
Glycerin	20	37.25	290°C
PG	34	65.5	188°C
Flavor*	0	5	-
Menthol*	0	2	212°C

*out of scope

Basic Concept:

Use a FTIR gas analyzer with heated sampling lead

- Heat the E-cig aerosol to 180°C for analysis
- Heating aerosol to 180°C is
  - sufficient to transfer droplets into gas phase
  but
  - low enough to not decompose key constituents and e.g. generate additional carbonyls

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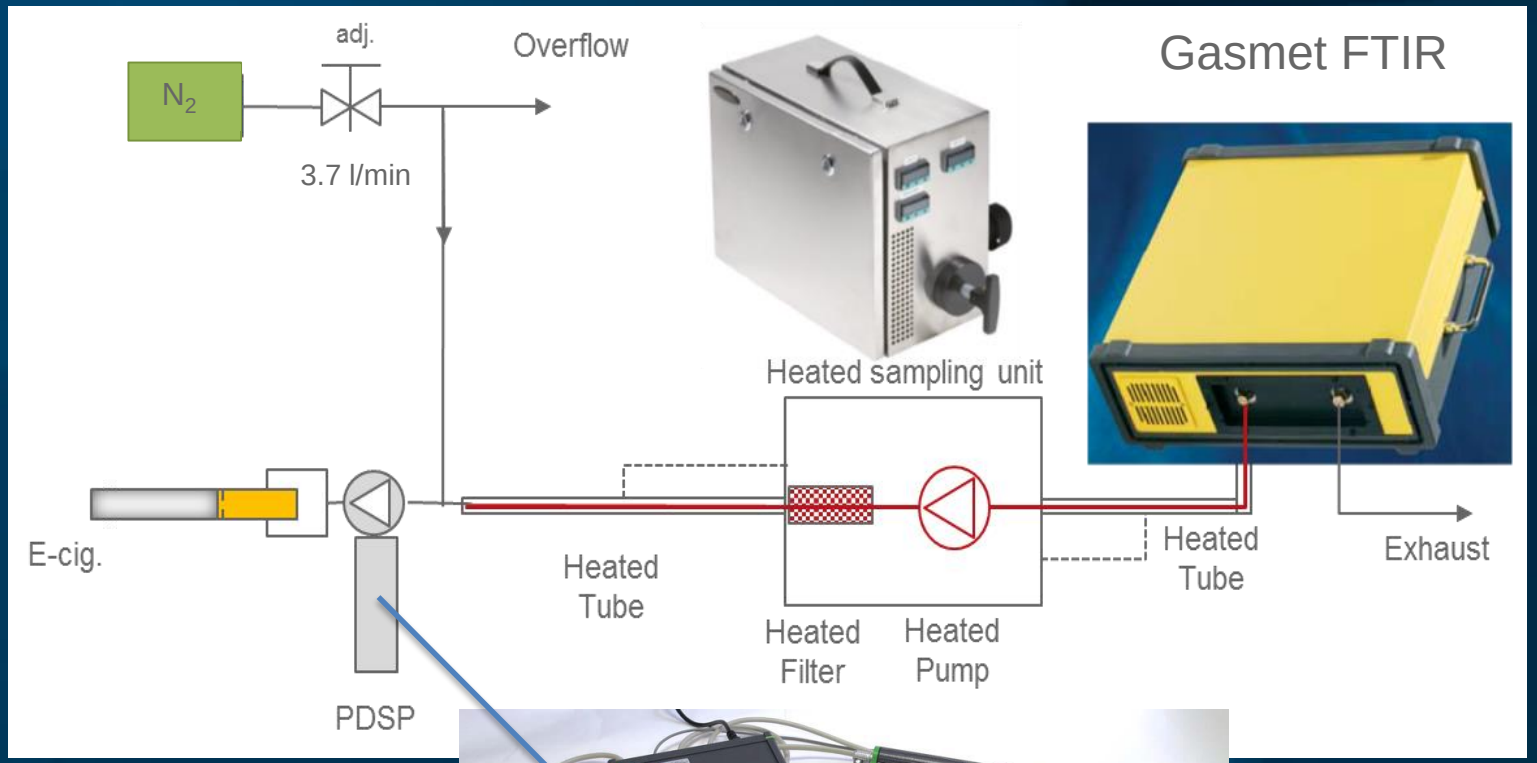
Experimental Setup

- Gasmet™ DX4000 FTIR Gas analyzer
- Gasmet™ Portable sampling system
  - Heating controller, heated pump & filter, heated sample lines, calibrator
- PC with Calcmet™ software
- Aerosol generation using PSSP: Programmable Single Syringe Pump



Principle of Operation

- Michelson Interferometer performs Fourier transformation on IR beam passing the sample chamber
- Full IR –spectrum measured at high speed (>1 spectrum/s)
- Calcmet™ software calculate factors for ref. spectra of selected gaseous compounds

Programmable Single Syringe Pump (PSSP)

