FTIR Method for E-Cigarette Aerosol Characterization

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Outline

- Introduction
  - Background
  - Motivation & Target
- Equipment & Method Concept
- Method Verification
  - Study design: Quantitative E-cig aerosol analysis
  - Results
- Summary
- Outlook

Background

- 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-cigarettes emissions needs 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 are known to be emitted by e-cigarettes, in various amounts depending on the design

Motivation for online e-cig screening method

- 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**
- Secondary: Quantify carbonyls during critical EoB/EoL e-cig operation

Key E-Cig Aerosol Constituents

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

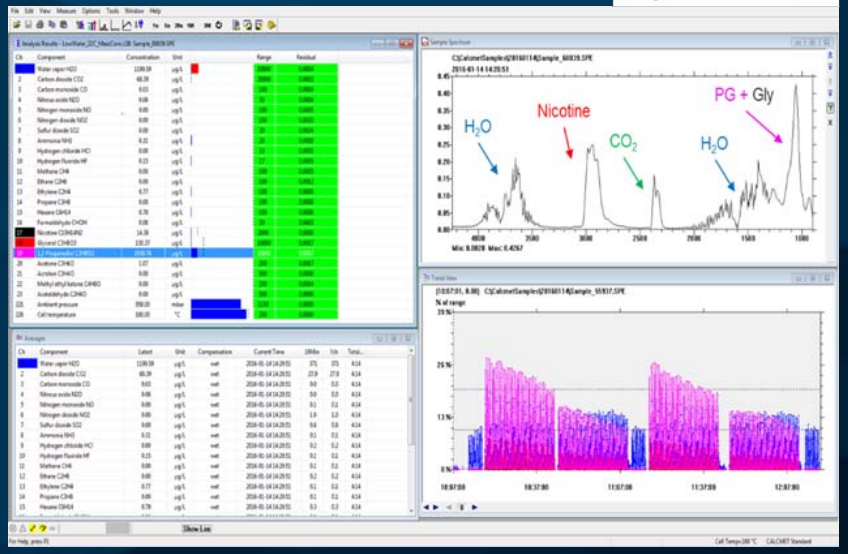
*out of scope

Selected FTIR System

- Gasmet™ DX4000 FTIR Gas analyzer
- Gasmet™ Portable sampling system
  - Heating controller, heated pump & filter, heated sample lines, calibrator
- PC with Calcmet™ software

