

Easier, cheaper, deeper A novel approach to tailpipe emissions measurement

Nick Molden 17 March2022

#### **Our Belief**

When it comes to the pursuit for improved air quality, we believe in the power of clarity, transparency and integrity. With real -world data we can meet emissions challenges – instilling trust and confidence in our industry partners and public.

It's with our commitment and independence we are able to make a significant contribution toward positive change and to achieve enduring results.



#### Unregulated tailpipe pollutants

#### Covid and future regulation

- COVID lockdowns showed that air pollution is not just a NO <sub>x</sub> problem
- Ultrafine particles and VOCs are perhaps now more important
- But Euro 7 is focusing too much on legacy issues such as  $NO_x$  and covering all driving scenarios
- Needs to tidy up the complexities and deficiencies of Euro 6
- But then what are the important pollutants to cover?
- What can now be measured in practice?



#### European Environment Agency...

# *"Concentrations of every air pollutant in Europe have declined since the year 2000, with the exception of ozone"*



#### Emissions Analytics' approach

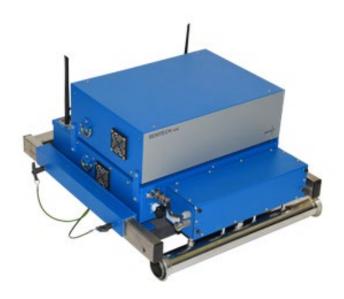
- Identify the priority pollutants in real -world conditions
- Develop novel techniques to enable measurement
- To avoid just regulating what is easy to measure
- Exhaust is a complex and diverse mixture of chemicals
- Separation, identification and quantification is vital
- Some low concentration compounds may have significant negative effects

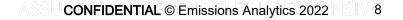


#### Test methodologies

#### Measurements – PEMS

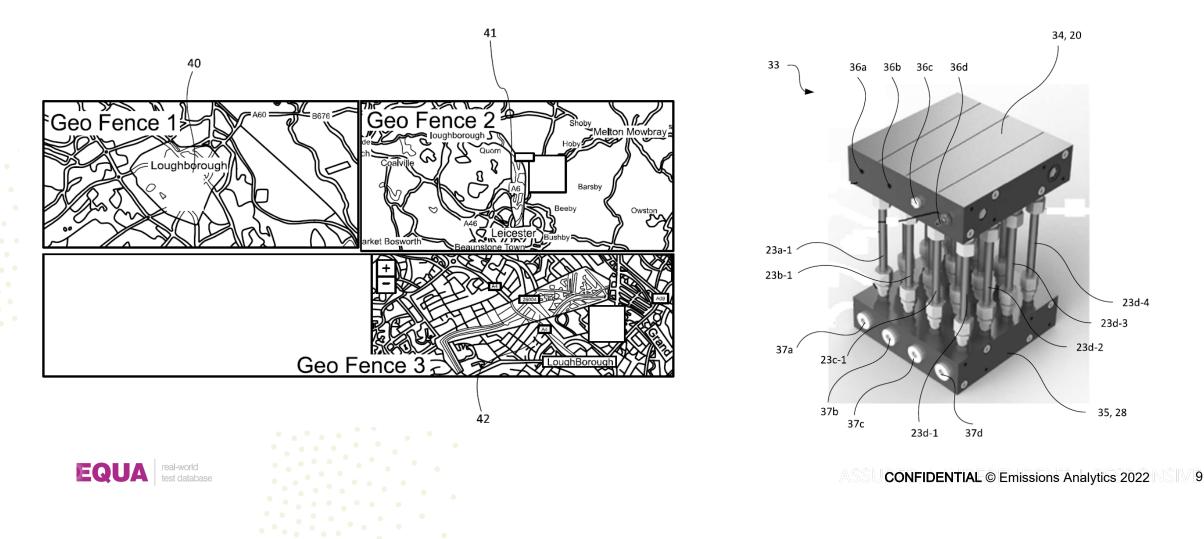
- Core: CO<sub>2</sub>, CO, NO, NO<sub>2</sub>, NO<sub>x</sub>, exhaust temperature
- Using regulatory -grade PEMS from Sensors, Inc
- Measurements at 1Hz
- Weather station: temperature, humidity, pressure
- OBD: typically speed, rpm, coolant temperature, engine load, throttle position, manifold pressure
- PN, particularly for EU gasoline and hybrids
- Custom integrated NH <sub>3</sub> sensor