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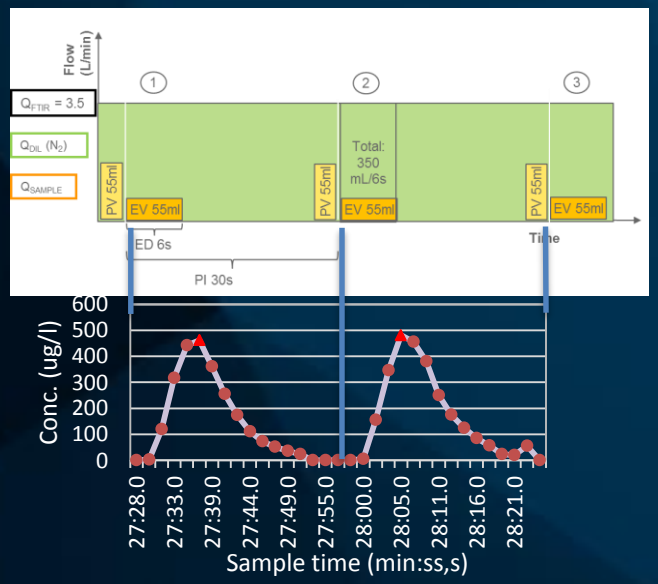
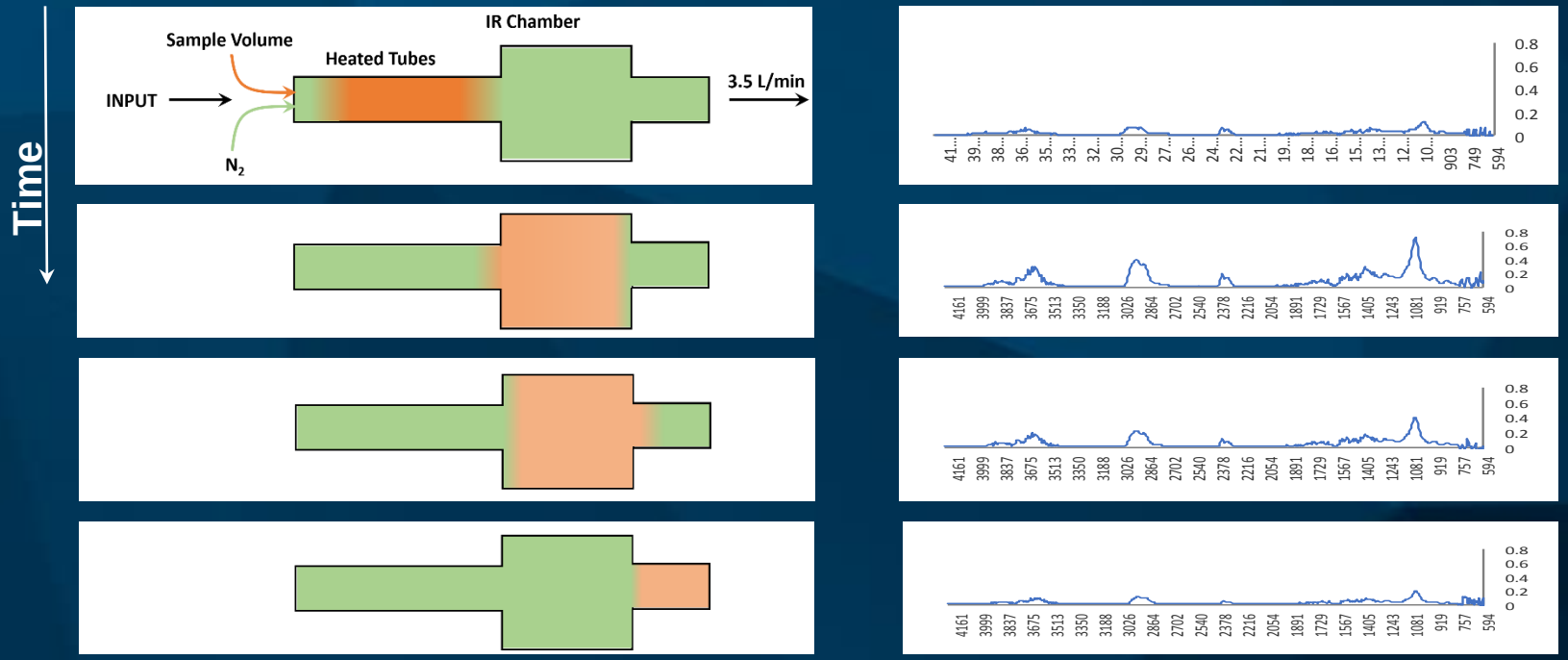
Sample Flow in the FTIR Instrument

Single Port Setup for Puff-to-Puff (P2P)

Aerosol generation (CORESTA Method N° 81):

Puff Volume (PV)	55ml
Puff Duration (PD)	3s
Puff Interval (PI)	30s
Puffing Profile (PP)	Square





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Tested E-Cig & E-Liquid Composition