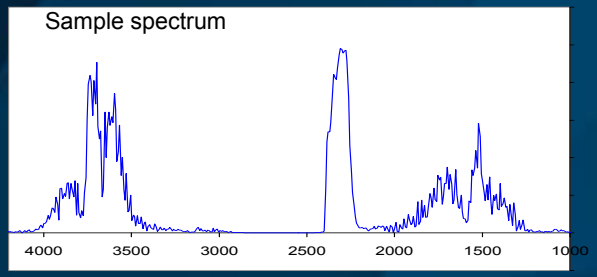
Principle of Operation

- 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



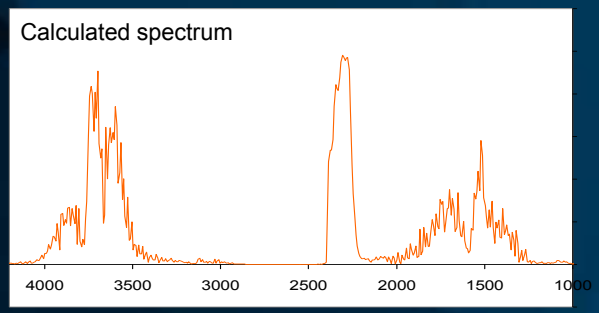
Analysis of FTIR Spectra

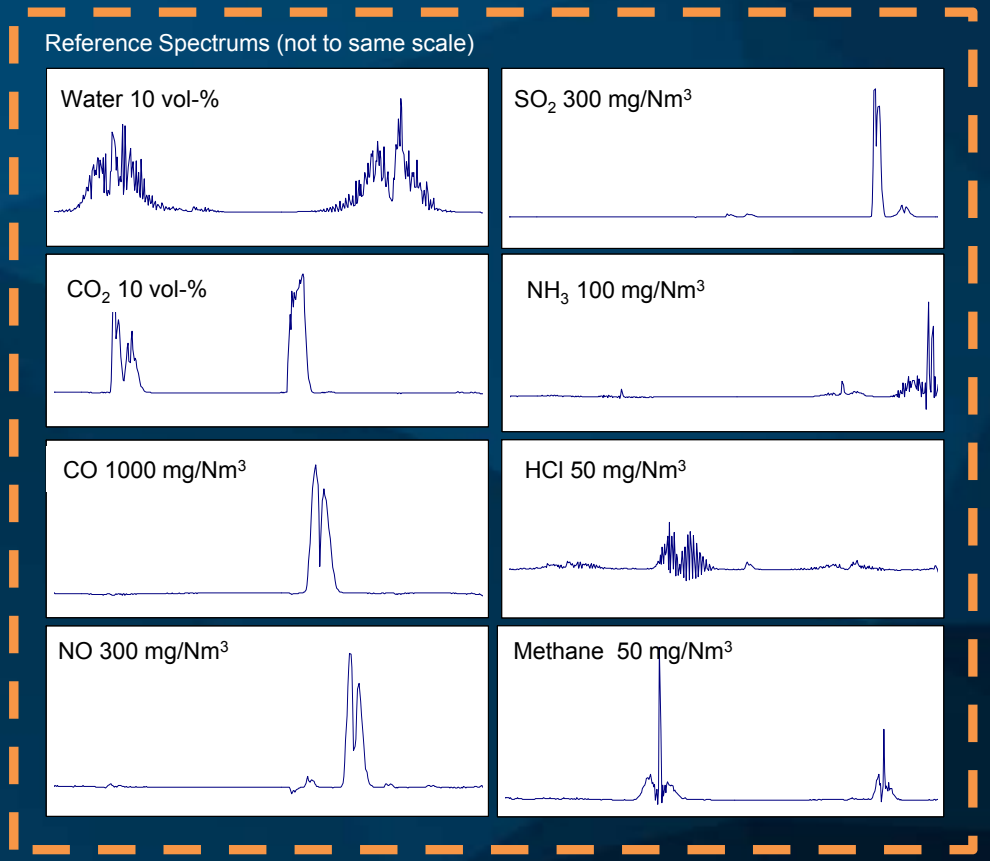
Quantification based on infrared (IR) absorption (wave number 900 cm-1 to 4200cm-1)



Analysis:

0.881 * Water 10 vol-%
1.112 * CO_2 10 vol-%
0.995 * CO 1000 mg/Nm^3
0.910 * NO 300 mg/Nm3
0.810 * SO_2 300 mg/Nm3
0.660 * NH_3 100 mg/Nm^3
0.082 * HCl 50 mg/Nm^3
0.210 * Methane 50 mg/Nm^3