#### Integrated sample collection on tubes



#### Measurements – volatile organic compounds

markes cor

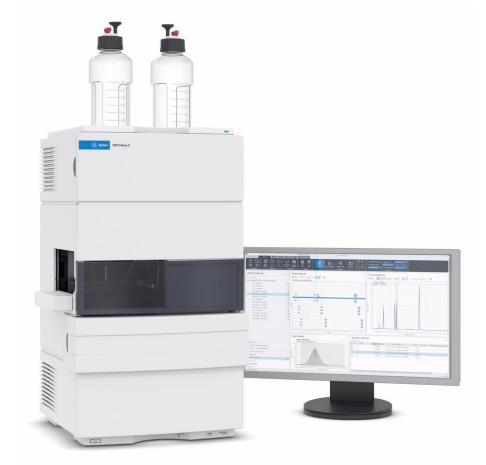
- Two-dimensional gas chromatography with mass spectrometry
  - INSIGHT flow modulator from SepSolve Analytical for separation
  - BENCH-TOF time-of flight mass spectrometer
  - Thermal desorption tube sampling from Markes International



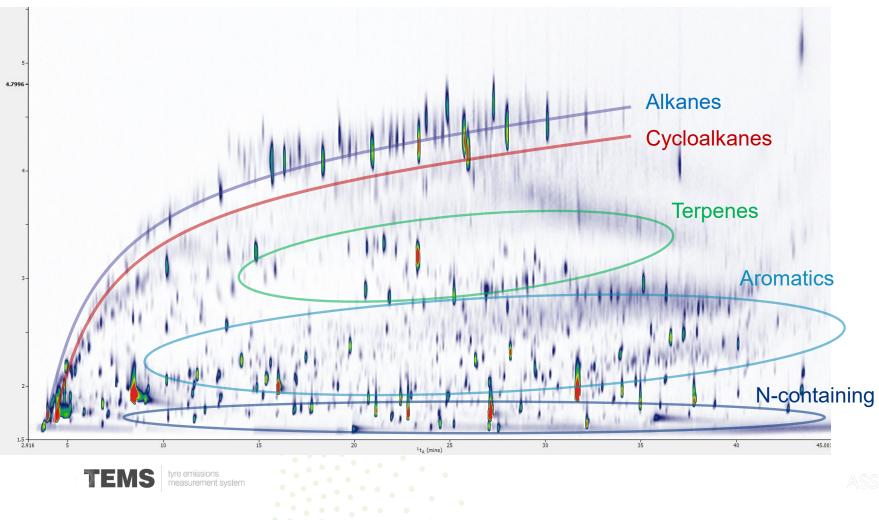


#### Measurements – formaldehyde

- High performance liquid chromatography
- Agilent 1220 Infinity II LC
- DNPH cartridges

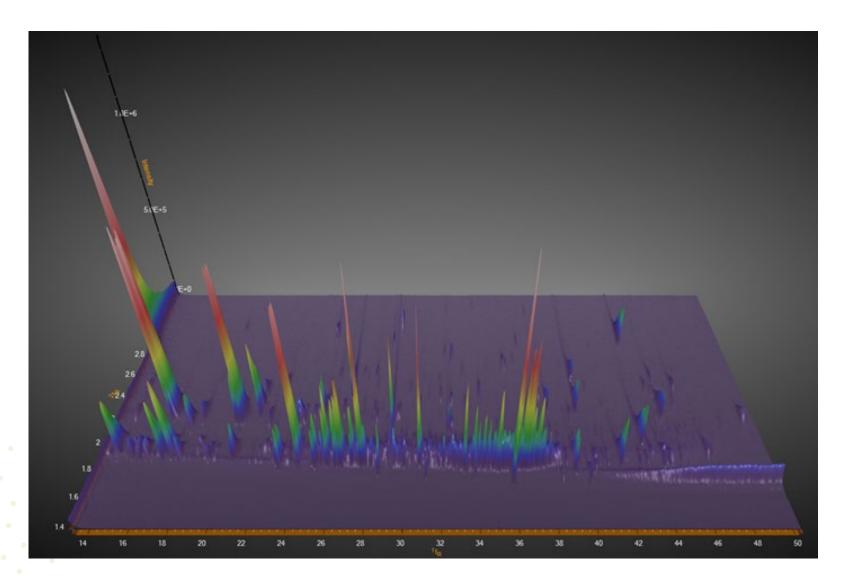


#### Typical two - dimensional chromatogram



- Wide-ranging analytes identified
- Alkanes: lungs, liver, kidney, brain
- Cycloalkanes: headaches, dizziness
- Terpenes: aromas
- Aromatics:
   carcinogens
- N-containing: carcinogens

