METEV

MEASUREMENT TECHNOLOGIES FOR EMISSIONS FROM ETHANOL FUELLED VEHICLES

AVL MTC 9711

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AVL MTC AB

2009/11

A REPORT FOR

INTERNATIONAL ENERGY AGENCY – ADVANCED MOTOR FUELS

ACKNOWLEDGEMENTS

This project is financed by the Swedish Road Administration and made in cooperation with the International Energy Agency – Advanced Motor Fuels Agreement.

Financing of the project as cost-sharing has been arranged by Department of Energy, USA, Tekes, Finland and National Resources Canada, Canada. The report is a contribution to Annex XXXVI, "Measurement technologies for emissions from ethanol fuelled vehicles, METEV".

The project has been commissioned by the Swedish Road Administration as the operating agent. AVL MTC is responsible for the execution of the project, Volvo Cars Corporation (VCC) and General Motors Powertrain (GMPT, Trollhättan) has participated on task sharing basis. VTT in Finland has been commissioned by AVL MTC to perform cold climate vehicle tests on chassis dynamometer.

SUMMARY

The interest of using alcohols, and especially ethanol, as vehicle fuel is high in Sweden. The advantages are many, such as; being renewable, the ethanol can be produced locally and it is easily mixed with gasoline. Alcohol fuels are considered to be a substantial part of the alternative fuel market, especially in Brazil, USA and Sweden.

With this growing interest it is of most importance to investigate the emission performance of vehicles fuelled with alcohols. The focus in this study is on measurement and calculation of hydrocarbon emissions.

The emission regulations in different countries have different ways to treat alcohol fuelled vehicles. When alcohols are used as blending components in gasoline, uncombusted alcohols from the fuel are emitted in the exhaust in various amounts. If a Flame Ionization Detector (FID) is used to measure hydrocarbons, the uncombusted alcohol will be included in the measurement. The alcohol is, per definition, however not a hydrocarbon (hydrocarbons contains only hydrogen and carbon). In the US regulations, the alcohol content is measured separately, and the FID measurement is adjusted for the alcohol part. This is not performed in the European regulations.

The aim of this project is to highlight the need for a discussion regarding the methodology for measuring hydrocarbon and alcohol emissions from flexible fuelled vehicles operating on alcohol fuel blends.

This project is divided in three main parts:

1. A literature survey on the topic "Measurement methodologies for alcohol fuelled vehicles". Regulations, instrumentation and measurement procedures has been investigated.

2. Measurement of ethanol calibration gases of different concentration and oxygen content. Different FID analyzers have been compared, and the response factor has been investigated.

3. An ethanol-fuelled vehicle has been tested on chassis dynamometer; measurements of regulated compounds, alcohol and aldehydes have been performed at three different temperatures.

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ABBREVIATIONS

C_2H_5OH	Ethanol
C3-C8	Substances containing 3-8 carbon atoms
CARB	California Air Resource Board
CFV	Critical Flow Venturi
CH_3CHO	Acetaldehyde
CH_3OH	Methanol
CH_4	Methane
CO	Carbon Monoxide
CO_2	Carbon Dioxide
CVS	Constant Volume Sampler
DNPH	DiNitroPhenylHydrazine
EU	European Union
EUDC	Extra Urban Driving Cycle
FFV	Flexible Fuelled Vehicle
FID	Flame Ionisation Detector
FTIR	Fourier Transform InfraRed
FTP75	Federal Test Procedure 75
GC	Gas Chromatography
GMPT	General Motors Powertrain
HCHO	Formaldehyde
HEPA	High Efficiency Particulate Air (Filter)
HPLC	High Performance Liquid Chromatography
LDV/LDT	Light Duty Vehicle / Light Duty Truck
LEV	Low Emission Vehicle
MS	Mass Spectrometer
MTBE	Methyl Tertier Butyl Ether
NEDC	New European Driving Cycle
NMHC	Non Methane Hydrocarbon
NMOG	Non Methane Organic Gases
NOX	Nitrogen Oxides
PAS	Photoacoustic sensor
PM	Particulate Matter
Ppm	Parts per million
ppmC	Parts per million of Carbon
RHO	Aldehydes
ROH	Alcohols
SAE	Society of Automotive Engineers International
SULEV	Super Ultra Low Emission Vehicle
THC	Total Hydrocarbon
UDC1	Urban Driving Cycle 1st part
UDC2	Urban Driving Cycle 2nd part
ULEV	Ultra Low Emission Vehicle
US EPA	Environmental Protection Agency
VCC	Volvo Car Corporation
VTT	Technical Research Centre of Finland

1 INTRODUCTION

In recent years, hydrocarbon, aldehyde and alcohol tailpipe emissions from flexible fuelled vehicles operated on alcohols, or blends of alcohols, have received an increased attention in Sweden together with an increased and expanding interest in alternative fuel for vehicle propulsion.

However, in the European regulations with respect to emission measurements from motor vehicles, the emission testing of flexible fuelled vehicles are based upon that the vehicles are fuelled by gasoline only. No special limit values for flexible fuelled vehicles are implemented in Euro 4 and earlier Euro-classes. Future EU emission regulations (Euro 5/6 for LDV) are adopted to also include regulations for flexible fuelled vehicles operated on E85. To evaluate emission performance of vehicles fuelled with alcohols, it has frequently been questioned how to define THC emissions – if the current THC measurement method is applicable for FFV tailpipe emission measurements (calibration gas, FID temperature, etc), and if it is necessary to include aldehydes and alcohol measurements into the regulation as in the US regulation.

Due to the fact that alcohol fuel blends have different fuel properties compared to conventional fuels such as gasoline/diesel, it is important to study factors which affect the reproducibility and repeatability of the THC measurement from such vehicles. It is therefore important that the instrumentation, test procedures and sampling methods are designed to cope with both conventional (fossil) fuels and alcohol fuels. In this study, parameters such as FID type and temperatures, measurement routines, maximum time between sampling (diluted exhaust gas in Tedlar bags) and analysis has been investigated.

The study was divided into three main parts.

Part 1: Literature survey of the topic measurement methodologies for alcohol fuelled vehicles

Comparison of regulations for alcohol fuelled vehicles in countries where alcohol fuels are commercially available in significant numbers. Calculations, measurement procedures and instrumentation were investigated.

Part 2: Measurement of ethanol calibration gases of different concentration and oxygen content, FID analysis

Different models of FID analyzers were tested, using ethanol gases of different concentration and oxygen content. The FID response to ethanol was investigated. The influence of storage time (in sample bags) was also studied.

Part 3: Vehicle tests

Tests were carried out with a flexible fuelled vehicle using ethanol blends as fuel. The vehicle tests were carried out on a chassis dynamometer according to 70/220/EG in accordance with NEDC driving cycle. The effects of different temperatures and exhaust dilution levels on exhaust emissions have been studied.

1.1 Introduction – alcohols and aldehydes

Aldehydes are formed in an oxidation reaction of primary alcohols, such as methanol and ethanol.

Basic reaction:

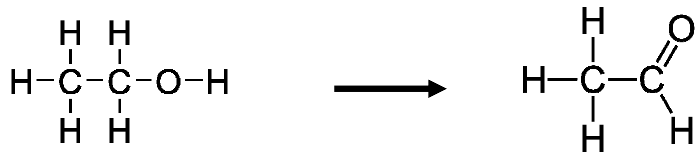

Figure 1: The ethanol molecule (C_2H_5OH) is oxidized into acetaldehyde (CH_3CHO).

Methanol (CH_3OH) is oxidized into formaldehyde (HCHO). In the exhausts from a flex fuelled vehicle using methanol, unburned methanol, formaldehyde and formic acid are present. In the exhausts from a vehicle using ethanol the exhausts contains unburned ethanol, acetaldehyde and acetic acid. The formaldehyde is a known carcinogen, whereas acetaldehyde is considered to be “probable” carcinogen.

The alcohols are by definition no hydrocarbons, because the molecule contains oxygen. The FID, which is used to measure the emissions of HC in certification testing of vehicles and engines, is however a non-selective detector and will respond to all substances being ionized in the flame, i.e. all substances containing carbon. For flex fuelled vehicles the THC will also include the substances mentioned above. This is further complicated by the fact that different substances have different response factors. For pure hydrocarbons without, for instance, oxygen, the FID response is proportional to the carbon atoms in the molecule. When another functional group, such as oxygen, is present the FID response is decreased. This means that the measured total hydrocarbons (by FID) is not correct for alcohol fuelled vehicles, since substances which should not be classified as hydrocarbons are included.

2 Part 1: Literature study

This part is divided into:

1. Regulations concerning emission measurement technology of exhaust emissions from E85 fuelled passenger cars including definitions of hydrocarbons (EU, CARB, US EPA, Brazil)
2. Measurement technology

2.1 Emission regulations

In this study we have chosen to look into the emission legislation in countries where ethanol fuelled vehicles are offered on a commercial basis. The focus is on hydrocarbon emissions, and alcohol / aldehyde emissions where applicable.

2.1.1 European Union

Table 1: Emission standards - EU

		Limit values - vehicle category M and N_1 class 1													
		CO		THC		NMHC		NO_X		THC + NO_X		PM (1)		Particle number (2)	
		mg/km		mg/km		mg/km		mg/km		mg/km		mg/km		mg/km	
		PI	CI	PI	CI	PI	CI	PI	CI	PI	CI	PI (3)	CI	PI	CI
Euro 4	*2005.01*	1000	500	100	-	-	-	80	250	-	300	-	25	-	-
Euro 5	*2009.09* (4)	1000	500	100	-	68	-	60	180	-	230	5,0/4,5	5,0/4,5	-	$6{,}0 \times 10^{11}$
Euro 6	*2014.09*	1000	500	100	-	68	-	60	80	-	170	5,0/4,5	5,0/4,5	-	$6{,}0 \times 10^{11}$

PI = Positive Ignition, CI = Compression Ignition
(1) A revised measurement procedure shall be introduced before the application of the 4,5 mg/km limit value.
(2) Euro 5: A new measurement procedure shall be introduced before the application of the limit value.
Euro 6: A number standard is to be defined for this stage for positive ignition vehicles.
(3) Positive ignition particulate mass standards shall apply only to vehicles with direct injection engines.
(4) 2011.01 for all models.

Driving cycle: New European Driving Cycle – NEDC (see Figure 2).

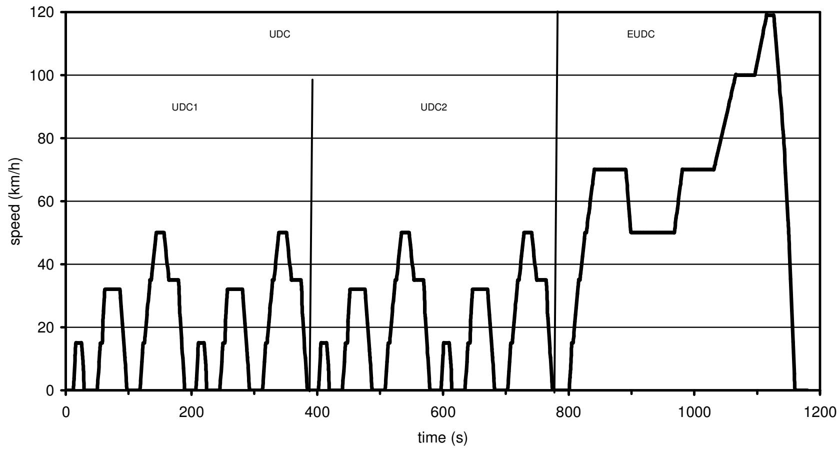

Figure 2: The New European Driving Cycle – NEDC.

The Euro 5 regulations is applicable from September 2009, and Euro 6 from September 2014. In Euro 4 and earlier regulations, the manufacturers of flexible fuelled vehicles were allowed to use only the conventional (fossil) fuel in the certification testing. From Euro 5 both fuels must be used at the certification testing. Testing at low ambient conditions (i.e. Type 6-testing) will be demanded for both fuels from 2011 (please see footnote in Table 2). The tests required for flexible fuelled vehicles are demonstrated in Table 2.

Table 2: Test requirements for type-approval and extensions (according to European Commission Regulation (EC) No 692/2008):

Vehicle category	***Vehicles with positive ignition engines including hybrids***
Reference fuel	***Flex fuel*** Petrol (E5) Ethanol (E85)
Test type	
Gaseous pollutants (Type 1 test)	Yes (both fuels)
Particulates (Type 1 test)	Yes (direct injection) (both fuels)
Idle emissions (Type 2 test)	Yes (both fuels)
Crankcase emissions (Type 3 test)	Yes (petrol)
Evaporative emissions (Type 4 test)	Yes (petrol)
Durability (Type 5 test)	Yes (petrol)
Low temperature emissions (Type 6 test)	Yes(2) (both fuels)
In-service conformity	Yes (both fuels)
CO_2 emissions and fuel consumption	Yes (both fuels)

(2) Test on petrol only for vehicles type-approved before 1 September 2011 for new types of vehicles and from 1 January 2013 for all new vehicles sold. The test will be performed with both fuels on or after these dates.

In EU regulations total emissions of hydrocarbons and non-methane hydrocarbons are regulated. The mandated measurement procedure is by using a FID-instrument, calibrated with propane in synthetic air. Flexible fuelled vehicles are tested according to the same procedure as gasoline fuelled vehicles.

The gas density used for calculation of emissions from gasoline fuelled vehicles is 0,619 g/dm^3, for E85 the gas density is 0,932 g/dm^3 (with hydrocarbon ratio of $C_1H_{2,74}O_{0,385}$).

The calculation:

$$M_i = \frac{V_{mix} \times Q_i \times k_H \times C_i \times 10^{-6}}{d}$$

M_i = mass emission of the pollutant i in grams per kilometre,

V_{mix} = volume of the diluted exhaust gas expressed in litres per test and corrected to standard conditions (273,2 K and 101,33 kPa),

Q_i = density of the pollutant i (for example hydrocarbons, where the density for gasoline is 0,619 g/dm^3, for E85 0,932 g/dm^3) in grams per litre at normal temperature and pressure (273,2 K and 101,33 kPa),

k_H = humidity correction factor used for the calculation of the mass emissions of oxides of nitrogen (there is no humidity correction for HC and CO),

C_i = concentration of the pollutant i in the diluted exhaust gas expressed in ppm and corrected by the amount of the pollutant contained in the dilution air,

d = actual distance corresponding to the operating cycle in km.

In reality, the change of Q_i for THC from 0,619 to 0,932 g/dm^3, leads to an increase of approximately 50% in the calculation of THC emissions from flexible fuelled vehicles.

2.1.2 USA

The federal emission standards (set up by US EPA) must be met by all new vehicles sold in the US. California has however been granted, by the Clean Air Act, to adopt its own emission standards which are stricter than the federal standards. These standards are set up by the Californian Air Resource Board (CARB). Some other states have followed and adopted the Californian standards.

The US emission standards are neutral regarding fuel and technology, meaning the same emission limits is applied regardless of the fuel and engine/vehicle technology.

2.1.2.1 US EPA

In the Tier 2 regulation, effective from 2004, the same emission standards apply to all vehicle weight categories, i.e. cars, minivans, light-duty trucks and SUVs have the same emission limit.

The Tier 2 emission standards are structured into different bins, where the vehicle manufacturer can choose to certify the vehicles to fit into any of the available bins. The manufacturer's fleet average on NO_X must however not average more than 0,07g/mile (equivalent to bin 5 level, full useful life).

Table 3: Emission standards – US EPA

Bin#	Intermediate life (5 years / 50,000 mi)					Full useful life				
	NMOG	**CO**	**NO_X**	**PM**	**HCHO**	**NMOG**	**CO**	**NO_X**	**PM**	**HCHO**
	g/mi	g/mi	g/mi	g/mi	g/mi	g/mi	g/mi	g/mi	g/mi	g/mi
Temporary Bins										
11						0.280	7.3	0.9	0.12	0.032
10	0.125	3.4	0.4	-	0.015	0.156	4.2	0.6	0.08	0.018
9	0.075	3.4	0.2	-	0.015	0.090	4.2	0.3	0.06	0.018
Permanent Bins										
8	0.100	3.4	0.14	-	0.015	0.125	4.2	0.20	0.02	0.018
7	0.075	3.4	0.11	-	0.015	0.090	4.2	0.15	0.02	0.018
6	0.075	3.4	0.08	-	0.015	0.090	4.2	0.10	0.01	0.018
5	0.075	3.4	0.05	-	0.015	0.090	4.2	0.07	0.01	0.018
4	-	-	-	-	-	0.070	2.1	0.04	0.01	0.011
3	-	-	-	-	-	0.055	2.1	0.03	0.01	0.011
2	-	-	-	-	-	0.010	2.1	0.02	0.01	0.004
1	-	-	-	-	-	0.000	0.0	0.00	0.00	0.000

Driving cycle: Federal Test Procedure – FTP75 (see Figure 3)

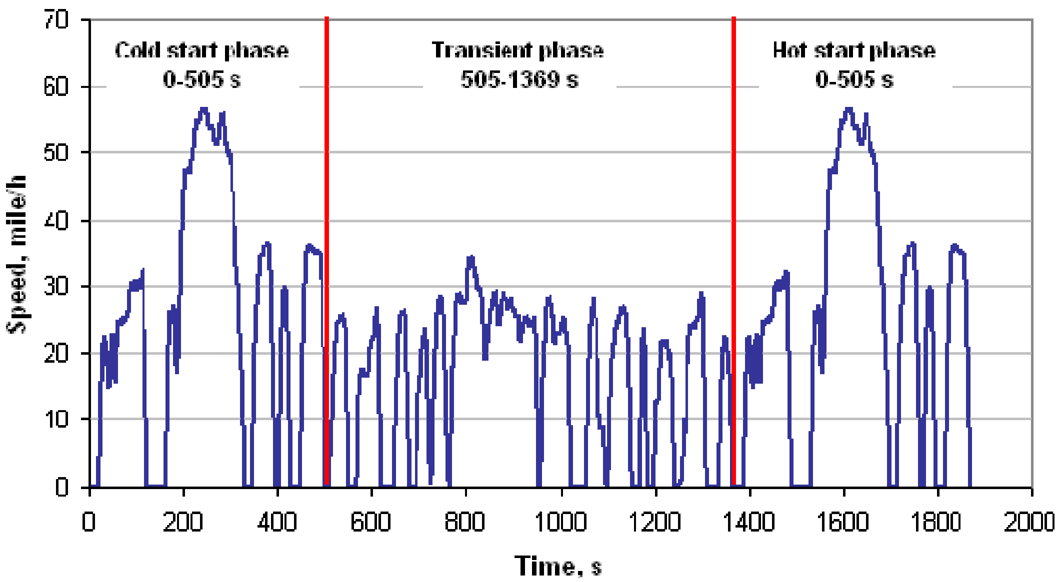

Figure 3: Federal Test Procedure – FTP75.

Besides the emission requirements presented in Table 3, where testing is performed using the FTP75 driving cycle, there are supplemental exhaust emission standards that needs to be fulfilled in the certification process. Here the US06 and SC03 driving cycles are used. The supplemental exhaust emission standards must however not be fulfilled for alternatively fuelled LDV/LDTs or flexible fuelled LDV/LDTs when operated on a fuel other than gasoline or diesel. The supplemental exhaust emissions standards are not presented in this report.

The EPA regulations for alcohol fuelled vehicles are based on methanol fuel; therefore the formaldehyde emissons are regulated.

As can be seen in Table 3, NMOG (NonMethane Organic Gases) are regulated. The definition of NMOG is the emissions of NonMethane Hydrocarbons (NMHC) and oxygenated hydrocarbons. The weighted mass (wm) emissions of NMOG shall be calculated as follows:

$$\mathbf{NMOG_{wm} = \Sigma NMHC_{wm} + \Sigma ROH_{wm} + \Sigma RHO_{wm}} \qquad (1)$$

ROH are the alcohol content in the exhaust emissions. The alcohol can be measured with Photoacoustic Sensor (PAS) or sampled by the impinger method (Method 1001, see Measurement Technology Specification for description). The impinger sample is thereafter analysed by Gas Chromatography.
RHO are the aldehydes (and ketones) content in the exhaust emissions. They are sampled in DNPH-cartridges (Method 1004, see Measurement Technology Specification for description). The cartridges are thereafter analysed by HPLC.

