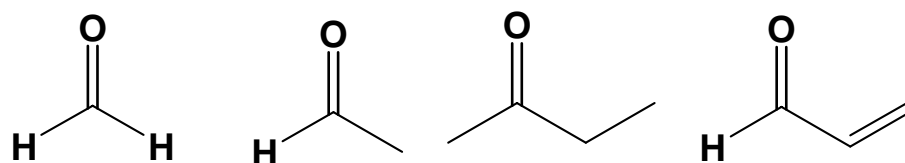


Carbonyl compounds and VOCs analysis from vehicle exhaust: Conventional and alternative methods of detection, analysis and quantification

- **Carbonyl Compounds** - (aldehydes and ketones) contain a carbon atom and an oxygen atom linked with a double bond (C=O). Some carbonyls are highly reactive and play a critical role in the formation of ozone. Other carbonyls have adverse chronic and acute health effects. In some cases, carbonyls can be both highly reactive and potentially toxic. The major sources of directly emitted carbonyls are fuel combustion, mobile sources, and process emissions from oil refineries. To date, the ARB monitors four carbonyls: formaldehyde, acetaldehyde, methyl ethylketone (MEK), and acrolein.



- **Volatile Organic Compounds** - VOCs are organic compounds that can vaporize easily at ambient temperatures. Some VOCs are highly reactive and play a critical role in the formation of ozone. Other VOCs have adverse, chronic, and acute health effects. In some cases, VOCs can be both highly reactive and potentially toxic. Sources of VOCs include motor vehicle exhaust, waste burning, gasoline marketing, industrial and consumer products, pesticides, industrial processes, degreasing operations, pharmaceutical manufacturing, and dry cleaning operations

Laboratory analyses of samples are conducted using state-of-the-art techniques.

- Carbonyl compounds are collected into adsorbent cartridges and analyzed by high performance liquid chromatography (HPLC). (SOP MLD022 - Determination of Carbonyl Compounds in Ambient Air Using High Performance Liquid Chromatography) and EPA/625/R-96/-1-b; Compendium Method TP-11A: Determination of Formaldehyde in Ambient Air Using Absorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC)
- VOC and oxygenated compound samples are collected in stainless steel canisters and are analyzed in the laboratory by two separate gas chromatography (GC) methods for butadiene, aromatic and halogenated, and oxygenated hydrocarbons.
- *Note that US EPA and CARB agencies have removed acrolein ($H-CO-CH=CH_2$) from the validated list for the measurement using DNPH-cartridge technique, due to its degradation in the presence of the collection media. Other methods have been suggested by other agencies; however none has been validated yet.*

Emission standard for MY 2004 and subsequent Medium-Duty Diesel Engines
CARB (California Environmental Protection Agency)

Table 5 - ARB Emission Standards for MY 2004 and Subsequent Medium-Duty Diesel Engines (grams per brake horsepower-hour)

Option	Formaldehyde
ULEV A	0.05
ULEV B	0.05
SULEV	0.025

The ARB's toxic air contaminant monitoring programs for hydrocarbon VOCs and Carbonyls are described in: Toxic Air Contaminants Monitoring

Source: <http://www.arb.ca.gov/aaqm/toxics.htm>

- Formaldehyde Test Methodologies

The Formaldehyde test method used in CALIFORNIA EXHAUST EMISSION STANDARDS AND TEST PROCEDURES FOR 2001 AND SUBSEQUENT MODEL PASSENGER CARS, LIGHT-DUTY TRUCKS, AND MEDIUM-DUTY VEHICLES is the DNPH impinger method or DNPH cartridge.

- Other than the DNPH impinger method, the extractive FT-IR method, and the aqueous acetylacetone impinger method (NCASI or Celanese Method) could be used to measure Formaldehyde.