Two dimensons are essential for good separation





#### EQUA test results

#### Test programme

- 8 gasoline vehicles
- Mix of hybridisation levels
- PHEV in engine mode
  2020 or 2021 model year
  EQUA test cycle
  Tested May-July 2021



- $\succ$  Three-way catalysts can produce N<sub>2</sub>O, CH<sub>2</sub>O
- > VOCs including aldehydes, ketones, alcohols and PAHs may also be generated



#### Regulated pollutant test results

Model Year	Make	Model	Fuel/powertrain	CO <sub>2</sub> (g/km)	CO (mg/km)	NO <sub>x</sub> (mg/km)	PN (x10^11
2021	Renault	Clio	Gasoline	124.6	61	6	0.015
2021	Volkswagen	Polo	Gasoline	130.2	14	6	0.083
2021	Kia	Rio	Gasoline MHEV	139.9	39	7	0.575
2021	Ford	Focus	Gasoline MHEV	126.5	194	3	0.620
2021	Skoda	Octavia	Gasoline	116.6	11	14	0.003
2020	Mini	Countryman	Gasoline PHEV	176.9	113	1	0.122
2021	Subaru	Forester	Gasoline FHEV	184.3	143	6	2.198
2021	Peugeot	208	Gasoline	134.1	251	8	0.685
Average				141.6	103	6	0.538
Average exc	ceedance factor			1.5	0.1	0.1	<i>O.</i> 1



#### • Powerful greenhouse gas

#### Nitrous oxide results

• Quantified using N<sub>2</sub>O standard

Model Yea	r Make	Model	Fuel/powertrain	N <sub>2</sub> O (mg/km)		)
				Urban	Rura	Motorway
2021	Renault	Clio	Gasoline	0.256	4.794	3.177
2021	Volkswagen	Polo	Gasoline	0.927	3.933	0.389
2021	Kia	Rio	Gasoline MHEV	0.678	2.335	1.742
2021	Ford	Focus	Gasoline MHEV	0.727	3.199	3.504
2021	Skoda	Octavia	Gasoline	1.085	4.588	3.978
2020	Mini	Countryman	Gasoline PHEV	0.718	2.778	1.753
2021	Subaru	Forester	Gasoline FHEV	0.141	2.194	1.624
2021	Peugeot	208	Gasoline	0.781	2.077	1.898
Average				0.664	3.237	2.258



#### • Carcinogen, serious irritant

#### Formaldehyde results

• Quantified using CH <sub>2</sub>O standard

Model Yea	r Make	Model	Fuel/powertrain	CH <sub>2</sub> O (mg/km)		ı)
				Urban	Rura	Motorway
2021	Renault	Clio	Gasoline	0.380	0.400	0.340
2021	Volkswagen	Polo	Gasoline	0.160	0.250	0.200
2021	Kia	Rio	Gasoline MHEV	0.130	0.110	0.110
2021	Ford	Focus	Gasoline MHEV	0.180	0.240	0.150
2021	Skoda	Octavia	Gasoline	0.170	0.330	0.260
2020	Mini	Countryman	Gasoline PHEV	0.110	0.210	0.110
2021	Subaru	Forester	Gasoline FHEV	0.190	0.430	0.170
2021	Peugeot	208	Gasoline	0.160	0.250	0.140
Average				0.185	0.278	0.185



### PAH and N-compounds

- Often carcinogenic
- Quantified using toluene equivalence

Model Yea	r Make	Model	Fuel/powertrain	PAH and N-compounds (r		s (ng/km)
				Urban	Rura	Motorway
2021	Renault	Clio	Gasoline	15.8	71.6	31.5
2021	Volkswagen	Polo	Gasoline	266.0	292.1	210.5
2021	Kia	Rio	Gasoline MHEV	294.0	227.2	205.0
2021	Ford	Focus	Gasoline MHEV	<b>281</b> .1	333.5	121.1
2021	Skoda	Octavia	Gasoline	428.1	322.4	205.0
2020	Mini	Countryman	Gasoline PHEV	214.3	285.0	126.3
2021	Subaru	Forester	Gasoline FHEV	287.8	259.0	182.4
2021	Peugeot	208	Gasoline	211.6	469.6	206.6
Average				249.9	282.6	161.0



# Alkanes, alkenes, alkynes and cyclo - results

- Affect lungs, liver, kidney, brain + headaches, dizziness
- Quantified using toluene equivalence