To calculate the NMOG emissions, the first step is to correct the FID measurements for the presence of methane and oxygenated hydrocarbons:

$$NMHC = {}_{FID}THC - (r_{CH4} \text{ x } CH_4) - (r_{C2H5OH} \text{ x } 2 \text{ x } C_2H_5OH)$$

${}_{FID}THC$ is the THC measured by FID in ppm C.

r_{CH4}, r_{C2H5OH} are the FID response factor for CH_4 and C_2H_5OH respectively. The response factors are determined by the use of gas bottles with known concentration (within ±2% of the specified concentration).

The pollutant concentration is presented in ppm C, hence the factor 2 for ethanol.

The FTP75 driving cycle is divided into three parts which are weighted differently. The mass emissions from the respective part are calculated as follows (alcohol is used in this example, can be applied to any of the pollutants with its respective density):

$$ROH_{mass} = ROH_{conc} * ROH_{dens} * 10^{-6} * V_{MIX}$$

To achieve the weighted mass emission of ROH, the different parts of the driving cycle are weighted as follows:

$$\mathbf{ROH_{wm}} = 0.43\left(\frac{ROH_{mass1} + ROH_{mass2}}{D_{phase1} + D_{phase2}}\right) + 0.57\left(\frac{ROH_{mass3} + ROH_{mass2}}{D_{phase3} + D_{phase2}}\right)$$

To calculate the NMOG, the oxygenated hydrocarbons are thereafter added back according to equation 1.

The densities of interest in this study:
Per CFR, calculations are based on standard temperature and pressure of 20°C (68°F) and 1 atm:

NMHC: 16,33 g/ft^3 (13,88 g/mole)
C_2H_5OH: 54,23 g/ft^3 (46,07 g/mole)
CH_3CHO: 51,85 g/ft^3 (44,05 g/mole)
HCHO: 35,34 g/ft^3 (30,03 g/mole)
CH_4: 18,88 g/ft^3 (16,04 g/mole)

Response factors:
The FID instrument response is calibrated for HC-only gas – typically propane. Because its response is different for oxygenated hydrocarbons and methane, its output must be corrected to account for the presence of these compounds in the measured exhaust. Measured response factors are determined for each compound known to be present and known to affect FID response.

The US EPA recommends the FID to be heated to 113 ºC for methanol fuelled vehicles (instead of 190 ºC which is used for gasoline and diesel fuelled vehicles).

2.1.2.2 California ARB

The emission standards in California differ from the US EPA, as can be seen in Table 4.

Table 4: Emission standards, passenger cars – California ARB

	50,000 miles / 5 years					120,000 miles / 11 years				
	NMOG	**CO**	**NO_X**	**PM**	**HCHO**	**NMOG**	**CO**	**NO_X**	**PM**	**HCHO**
	g/mi	g/mi	g/mi	g/mi	g/mi	g/mi	g/mi	g/mi	g/mi	g/mi
LEV	0.075	3.4	0.05	-	0.015	0.090	4.2	0.07	0.01	0.018
ULEV	0.040	1.7	0.05	-	0.008	0.055	2.1	0.07	0.01	0.011
SULEV	-	-	-	-	-	0.010	1.0	0.02	0.01	0.004

Driving cycle: FTP75 (see Figure 3)

As in the US EPA regulation, the hydrocarbons are part of the NMOG emissions. The calculations are the same, but California has regulations concerning both methanol and ethanol fuelled vehicles. The response factor for the respective alcohol is determined and applied in the calculation.

As in the federal regulations, there is a fleet average to consider for the vehicle manufacturer. In California the fleet average is for NMOG emissions.

2.1.3 Brazil

Brazil has an extensive production of ethanol, and ethanol fuelled vehicles is commonly used. All gasoline sold is blended with 20-25% ethanol, and almost nine of every ten new cars sold in the Brazilian market are Flex Fuelled Vehicles. There is a wide range of fuels on the market, where:
E100 (93% ethanol + 7% water)
E22 (22 ± 2% ethanol + gasoline)
Certification required with E22 fuel for E22 vehicle, E22/E60/E100 for a flex fuel vehicle, E22/E60/E100 and CNG for a tri-fuel vehicle. The calculations for E22/E60/E100 are the same.

Table 5: Emission standards, passenger cars – Brazil

		Limit values - Passenger cars					
		CO	**HC**	**NO_X**	**PM**	**RCHO**	**Idle CO**
		g/km	g/km	g/km	g/km	g/km	(% vol)
Proconve L-4	*2005.01* [1]	2.0	0.16[4]	0.25[6]	0.05	0.03	0.5
	2006.01 [2]	2.0	or	or	0.05	0.03	0.5
	2007.01 [3]	2.0	0.30[5]	0.60[7]	0.05	0.03	0.5
Proconve L-5	*2009.01*	2.0	0.05[4] or 0.30[5]	0.12[6] or 0.25[7]	0.05	0.02	0.5

Idle CO limits apply to Otto cycle engines only
PM limits apply to Diesel cycle engines only
RCHO limits apply to Otto cycle engines only; Natural gas vehicles exempted
(1) At least 40% of annual production (passenger vehicles + light commercial vehicles
(2) At least 70% of annual production (passenger vehicles + light commercial vehicles
(3) 100% of annual production (passenger vehicles + light commercial vehicles
(4) NMHC
(5) THC; limits apply to natural gas vehicles only
(6) Otto cycle engines
(7) Diesel cycle engines

Driving cycle: FTP75 (see Figure 3)

The calculation for NMHC is:

$$NMHC = THC - CH_4$$

The density for THC is 576,8 g/m^3, regardless of fuel type.

The vehicle manufacturer has however the right to measure the unburned ethanol and discount this value from the NMHC emissions. In this case the calculations are similar to the US EPA. The ethanol is sampled with impingers and the distilled water from the impingers is analyzed with Gas Chromatography (GC). A response factor for the ethanol is measured by using gas bottles with known concentration of ethanol.

2.2 Measurement technology specification

Instruments and sampling methodologies used for emission measurements of flexible fuelled vehicles will be presented in this chapter. The focus will be on instruments and methods measuring hydrocarbons, alcohols and aldehydes in the emission regulations presented in the previous chapter.

2.2.1 Flame Ionization Detector (FID)

Used for: Hydrocarbons.

The technique of flame ionization detection (FID) relies on the ionization of molecules during high temperature combustion in the reaction zone of the FID-flame to determine the total hydrocarbon concentration within a gaseous sample. The analyzer has an adjustable heated oven (60 to 200° C) which contains a heated sample pump and burner in which a small flame is elevated and sustained by regulated flows of air and 100% hydrogen or a 40/60% mixture of hydrogen and helium. The burner jet is used as an electrode and is connected to the negative side of a precision power supply. An additional electrode, known as the "collector", is connected to a high impedance, low noise electronic amplifier. The two electrodes establish an electrostatic field. When a gaseous sample is introduced to the burner, it is ionized in the flame and the electrostatic field causes the charged particles (ions) to migrate to their respective electrodes. The migration creates a small current flow between the electrodes. This current is measured by the precision electrometer amplifier and is directly proportional to the hydrocarbon concentration of the sample.

2.2.2 Mass Spectrometer (MS)

Used for: Ethanol

The Mass Spectrometer separates molecules in a gas stream by using the quote between the mass and the charge of the molecules (when ionised).

Measurement with the Mass Spectrometer is not a regulated procedure and is mostly used for research purposes for determination of unregulated emissions.

Basic principle:
The MS consists of four parts and the incoming molecules are treated in the different stages; the ionisation, the accelerator, the separator and the detector stage.

In the MS the atoms/molecules are first ionised, by force, into positive ions. The ions are then accelerated and thereafter immediately deflected in a curved magnetic field according to their masses. The lighter molecules are deflected more than the heavier ones. The level of deflection is also dependent of the positive charge of the molecule – if more than one electron has been knocked off, the molecule has a stronger charge – and is more deflected. It is only the ions with the correct mass/charge relationship that passes through to the detector stage. By varying the magnetic field ions with different mass/charge relationship can be analyzed.

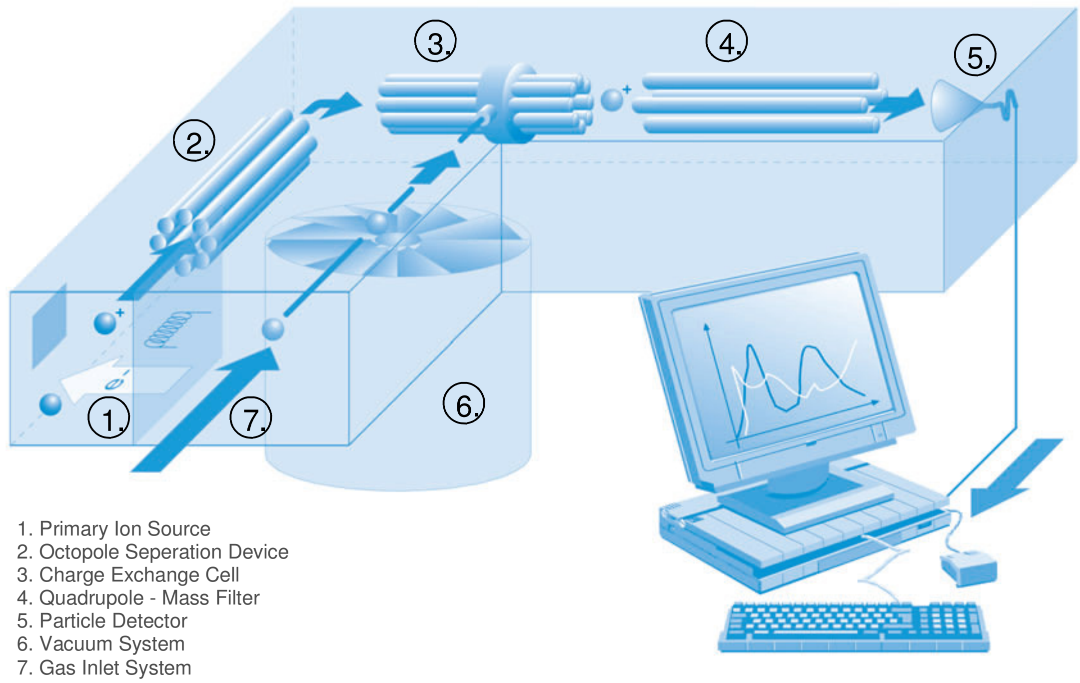

Figure 4: Schematic view of the V&F Airsense mass spectrometer (Source: vandf.agindo.info).

The MS is a fast response instrument; it is possible to get modal measurement at a speed of up to 50 Hz. This makes it possible to measure at transient conditions. It can be used for raw exhausts as well as for diluted exhausts.

It is possible to detect many different molecules with the MS, different molecules will be distinguished through their different molecule weight. If however the concentration of specific substance is an issue, the instrument needs to be calibrated with a known concentration of the specific substances.

2.2.3 Fourier Transform InfraRed (FTIR)

Used for: Ethanol, methanol, acetaldehyde and formaldehyde.

Measurement of alcohols and aldehydes with FTIR is not a standard procedure, and is used mainly for research purposes.

The FTIR uses the fact that different substances absorb different frequencies of infrared light unequally. The FTIR analysis produces absorption peaks corresponding to the frequencies of vibrations between the bonds of the atoms in a molecule. Since different molecules are consisting of different combinations of atoms, the infrared spectrum is unique for a specific substance. This makes FTIR very useful for analyzing many different compounds. The size of the peaks is also corresponding to the amount of the substance.

The infrared beam from the source is divided by a beamsplitter, dividing the beam into two optical beams. One of the beams is reflected off of a non-mobile mirror back to the beamsplitter. The other beam is reflected off of a flat mirror which is mobile (only a few millimeters) back to the beamsplitter. The mobile mirror makes it possible to differentiate the beams. The two reflected beams are recombined at the beamsplitter, and the signal exiting the "interferometer" is a result of these two beams "interfering" with each other. The resulting signal is called an interferogram, which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source. This means that as the interferogram is measured, all frequencies are being measured simultaneously.

The analyzer requires a frequency spectrum in order to make an identification. This means that the individual frequencies need to be "decoded", which is accomplished via a well-known mathematical technique called the Fourier transformation.

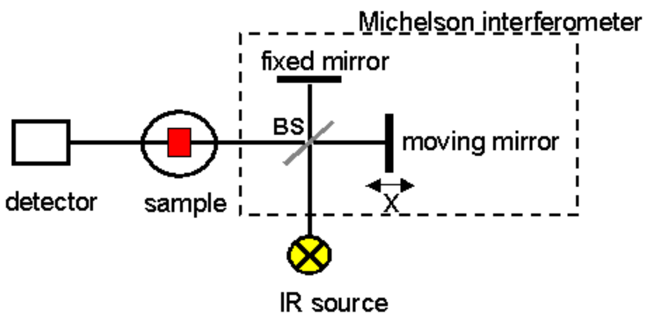

Figure 5: Schematic view of the principles of the FTIR (Source: www.uni-ulm.de).

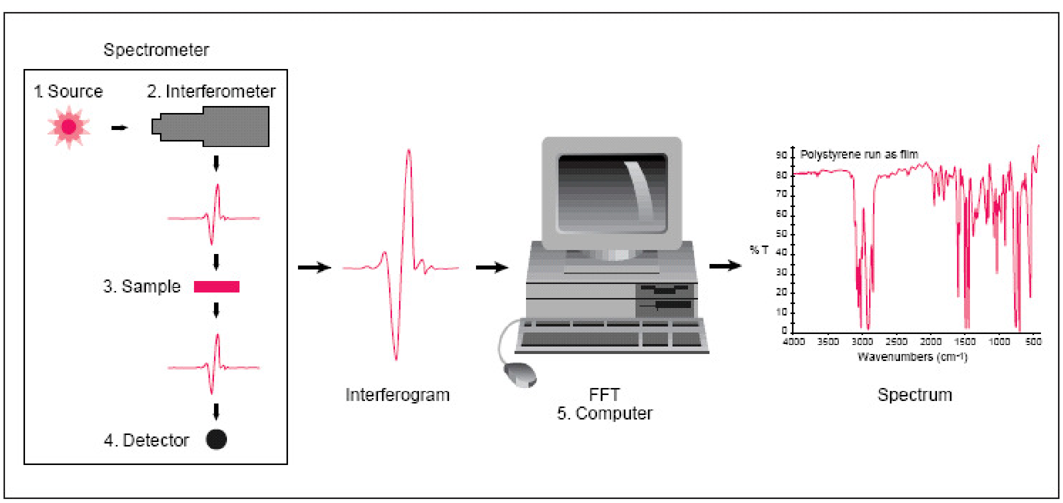

Figure 6: The working principle of the FTIR (Source: www.mmrc.caltech.edu).

The FTIR measurement is performed on raw exhaust emissions.

One advantage with the FTIR instrument is that it is possible to measure many substances at the same time, with a fast response.

2.2.4 Photoacoustic sensor (PAS)

Used for: Ethanol

The Photoacoustic sensor is approved by the US EPA and California ARB for measuring ethanol emissions in vehicle exhaust.

The principle of the PAS is based on the fact that different substances absorb different frequencies of infrared light unequally, similar to the FTIR instrument.

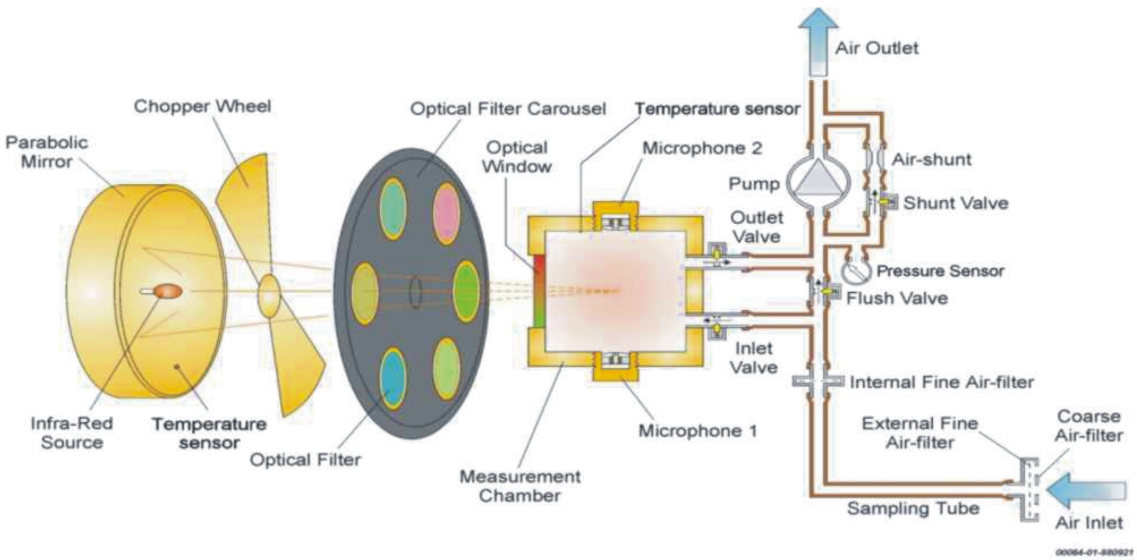

Figure 7: Schematic view of the Photoacoustic Sensor (Source: www.lumasense.dk).

The sample is drawn into the measurement chamber by an internal pump. Light from an infrared light source is reflected off a mirror, passed through a mechanical chopper, which pulsate it, and then through one of the optical filters in the filter wheel.
The gas being monitored, causing the temperature of the gas to increase selectively, absorbs the light transmitted by the optical filter. Because the light is pulsating – the gas temperature increases and decreases – causing an equivalent increase and decrease in the pressure of the gas (an acoustic signal) in the closed cell.
Two microphones mounted in the cell wall measure this acoustic signal, which is directly proportional to the concentration of the monitored gas present in the cell.
The filter wheel turns so that light is transmitted through the next optical filter, and the new signal is measured. The number of times this step is repeated is dependent on the number of gases being measured.

The PAS measures from bag after the end of the test cycle, online measurement is not possible.

2.2.5 Methods used for sampling alcohols and aldehydes

2.2.5.1 Method 1001: Sampling alcohols with Impinger sampling system

Sampling alcohol in impingers are a standardized procedure (Method 1001) approved by both the US EPA and California ARB.

The impingers are filled with deionised water and placed on ice to reduce vaporization of water. Diluted exhausts are led into the upper part of the impinger, through a tube down into the water where the gas is bubbled; the ethanol is hence dissolved into the water.

After the test, the sample is transferred to bottles and is kept below 4ºC. According to Method 1001 the sample should be analyzed within 6 days. The sample is analyzed through Gas Chromatography.

The method recommends two impingers in series (for each phase of the FTP75 test cycle), to prevent eventual breakthrough.

2.2.5.2 Method 1004: Sampling aldehydes with DNPH

Sampling aldehydes by using DNPH (2,4-DiNitroPhenylHydrazine) is a standardised procedure (Method 1004) approved by both the US EPA and California ARB.

The DNPH can be either as liquid or in a cartridge.

Liquid DNPH:
This procedure is similar to the impinger sampling described above (Method 1001: Impinger sampling system), but the ionized water is replaced by the absorbent 2,4-DiNitrophenyl-Hydrazine mixed with sulphuric or perchloric acid. After the test, if sulphuric acid has been used, the impingers should be kept, without the lid on, in a waterbath with temperature of 70-80ºC for 30min. If perchloric acid has been used, this is not necessary. The impingers should be allowed to cool in room temperature before transferred to glass bottles.

The liquid sample is analyzed through HPLC.

DNPH-cartridge:
The liquid is replaced by a cartridge containing the DNPH absorbent. For the first phase of the test cycle, two cartridges in series should be used in case of breakthrough.