- EtOH Emissions Measurement

CARB is measuring EtOH emissions by the impinger method

Other examples: Brazilian legislation RCHO emission limits

Tabela 28 – Limites máximos de emissão para veículos leves novos¹

ANO	CO (g/km)	HC (g/km)	NOx (g/km)	RCHO ² (g/km)	MP ³ (g/km)	EVAP. ⁴ (g/teste)	CÁRTER	CO-ML (% vol)
89 - 91	24	2,10	2,0	--	--	6	nula	3
92 - 96 ⁶	24	2,10	2,0	0,15	--	6	nula	3
92 - 93	12	1,20	1,4	0,15	--	6	nula	2,5
mar/94	12	1,20	1,4	0,15	0,05	6	nula	2,5
jan/97	2	0,30	0,6	0,03	0,05	6	nula	0,5
mai/03	2	0,30	0,6	0,03	0,05	2	nula	0,5
jan/05 (40%)	2	0,16 ⁵	0,25 ⁷	0,03	0,05	2	nula	0,5 ⁷
jan/06 (70%)	2	ou	ou	0,03	0,05	2	nula	0,5 ⁷
jan/07 (100%)	2	0,30 ⁶	0,60 ³	0,03	0,05	2	nula	0,5 ⁷
jan/09	2	0,05 ⁵ ou	0,12 ⁷ ou	0,02	0,05	2	nula	0,5 ⁷
jan/09	2	0,30 ⁶	0,25 ³	0,02	0,05	2	nula	0,5 ⁷

1 - Medições de acordo com a NBR6601 (US-FTP75), e conforme as Resoluções CONAMA n° 15/95 e n° 315/02.

2 - Apenas para veículos do ciclo Otto. Aldeídos totais de acordo com a NBR 12026.

3 - Apenas para veículos do ciclo Diesel.

4 - Apenas para veículos do ciclo Otto, exceto a GNV.

5 - Hidrocarbonetos não metano (NMHC).

6 - Hidrocarbonetos totais somente para veículos a GNV, que também atendem ao item (5).

7 - Apenas para veículos do ciclo Otto, inclusive a GNV.

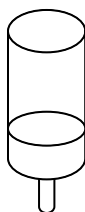
In conformity with Brazilian Resolution CONAMA no. 15/95 & no. 315/02



Sep-Pak® DNPH-Silica cartridge



ELUTION OF
CARTRIDGE



5 ml of fresh prepared
solution of:
CH₃CN / H₂O milliQ (50:50)