Model Yea	r Make	Model	Fuel/powertrain	Alkan	Alkanes etc(ng/km)	
				Urban	Rura	Motorway
2021	Renault	Clio	Gasoline	1627.2	5817.′	3333.7
2021	Volkswagen	Polo	Gasoline	2872.2	6309.3	4564.0
2021	Kia	Rio	Gasoline MHEV	3250.6	3877.2	3448.7
2021	Ford	Focus	Gasoline MHEV	4873.7	5515.´	3232.6
2021	Skoda	Octavia	Gasoline	2890.9	2891.6	1775.5
2020	Mini	Countryman	Gasoline PHEV	972.4	2774.5	1193.8
2021	Subaru	Forester	Gasoline FHEV	4089.4	14287.7	8111.6
2021	Peugeot	208	Gasoline	6142.8	6834.5	5997.0
Average				3339.9	6038.4	3957.1



#### Common compounds

## • Most prevalent compounds common to the vehicles

Compound	Group	Toxicity
Tridecane	Alkane, alkene, alkyne andcyclo	Damaging to lungs
Tetradecane	Alkane, alkene, alkyne andcyclo	Damaging to lungs
Dodecane	Alkane, alkene, alkyne andcyclo	Damaging to lungs
Toluene	Aromatics, aldehydes and ketones	Damaging to lungs; skin irritant; dizzines:
Pentadecane	Alkane, alkene, alkyne andcyclo	Damaging to lungs
Benzene, 1,3 dimethyl-	Aromatics, aldehydes and ketones	Damaging to eyes and skir
°p-Xylene	Aromatics, aldehydes and ketones	Damaging to lungs; skin and eye irritan
Undecane	Alkane, alkene, alkyne andcyclo	Damaging to lungs
Octane	Alkane, alkene, alkyne andcyclo	Damaging to lungs; skin irritant; dizzines:



#### Differentiating compounds

 Compounds particularly prevalent in each compound

Model Year	Make	Model	Fuel/powertrain	Compound	Toxicity
2021	Renault	Clio	Gasoline	2-Pentene	Lungs, skin and eye irritation
2021	Volkswagen	Polo	Gasoline	Benzene, 1,3 dimethyl-	Damaging to eyes and skin
2021	Kia	Rio	Gasoline MHEV	Nonane, 2,2,4,4,6,8,8-heptamethyl-	Damaging to eyes and lungs; carcinogenic
2021	Ford	Focus	Gasoline MHEV	cis-11Hexadecenal	Lung and eye irritation
2021	Skoda	Octavia	Gasoline	Pentadecane	Damaging to lungs
2020	Mini	Countryman	Gasoline PHEV	Heptadecane	Damaging to lungs
2021	Subaru	Forester	Gasoline FHEV	Pentadecane	Damaging to lungs
2021	Peugeot	208	Gasoline	Benzene, 1,3 dimethyl-	Damaging to eyes and skin



#### Summary results

Model Year	Make	Model	Fuel/powertrain	N <sub>2</sub> O (mg/km)	CO <sub>2</sub> - equivalent (g/km)	· · · /		Alkanes (mg/km)
2021	Renault	Clio	Gasoline	2.742	0.686	0.373	0.40	3592.7
2021	Volkswagen	Polo	Gasoline	1.750	0.437	0.203	0.256	4581.8
2021	Kia	Rio	Gasoline MHEV	1.585	0.396	0.117	0.242	3525.5
2021	Ford	Focus	Gasoline MHEV	2.476	0.619	0.190	0.245	4540.5
2021	Skoda	Octavia	Gasoline	3.217	0.804	0.253	0.318	2519.3
2020	Mini	Countryman	Gasoline PHEV	1.750	0.437	0.143	0.208	1646.9
2021	Subaru	Forester	Gasoline FHEV	1.320	0.330	0.263	0.243	8829.6
2021	Peugeot	208	Gasoline	1.585	0.396	0.183	0.295	6324.8
Average				2.053	0.513	0.216	231.2	4445.1



#### Conclusion

- Priorities for tailpipe regulation are shifting
- VOCs, together with ultrafine particles, should gain greater focus for future air quality policy
- Speciation of VOCs is necessary to reveal highly toxic but low concentration compounds
- Gasoline vehicles are more problematic than diesels
- These can be measured practically in real-world conditions
- GCxGC-TOF-MS gives best combination of breadth and depth of measurement



#### Thank you.

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