The cartridge is kept in a freezer both before and after the test, and should be analyzed within 2 weeks after the test. The cartridge is also analyzed through HPLC.

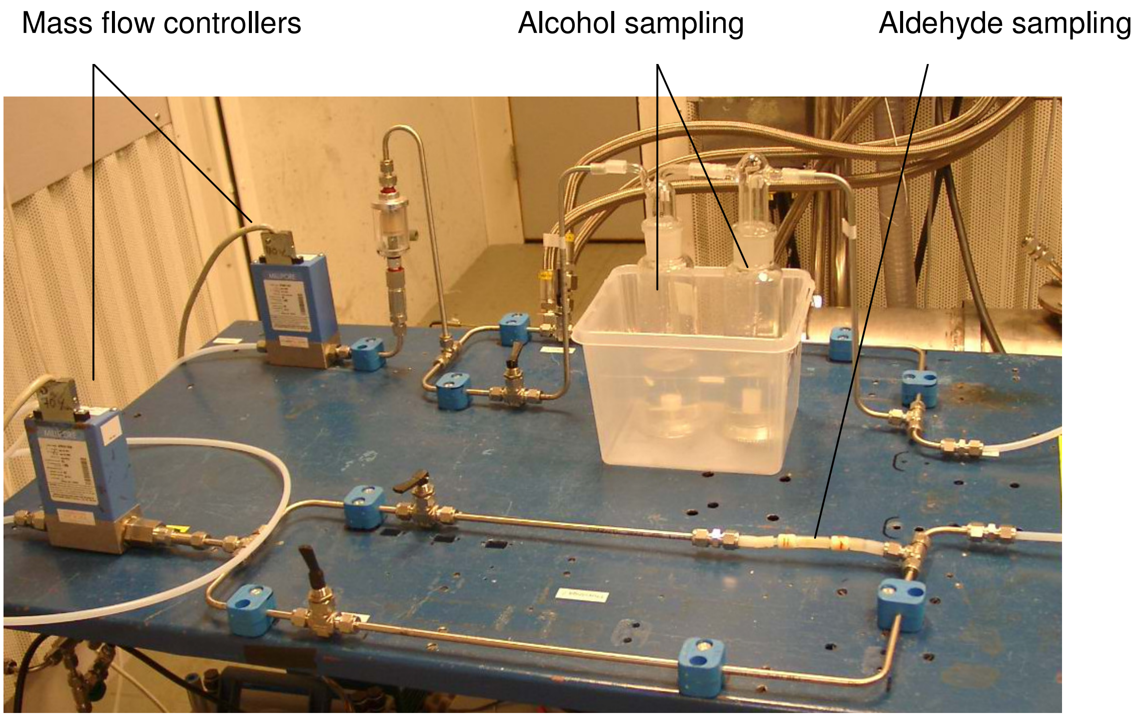

Figure 8: Setup of the alcohol and aldehyde sampling system in the METEV project. The alcohol is sampled by impingers (two in series), the aldehydes are sampled with DNPH-cartridges (two in series).

3 Part 2: Calibration gas measurement

The US EPA recommends the FID to be heated to 113 ºC for methanol fuelled vehicles (instead of 190 ºC which is used for gasoline and diesel fuelled vehicles). This is based on the fact that exhaust from methanol-fuelled vehicles generally has much higher water vapor content than conventional vehicles, which can lead to water condensation under certain testing conditions. Since both methanol and formaldehyde are soluble in water, this can be an accuracy problem in the testing. The temperature should not be too hot since the methanol can undergo decomposition reactions.

In the European regulation, the alcohol fuelled vehicles are tested in the same way as for gasoline fuelled vehicles.

The FID instrument response is calibrated for HC-only gas – typically propane. Most hydrocarbons respond nearly identically as propane with notable exceptions being oxygenated hydrocarbons such as alcohols and aldehydes commonly found in engine exhaust. See Table 6 for FID sensitivity.

Table 6: Sensitivity of the FID towards selected compounds relative to the hydrocarbon n-heptane (C_7H_{16}), which is set to 1.00 (Dietz, 1967).

Hydrocarbons:		**Alcohols:**		**Organic acids:**	
Methane	0.97	Methanol	0.23	Formic acid	0.01
Ethane	0.97	Ethanol	0.46	Acetic acid	0.24

In the European regulation, the FID is assumed to respond to all hydrocarbons identically as it responds to propane in determining the concentration of carbon atoms in a gas sample.

In the US EPA regulation, the difference in response is taken into account and response factors are established for oxygenated hydrocarbons and methane. The measurements are thereby corrected for the presence of these compounds in the measured exhaust. Measured response factors are determined for each compound known to be present, and to affect, the FID response.

Response factors should be measured directly on the FID instrument being used for HC measurement. Note that FID response to ethanol may be slow due to ethanol adsorption on walls of supply tubing. This should be taken into account when determining FID response and when determining sample time for THC measurement to be certain an accurate response to ethanol is obtained.

According to US EPA, the FID response factor to methanol is calculated as follows:

r = FIDppm / SAMppm

r = FID response factor
FIDppm = FID reading in ppmC
SAMppm = methanol concentration in the sample, or gas bottle, in ppmC

In order to test the FID response of ethanol tests were performed with calibration gas bottles with a known concentration. A total of 5 gas bottles with different concentrations of ethanol was used in this study, and 6 ethanol concentrations were studied.

Gas bottles specification:

- 30ppm ethanol in synthetic air
- 30ppm ethanol in 6% oxygen / 94% nitrogen
- 30ppm ethanol in 12% oxygen / 88% nitrogen
- 70ppm ethanol in synthetic air
- 15ppm ethanol / 7ppm propane

A gas divider was also used to produce a concentration of 5ppm ethanol.

The FID was calibrated with its ordinary calibration gas.

The study was divided into different parts:
1. Measurement of ethanol calibration gases with different concentration and oxygen content
2. Measurement of ethanol calibration gases in bags with different waiting time
3. Measurement of ethanol calibration gases using different types and individuals of FID instruments

3.1 Measurement of ethanol calibration gases in bags with different concentration and oxygen content

The FID response curve for ethanol is prolonged because of ethanol adsorption in the measurement system. In this part, the response curve can be observed as well as the effect of FID oven temperature.

Experimental

The gas bottle was connected to the sampling bag inlet, and the sampling bag was filled with the calibration gas. The FID instrument was thereafter used to analyze the sampling bag. No time limit was set; all gas in the bag was analyzed.

3.1.1 Effect of FID oven temperature

The FID response was studied using two different temperatures: 113°C and 190°C. In the US, 113°C are specified for methanol-fuelled vehicles. 190°C is the usual setting for the FID oven for gasoline- and diesel-fuelled vehicles. In the EU there is no change in this setting for alcohol fuelled vehicles.

Please note that the concentration is presented as ppmC1. In practice, this means that the concentration of the ethanol gas is multiplied by 2 since the ethanol molecule contains two carbon atoms (C_2H_5OH).

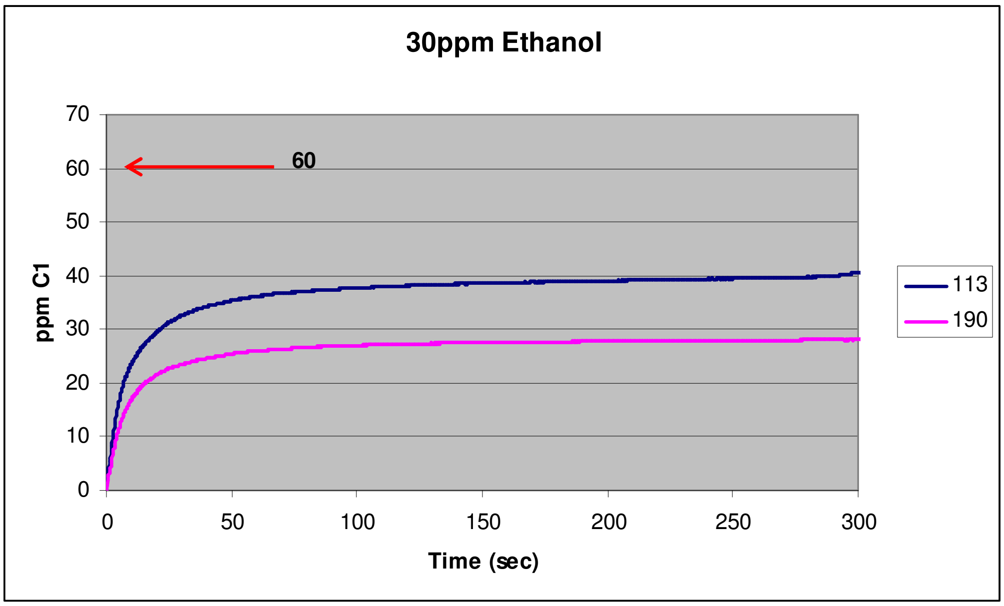

Figure 9: Comparison of FID response curve due to different FID temperatures. In this figure, the 30 ppm ethanol gas bottle is presented. The arrow points out the actual concentration of C1 in the ethanol gas.

If the concentration after a sampling time of 90 seconds is used, the response factors for the different temperatures are:

Rf: 0,67 (113 ºC)
Rf: 0,48 (190 ºC)

The response factor for the bottles with different concentration of ethanol is presented in Figure 10.

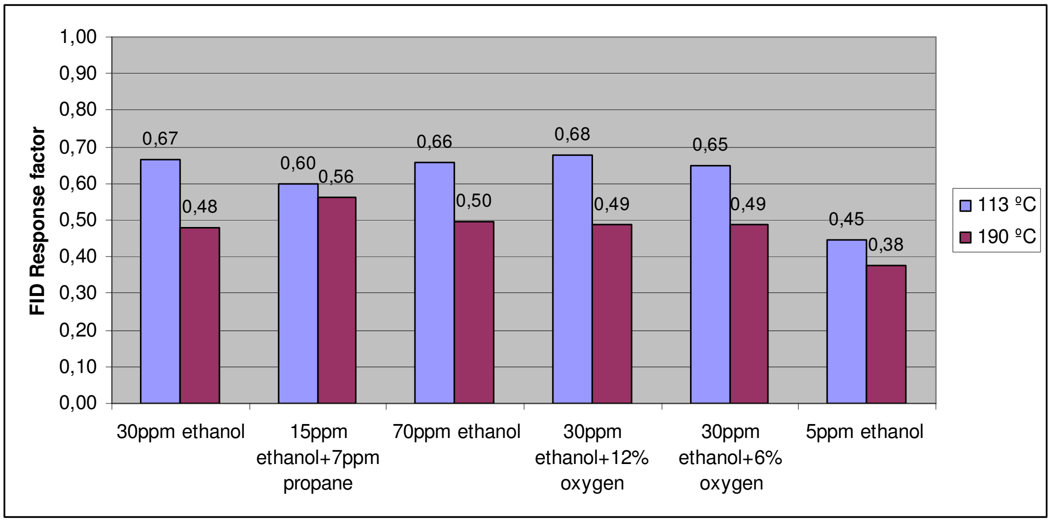

Figure 10: Comparison of FID response to different ethanol concentrations and FID temperature.

The US EPA recommendation of FID oven temperature set to 113 ℃ (for methanol-fuelled vehicles) is based on the higher water vapor of methanol, and the fact that methanol can undergo decomposition reactions if the oven is too hot.

3.1.2 Effect of oxygen concentration

The effect of oxygen concentration in the gas bottles was also investigated. Three gas bottles containing 30ppm ethanol together with different concentrations of oxygen was used.

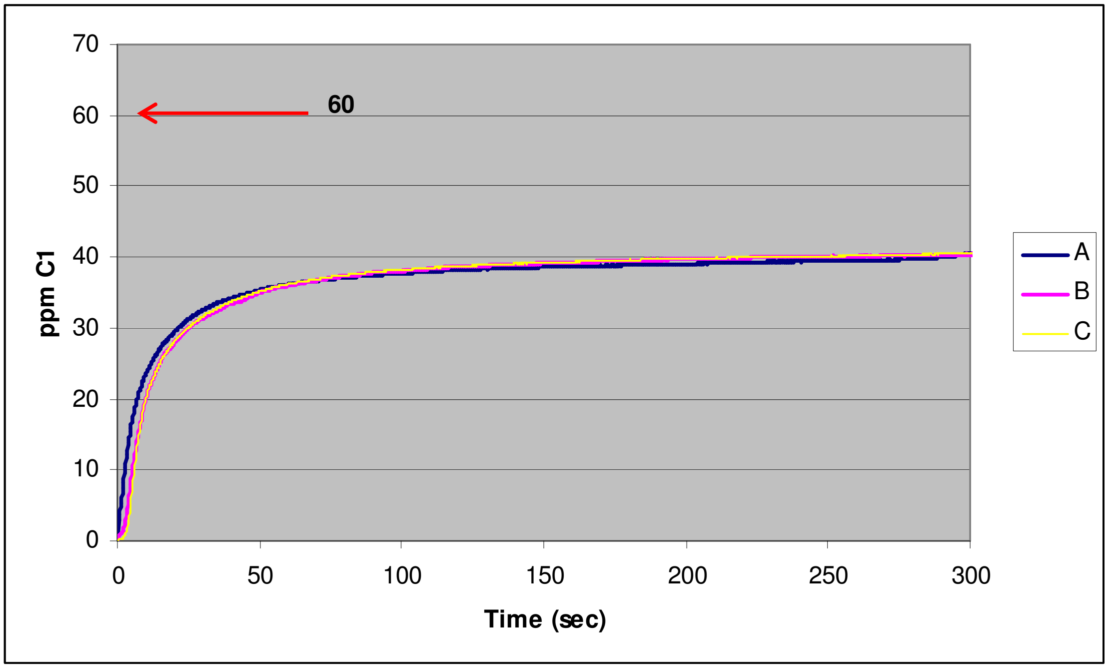

Figure 11: Comparison of FID response measurements at 113 ºC with gas bottles containing different concentration of oxygen. The arrow points out the actual concentration of C1 in the ethanol gas.
A - 30ppm Ethanol (+ synthetic air (20% Oxygen))
B - 30ppm Ethanol + 6% Oxygen + 94% Nitrogen
C - 30ppm Ethanol + 12% Oxygen + 88% Nitrogen

No effect of FID response to different oxygen content in the ethanol could be observed.

3.2 Measurement of ethanol calibration gases in bags with different waiting time

The NEDC test cycle is 1180 sec, or almost 20 min, long. As can be seen in the following chapter where the vehicle tests have been presented, most of the emissions are emitted at the cold start phase of the test cycle. The bags are analyzed after the finish of the test cycle. In this part we wanted to see if the concentration changed during the waiting time.

Experimental

The bag was filled with gas from the gas bottles. After 15 min the valve was opened and the bag was analyzed for 150 sec before closing of the valve. This was repeated after 20 min and after 25 min. At 25 min the rest of the gas present in the bag was analyzed, and therefore the valve was not closed after 150 sec. The results from this part are presented in Figure 12.

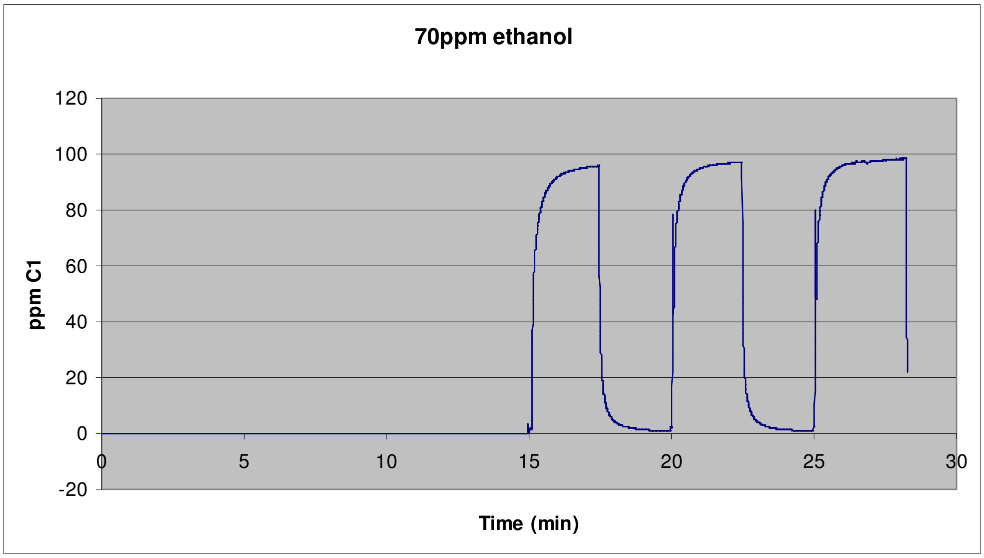

Figure 12: The gas was analyzed after 15 min, 20 min and 25 min.

In Figure 12, it can be observed that the FID response is so prolonged for the ethanol gas and the measurement has not reached stabilization after the first 150 seconds (at the 15 min reading). After 20 min the curve almost reaches stabilization. This is probably due to the adsorption characteristic of ethanol, where the measurement system (i.e. bags, tubing etc) has been saturated in the first measurement.

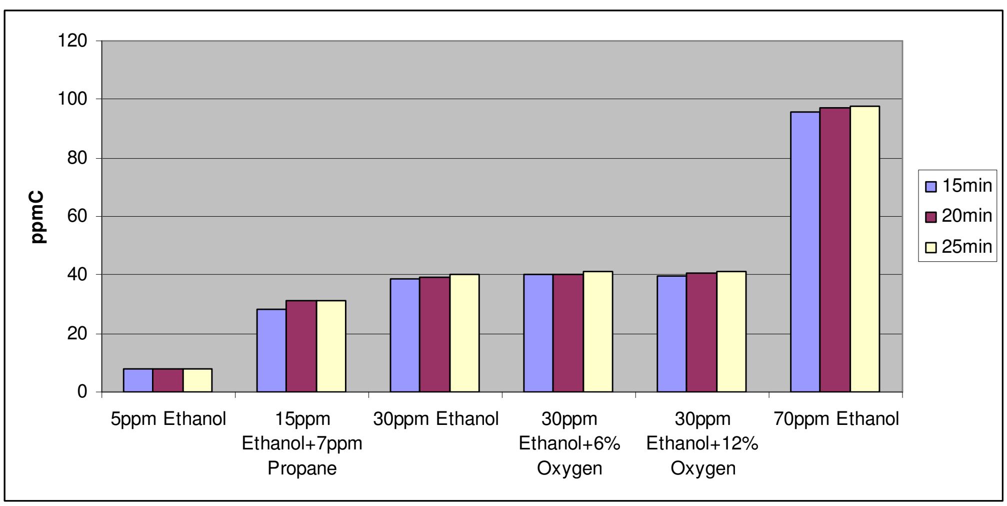

Figure 13: Results from measurement of ethanol gases in bags with different waiting time.

In the results presented in Figure 13, it appears that the concentration readings are higher the more prolonged the waiting time. Taking Figure 12 into account, it is clear that stabilization was not reached (especially in the first reading, after 15 min). The conclusion is therefore that the ethanol gas is not affected by the waiting time in the bag.

3.3 Measurement of ethanol calibration gases using different types and individuals of FID instruments

The FID has a low response for ethanol (see Table 6), but is this depending on the type and individual of the FID? This was investigated in this part of the study. The different laboratories participating in this project, except for VTT, analyzed the gas bottles with different FID:s, and the result from the analyzes of the gas bottle with 30ppm ethanol is presented in Figure 14.