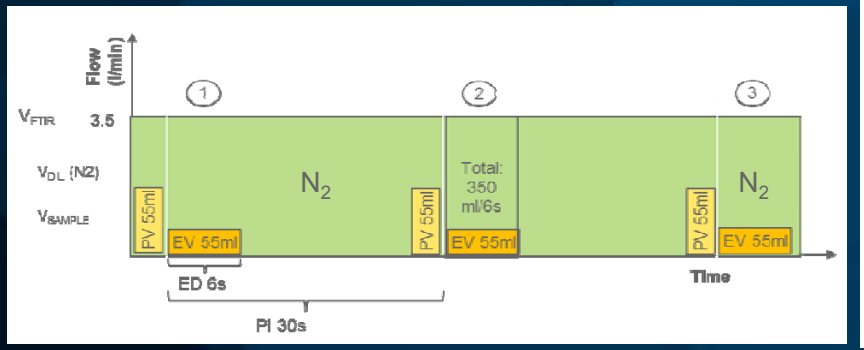


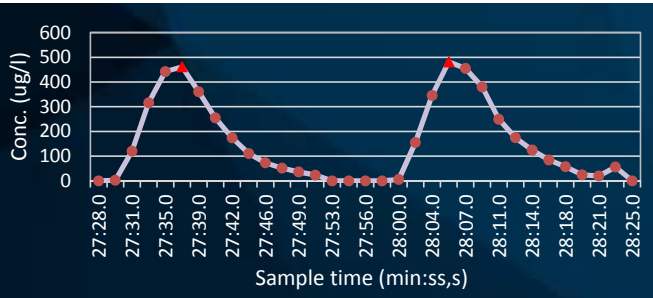
Experimental Setup

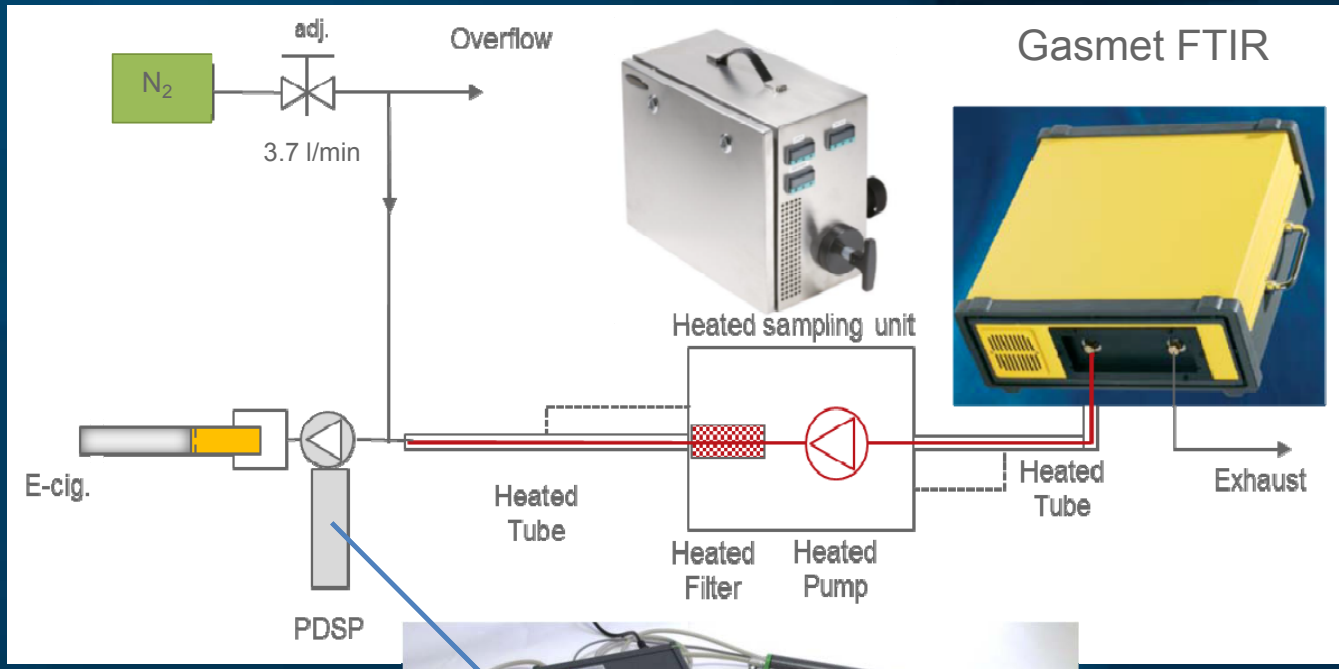
Single Port Setup for Puff-to-Puff (P2P)

Aerosol generation (CORESTA Method N° 81):

