RESEARCH REPORT

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# Development and validation of comprehensive emission measurement methods for alternative fuels at VTT

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**Summary**

Emission measurement methods have been developed for vehicles using traditional fuels, and they do not necessarily suit, or are not sufficient, for alternative fuels and technologies. New fuels, engines and emission control devices may lead to alterations in the exhaust gas composition, and to the formation of new emission species. Due to the tight emission regulations, emissions have decreased and their quantitative analysis has become more challenging. Therefore, in addition to improving and developing of the traditional analysis methods, it has also become essential to find new comprehensive analysis methods and principles to evaluate for exhaust gas emissions.

The aim of this project was to review, improve, develop, and validate emission measurement methods for more comprehensive characterization and impact assessment of the exhaust gas emissions from low-emitting cars and vehicles using alternative fuels. For example, a new comprehensive method for the estimation of oxidative potential in particulate matter and the semivolatile organic samples was introduced (DTT assay), as well as, microAmes test for mutagenicity. Exhaust volume based dosing was developed instead of mass based dosing to enable testing of low-emitting cars with reasonable number of replicate tests. The methods were validated in the measurement campaign. New information was collected, and new methods and tests will be used in the future projects.

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## Preface

Emission measurement methods have been developed for traditional vehicles and fuels, and they are not necessarily compatible with new vehicles and alternative fuels. Alternative fuels and new engine and emission control technologies can lead to alterations in the exhaust gas composition and to the possible formation of the new emission species. Chemical characterization of all individual compounds of exhaust gas is not possible using reasonable set of instruments. In addition, quantitative analysis of emissions is challenging for modern low-emitting cars and vehicles, and some exhaust species may be toxic or mutagenic at concentrations below detection limits. As a consequence, comprehensive analysis methods are needed in addition to improved traditional analysis methods.

The aim of this project was to review, improve, develop, and validate the emission measurement methods for more comprehensive characterization and impact assessment of the exhaust gas emissions. Existing methods were reviewed and improved to take into account alternative fuels and new engines and emission control technologies. For example, many methods for gaseous emissions were updated and collection method for the semivolatile organic fraction of the exhaust gas was developed. A microAmes test was introduced for small sample sizes and a new comprehensive method for the estimation of oxidative potential in PM and semivolatile samples. New approach basing on exhaust volume instead of particulate mass was introduced for dosing of samples from low emitting cars and vehicles. Methods to characterize exhaust gases from alternative fueled cars and vehicles were validated in an extensive measurement campaign with Euro 6 diesel, E10 E85, and CNG fueled cars and with Euro 2 diesel car. Several methods were also validated in the IEA AMF Annex 44 ”Unregulated Pollutants Emissions of Vehicles Fuelled with Alcohol Alternative Fuels” (Operating Agent CATARC, China), in which VTT studied emissions from two FFVs using three fuels (E10, E85, and E100) at +23 ja -7 °C. New measurement methods will be used in the future evaluations of the direct and indirect effects of the alternative fuels on human health and environment.

“Development and validation of emission measurement methods for alternative fuels”- project was a part of a larger project “New biofuel options to supplement diesel fuels – Collaboration, networking and piloting, 2GBIO-PILOT” project financed by Tekes, VTT Ltd, and different companies. Nils-Olof Nylund is acknowledged for inspiration within the 2GBIO-PILOT project.

All authors contributed in the development of new methods. Authors are grateful to Heidi Hellén from the Finnish Meteorological Institute for providing Tenax-tubes and for their analyses. Service providers (Chapter 4.4.6) are acknowledged for their efforts. Maija-Riitta Hirvonen and Pasi Jalava from UEF are acknowledged for discussions and cooperation when planning the oxidative potential testing. Personnel at VTT, particularly Pekka Piimäkorpi, Reijo Mikkola, and Tommi Hangasmaa are acknowledged for their contributions in the emission testing. IEA AMF Annex 44 partners are acknowledged for cooperation.