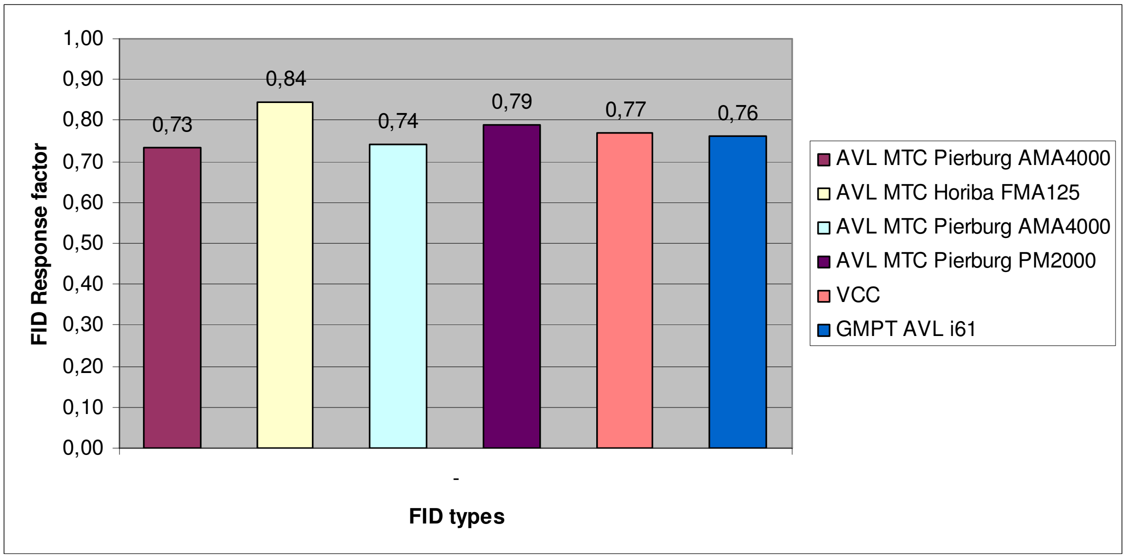

Figure 14: Comparison of FID analyzers and the response factor for ethanol. In this comparison, the gas bottle with 30ppm ethanol was analyzed.

The response factor varies between 0,73 to 0,84 for ethanol beween the different FID:s. In this comparison the calibration gas inlet on the analyzers was used.

4 Part 3: Vehicle tests

4.1 Experimental

The vehicle tests have been performed at three different laboratories – AVL MTC, VCC and VTT. At AVL MTC the effect of different ambient temperatures has been investigated. The testing at VCC has investigated whether the dilution of exhausts (by using different venturies in the CVS) is affecting the results. At the VCC testing, GMPT has been assisting by measuring alcohol emissions with their INNOVA Photoacoustic detector. The testing at VTT has been performed at cold climate conditions. For comparison between the different test laboratories, all test labs have performed tests at +22°C.

Since the focus has been on E85 testing, no testing with gasoline has been performed in this project.

4.1.1 Test program

Test lab	Temperature	Fuel	Flow rate (m^3/min)	HC	Alcohols	Aldehydes
AVL MTC	**+22°C**	E85	9	FID Diluted: bag, CVS online Raw: online	FTIR, MS, Impinger	FTIR, DNPH-cartridges
AVL MTC	**+10°C**	E85	9	FID Diluted: bag, CVS online Raw: online	FTIR, MS, Impinger	FTIR, DNPH-cartridges
AVL MTC	**-7°C**	E75	9	FID Diluted: bag, CVS online Raw: online	FTIR, MS, Impinger	FTIR, DNPH-cartridges
VCC (GMPT)	+22°C	E85	**9**	FID Diluted: bag, CVS online Raw: online	FTIR, MS, Innova photoacoustic detector	FTIR, DNPH-cartridges
VCC (GMPT)	+22°C	E85	**12**	FID Diluted: bag, CVS online Raw: online	FTIR, MS, Innova photoacoustic detector	FTIR, DNPH-cartridges
VCC (GMPT)	+22°C	E85	**15**	FID Diluted: bag, CVS online Raw: online	FTIR, MS, Innova photoacoustic detector	FTIR, DNPH-cartridges
VTT	+23°C	E85		FID Diluted: bag, CVS online	FTIR	FTIR, DNPH-cartridges
VTT	**-7°C w/o blockheater**	E75		FID Diluted: bag, CVS online	FTIR	FTIR, DNPH-cartridges
VTT	**-7°C with blockheater**[1)]	E75		FID Diluted: bag, CVS online	FTIR	FTIR, DNPH-cartridges
VTT	**-15°C with blockheater**[2)]	E75		FID Diluted: bag, CVS online	FTIR	FTIR, DNPH-cartridges

1) Blockheater used for 1 hour prior to testing.
2) Blockheater used for 2 hours prior to testing.

At VTT, the testing at cold climate was performed both without and with engine block heater. In the -7°C tests, when the engine block heater was active for 1 hour, the temperature of the engine was -3°C at the start of the tests. In the -15°C tests, when the engine block heater was active for 2 hours, the temperature of the engine was -4°C at the start of the tests.

4.1.2 Test vehicle

A Skoda Octavia FFV, certified to the Euro 4 emission standard, was used in the testing. The road load curve for the vehicle was kindly supplied by the vehicle manufacturer.

Table 7: Vehicle specification

Make	Skoda
Model	Octavia 1,6
Model year	2008
Emission standard	Euro 4
Odometer (km)	9903
Inertia mass (kg)	1350
Displacement (cm3)	1595
Power (kW)	75
Gearbox	M5
Fuel	Gasoline / E85

4.1.3 Test fuel

The vehicle was fuelled with E85 for the tests performed above zero degrees, for the tests at -7°C and -15°C E75 fuel was used. For E85 fuel specifications, see Table 8.

Table 8: Fuel specification

Parameter	**Unit**	**Spec according to SS 155480**	**Result of fuel analysis**
Density	g/ml	-	0,7855
Water content	% w/w	max 0,3 vol%	0,25 = 0,15 vol%
pHe	pH	6,5-9	6,7
Ethanol (see below)	% w/w	min 70 vol%	86,4 = 85,95 vol%
Methanol	% w/w	max 1,0 vol%	0,3 = <0,1 vol%
Isobuthanol	% w/w	-	0,4
MTBE	% w/w	ethers max 5,2 vol%	2,2 = 2,3 vol%
Petrol	% v/v	min 14 vol%	14,05*
Ethanol:			
Sulphur	mg/kg	max 10 mg/kg	0,78
C3-C8	mg/kg	max 2,0 vol%	1782 = 0,2 vol%
Chlorides	mg/l	max 1 mg/l	<0,1
Appearance	-	clear liquid	-

* According to SS 155422 Petrol, MTBE and Isobuthanol are counted as petrol components.

4.1.4 Driving cycle

The vehicle was tested according to the legislative NEDC test cycle, this test cycle is used for emission certification of light duty vehicles in Europe. The first part of the cycle includes four identical parts, representing the Urban Driving Cycle (UDC). The UDC can be further divided into two parts, UDC1 and UDC2. This enables you to look at cold start performance compared to the warm engine. The UDC part is followed by a part with higher speed, the Extra Urban Driving Cycle (EUDC). The total length of the test cycle is 1180 s.

Before the start of the test cycle, the vehicle was preconditioned by driving an NEDC cycle before soaked in a temperature-controlled area, until the engine oil temperature did not differ more than ±2°C from the ambient temperature.

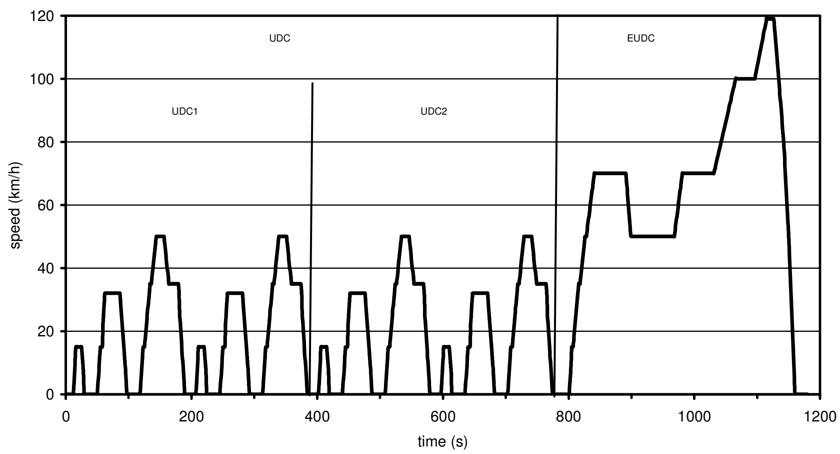

Figure 15: The NEDC driving cycle.

4.2 Test conditions – AVL MTC

4.2.1 Chassis dynamometer

The vehicle was tested on an electric Clayton DC500 500mm double roller chassis dynamometer. The dynamometer settings were applied according to the corresponding regulation 98/69/EC.

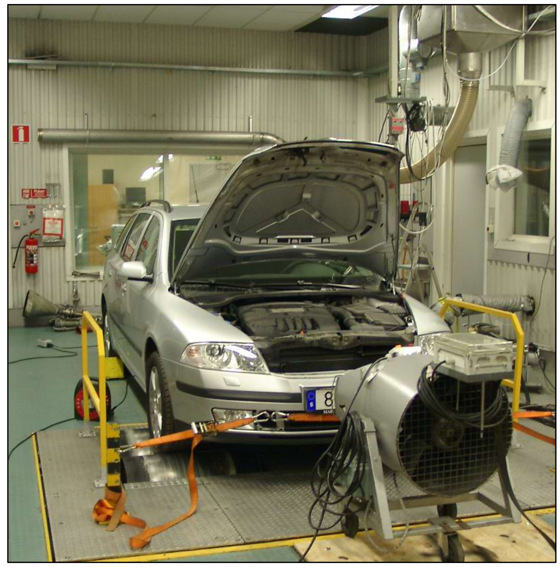

Figure 16: The test vehicle on the chassis dynamometer.

4.2.2 Exhaust sampling system

A Constant Volume Sampler (CVS) (Horiba CVS-9300T) was used in the study. The dilution tunnel (total length of 3150mm, inner diameter 250mm) is connected to the tailpipe. Cleaned and HEPA filtered test cell air is introduced into the exhaust stream. The dilution tunnel flow rate is controlled by the use of a 9 m^3/min critical venturi.

4.2.3 Emission measurement

The regulated emissions were measured according to the test procedures corresponding to the current emission regulation (98/69/EC). A Horiba Mexa 9000 series (9400D) was used for CO, HC, NO_X and CO_2 analysis. The measurement principles for the different components are presented in Table 9. The diluted exhausts were sampled in three bags for the different parts of the NEDC test cycle (UDC1, UDC2 and EUDC).

Figure 17: Horiba MEXA measurement system.

Table 9: Measurement principles

Emission component	Measurement principle
Total hydrocarbons (THC)	FID (flame ionization detector, detector temp 190°C)
Carbon monoxide (CO)	NDIR (Non-dispersive infrared analyzer)
Nitrogen oxides (NO_X)	CLA (Chemi-luminescence)
Carbon dioxide (CO_2)	NDIR (Non-dispersive infrared analyzer)
Fuel consumption (FC)	Carbon balance of HC, CO and CO_2

4.2.4 Online measurements of regulated components

The regulated emissions were also measured via sampling from the CVS. The same instrumentation was used as for the bag measurements.

4.2.5 Unregulated emissions

4.2.5.1 Ethanol

Ethanol was analyzed with FTIR, MS and by the use of impingers. By using the FTIR and MS one can get second-by-second analysis of the ethanol emissions. The impingers collect through the total cycle. The impinger sampling system consists of two glass impingers containing distilled water. After the test, the distilled water (containing the alcohol) is sent for analysis to an external laboratory. No breakthrough was observed between the two glass impingers.
The MS and impinger system samples from the CVS tunnel.
The FTIR samples from the raw emissions.

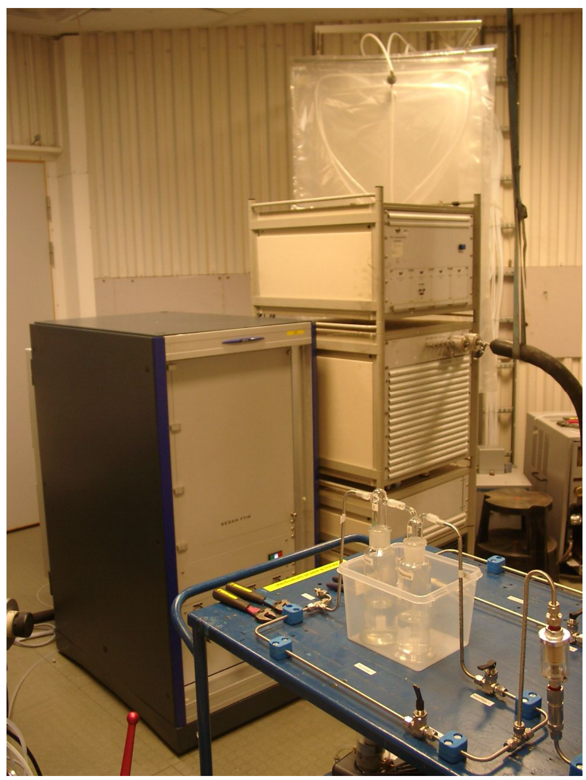

Figure 18: The FTIR, MS and Impinger measurement systems.

4.2.5.2 Aldehydes

Aldehydes are formed in an oxidation reaction of primary alcohols, such as methanol (formaldehyde) and ethanol (acetaldehyde).

The aldehydes were analyzed with FTIR and DNPH (2,4-dinitrophenyl hydrazine) cartridges. The FTIR gives second-by-second emissions, and the aldehydes sampled in the cartridges give a total value for the test cycle.

Two DNPH cartridges in series were used over each individual NEDC cycle, thus the emissions are given as an integrated value over the test cycle. After sampling, the cartridges were stored in a freezer and thereafter sent to an external analysis laboratory. No breakthrough was observed between the two cartridges.

The DNPH-cartridges samples diluted exhausts emissions from the CVS tunnel. The FTIR samples from the raw exhaust emissions.

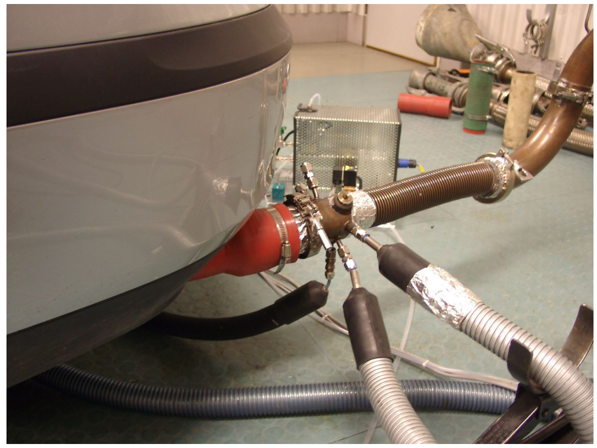

Figure 19: Sampling of raw exhaust emissions from the tailpipe.

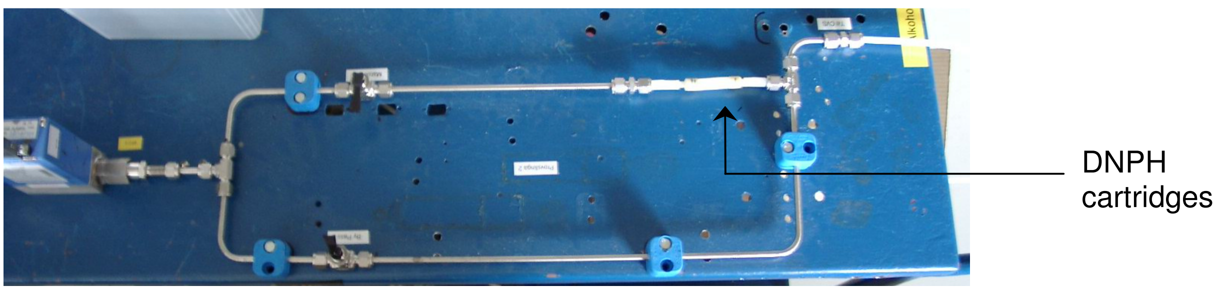

Figure 20: Aldehyde sampling system.

Figure 21: DNPH cartridges used for aldehyde sampling, two in series.

4.3 Test conditions – Volvo Car Corporation

4.3.1 Chassis dynamometer

At VCC the vehicle was tested on a 1220 mm MAHA IP-ECDM 48L 2WD chassis dynamometer. The dynamometer settings were applied according to the corresponding regulation 98/69/EC.

4.3.2 Exhaust sampling system

A Constant Volume Sampler (CVS) (Horiba CVS 7200 SLE) was used. Before the CVS, the exhausts are mixed with dilution air through a low loss mixing tee system. Four different CFVs can be combined to achieve the wanted flow. In this study three different flows were used; 9, 12 and 15 m^3/min.

Figure 22: Horiba CVS-7200SLE sampling system.

Figure 23: Critical flow venturi.

4.3.3 Emission measurement

The regulated emissions were measured according to the test procedures corresponding to the current emission regulation (98/69/EC). A Horiba Mexa 7200 SLE was used for CO, HC, NO_X and CO_2 analysis. The diluted exhausts were sampled in two bags for the different parts of the NEDC test cycle (UDC and EUDC).

4.3.4 Online measurements of regulated components

The regulated emissions were also measured via sampling from tailpipe. The instrumentation used for tailpipe analysis is a Horiba Mexa 7100 D.

4.3.5 Unregulated emissions

4.3.5.1 Ethanol

Ethanol was measured online with FTIR and MS. The FTIR is an MKS, Multigas analyzer, 2030 model. The MS is a V&F Analystechnik, Airsense 2000 model. These instruments sampled from tailpipe using heated lines.

Figure 24: The MS measures ethanol concentration online.

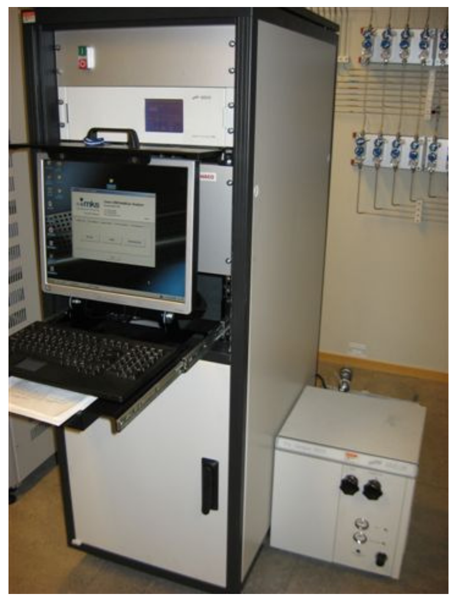

Figure 25: The FTIR measures ethanol and aldehydes concentrations online.

The ethanol content was also analyzed with an INNOVA 1314 photoacoustic detector. This instrument belongs to General Motors Powertrain (GMPT), and representatives from GMPT were present at the testing at VCC.

The INNOVA photoacoustic detector measures ethanol concentration in bag emissions. After the bag analysis was finished, the INNOVA was connected to the bags (Figure 26) in the following order: UDC (exhaust), EUDC (exhaust), UDC (dilute), EUDC (dilute). The ethanol concentration was measured for a minimum of 3 sample points per bag.

Figure 26: Switch between bag analysis and INNOVA.

Figure 27: INNOVA 1314 photoacoustic detector.

4.3.5.2 Aldehydes

VCC has a Horiba NMOG sample cart system for aldehyde sampling. A heated sample line is used for sampling the diluted exhausts. For the sampling of ambient air, the line is not heated. The number of cartridges makes it possible to differentiate the emissions from different parts of the test cycle. See Figure 28.

Figure 28: Horiba NMOG sample cart system (VCC).

4.4 Test conditions – VTT

4.4.1 General

The testing at VTT was conducted using European test method as a guideline, and all equipment listed for regulated emissions testing were fulfilling the requirements for Euro 4. In principle, the laboratory has an official accreditation to perform such testing (FINAS, T001)[1].
The testing was conducted in a climatic test cell, where ambient temperature can be controlled between +30°C and -30°C.

Figure 29: The test vehicle on the chassis dynamometer.

4.4.2 Chassis dynamometer

The vehicle was tested on a chassis dynamometer (FroudeConsine), single roller with a diameter of 1,0 m. The dynamometer settings were applied according to the corresponding regulation 98/69/EC.