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

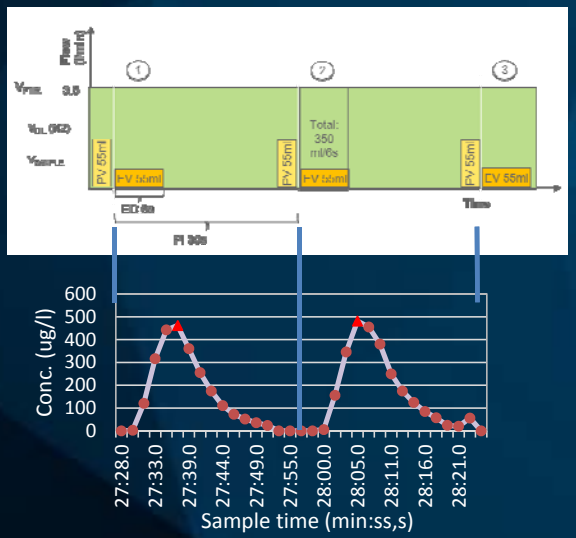


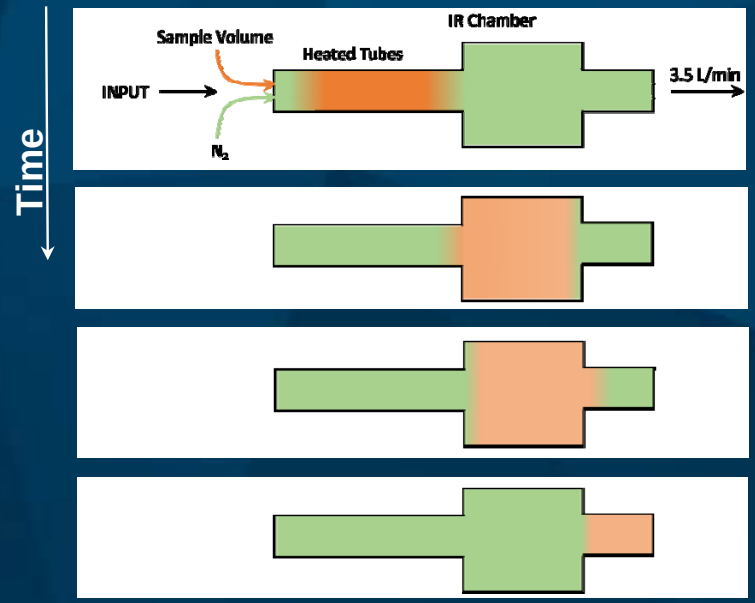




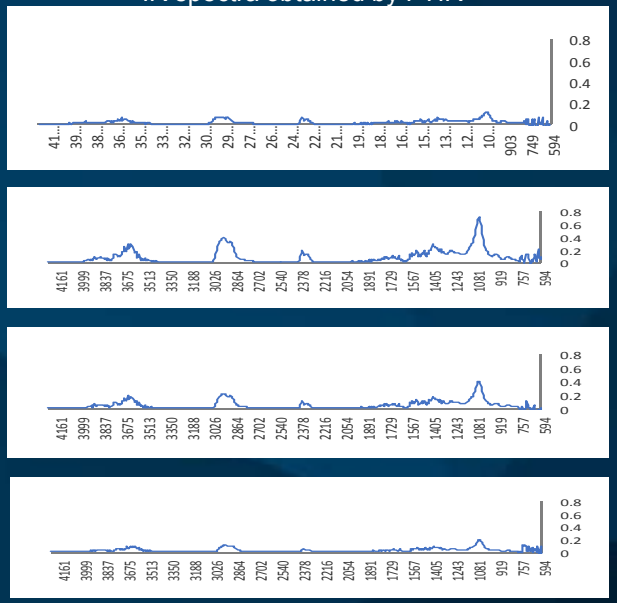
Programmable Dual Syringe Pump (PDSP)