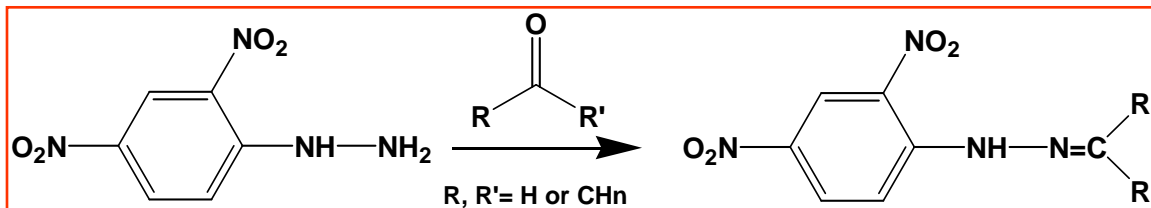
ELUTED sample

1 mL



HPLC-UV

DNP Cartridge

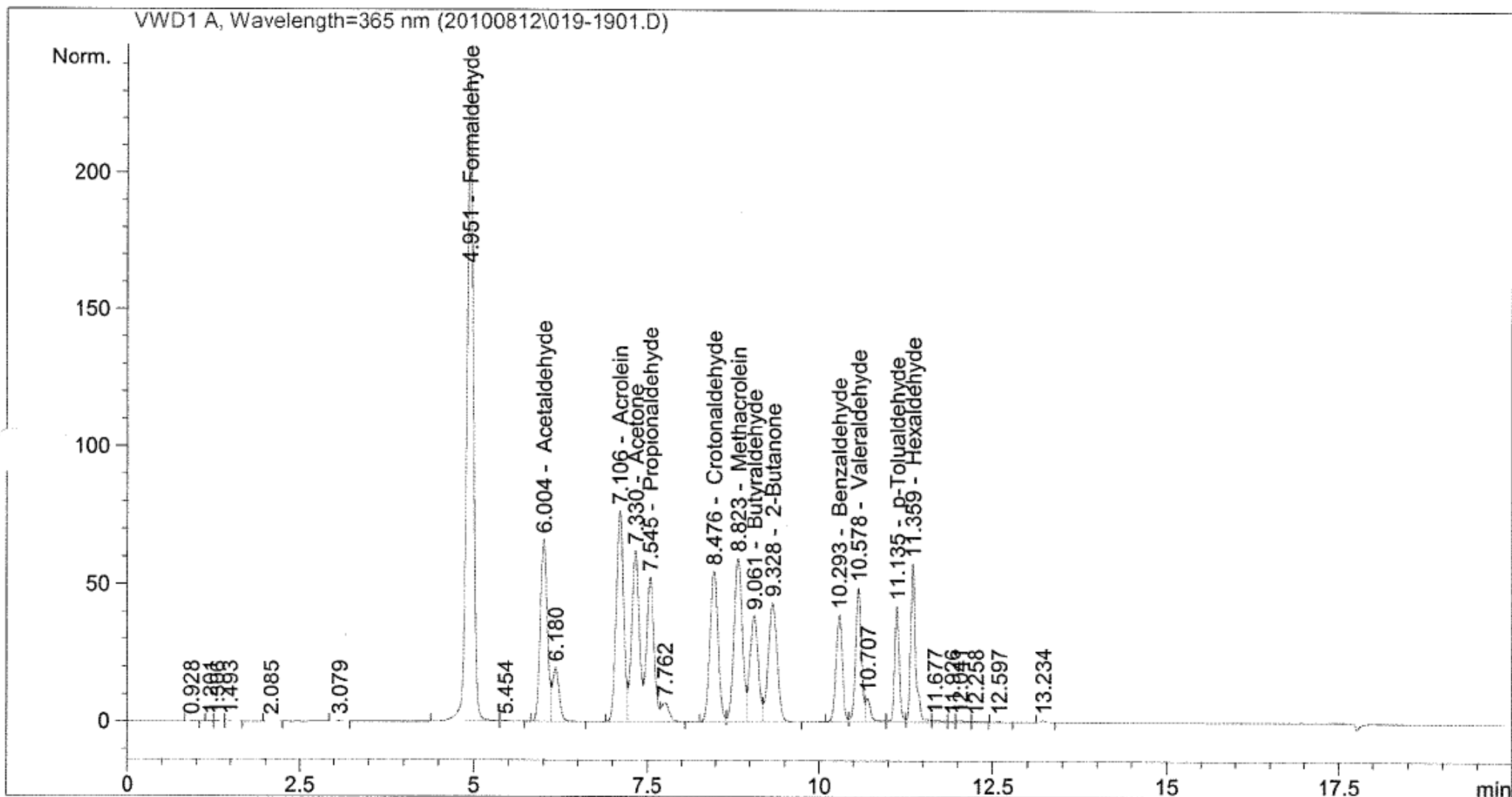


The method described has been developed on the basis of the “compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (2nd Edition)”

[EPA/625/R-96/-1-b; Compendium Method TP-11A: Determination of Formaldehyde in Ambient Air Using Absorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC)]