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## Abbreviations

| | |
|---|---|
| BC | Black carbon |
| BTEX | Benzene, toluene, ethylbenzene, and xylenes |
| CAFÉ | Corporate Average Fuel Economy |
| CE | Capillary electrophoresis |
| $CH_4$ | Methane |
| CI | Compression ignition (Diesel) |
| CLD | Chemiluminescence |
| CNG | Compressed natural gas |
| $CO_2$ | Carbon dioxide |
| CO | Carbon monoxide |
| CPC | Condensation particle counter |
| CVS | Constant volume sampler |
| DCM | Dichloromethane |
| DGI | Dekati Gravimetric Impactor |
| DI | Diesel |
| DLPI | Dekati Low Pressure Impactor |
| DMSO | Dimethyl sulphoxide |
| DNPH | Dinitro phenyl hydrazine |
| DOC | Diesel oxidation catalyst |
| DPF | Diesel particle filter |
| DR | Dilution ratio |
| DTT | Dithiothreitol |
| E10 | Fuel containing max. 10% ethanol and min. 90% gasoline |
| E85 | Fuel containing max. 85% ethanol and min. 15% gasoline |
| EC | Elemental carbon |
| ED95 | 95% ethanol, ignition improver and other additives |
| EGR | Exhaust gas recirculation |
| ELPI | Electric Low Pressure Impactor |
| EUDC | Extra-urban driving cycle |
| FAME | Fatty acid methyl ester |
| FFV | Flex-fuel cars |
| FID | Flame ionization detector |
| FSN | Filter Smoke Number |
| FTIR | Fourier transformation infrared |
| FTP | Federal Test Procedure |
| GC | Gas chromatograph |
| GHG | Greenhouse gases |
| $H_2O_2$ | Hydrogen peroxide |
| HC | Hydrocarbons |
| $HNO_3$ | Nitric acid |
| HONO | Nitrous acid |
| HPLC | High-performance liquid chromatography |
| IC | Ion chromatography |
| ICP-MS | Inductively coupled plasma mass spectrometry |
| INAA | Instrumental Neutron Activation Analysis |
| IR | Infrared |
| LD | Light-duty |
| MCT | Mercury Cadmium Telluride (HgCdTe) |
| MIR | Maximum incremental reactivity |

| | |
|---|---|
| MSAT | Mobile-source air toxics |
| MTBE | Methyl tert-butyl ether |
| NEDC | New European Driving Cycle |
| NGV | Natural gas vehicle |
| $NH_3$ | Ammonia |
| NMHC | non-methane hydrocarbons |
| NMOG | Non-methane organic gases |
| $NO_2$ | Nitrogen dioxide |
| $NO_3$ | Nitrates |
| $NO_x$ | Nitrogen oxides (NO and $NO_2$ calculated as $NO_2$) |
| $N_2O$ | Nitrous oxide |
| $O_3$ | Ozone |
| OC | Organic carbon |
| o.d. | Outer diameter |
| OFP | Ozone-forming potential |
| PAH | Polyaromatic hydrocarbons |
| PIXE | Particle-induced X-ray emission |
| PM | Particulate matter |
| PN | Particle number |
| POM | Polycyclic organic matter |
| PTD | Porous tube diluter |
| PTFE | Polytetrafluoroethylene |
| SCR | Selective catalytic reduction |
| SEM | Scanning electron microscope |
| SFOC | Specific fuel oil consumption |
| SIM | Selected Ion Monitoring |
| SMPS | Scanning Mobility Particle Sizer |
| SNR | Noise to signal ratio |
| SOA | Secondary organic aerosols |
| SOF | Soluble organic fraction |
| $SO_x$ | Sulphur oxides |
| $SO_4$ | Sulphates |
| SPE | Solid phase extraction |
| SVOC | Semivolatile organic compounds |
| TC | Turbo charger |
| TD | Thermodenuder |
| TEF | Toxic equivalency factor |
| TEM | Transmission electron microscopy |
| THC | Total hydrocarbons |
| TWC | Three-way catalyst |
| UP | Ultrafine particles, below 100 nm |
| UV | Ultraviolet |
| VOC | Volatile organic compounds |

# 1. Introduction

New renewable and alternative fuels are introduced in the transport sector. Valid and comparable data is needed both on the direct and indirect effects of the new technologies to enable wide-ranging decision-making to increase competitiveness of the best low-emission technologies and to avoid investment in the harmful development, which could lead to new emission related problems. The aim of this project was to improve, develop, and validate emission measurement methods for more comprehensive characterization and impact assessment of the exhaust gas emissions for cars and vehicles using alternative fuels.