E-Cigarette			Name	H_2O (% w/w)	Nic (% w/w)	Gly (% w/w)	PG (% w/w)	∑ Key Constituent (% w/w)	Flavor (% w/w)	Menthol (% w/w)
Recharchable battery, replacable cartomizer		Empty cartomizer, filled with test liquids	Test 1.1.	**20**	**0.5**	**37.25**	**37.25**	**95**	5	0
			Test 1.2.	**20**	**7**	**34**	**34**	**95**	5	0
			Test 1.3.	**20**	**1.8**	**36.6**	**36.6**	**95**	5	0
			Test 1.4.	**20**	**3.5**	**35.75**	**35.75**	**95**	5	0
			Test 3.1.	**6**	**1**	**20**	**66**	**93**	5	2
			Test 3.2.	**6**	**4**	**20**	**63**	**93**	5	2
			Test 3.3.	**6**	**1.5**	**20**	**65.5**	**93**	5	2
		Commercial Product	Liquid H	**5.96***	**1.26***	**20.2***	**74.1***	**101.6**	nd	nd
			Liquid M	**6.91***	**0.91***	**17.6***	**65.9***	**91.4**	nd	nd
			Liquid L	**7.28***	**0.45***	**17.4***	**64.1***	**89.3**	nd	nd

*Ratios taken from TPM filter analysis, Sep 2014

nd – not determined

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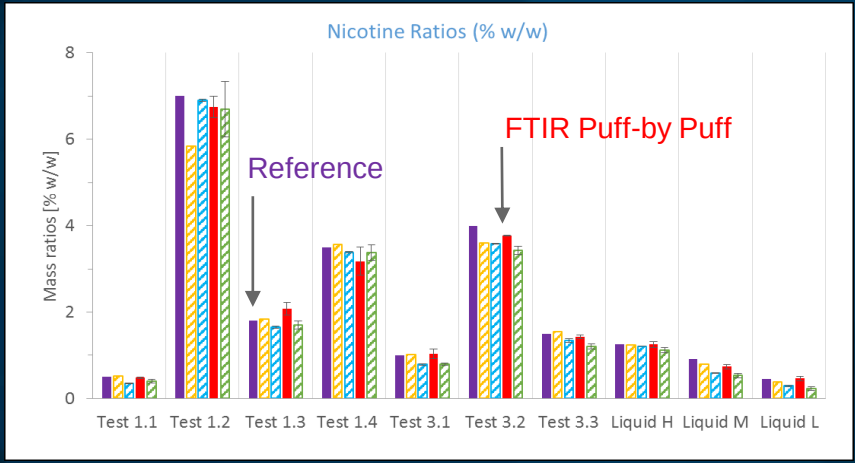
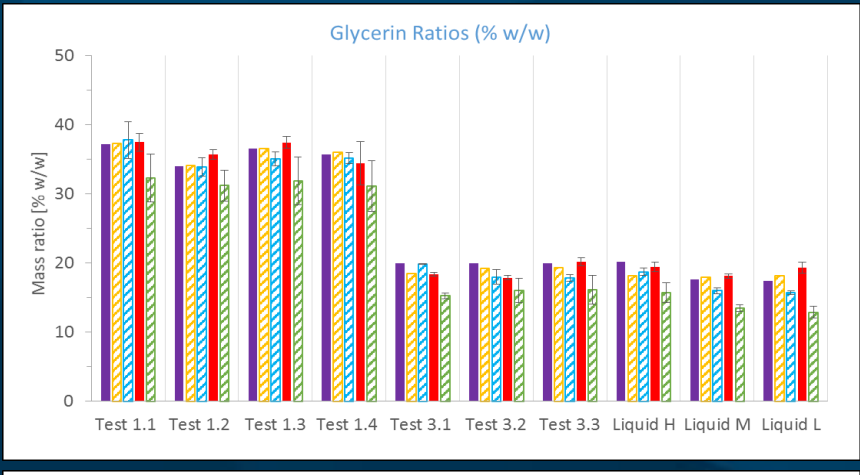
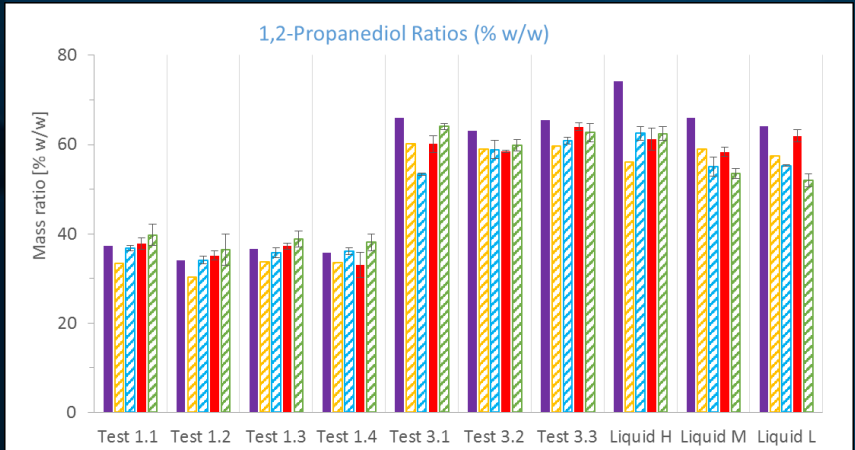
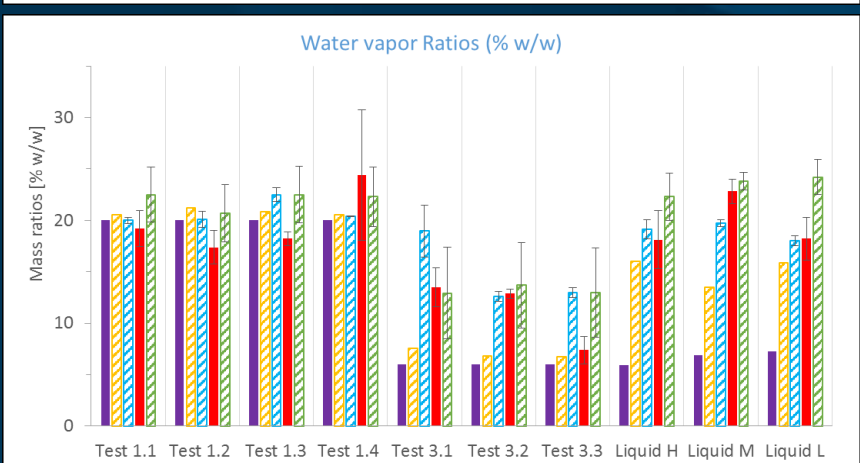
FTIR Puff-by-Puff Results: Mass Ratios