4.4.3 Exhaust sampling system

A Constant Volume Sampler (CVS) (Pierburg 12.5 WT) was used in the study.

Figure 30: Pierburg AMA 2000 measurement system.

4.4.4 Emission measurement

The regulated emissions were measured according to the test procedures corresponding to the Euro 4 emission regulation (98/69/EC). A Pierburg AMA 2000 system was used for CO, HC, NO_X and CO_2 analysis. The diluted exhausts were sampled in three bags for the different parts of the NEDC test cycle (UDC1, UDC2 and EUDC).

[1] A new reference number shall be assigned starting 1.1.2010.

4.4.5 Online measurements of regulated components

The regulated emissions were also measured via continuous sampling from the CVS. For analysis, the same instrumentation was used as for the bag measurements.

4.4.6 Unregulated emissions

4.4.6.1 FTIR

The FTIR was a Gasmet CR2000, sampling from raw exhausts immediately after the exhaust tailpipe. The FTIR was used to analyze ethanol and aldehyde emissions.

Figure 31: Sampling from exhaust pipe, FTIR and AMA.

4.4.6.2 DNPH cartridges sampling (aldehydes)

A system for sampling diluted exhausts with DNPH-cartridges was also used.

Two cartridges were used, separately for the UDC and EUDC parts, respectively, of the NEDC test cycle. After the tests, the cartridges were analyzed for aldehydes by HPLC.

Figure 32: The FTIR (left) and the DNPH cartridges sampling system (right) at VTT.

4.5 Test results

In this part of the project the focus is on emissions of concern for this study. The hydrocarbon emissions, and unregulated emissions of alcohols and aldehydes are presented here. Emissions of CO, NO_X, CO_2 and fuel consumption is included in the Appendix.

The vehicle has been tested at three different test sites and to be able to compare the results it is important that the vehicle has been treated in the same way during the testing. The vehicle manufacturer provided the road load curve for the vehicle, which was used by all the test sites. In figure 33, the fuel consumption at tests performed at room temperature are shown, and can be used for reason of comparison.

Please note that the scales can be different in the diagrams.

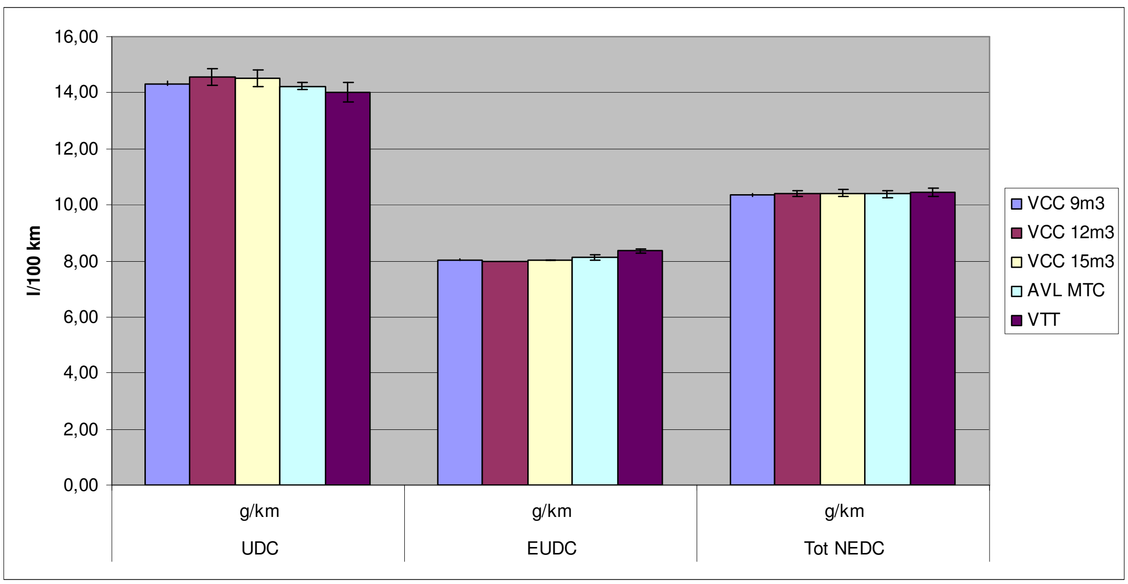

Figure 33: Fuel consumption (in l/100km) from tests performed at room temperature.

4.5.1 Emissions of Hydrocarbons

Hydrocarbons are calculated using the density (0,619 g/dm^3) defined for the calculations of HC in Euro 4 emissions standard. The hydrocarbons are measured by FID.

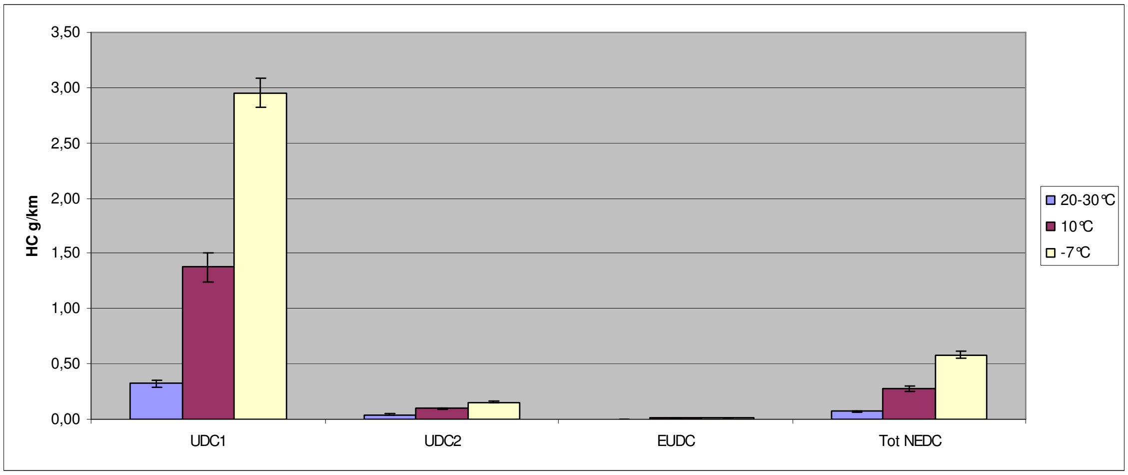

Figure 34: AVL MTC: HC emissions, effect of different ambient temperatures, presented for each part of the NEDC and for total NEDC.

As can be seen in figure 34, the emissions of hydrocarbons are depending on the ambient temperature. Almost all hydrocarbons are emitted during the first part of the NEDC test cycle (UDC1), the cold start.

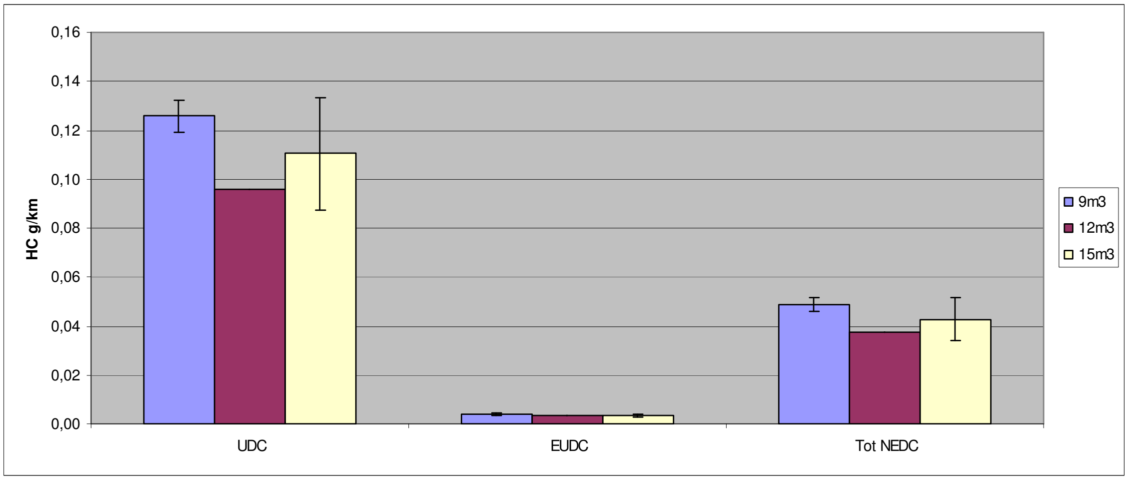

Figure 35: VCC: HC emissions, effect of different dilution ratios, presented for each part of the NEDC and for total NEDC.

In the testing performed at VCC, different venturies were used. This can be studied in Figure 35. The emissions of hydrocarbons do not seem to be dependent on dilution of the exhausts.

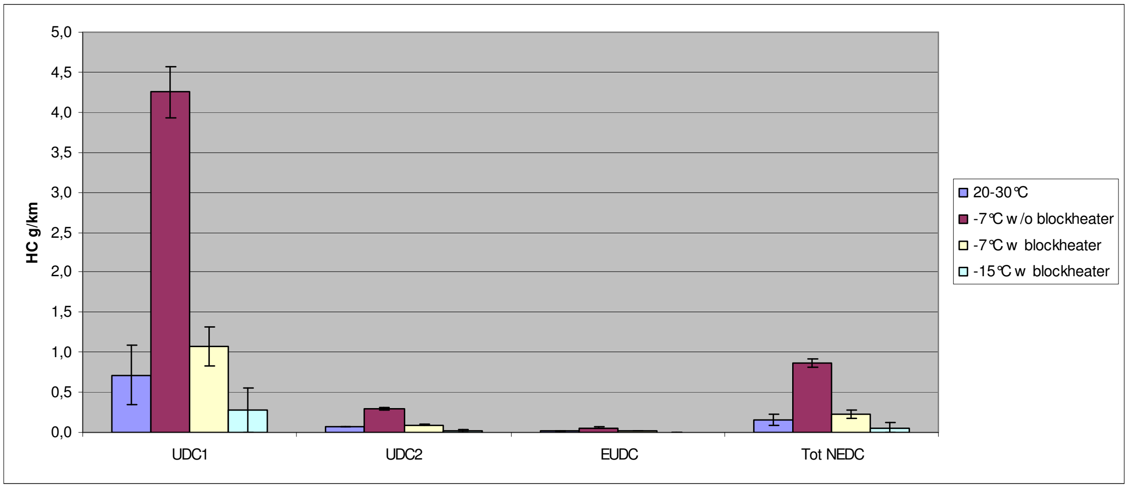

Figure 36: VTT: HC emissions, effect of different ambient temperature and the use of block heater. The emissions are presented for each part of the NEDC and for total NEDC.

The testing at VTT in Finland included low temperature testing, with and without the use of block heater. A similar pattern can be seen in the VTT testing as in the tests performed at AVL MTC, emissions of hydrocarbons is very much dependent on ambient temperature. The absolute maximum is reached in the cold start phase (UDC1) at -7ºC. The use of block heater at the same temperature lowers the emissions significantly.

4.5.2 Alcohol emissions

Online emissions, measured by MS and FTIR, are presented in this first part. Comparisons are made between different methods for measuring the alcohol content in the emissions.

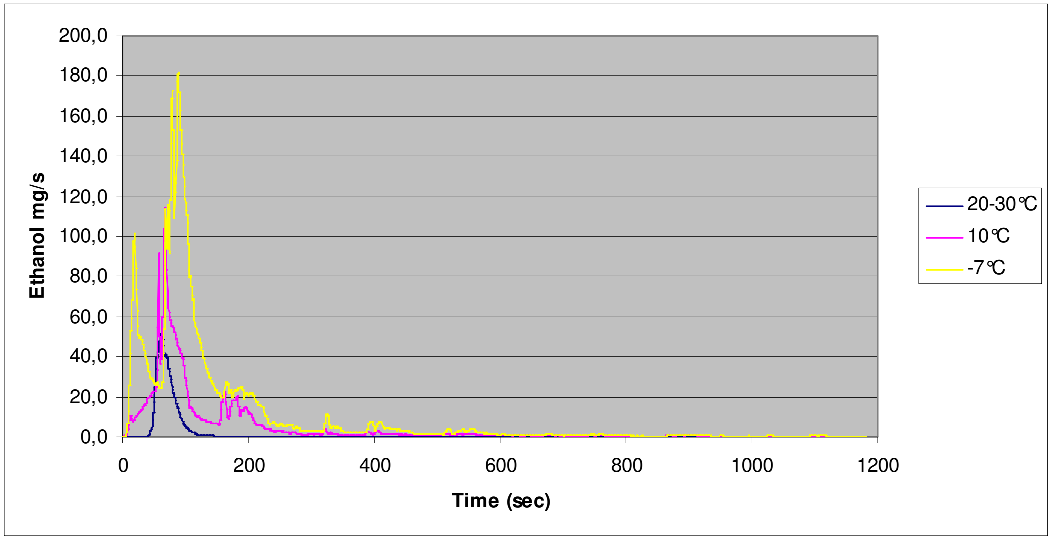

Figure 37: Ethanol emissions, measured by MS (AVL MTC)

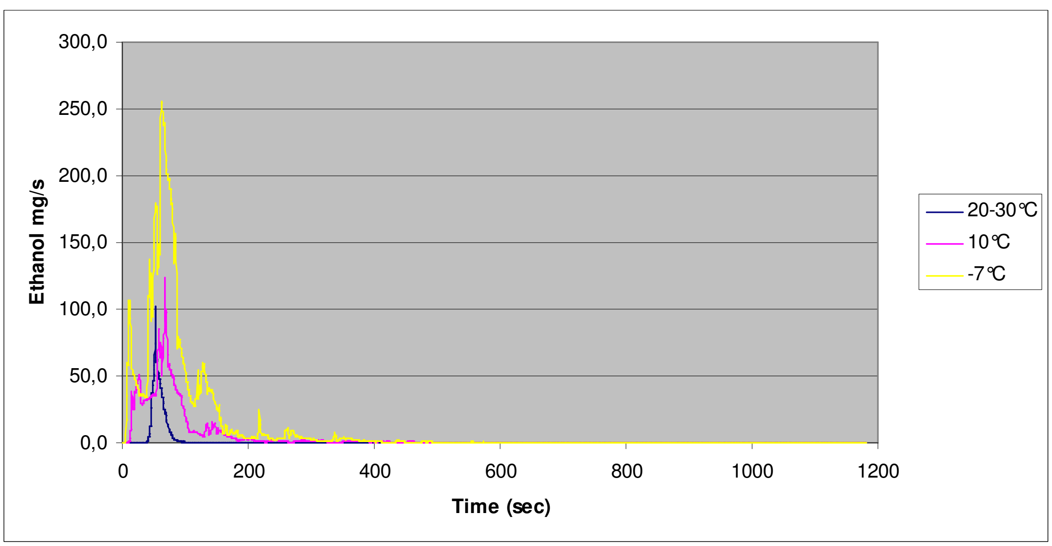

Figure 38: Ethanol emissions, measured by FTIR (AVL MTC).

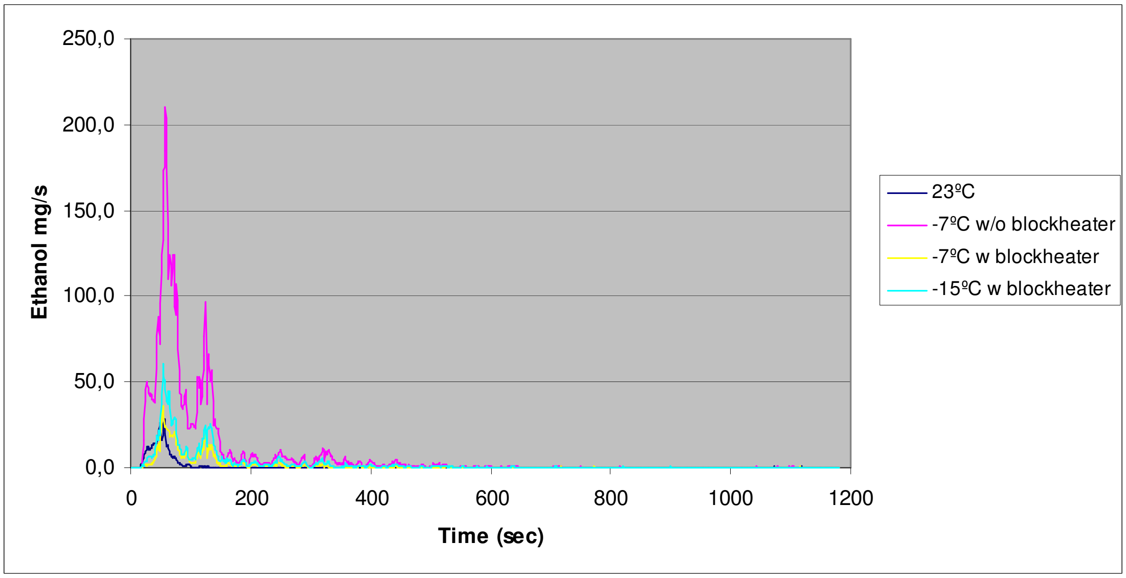

Figure 39: Ethanol emissions, measured by FTIR (VTT).

The ethanol emissions were measured online by MS and FTIR at AVL MTC, and FTIR at VTT in Finland. The patterns are similar both between the instruments as well as between the test sites. Almost all ethanol is emitted during the starting phase of the test cycle.

The alcohol emissions are also (as well as the hydrocarbon emissions discussed earlier) temperature dependent, and tests performed at low ambient temperatures yields elevated alcohol emissions. Tests performed at AVL MTC and VTT shows this temperature dependency.

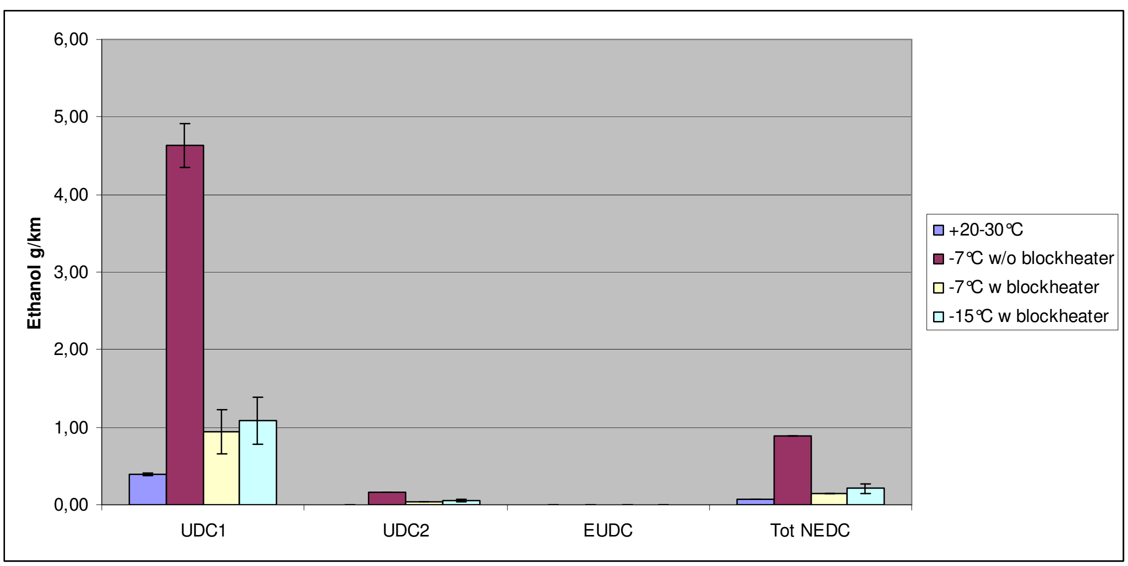

Figure 40: Ethanol emissions in the different parts (UDC and EUDC) of the NEDC cycle, and total NEDC – different ambient temperatures. Ethanol concentration is measured with FTIR (VTT).