Sample Flow in the FTIR Instrument

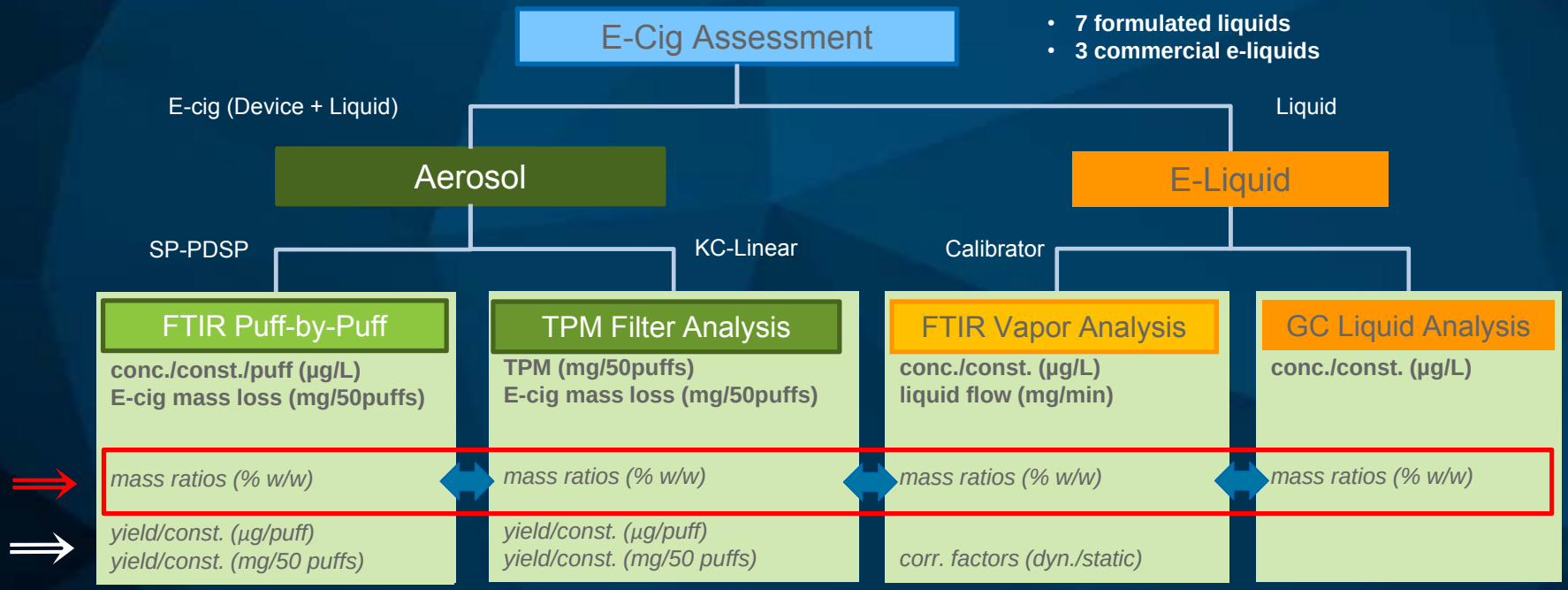




IR spectra obtained by FTIR



Method Verification: Study Design



Remarks:
**Italic: Calculated values*

Flavors & Menthol ratios deducted or not considered

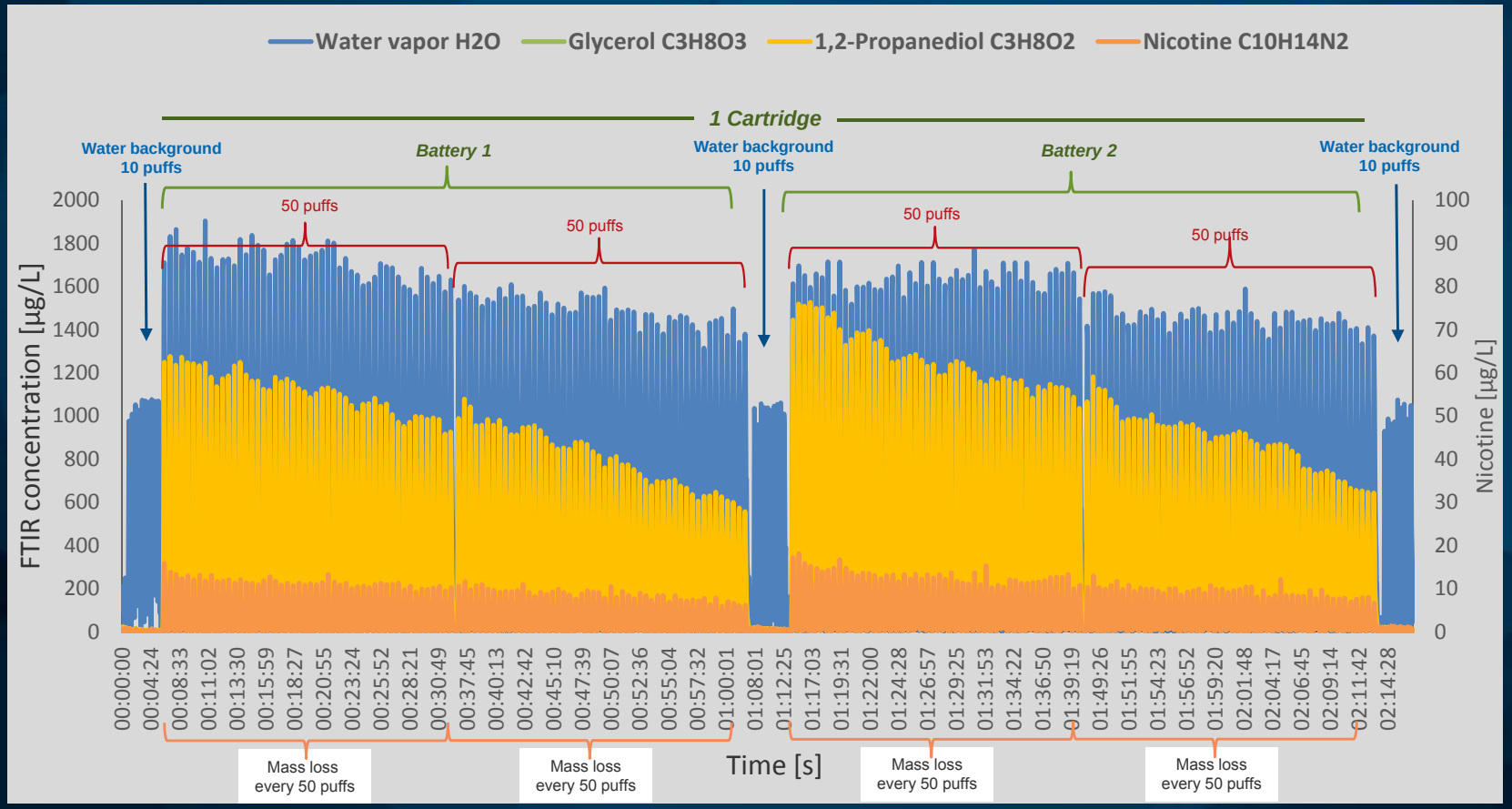
Tested E-Cig & E-Liquid Composition

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

FTIR Puff-to-Puff Sampling Sequence



FTIR Yield & Ratio Evaluation Approach

FTIR Concentrations

AVG Peak Conc. (µg/L)				
# puffs	H_2O	Nic	Gly	PG
50	667.2	11.4	915.8	1112.3
100	439.8	8.6	686.9	802.2
150	605.6	12.9	1098.7	1263.3
200	419.4	9.3	688.4	884.4
AVG	**533.0**	**10.5**	**847.4**	**1015.6**

Average FTIR Yields

FTIR Mass (mg/50puff)					
# puffs	H_2O	Nic	Gly	PG	Sum
50	11.74	0.20	16.12	19.58	47.64
100	7.74	0.15	12.09	14.12	34.10
150	10.66	0.23	19.34	22.23	52.46
200	7.38	0.16	12.12	15.57	35.23
AVG	9.38	0.19	14.91	17.87	42.36

Liquid Composition Ratios (%w/w)

Ratios based on FTIR (%)					
# puffs	H_2O	Nic	Gly	PG	Sum
50	23.42	0.40	32.14	39.04	95
100	21.56	0.42	33.68	39.34	95
150	19.30	0.41	35.02	40.27	95
200	19.91	0.44	32.67	41.98	95
AVG	**21.0**	**0.42**	**33.45**	**40.09**	**95**