E-liquid Formulation | Analysis of used Liquids | Offline TPM filter analysis
FTIR Puff-by-Puff (Device) | FTIR Liquid Evaporation (Calibrator)









FTIR and TPM analysis: error bars represent +/- SD; n=4

Potential Carbonyl Generation

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- Secondary e-cig aerosol constituents result from thermal decomposition of primary liquid constituents
  - Known thermal decomposition routes:
    PG: (methyl glyoxal=>) **acetaldehyde, formaldehyde**
    Glycerin: (glycidol=>) **acrolein, formaldehyde**
  - Overheating mainly occurs during insufficient liquid supply (end of liquid), uncontrolled/increase power, poor device maintenance, uncontrolled system configurations (e-liquids, device components, etc.), missing/insufficient/failed temperature control systems

⇒ Special situation investigation (end of battery, end of liquid) and single puff aerosol analysis helps understanding the root causes

- Online, fast FTIR method allows assessment of e-cig performance on single puff basis

  - Method identifies those puffs contributing to increased average carbonyl concentrations

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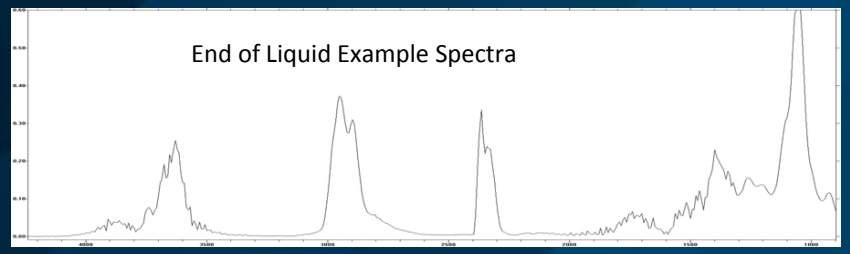
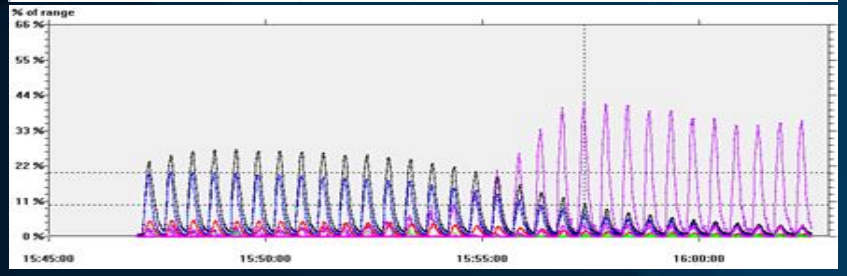
E-Cigarette Aerosol FTIR Analysis

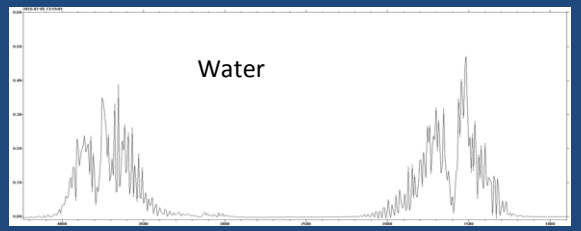
Quantification based on infrared (IR) absorption (wave number 900 cm-1 to 4200cm-1): End of Liquid (EoL) Example