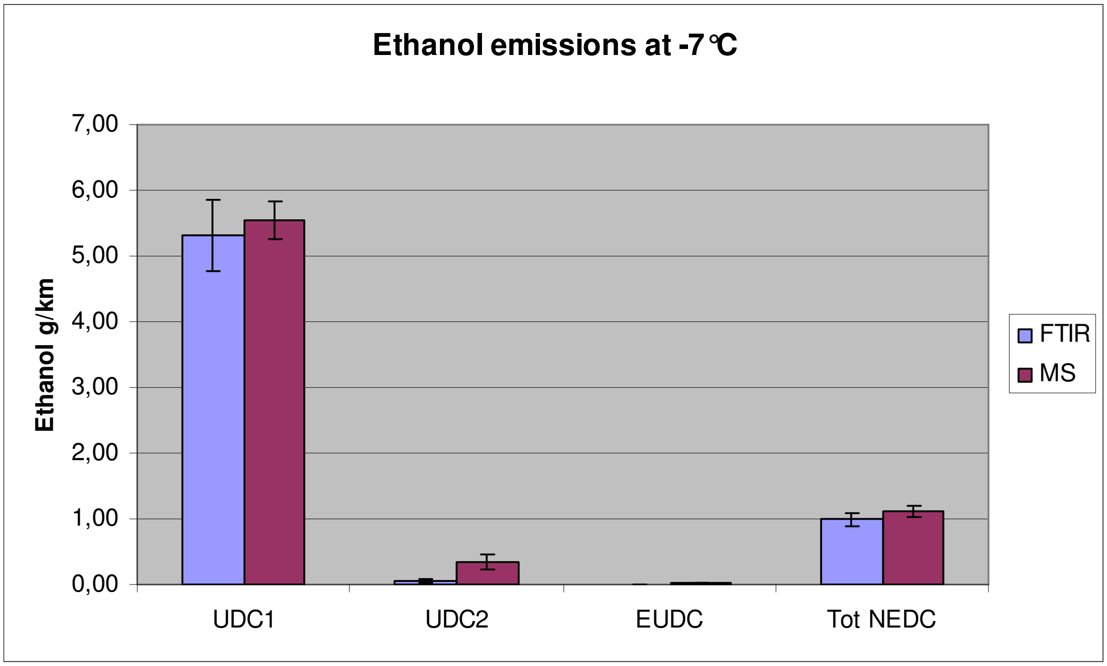

Figure 41: Ethanol emissions at -7°C, comparison between measurements performed with FTIR and MS. The different parts (UDC1, UDC2 and EUDC) and total of the NEDC cycle are presented (AVL MTC).

The ethanol emissions emitted in the different parts of the NEDC cycle, measured with FTIR and the MS at AVL MTC. The analyzing methods show a good correlation, as can be studied in Figure 41.

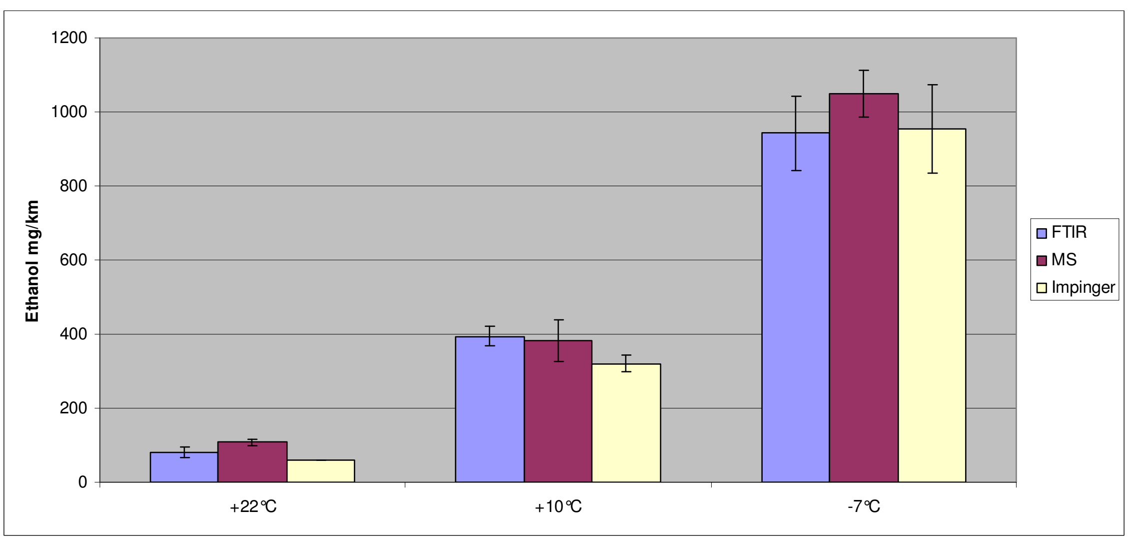

Figure 42: Ethanol emissions, comparison between measurements performed with FTIR, MS and the impinger sampling method (AVL MTC).

Figure 42 shows a comparison between different ethanol emission measurements. The FTIR and the MS instruments were used, and the exhausts were also sampled in impingers. Since

the impinger sampling (and further analyzed by HPLC) is the only approved method this should be considered to be the “reference method” in this comparison.
The correlation between the different methods is quite good.

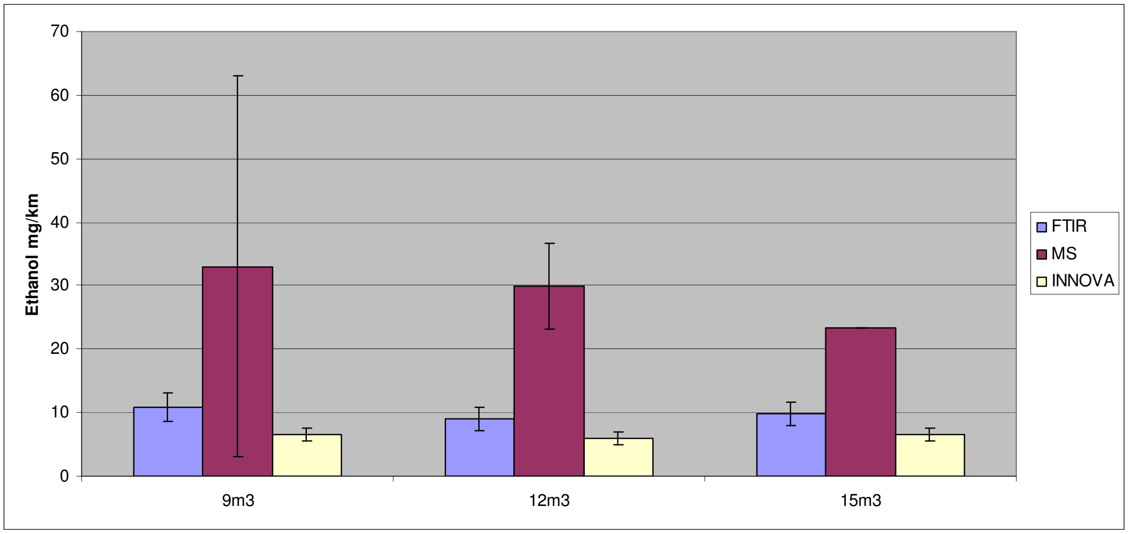

Figure 43: Ethanol emissions measured at VCC. Comparisons are made between measurements performed with FTIR and MS (by VCC) and the INNOVA photoacoustic detector (by GMPT). The tests were performed at VCC with the help from representatives from GMPT.

Figure 43 shows a comparison between the different ethanol emission measurements performed at VCC, where different dilution ratios were studied. FTIR, MS and INNOVA (Photoacoustic Sensor) is compared. Since the Photoacoustic Sensor is the only approved method among these, this should be considered to be the “reference method” in this comparison.

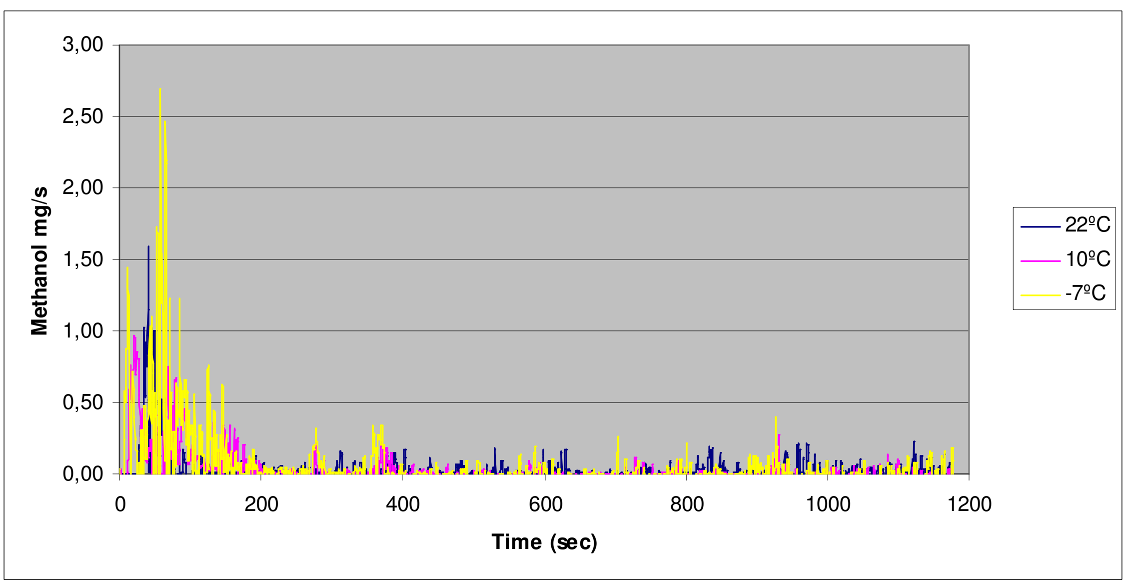

Figure 44: Methanol emissions, measured by FTIR (AVL MTC).

The methanol emissions are very low, and are not an issue in this study. The emissions of formaldehyde is however more interesting, even at low levels, because of its carcinogenic properties.

4.5.3 Aldehyde emissions

The aldehyde emissions show the same pattern as the alcohol emissions; almost all is emitted at the cold start phase. It can also be seen that the emissions are very much dependent on ambient temperature; low ambient temperature leads to much higher levels of aldehyde emissions. See Figure 46 and 47.

Tests at different temperatures were performed by both AVL MTC and VTT. Unfortunately, the acetaldehyde emissions measured with the FTIR at AVL MTC were incorrect and will not be presented in this report. This was due to a defective calibration gas bottle, and the supplier informed AVL MTC about this error after the testing was finished.

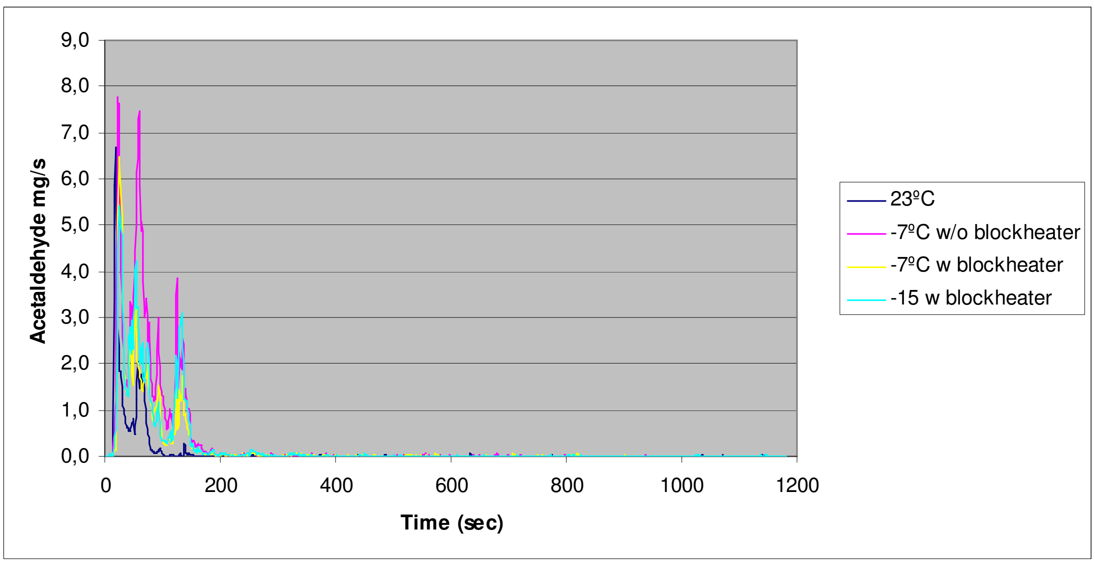

Figure 46: Acetaldehyde emissions, measured by FTIR (VTT).

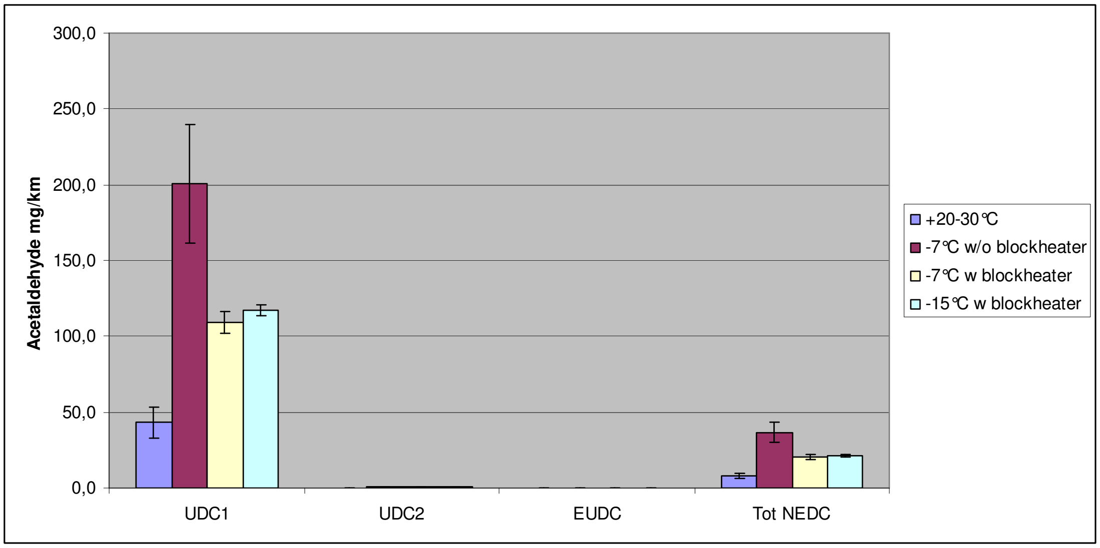

Figure 47: Acetaldehyde emissions in the different parts (UDC1, UDC2 and EUDC) of the NEDC cycle, and total NEDC – different ambient temperatures. Acetaldehyde concentration is measured with FTIR (VTT).

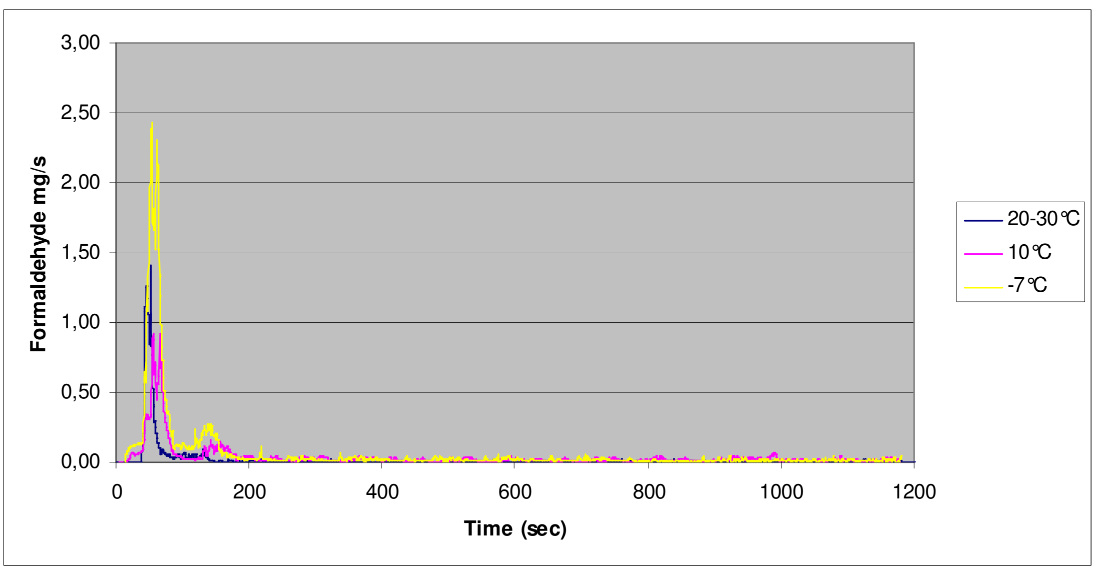

Figure 48: Formaldehyde emissions, measured by FTIR (AVL MTC).

The emissions of formaldehyde are also temperature dependent, as can be seen in figure 47. For an ethanol fuelled vehicle, the levels of formaldehyde are very low.

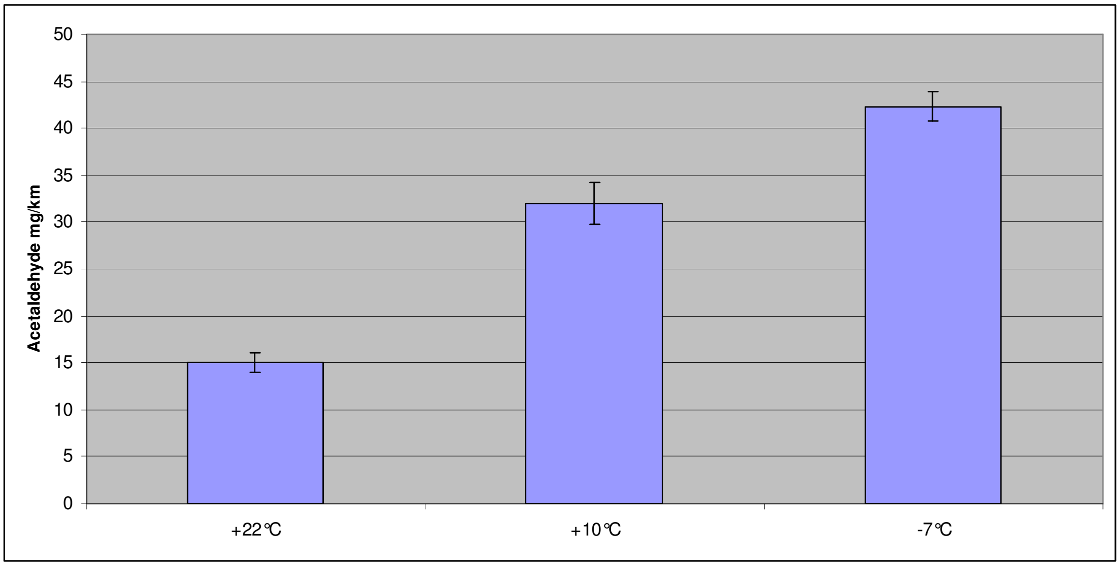

Figure 49: Acetaldehyde emissions sampled with DNPH-cartridges, different ambient temperatures (AVL MTC).