Traditional emission measurement methods have been developed for traditional vehicles and fuels and they are not necessarily compatible with the new technologies and different alternative fuel options. The composition of the exhaust gases depends on the fuel properties, for example, on the oxygen content of fuel. Some of the existing measuring methods give inaccurate results when new components are present in the exhaust gas for alternative fuels. For example, oxygen containing compounds in the exhaust disturb analysis of the hydrocarbon emissions.

New technologies and alternative fuels can lead to alterations in combustion processes and hence lead to the formation of new type of emission components/compounds. Due to tighter regulations, the concentrations of individual exhaust gas compounds have decreased and their quantitative analysis has become more and more challenging. Therefore, in addition to improving and developing of the traditional analysis methods for cars and vehicles using alternative fuels, it has also become essential to find new comprehensive analysis methods for the exhaust gas emissions, such as biological tests.

Real-time measurements are increasingly important both for gaseous and particle emissions to monitor emissions during transient driving and over cold-starts, when the emission level is typically at the highest. For alternative fuels, composition of the particulate matter (PM) and semivolatile organic compounds (SVOCs) can be very different from that for the traditional fuels. Phase partitioning of semivolatile organic compounds vary depending on their concentration and saturation pressure, and on the other constituents of particulate matter. Traditionally toxicity, mutagenicity, and carcinogenicity of samples are evaluated using PAH analyses and Ames tests, but there are various analysis methods available, for example DTT assay to monitor oxidative potential.

The goal of this project was to review current methods in-use at VTT, and to improve and develop analysis methods for reliable characterization and impact assessment of alternative fuels for on-road vehicles. The following analyses were improved/developed:

- Hydrocarbons: GC-FID procedure improved; feasibility of a microGC studied
- Carbonyl compounds: $NO_2$ interference taken into account
- FTIR: new methods for alternative fuels developed
- Semivolatile sampling method developed
- EC/OC analyses for oxygen containing fuels tested
- MicroAmes method for introduced
- Oxidative potential testing with DTT assay introduced
- New dosing method principle developed

Validation of the methods was carried out preliminarily in the IEA AMF Annex 44 ”Unregulated Pollutants Emissions of Vehicles Fuelled with Alcohol Alternative Fuels”

(Annex 44, Operating Agent CATARC, China), in which VTT studied emissions from two FFVs using three fuels (E10, E85 and E100) at +23 and -7 °C (Aakko-Saksa 2014). New measurements presented in this report covered measurement campaign conducted with four Euro 6 passenger cars using gasoline, diesel, E85 and CNG and one Euro 2 diesel car.

# 2. Significance of emissions

## 2.1 General

Reduction of adverse health and environmental effects related to air quality has been the primary driving force for tightening the exhaust emission limits of transport sector for decades. While struggling with the emission regulations and challenging targets for engine efficiency, ever cleaner cars and engines equipped with dedicated emission control technologies have been introduced. At the same time, concerns on energy security and global warming are driving towards new liquid and gaseous fuel alternatives. All new technologies should meet "no harm to health and environment" principle. However, verification of this is challenging for a spectrum of technologies with potential presence of new, unknown species in the exhaust gases.

## 2.2 Composition of exhaust gas

Complete combustion of hydrocarbons produces only carbon dioxide ($CO_2$) and water, while constituents called traditionally "emissions" represent only a small share of the total exhaust gas, below 0.5% (V/V). The major constituents of diesel exhaust are nitrogen, oxygen, water, and $CO_2$. Exhaust gas from gasoline fueled cars does not contain oxygen, because spark-ignited Otto engines typically operate close to the stoichiometric air to fuel ratio (AFR~1) and therefore oxygen is consumed in combustion. Instead, diesel engines use excess air (lean, AFR>1),

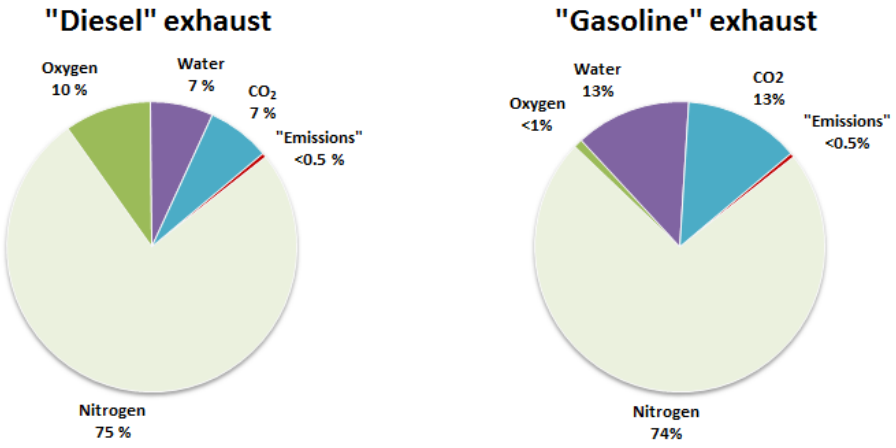



*Figure 1. Examples of composition of the exhaust gas from "diesel" combustion using excess air and stoichiometric spark-ignited "gasoline" combustion. Concentrations are shown as %(V/V).*