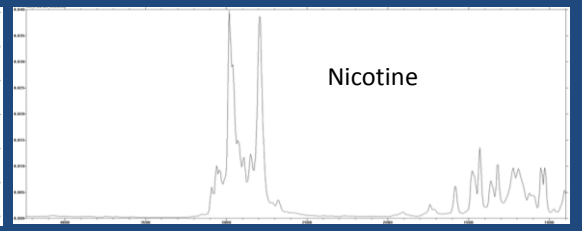


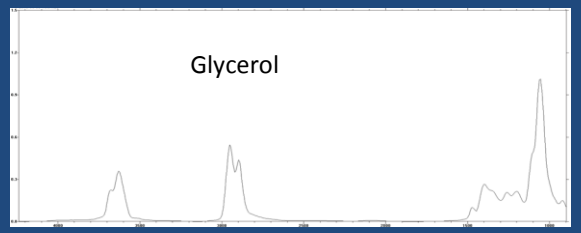
Ch	Component	Concentration	Unit	Range	Residual
1	Water vapor H2O	911.74	µg/L	10000	0.0010
2	Carbon dioxide CO2	174.55	µg/L	20000	0.0024
3	Carbon monoxide CO	21.57	µg/L	500	0.0008
4	Nitrous oxide N2O	0.18	µg/L	50	0.0076
5	Nitrogen monoxide NO	6.01	µg/L	100	0.0018
6	Nitrogen dioxide NO2	0.00	µg/L	100	0.0058
8	Ammonia NH3	0.13	µg/L	20	0.0018
9	Triacetin C9H14O6	0.58	µg/L	100	0.0068
10	Butyraldehyde C4H8O	0.00	µg/L	100	0.0025
11	Acetic Acid C2H4O2	0.00	µg/L	100	0.0065
13	Ethylene C2H4	0.00	µg/L	100	0.0018
15	Hexane C6H14	2.55	µg/L	100	0.0022
16	Formaldehyde CH2O	20.66	µg/L	50	0.0004
17	Nicotine C10H14N2	31.27	µg/L	2000	0.0022
18	Glycerol C3H8O3	942.63	µg/L	10000	0.0020
19	1,2-Propanediol C3H8O2	687.90	µg/L	10000	0.0020
20	Acetone C3H6O	0.00	µg/L	200	0.0014
21	Acrolein C3H4O	0.00	µg/L	500	0.0021
22	Methyl ethyl ketone C4H8O	0.00	µg/L	200	0.0016
23	Acetaldehyde C2H4O	17.90	µg/L	500	0.0022
24	Isoprene C5H8	8.12	µg/L	100	0.0025
221	Ambient pressure	983.00	mbar	1150	0.0000
226	Cell temperature	180.00	°C	200	0.0000
231	Source intensity	0.00		110	0.0000

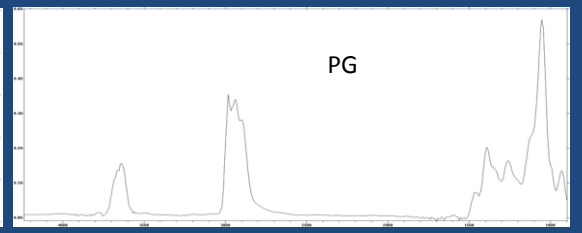


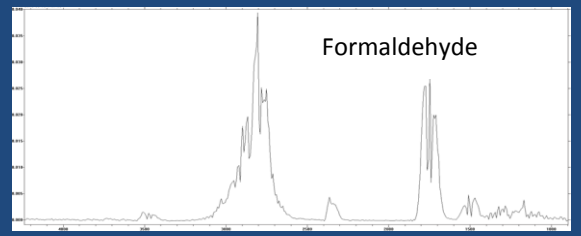
Reference Spectrums (not to same scale)