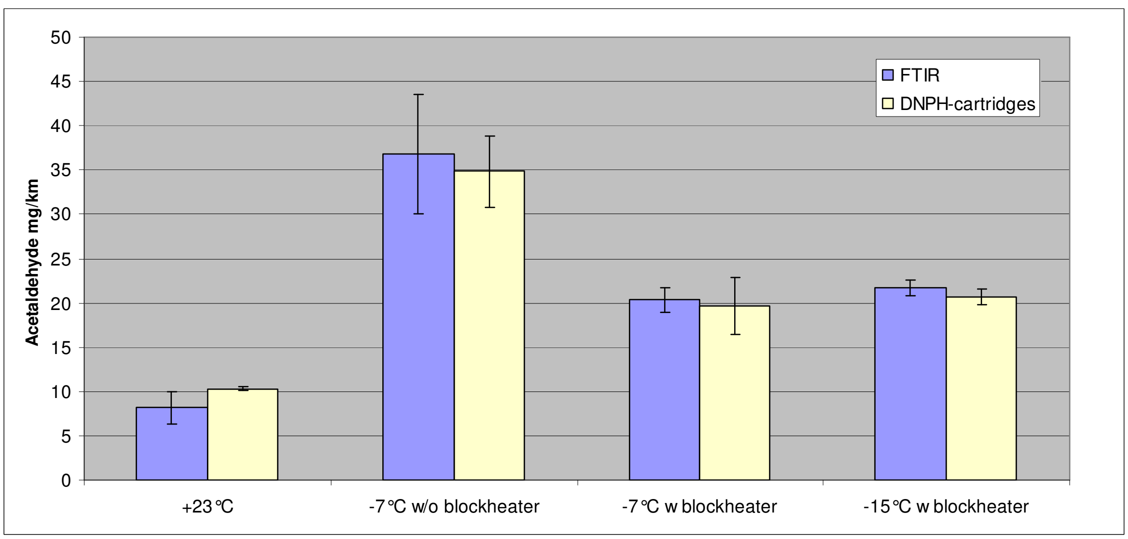

Figure 50: Acetaldehyde emissions, comparison between measurements performed with FTIR and DNPH-cartridges sampling method (VTT).

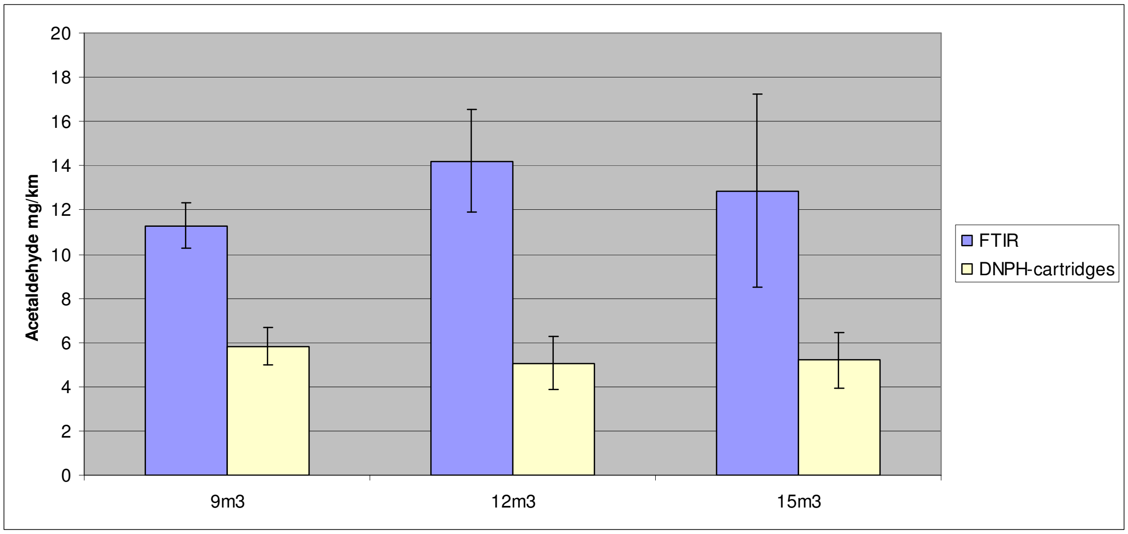

Figure 51: Acetaldehyde emissions, comparison between measurements performed with FTIR and DNPH-cartridges sampling method (VCC).

In Figure 49 and 50, comparisons have been made between acetaldehyde emissions measured by the FTIR and sampled by DNPH-cartridges. The DNPH-cartridge sampling method should be considered to be the reference method since it is approved by the US EPA and California ARB.

4.5.4 Hydrocarbon emissions from flexible fuelled vehicles calculated according to Euro 5

The Euro 4 and Euro 5 emission standards are treating the flex-fuelled vehicles very differently:

In ***Euro 4*** the vehicle manufacturer performs the certification tests using gasoline and no requirements for flex fuelled vehicles are applicable. The density for HC used in Euro 4 is 0,619 g/dm^3.

In ***Euro 5*** the vehicle manufacturer needs to perform the certification tests using both fuels for a flex-fuelled vehicle. For gasoline the HC density is 0,631 g/dm^3, for E85 the HC density is 0,932 g/dm^3. This leads to highly elevated HC emission levels only due to the difference in calculation.

In Figure 51, for the sake of comparison, the THC emissions have been calculated with the two different densities applicable in Euro 5.

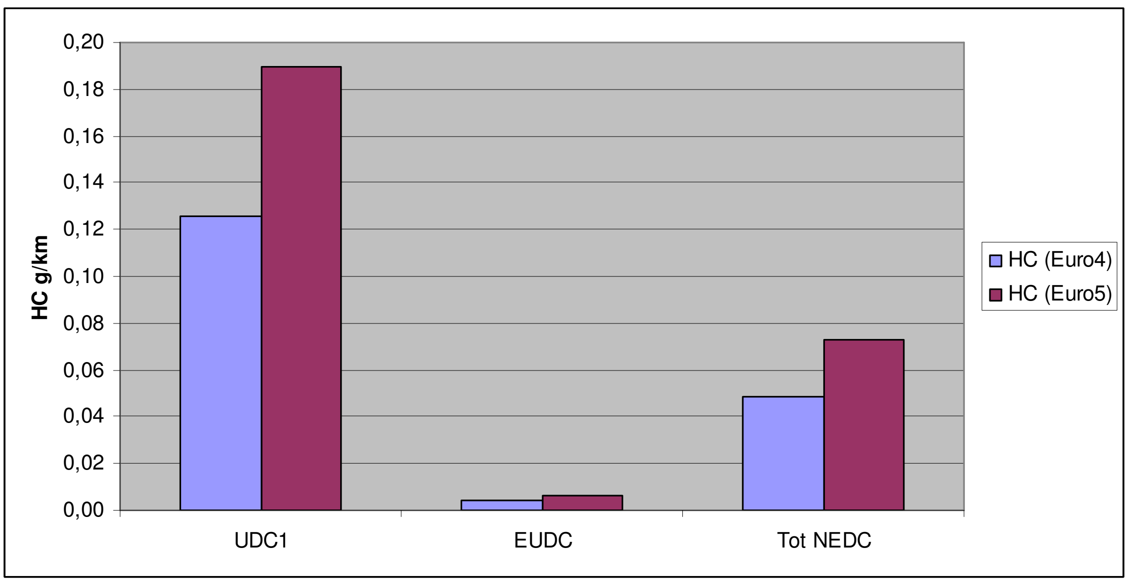

Figure 52: Comparison of THC emissions calculated according to Euro4 and Euro5.

4.5.5 Calculations according to US regulations

In USA, both the federal EPA regulations and the regulations set up by CARB in California, have included the hydrocarbon emissions in NMOG – Non Methane Organic Gases. The US regulations are presented in the literature study, chapter 2.1.2. In this part, the emissions have been calculated according to the US regulations regarding NMOG. Please note that the vehicle used in this study is certified according to the Euro 4 emission standard.

The NMOG comprises of:

NMOG = ΣNMHC + ΣROH + ΣRHO

The FID have measured hydrocarbons, alcohols and aldehydes during the test. The alcohols and aldehydes have also been measured separately with impingers and DNPH-cartridges, respectively. The FID measurement is corrected for the methane and alcohol part of the emissions:

$NMHC = {}_{FID}THC – (r_{CH4} \times CH_4) – (r_{C2H5OH} \times 2 \times C_2H_5OH)$

where,

${}_{FID}THC$ is the THC measured by FID in ppm C.

r_{CH4}, r_{C2H5OH} are the FID response factor for CH_4 and C_2H_5OH respectively. The response factor for methane has not been investigated in this study. For reason of comparison, the response factors used for these calculations are from a sample calculation of a M85 vehicle in "California Non-Methane Organic Gas Test Procedures".
$r_{CH4} = 1,04$
$r_{CH3OH} = 0,66$

According to the response factor study in this report, the response factor for ethanol is between 0,5-0,7.

To calculate the NMOG the oxygenated hydrocarbons are thereafter added back. The densities used in the calculation are from the US regulations. The NMOG emissions are presented in grams per mile.

$NMOG = \{[NMHC_{conc} * NMHC_{dens}] + [C_2H_5OH_{conc} * C_2H_5OH_{dens}] + [CH_3CHO_{conc} * CH_3CHO_{dens}] + [HCHO_{conc} * HCHO_{dens}]\} * 10^{-6} * V_{MIX} / miles$

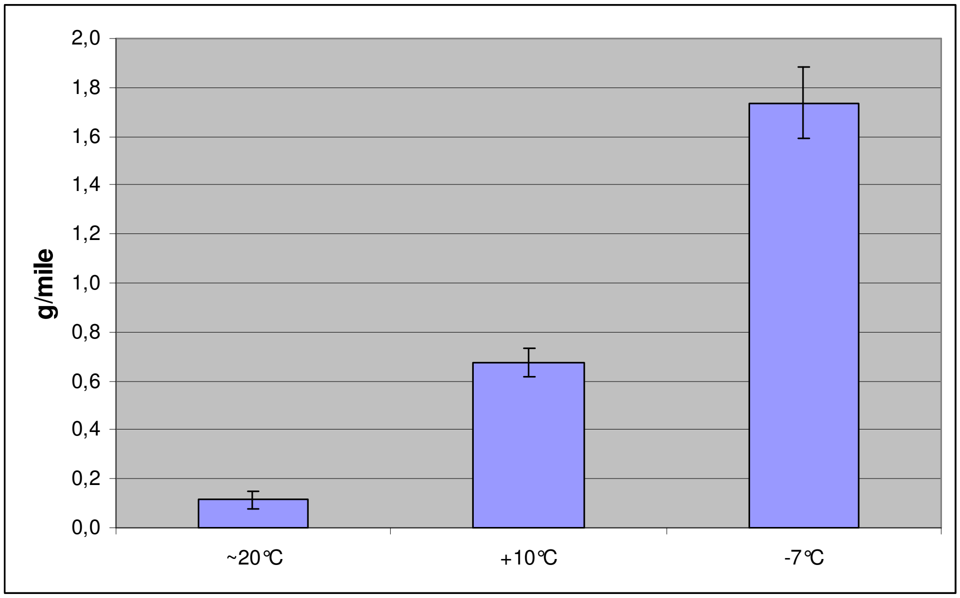

Figure 53: Comparison of NMOG emissions at different ambient temperatures (AVL MTC).

When the vehicle test is performed using the FTP75 driving cycle, the emissions are weighed for the different parts of the test cycle. This can not be applied to the NEDC test cycle used in this study. It is therefore not possible to compare the NMOG results with the US emission standards.

The general principle is however interesting when comparing the US and EU regulations. In the US the alcohol part is treated separately by separate sampling, measurement and calculation. The alcohol measured by the FID is also taken into consideration, when subtracting the alcohol emissions with its respective response factor.

5 DISCUSSION AND CONCLUSIONS

When alcohols are used as blending components in gasoline, uncombusted alcohols from the fuel are emitted in the exhaust in various amounts. There is therefore a risk that the FID reading is overestimated, leading to estimates of "hydrocarbon" emissions from flexible fuelled vehicles to be higher than they really are. To be able to make a valid comparison of hydrocarbon emissions from gasoline and flexible fuelled vehicles, the hydrocarbons and alcohols should be detected separately.

The emissions from alcohol fuelled vehicles are treated very differently in different countries and regulations. The US has specifications only applied to alcohol fuelled vehicles; such as FID oven temperature, establishment of response factors, sampling procedures for alcohols and aldehydes etc. This is also taken into account when calculating the total emissions, where the emissions of alcohols and aldehydes are included separately.

In the European regulation all "hydrocarbons" (thereby also including alcohols which are not, per definition, a hydrocarbon) are measured with the FID. There are however different densities for hydrocarbons depending on which type of fuel used in the testing.

In the Brazilian regulation, the vehicle manufacturer has the possibility to sample alcohols separately in the same way as in the US regulation.

It is a known fact that the FID has a low response to oxygenated compounds, such as alcohols. The FID response to ethanol is also very slow due to the adsorption of ethanol in the measurement system. This was further investigated in this study.

In the US regulations, this discrepancy is adjusted through measurement, and establishment, of FID response factors for alcohols and aldehydes. These FID response factors are used in the test result calculations. In the European regulation, no special adjustments are performed regarding this.

In the European Euro 5 emission standard a different density will be applied in the calculations of hydrocarbons, when the test is performed on E85 fuel. The higher density is used since the ethanol molecule also contains oxygen (besides carbon and hydrogen). This change in the calculation will automatically lead to an almost 50% increase of calculated "hydrocarbon" emissions. The combination of higher FID reading (due to uncombusted alcohol from the fuel) and the higher density used for calculation will make it more difficult for ethanol fuelled vehicles to comply with the Euro 5 emission standard. This will be even more difficult when low ambient temperature (Type 6) test is added for E85.

REFERENCES

Arlitt B. Fourier Transform Infrared Spectroscopy – Simultaneous measurement of regulated and unregulated Exhaust Emission Components. Perspectives of Exhaust Measurement, FAD Dresden July 2008.

Baronick J. et al. Modal Measurement of Raw Exhaust Volume and Mass Emissions by SESAM. SAE 980047. 1998.

Bolin A. Utveckling av ett provtagningssystem för alkohol och aldehyder i fordonsemissioner. Examensarbete, KTH. 2007.

Burkardt A., Hinterhofer K., Jacob E. FTIR based modal and multi-component exhaust gas analysis applications.

California Environmental Protection Agency. Procedure for the direct determination of total non-methane hydrocarbons and methane in motor vehicle exhaust using cryogenic preconcentration and flame ionization detection. May 2001.

California Non-Methane Organic Gas Test Procedures, as amended July 30, 2002.

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition. Compendium Method TO-11A. Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology]. January 1999.

de Serves C. Emissions from Flexible Fuel Vehicles with different ethanol blends. AVL MTC 5509. 2005.

Egebäck K.-E. et al. Blending of ethanol in gasoline for spark ignition engines. MTC 5407, ISSN: 1103-0240, ISRN: ASB-MTC-R--05/2—SE, 2005.

Electronic Code of Federal Regulation, current as of June 6, 2008.

Engeljehringer K. NMOG Non-Methane Organic Gas. AVL, 2008.

EU, Commission Regulation (EC) No 692/2008 of 18 July 2008 implementing and amending Regulation (EC) No 715/2007 of the European Parliament and of the Council on type-approval of motor vehicles with respect to emissions from light passenger and commercial vehicles (Euro 5 and Euro 6) and on access to vehicle repair and maintenance information. Official Journal of the European Union, 2008.

EU, Council Directive on the approximation of the laws of the Member States on measures to be taken against air pollution by emissions from motor vehicles (70/220/EEC), as last amended in 2006. Office for Official Publications of the European Communities. 2006.

Dieselnet, Emission standards, available on Internet at: *www.dieselnet.com* (accessed in November 2008).

Durbin T.D. et al. Effects of Ethanol and Volatility Parameters on Exhaust Emissions. Final Report. CRC Project No. E-67. University of California. 2006.

FTIR, figure 5 in the report, from *www.uni-ulm.de*

FTIR, figure 6 in the report, from *www.mmrc.caltech.edu*

Haupt D. et al. Vad är det vi mäter med en HFID när vi kör en 11-liters etanoldriven bussmotor? Luleå Tekniska Universitet, 1997.

Karlsson H. et al. Regulated and Non-regulated Emissions from Euro 4 Alternative Fuel Vehicles. SAE 2008-01-1770. 2008.

Larsen U., Johansen T., Schramm J. Ethanol as a Fuel for Road Transportation. IEA-AMF, 2009.

Li H. et al. Evaluation of a FTIR Emission Measurement System for Legislated Emissions Using a SI car. SAE 2006-01-3368. 2006.

Loo Jeffrey F., Parker David T. Evaluation of a Photoacoustic Gas Analyzer for Ethanol Vehicle Emissions Measurement. SAE Technical Paper Series 2000-01-0794.

LumaSense Technologies. Photoacoustic Multi-gas Monitor – INNOVA 1314.

Mass spectrometer, figure 4 in the report, from *vandf.agindo.info*

Photoacoustic Sensor, figure 7 in the report, from *www.lumasense.dk*

Reading A.H., Norris J.O.W., Feest E.A., Payne E.L. Ethanol Emissions Testing. AEAT Unclassified. 2002.

United States Environmental Protection Agency. Conversion Factors for Hydrocarbon Emission Components. EPA420-R-05-015. December 2005.

West B. et al. Effects of Intermediate Ethanol Blends on Legacy Vehicles and Small Non-Road Engines, Report 1. Oak Ridge National Laboratory. 2008.

West B. et al. Fuel Economy and Emissions of the Ethanol-Optimized Saab 9-5 Biopower. Oak Ridge National Laboratory. SAE 2007-01-3994. 2007.

Appendix

AVL MTC:

The averaged test results are based on three tests at the same temperature.

The results are presented for each part of the NEDC, which gives a good picture of the difference between emissions emitted from a cold engine (UDC1 phase) compared to a warm engine.

Emissions of CO, NO_X, CO_2, and fuel consumption:

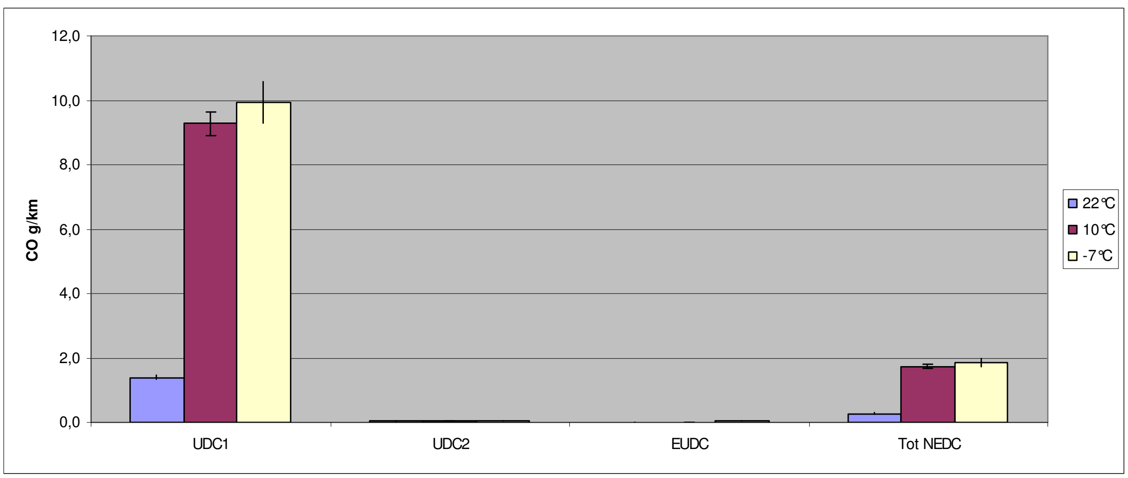

Figure A1: CO emissions, presented for each part of the NEDC and for total NEDC.

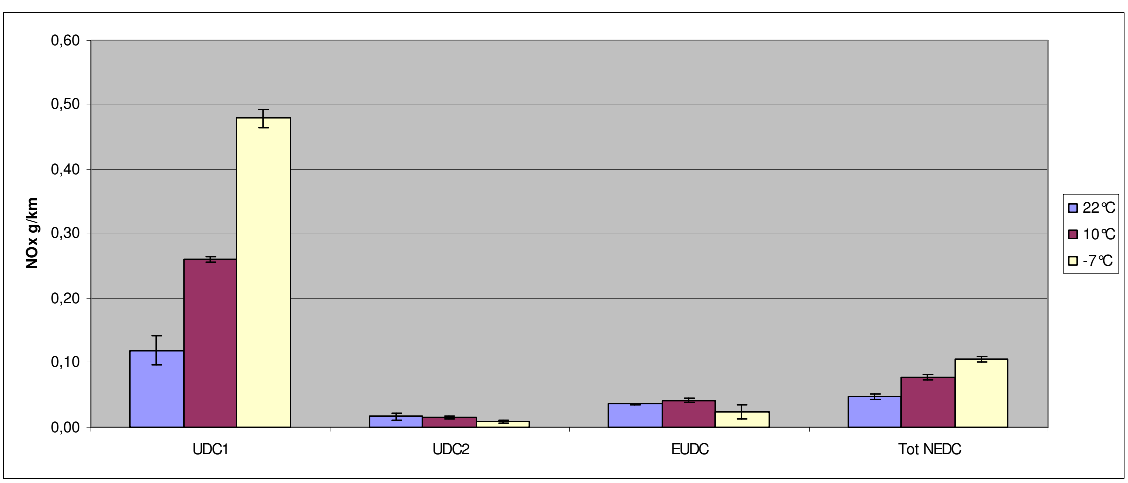

Figure A2: NO_X emissions, presented for each part of the NEDC and for total NEDC.