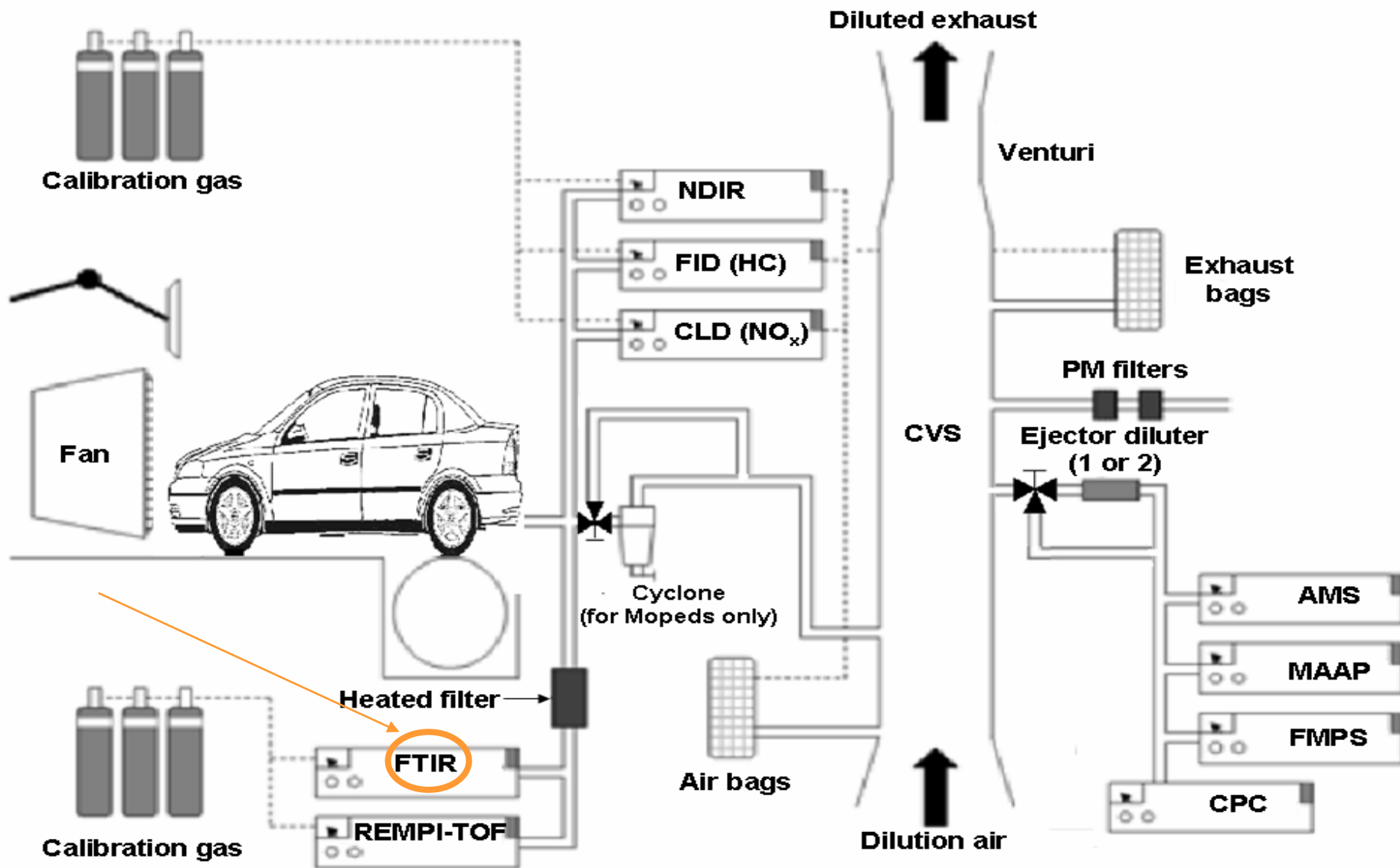
- Carbonyl compounds are measured up-stream of the vehicle exhaust. The diluted exhaust was drawn through 2,4-dinitrophenyl-hydrazine coated silica cartridges (Waters™ Sep-Pak® DNPH-cartridges). Aldehydes and ketones present in the exhaust flow are collected as their non-volatile 2,4-dinitrophenylhydrazone derivatives. The cartridges are then eluted with 2.5mL acetonitrile and 2.5 mL water and analyzed by HPLC-UV ($\lambda=365\text{nm}$).
- The cartridges are then eluted with 2.5mL of acetonitrile, diluted with 2.5 mL of water and stored at 5°C until analysis.
- Samples were analysed by HPLC-UV (high performance liquid chromatography) with a temperature stabilized (20°C). The column used was 30 cm x 3.9mm C18 -coated silica gel (*Several possible columns and sizes have been proposed lately for improvement of separation and rapidity of the analysis*) run in gradient mode (0.9 ml/min). Eluents were H₂O (A-eluent) and acetonitrile (B-eluent). The gradient was programmed from 50% to 90%. Detection and quantification were carried out at 365 nm.