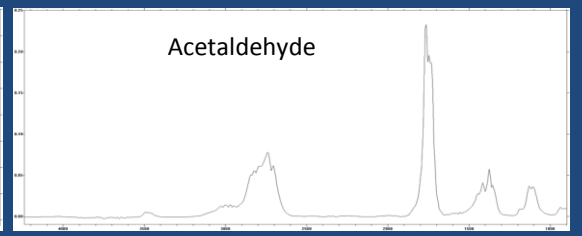


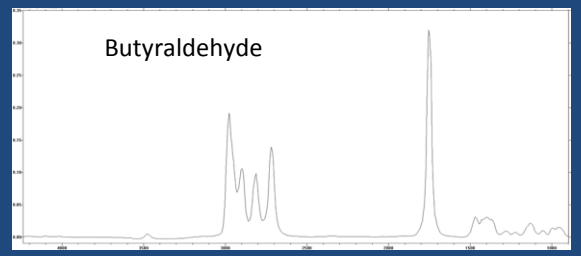


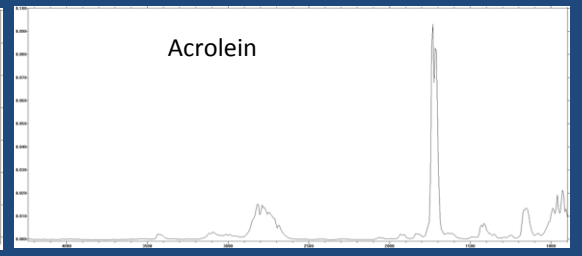












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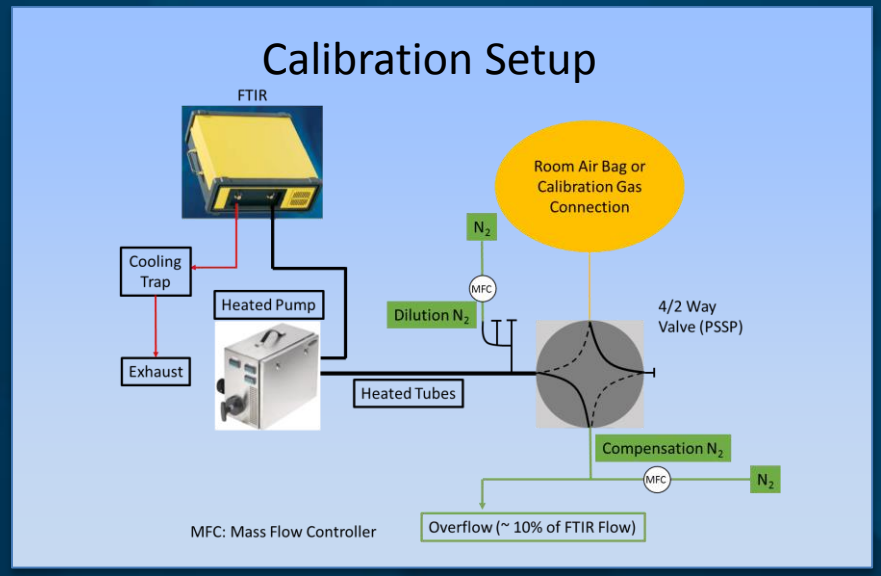
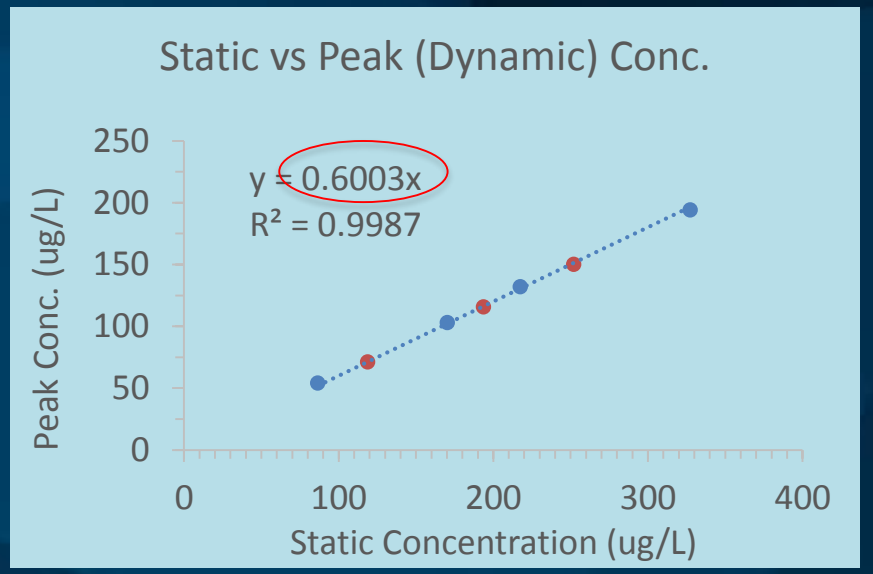
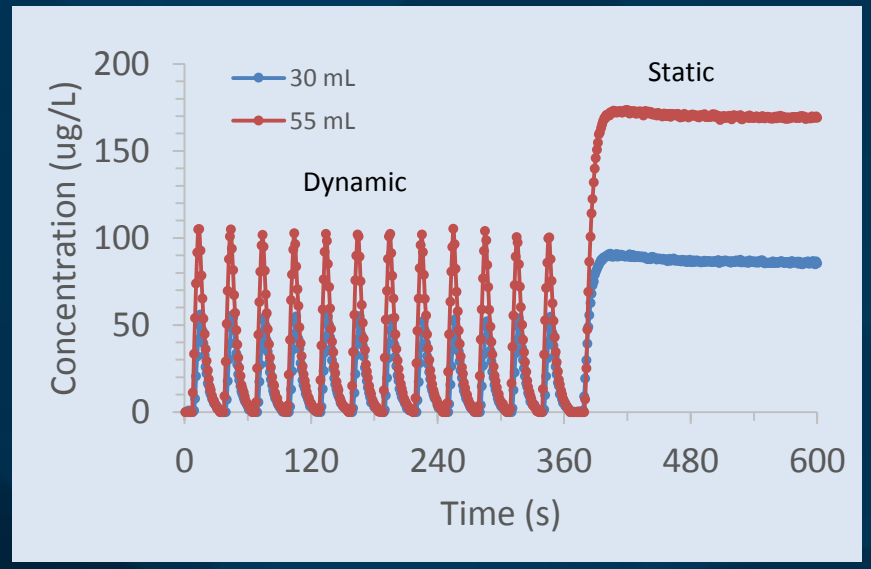
Carbonyl Calibration: Acetaldehyde