Correction Factor Static vs Dynamic

Ratio AVG FTIR Mass/Weight Loss				
# puffs	H2O	Nic	Gly	PG
50	72%	49%	53%	65%
100	66%	51%	55%	65%
150	56%	48%	55%	63%
200	59%	52%	52%	67%
AVG_{Ratio}	**63%**	**50%**	**54%**	**65%**
Dyn_{corr}	**64%**	**51%**	**52%**	**64%**

Corrected Average FTIR Yields

$FTIR_{corr}$ Mass (mg/50puff)					
# puffs	H_2O	Nic	Gly	PG	sum
50	18.35	0.39	31.00	30.59	80.33
100	12.09	0.30	23.25	22.06	57.70
150	16.65	0.45	37.19	34.74	89.03
200	11.53	0.32	23.30	24.32	59.48
AVG	14.66	0.36	28.68	27.93	71.63

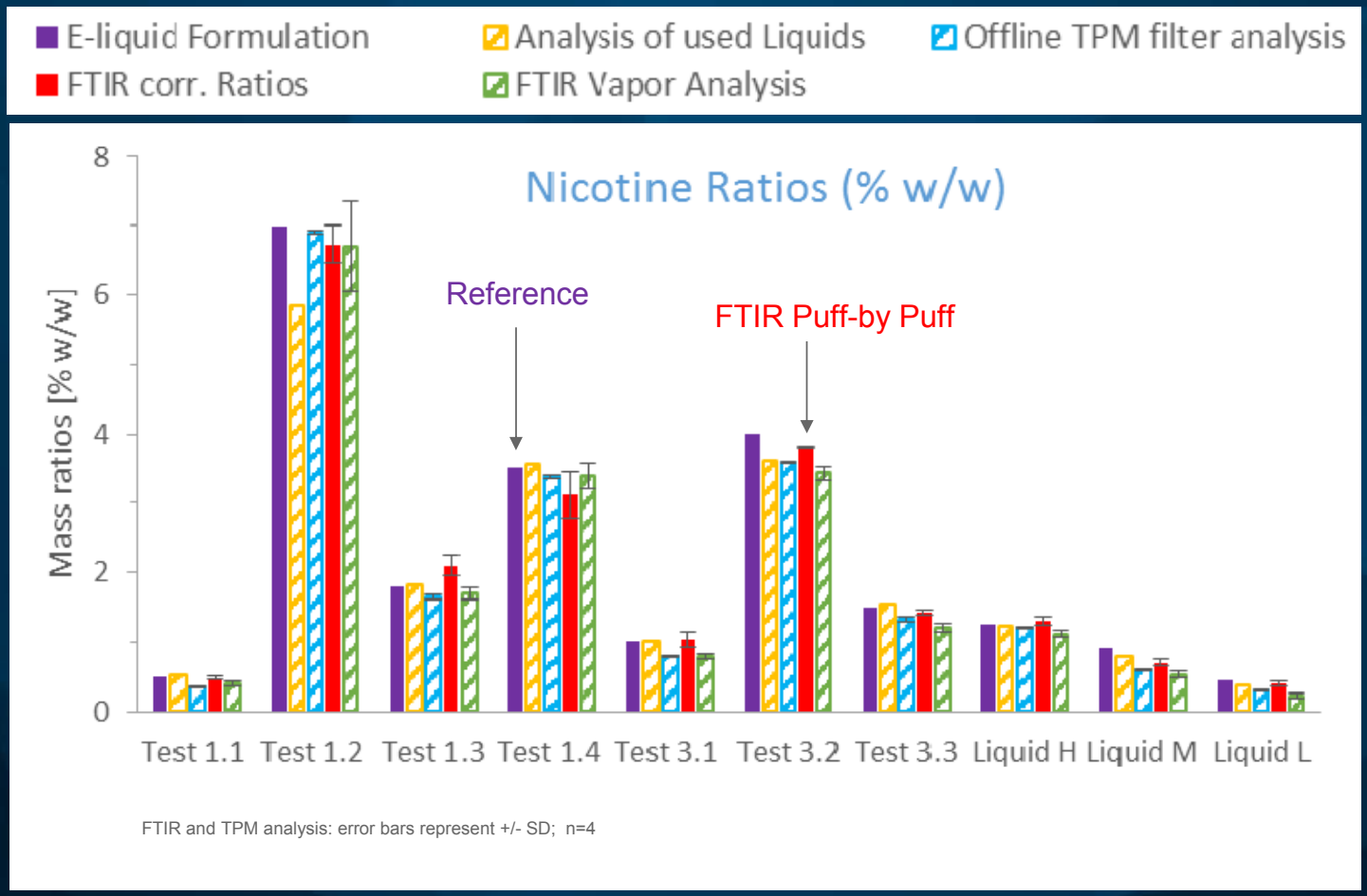
Corrected Liquid Composition Ratios (%w/w)