(Source: Clairotte, 2010-JRC Transport and Air Quality Unit)



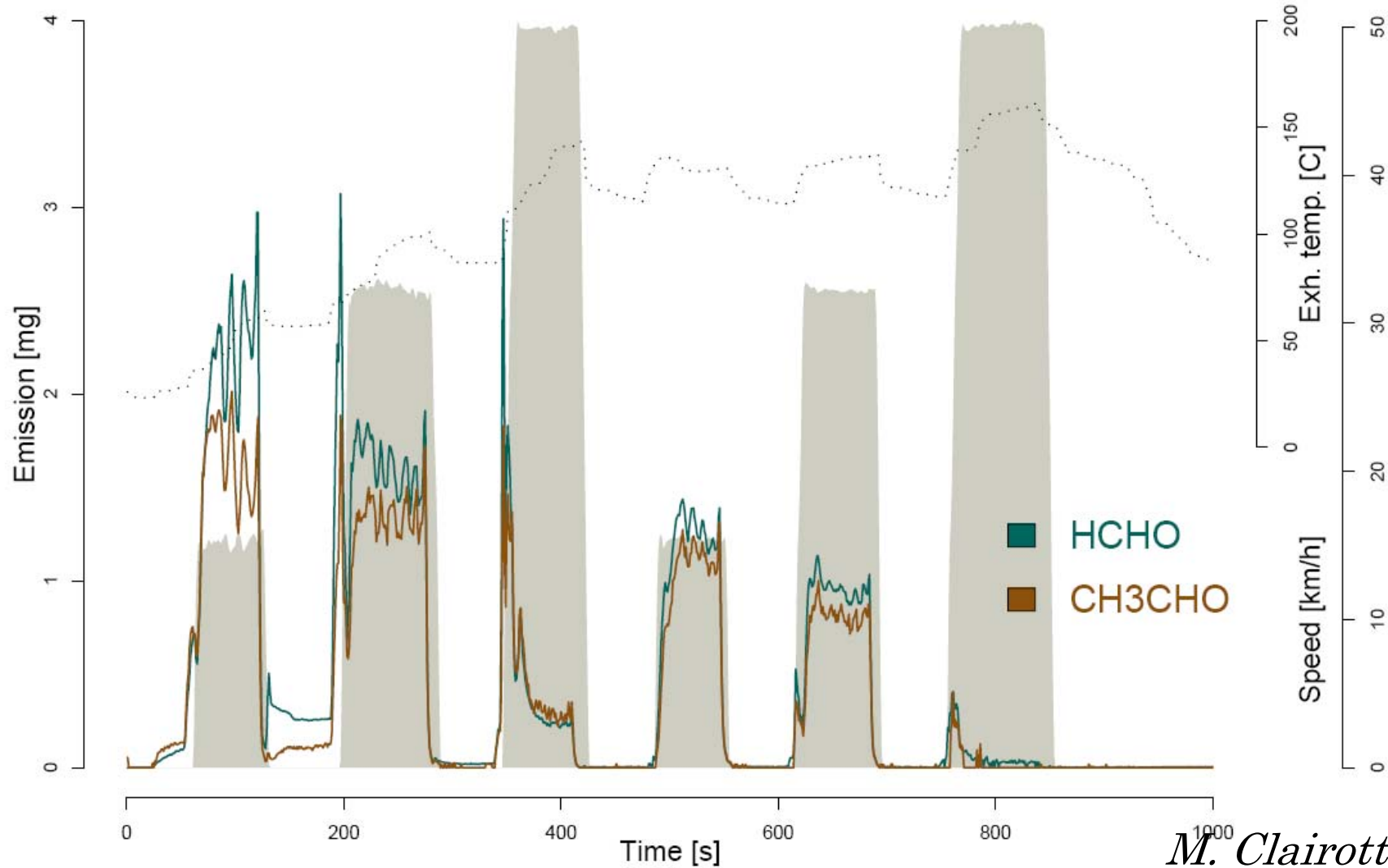
Standard chromatogram, all compounds at 0.6mg/L except formaldehyde (1.2mg/L)

- On line measurements, FT IR.
- Taking advantage of new online real time measurements we may be able to assess more accurately sources and origin of this class of compounds. Formaldehyde and Acetaldehyde have been monitored by a High Resolution Fourier Transforms Infrared spectrometer (HR-FTIR - Multigas analyzer).