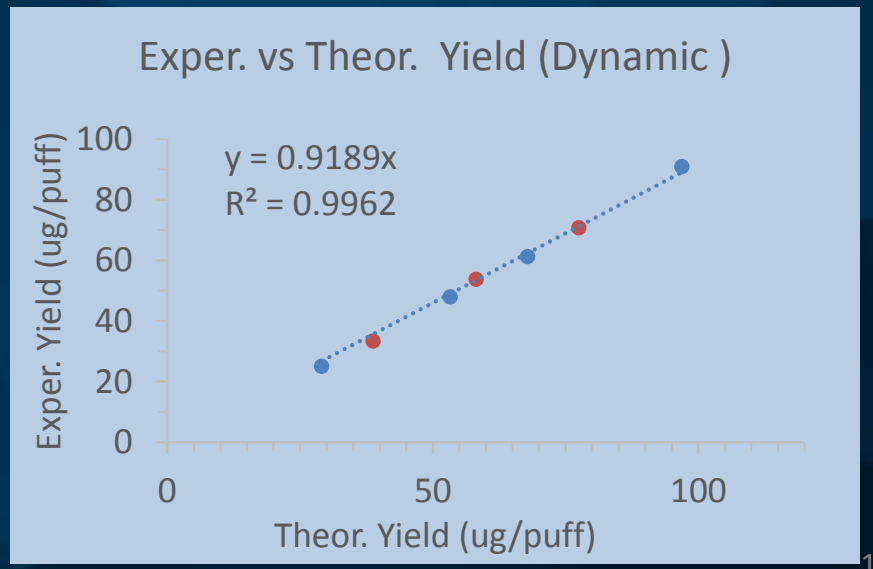
Gas Calibration Method:

- Basis: Calibration gas in cylinder (500ppm)
- Pump/Valve setup run with different dilutions:
  - changing flow
  - comparing switching valve (dynamic) situation with constant flow response
- Calculating yields









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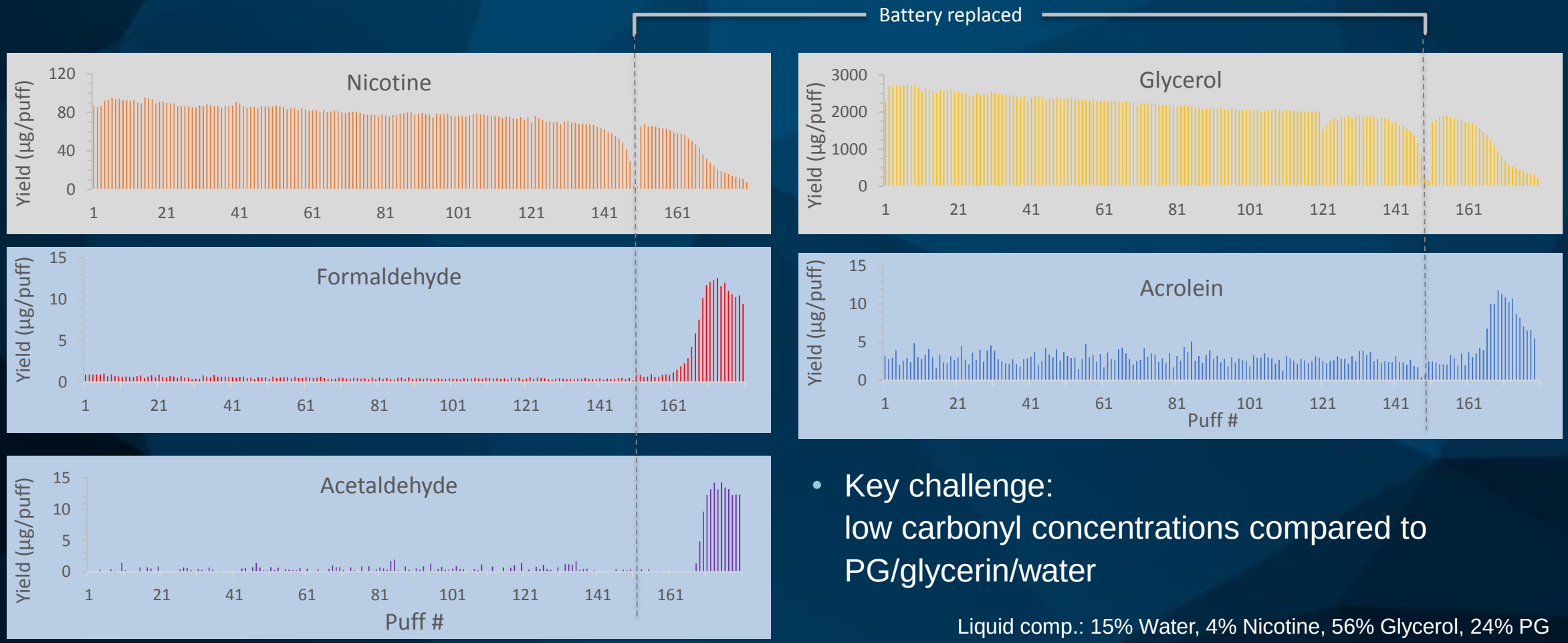
Example 1: Carbonyls at “End of Cartridge”



- Key challenge:
  low carbonyl concentrations compared to PG/glycerin/water

Liquid comp.: 15% Water, 4% Nicotine, 56% Glycerol, 24% PG
Aerosol Gen.: PV 55ml/PD 5s/PI 30s/PP rectangular