Air to fuel ratio (AFR) is one of the parameters affecting the exhaust emissions from internal combustion engines (Figure 2). In diesel combustion, nitrogen oxide emissions ($NO_x$) and PM emissions tend to be elevated, while emissions of total hydrocarbons (THC) and carbon monoxide (CO) are typically at low level. Spark-ignited gasoline cars operating close to stoichiometric air to fuel ratio can use three-way catalyst (TWC), which efficiently reduces CO, HC, and $NO_x$ emissions. Complicated emission control systems consisting of e.g. selective catalytic reduction (SCR) and diesel particulate filter (DPF) are required for diesel

engines to achieve low $NO_x$ and PM emissions. Alternative fuels can be used in both diesel and Otto engines. Some alternative fuels can assist performance of existing emission control systems, while others may require development/adjustment of the after treatment technologies.

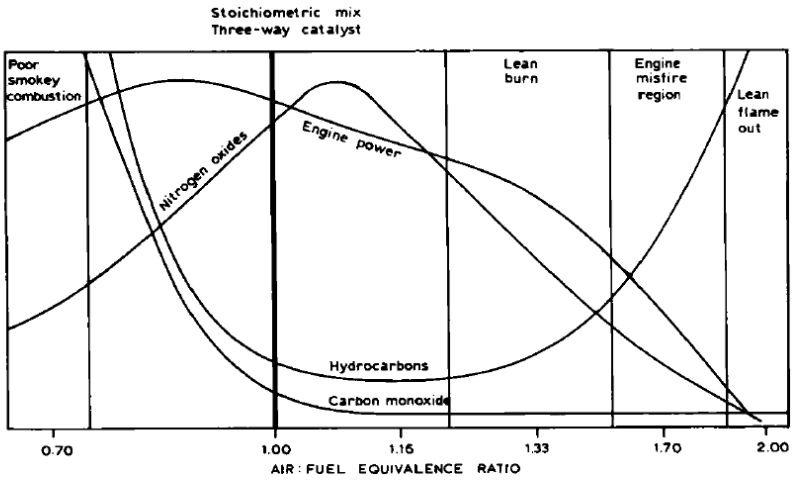



*Figure 2. Engine-out emissions from internal combustion engines at different air to fuel ratios (Windawi 1992).*

"Emissions", representing less than 0.5% (V/V) of the exhaust include, for example, the following constituents:

- Carbon monoxide (CO)
- Nitrogen oxides and other nitrogen containing compounds, such as ammonia ($NH_3$) and nitrous oxide ($N_2O$)
- Particulate matter consisting of elemental carbon, organic compounds, anions (sulphates, nitrates), and metals
- Hundreds of hydrocarbons, some of them toxic, for example benzene and 1,3-butadiene, or greenhouse gases, such as methane
- Carbonyl compounds, for example formaldehyde, acetaldehyde, and acrolein
- Polycyclic aromatic compounds, for example, polyaromatic hydrocarbons (PAHs), nitro-PAHs, and oxy-PAHs

Most of these emission species are fuel- and engine-dependent, but some of them are formed in emission control devices ($NH_3$, $N_2O$). Methane is emitted from engines and vehicles, particularly when fueled with natural gas or biomethane. $N_2O$ is induced by catalyst chemistry of TWC of the spark-ignited gasoline cars. Another catalyst induced emission is $NH_3$, which is present in the exhaust gases after TWC catalysts and the urea-based SCR[1] systems. However, $NH_3$ originates mainly from agricultural sources. (Meija-Centeno 2007, EEA 2012b).