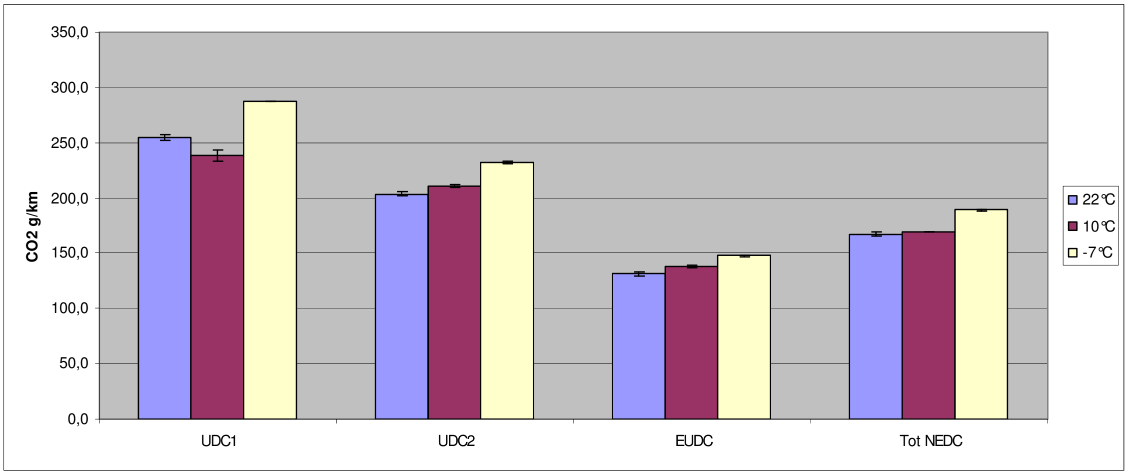

Figure A3: CO_2 emissions, presented for each part of the NEDC and for total NEDC.

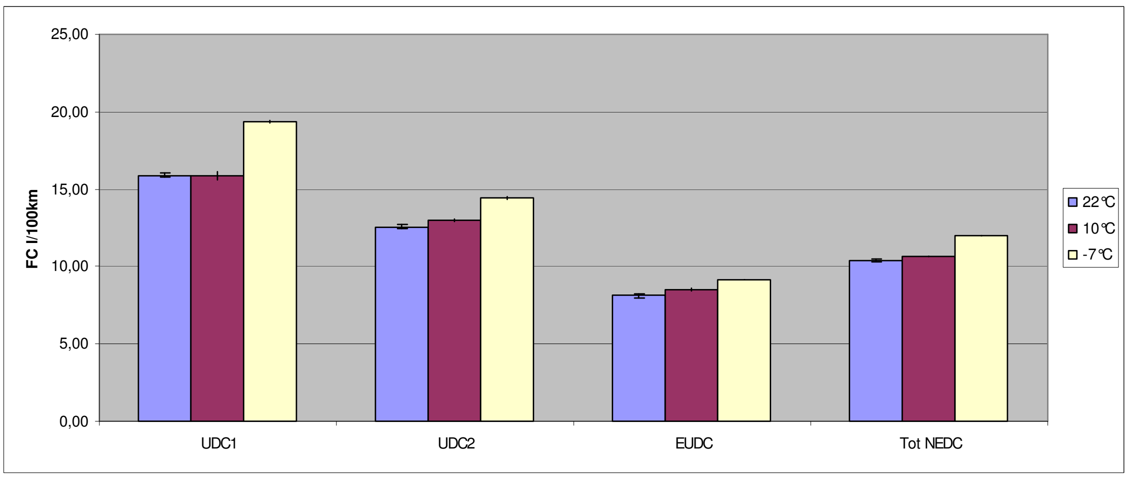

Figure A4: Fuel consumption, presented for each part of the NEDC and for total NEDC.

VCC:

The averaged test results are based on two tests for venturi setting 9 and 15 m^3, and one test for 12 m^3.

Emissions of CO, NO_X, CO_2, and fuel consumption:

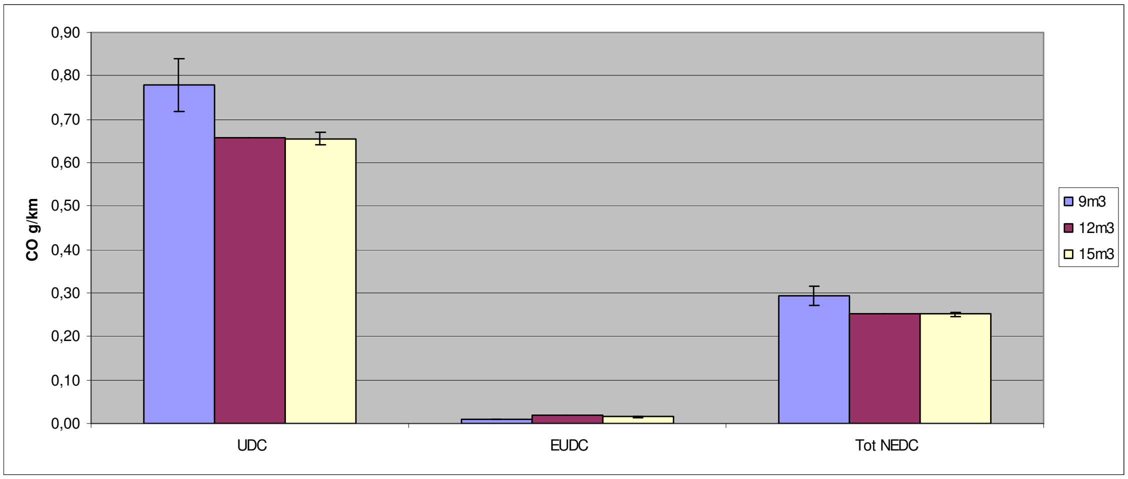

Figure A5: CO emissions, presented for each part of the NEDC and for total NEDC.

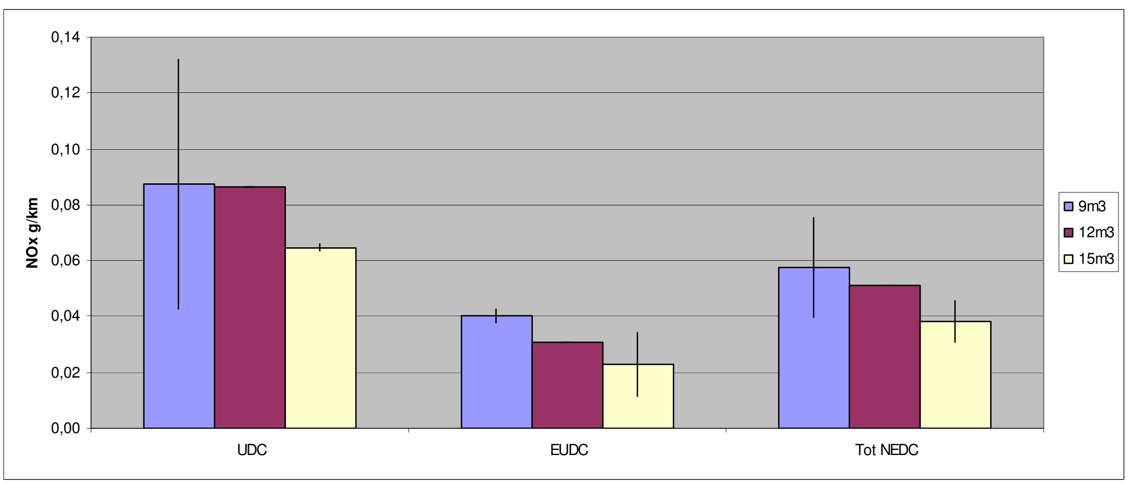

Figure A6: NO_X emissions, presented for each part of the NEDC and for total NEDC.

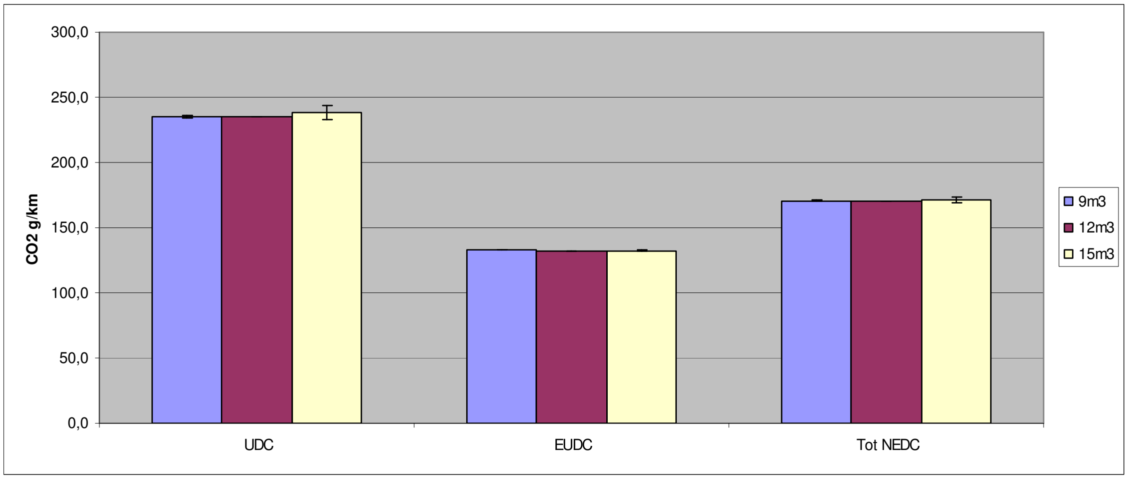

Figure A7: CO_2 emissions, presented for each part of the NEDC and for total NEDC.

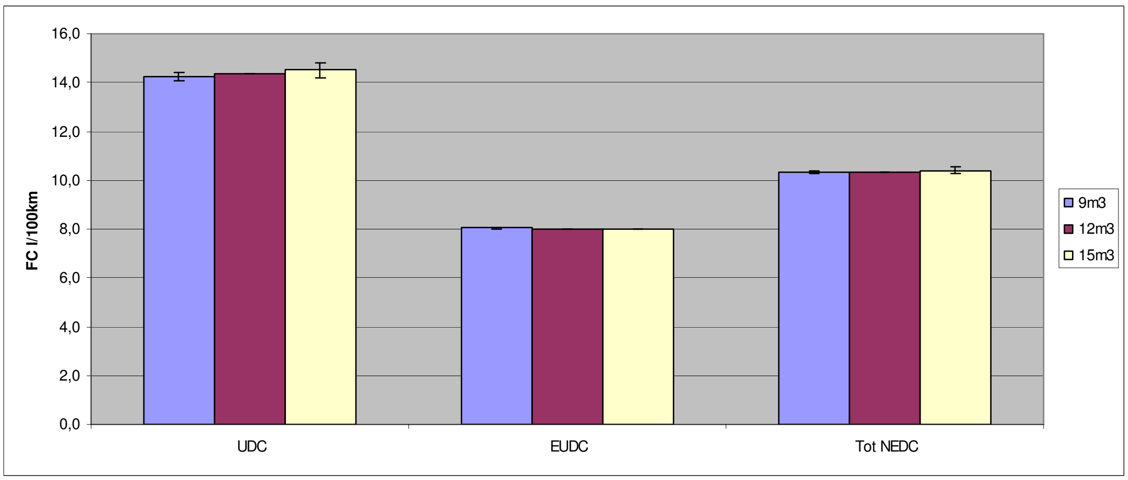

Figure A8: Fuel consumption, presented for each part of the NEDC and for total NEDC.

VTT:

The averaged test results are based on two tests using the temperature setting.

Emissions of CO, NO_X, CO_2, and fuel consumption:

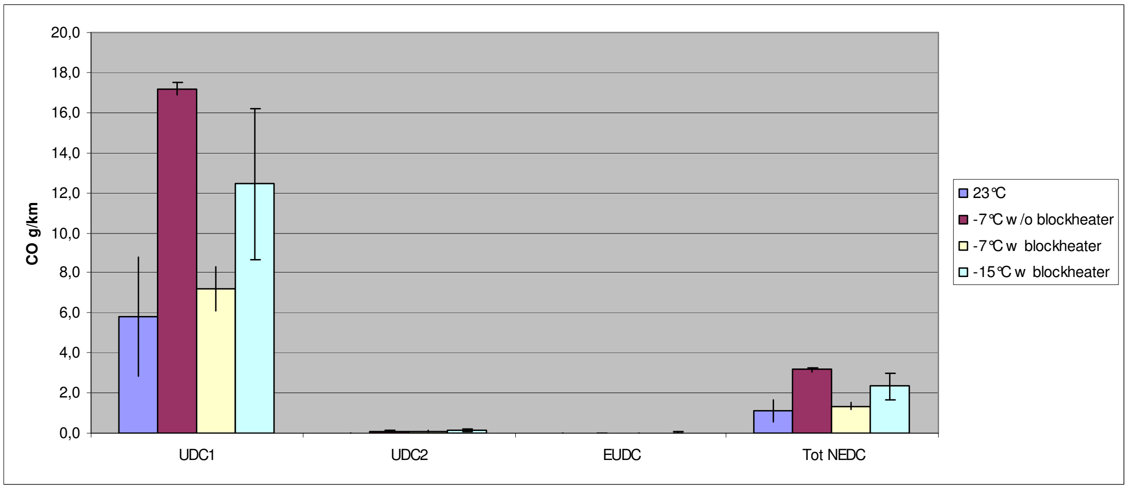

Figure A9: CO emissions, presented for each part of the NEDC and for total NEDC.

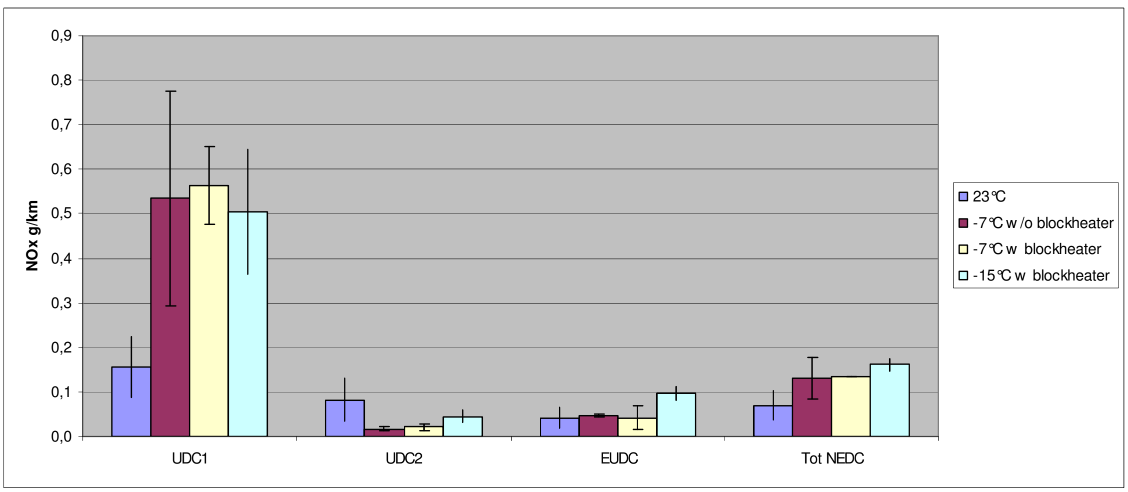

Figure A10: NO_X emissions, presented for each part of the NEDC and for total NEDC.

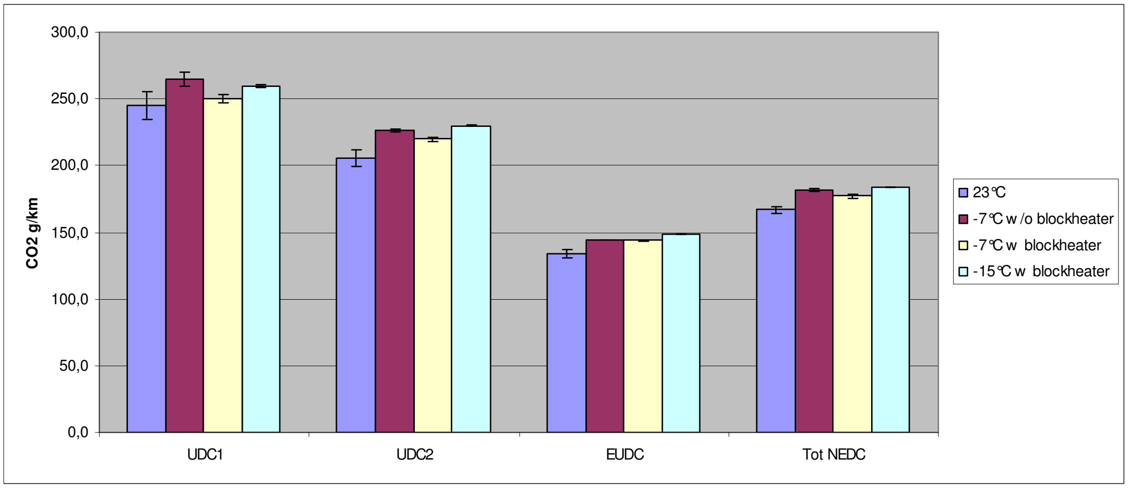

Figure A11: CO_2 emissions, presented for each part of the NEDC and for total NEDC.

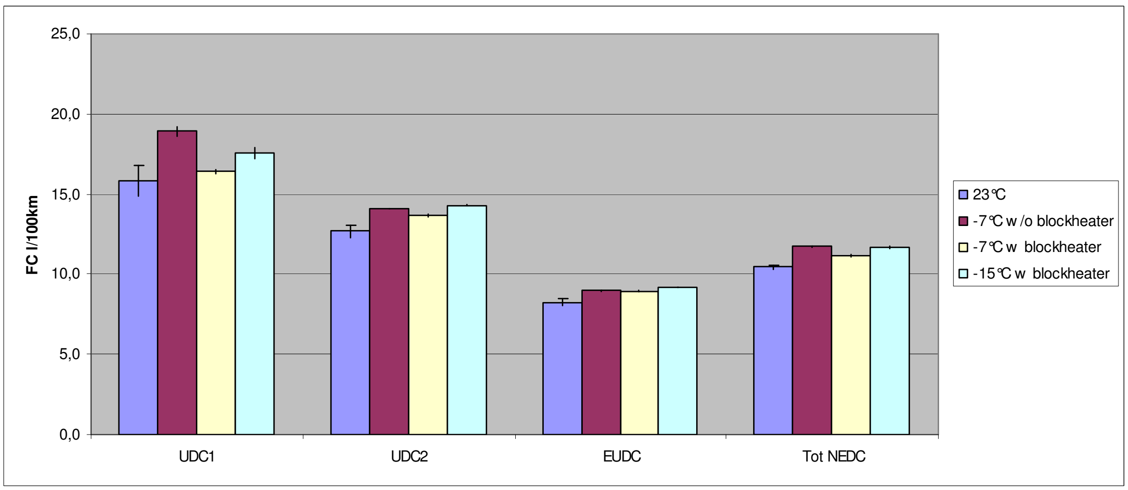

Figure A12: Fuel consumption, presented for each part of the NEDC and for total NEDC.