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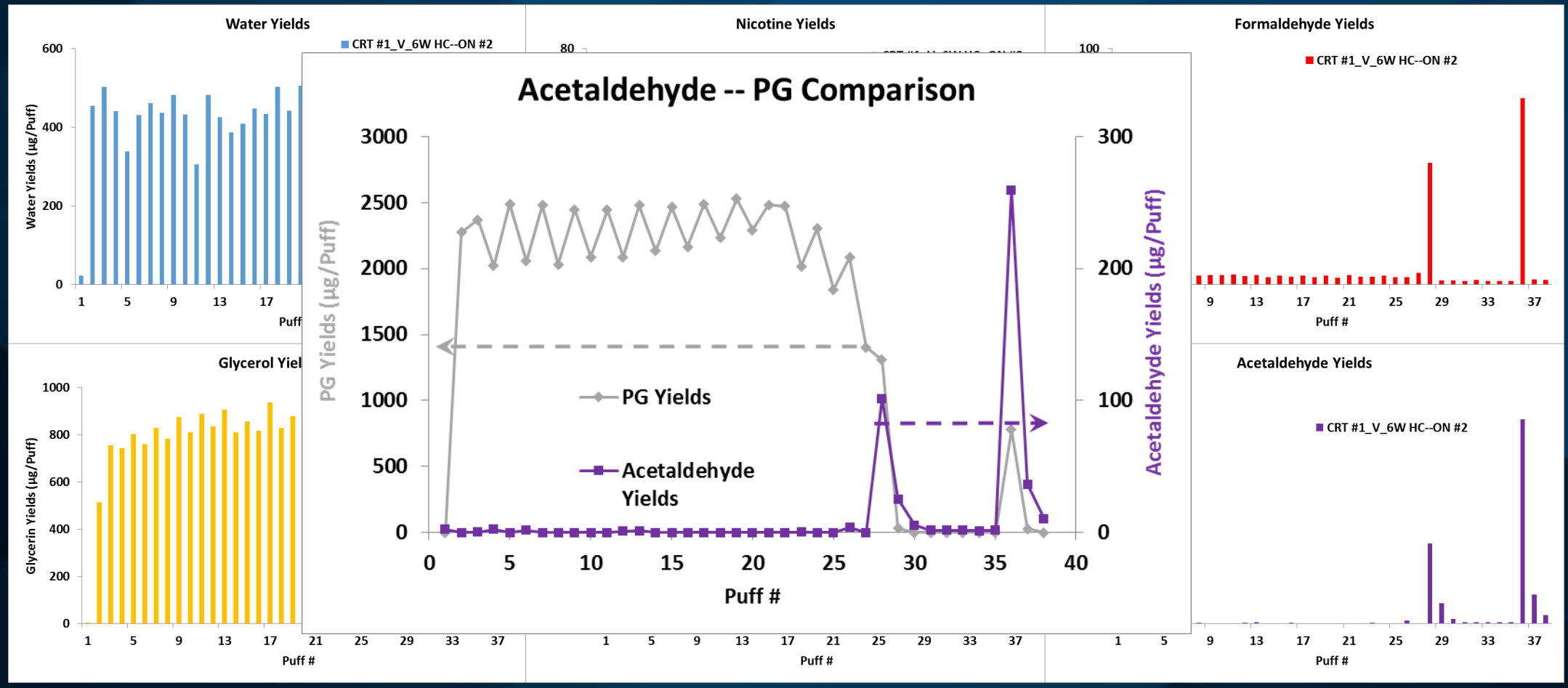
Example 2: Carbonyls at "End of Cartridge"

Test Liquid Composition: **20% Glycerol, 72.2% PG, 6% Water, 1.8% Nicotine**
Test Setup: **E-cig vertical orientation, Temperature controlled**



Summary

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- FTIR puff-by-puff method delivers reliable results for key e-cig constituents and yields can be quantified for nicotine, glycerin, PG and water on a per puff basis
- Carbonyls as potential thermal e-liquid decomposition products
  - can be quantified in case of overheating during critical end-of-liquid operation phase
  - yields per puff are close or below LOQ/LOD during normal e-cig operation

	Concentration (µg/l) (1)			Yield (µg/puff) (2)		
	Formaldehyde	Acetaldehyde	Acrolein	Formaldehyde	Acetaldehyde	Acrolein
LOD	3.49	3.27	0.20	0.192	0.180	0.011
LOQ	10	9.3	0.57	0.550	0.512	0.031

(1) Signal-to-noise Method
Blank (N2 flow only) for noise determination

(2) Calc. base: 55ml puff (CORESTA, CRM Nº 81)

- FTIR puff-by-puff method enables fast online assessment of e-cig performance on single puff basis
- Automated online FTIR data post processing and evaluation method reduces time-to-results compared to classical trapping/offline analysis methods

The end, la fin, das Ende, la fine, ……

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Thanks to

Roberto Monni

and

Andree Stoop

Thank you for listening

Further discussions possible at poster:

T310N206	**Novel FTIR online method for e-cigarette aerosol characterization**
	F. Radtke, R. Monni, A. Susz, A. Stoop, J. Verbeeck, and S. Maeder