IARC classification of diesel engine exhaust is carcinogenic to humans (Group 1), and classification of gasoline exhaust is possibly carcinogenic to humans (Group 2B) (IARC 2013). This classification is based on the results with older diesel engines. HEI (2015) found emissions from a 2007-technology engine to be not carcinogenic in the animal study (rat). A few effects in rat lungs were observed resembling changes seen in earlier studies after long-

[1] SCR is needed for $NO_x$ control of diesel vehicles.

term exposures to gaseous oxidant pollutants, in particular $NO_2$. The results showed that the 2007 compliant diesel engines equipped with exhaust gas recirculation (EGR), diesel oxidation catalyst (DOC), and DPF significantly reduced levels of PM (90%), VOCs and SVOCs (> 90%) compared with emissions from old engines. The $NO_x$ reduction seen for 2010 engines equipped with urea-SCR was over 90% compared with 2007 engines.

## 2.3 Emission regulations

CO, THC, $NO_x$, and PM emissions from transport applications are typically limited by legislation. In addition to these "regulated" emission species, the following emission regulations are implemented:

- In Europe, a limit to solid particulate number emissions (SPN) was introduced in 2011 for diesel engines (Euro 5b) and in 2014 for petrol engines (Euro 6).
- An $NH_3$ concentration limit of 10 ppm applies to Euro VI diesel and gas engines, but not to cars in Europe.
- Formaldehyde emission has been regulated for decades in the US.
- Greenhouse gas emissions are regulated in the US.
- $NO_2$ is limited for retrofitted heavy-duty engines in the US.
- Sulphur oxide ($SO_x$) emissions are limited through regulations on the sulphur content of fuel. In Europe, sulphur content of diesel fuel and gasoline is limited to 10 mg/kg and in the US to 15 mg/km.

The most stringent emission regulations are implemented in California, such as LEV III emission categories (Table 1).

*Table 1. LEV III emission standards in California phased-in over the 2015-2025 (FTP-75 test) (www.dieselnet.com 5.7.2016).*

| | | NMOG + $NO_x$ g/mi | CO g/mi | Formaldehyde mg/mi | PM[a] g/mi |
|---|---|---|---|---|---|
| Passenger cars<br>LD trucks ≤ 8500 lbs GVW[a]<br>Medium-duty passenger vehicles | LEV160 | 0.160 | 4.2 | 4 | 0.01 |
| | ULEV125 | 0.125 | 2.1 | 4 | 0.01 |
| | ULEV70 | 0.070 | 1.7 | 4 | 0.01 |
| | ULEV50 | 0.050 | 1.7 | 4 | 0.01 |
| | SULEV30 | 0.030 | 1.0 | 4 | 0.01 |
| | SULEV20 | 0.020 | 1.0 | 4 | 0.01 |

[a] The PM emission standards will be tightened to 3 mg/mi with phase-in from 2017 to 2021.

The United States has limits for greenhouse gas emissions (Table 2). The $CO_2$-equivalent in this rule is calculated by using $CO_2$ equivalence factors of 298 for $N_2O$ and of 25 for $CH_4$. In addition, the rule includes limits for tailpipe $N_2O$ and $CH_4$ emissions to prevent increase in these emissions in future vehicles (www.dieselnet.com 5.7.2016):

- $N_2O$: 0.010 g/mile
- $CH_4$: 0.030 g/mile

*Table 2. Projected 2012 – 2016 Fleet-Wide $CO_2$ and Fuel Economy Compliance Levels in the US. (www.dieselnet.com 5.7.2016).*

| | | Model Year | | | | |
|---|---|---|---|---|---|---|
| | | 2012 | 2013 | 2014 | 2015 | 2016 |
| Passenger cars | $CO_2$, g/mi | 263 | 256 | 247 | 236 | 225 |
| | $CO_2$ equiv. mpg [a] | 33.8 | 34.7 | 36.0 | 37.7 | 39.5 |
| | CAFE mpg | 33.3 | 34.2 | 34.9 | 36.2 | 37.8 |

[a] In the $CO_2$-equivalent standard, the $N_2O$ and $CH_4$ emissions are added to the $CO_2$ emissions using a $CO_2$ equivalence factor of 298 for $N_2O$ and of 25 for $CH_4$.

There are differences in the regulations on the exhaust emissions in Europe and in the US. In Europe, greenhouse gases from vehicles are not regulated, while targets for their $CO_2$ emissions are defined. Progress of the $NO_x$ standards have been slower in Europe than in the US. $NO_2$ levels are high in certain urban areas in Europe (EEA 2015). The Euro 6/VI regulations are expected to alleviate this situation by wider use of the SCR technology (Health Effects Institute 2015). Limits for formaldehyde, $N_2O$, or $CH_4$ emissions are not implemented in Europe, while they are limited in the US. PN limit is not included in the US regulation, while solid PN limit is in place in Europe.