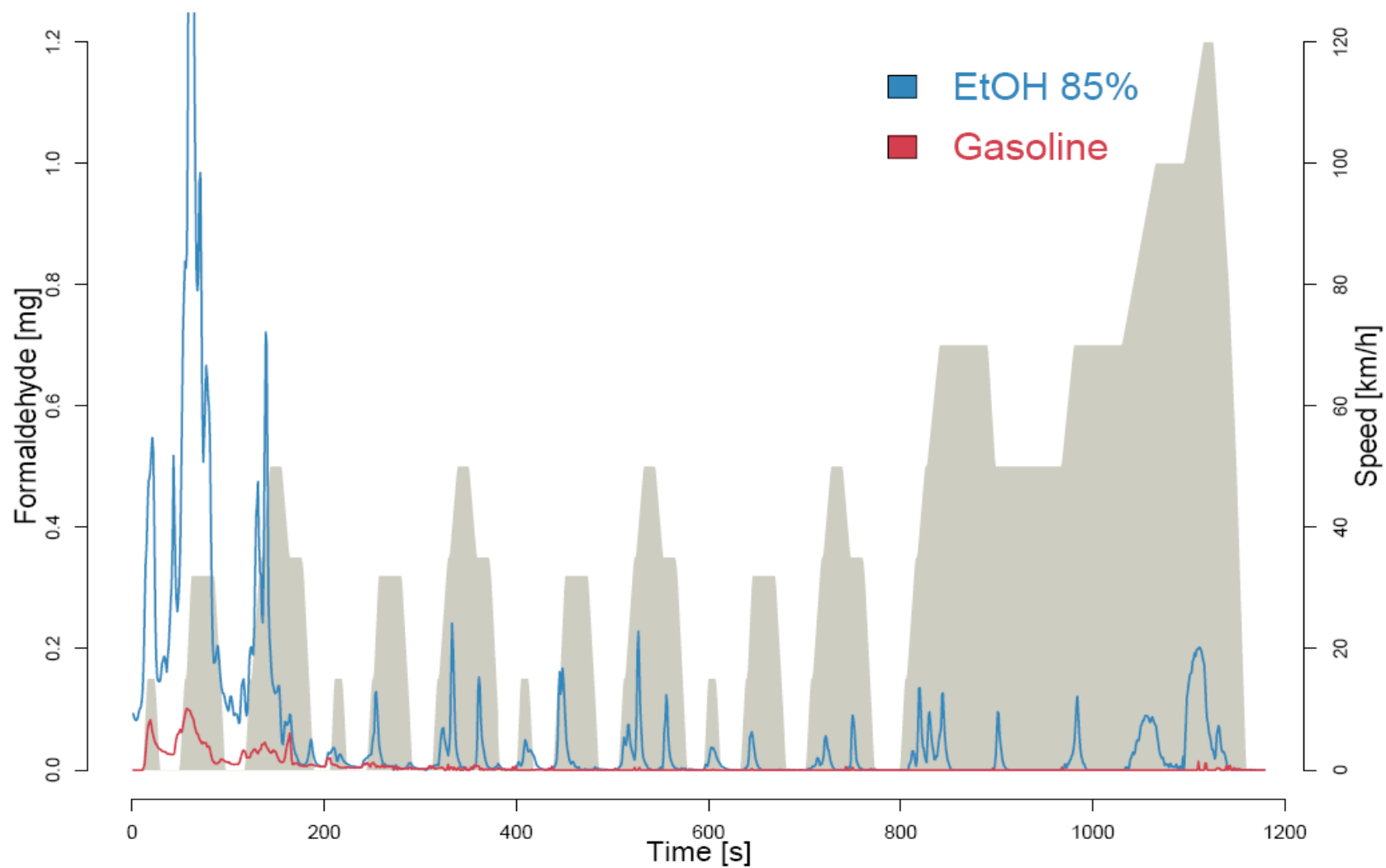
Source: M. Clairotte 2010

Formaldehyde and Acetaldehyde emission from MD E3 vehicle – Intense Traffic cycle – BIO30%