Ratios based on $FTIR_{corr}$ (%)					
# puffs	H_2O	Nic	Gly	PG	Sum
50	22.3	0.48	36.0	36.3	95
100	20.4	0.50	37.6	36.5	95
150	18.3	0.49	39.0	37.3	95
200	18.9	0.53	36.5	39.0	95
AVG	**20.0**	**0.50**	**37.26**	**37.27**	**95**

Liquid Formulation Ratios [%w/w]

H2O	Nic	Gly	PG	Flavor
20	0.5	37.25	37.25	5

FTIR Puff-by-Puff Results: Mass Ratios



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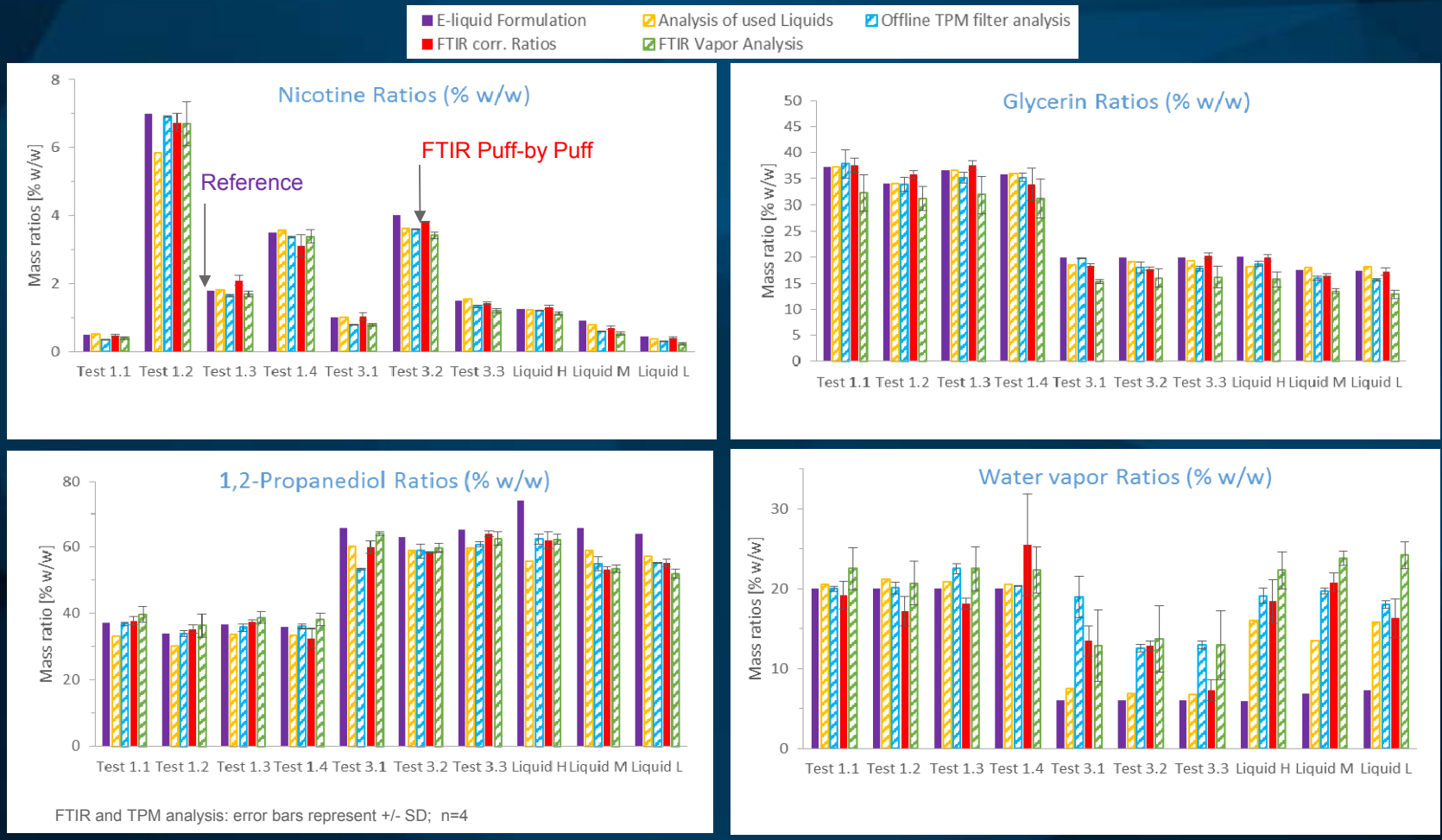


FTIR and TPM analysis: error bars represent +/- SD; n=4

Summary

- FTIR puff-by-puff method delivers reliable results for key e-cig constituents
- Ratios of key aerosol constituents match with reference liquid ratios, except H_2O: dynamic change due to water uptake in e-liquid
- E-cig yields can be quantified with FTIR method for

  Nicotine
  Glycerin
  PG
  H_2O

  } < ±10% differences to TPM filter analysis

Developed FTIR puff-by-puff method demonstrated:

- Fast online assessment of e-cig performance on single puff basis
- Quantitative assessment of key aerosol constituent yields by automated FTIR data post processing and evaluation

Outlook

- Improve FTIR performance
  - Increase sample rate 0.5 => 5-10 spectra/s (upgrade system)
- Integrate FTIR in a multiport e-cig test station concept
- Extend applications
  - Extend FTIR method for other RRP* aerosol matrices
  - Quantify toxicological relevant constituents like e.g. carbonyls

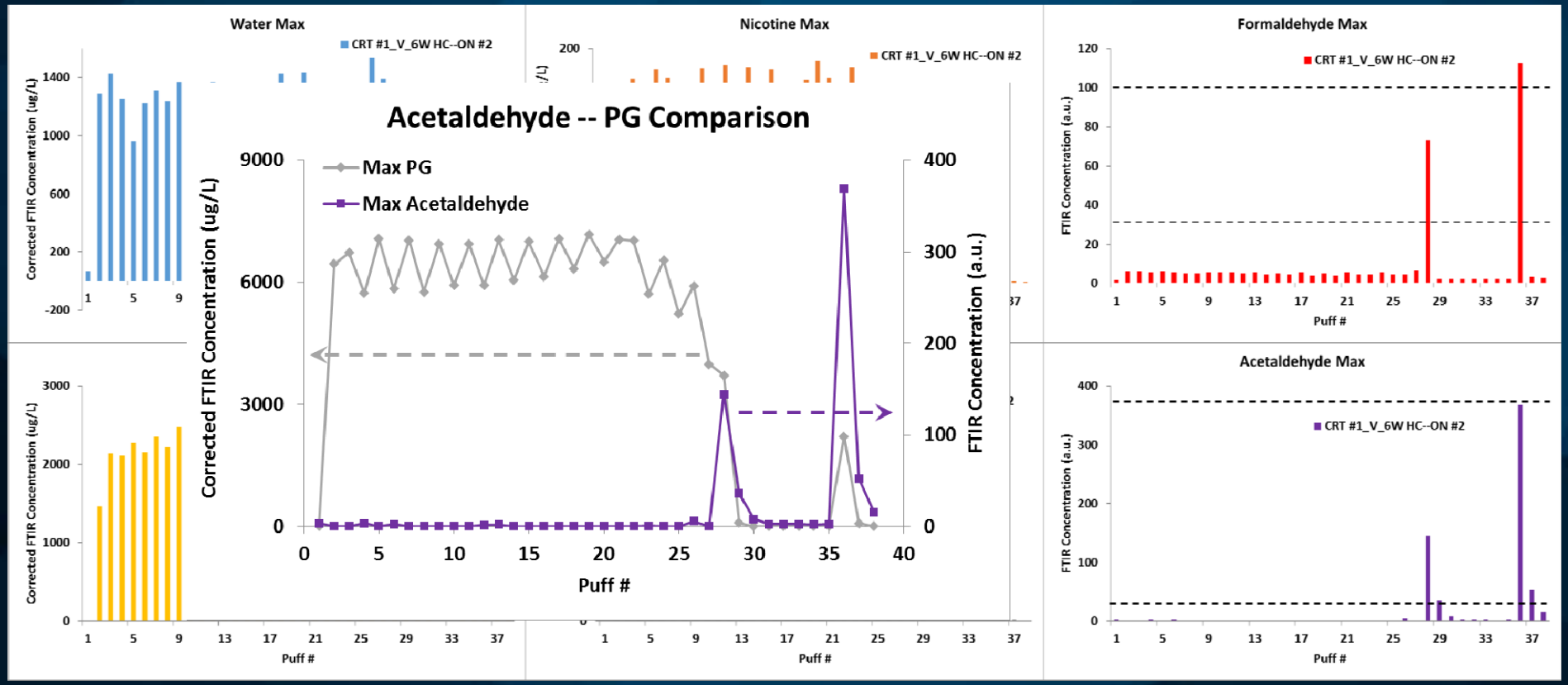
*Reduced-Risk Products ("RRPs") is the term the company uses to refer to products with the potential to reduce individual risk and population harm in comparison to smoking cigarettes.

PMI's RRPs are in various stages of development and commercialization, and we are conducting extensive and rigorous scientific studies to determine whether we can support claims for such products of reduced exposure to harmful and potentially harmful constituents in smoke, and ultimately claims of reduced disease risk, when compared to smoking cigarettes.

Before making any such claims, we will rigorously evaluate the full set of data from the relevant scientific studies to determine whether they substantiate reduced exposure or risk. Any such claims may also be subject to government review and authorization, as is the case in the United States today.

Example: Carbonyls at “End of Cartridge”

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



The end, la fin, das Ende, la fine, koniec.....

Thanks to

Anna Susz

and

Roberto Monni

Thank you for listening