M. Clairotte 2010

Formaldehyde emission from FLEXI EURO4



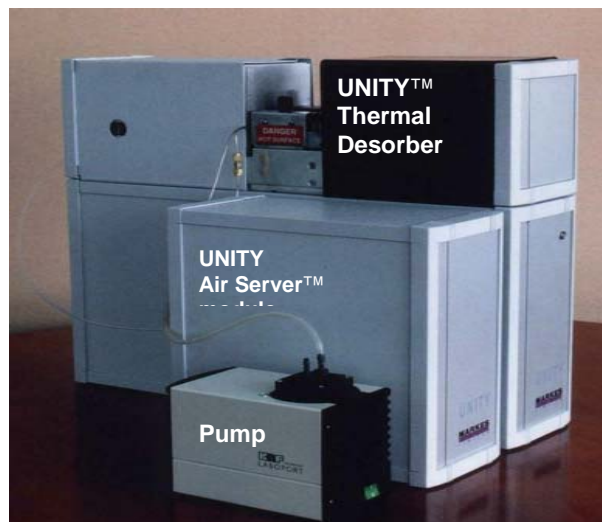
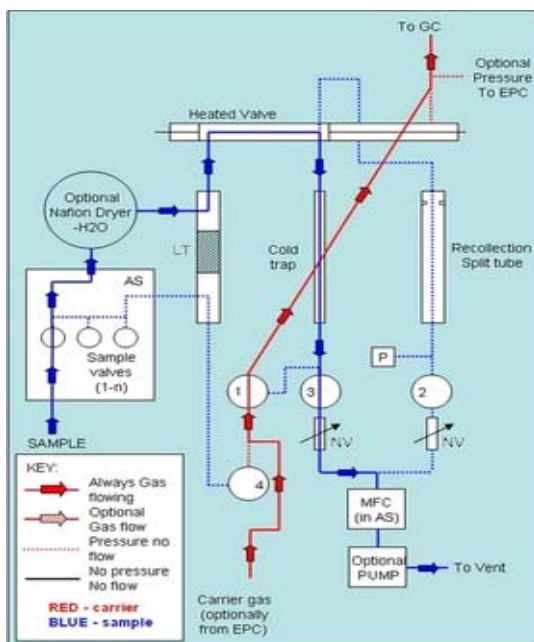
Mean of 3 tests

M. Clairotte 2010

Table - 30 hydrocarbon species (VOCs) recommended to be measured by the Ozone Directive 2002/3/EC.

ethane	1,3-butadiene	isooctane (2,2,4-trimethyl pentane)
ethene (ethylene)	n-pentane	benzene
ethyne (acetylene)	isopentane (2-methylbutane)	toluene
propane	1-pentene	ethylbenzene
propene	<i>trans</i> -2-pentene	<i>m+p</i> -xylene
n-butane	isoprene (2-methyl-1,3-butadiene)	<i>o</i> -xylene
isobutane (2-methyl propane)	n-hexane	1,2,4-trimethylbenzene
1-butene	i-hexane (2-methylpentane)	1,2,3-trimethylbenzene
<i>trans</i> -2-butene	n-heptane	1,3,5-trimethylbenzene
<i>cis</i> -2-butene	n-octane	

- Once emitted in the air, each VOC reacts at a different rate and with different reactions mechanisms, and therefore, it can influence differently the ozone formation at ground level. In urban areas, the major contributor to ozone precursors is road traffic, which is why determining the contribution of hydrocarbons from vehicle emissions is of high importance.



Vehicle was driven on a chassis dynamometer (Zoellner GmbH) with a constant volume sampler (flow 7.5 m³/min).

Exhaust samples of the vehicle were collected in Tedlar™ bags during the driving cycle test and analysed straight ahead after the sample collection. A sample volume of 80 ml out of the 10 liters collected in the bags was needed for the analysis, allowing replicate analysis when necessary.

A thermal desorption unit (UNITY™) and an auxiliary sampling device (Air Server™, Markes International, Pontyclun, UK) were used to collect the samples from the bags.

Chromatographic separation and detection were performed with a GC 6890 (Agilent, Wilmington, USA) equipped with a dual flame ionization detector (FID).

The original work showed here has been performed at the VELA Laboratory
Transport & Air Quality Unit,
Institute for Environment and Sustainability
EC-DG JRC, Ispra (IT)



THANKS FOR YOUR ATTENTION,

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