Schematic figure of the emission regulation in Europe over the past decades is shown in Figure 3. Emission regulations have been tightening since 1992 in Europe. The HC and $NO_x$ emissions are below 20%, PM emissions below 10%, and CO emissions below 40 of the level of 1992.

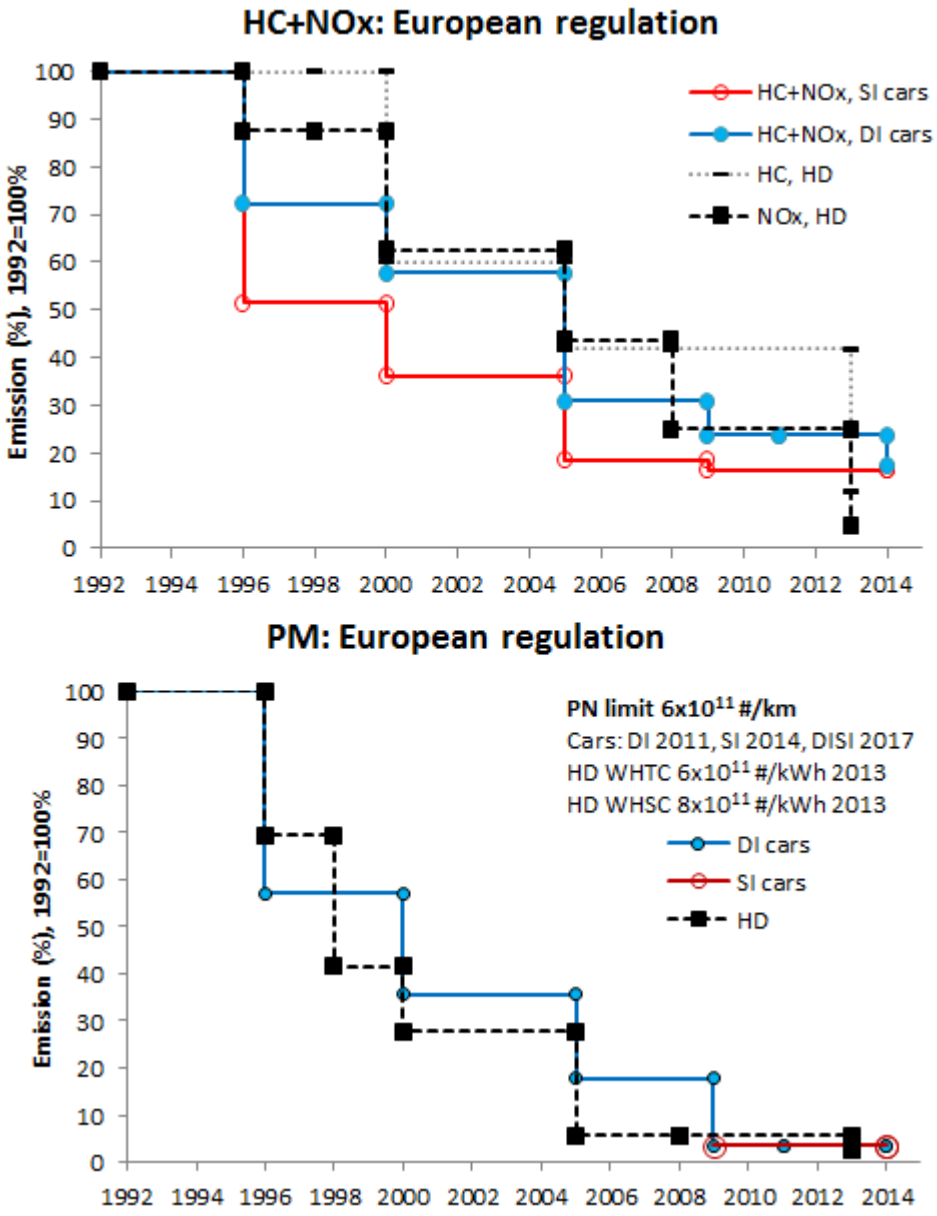



*Figure 3. Emission regulations have been tightening since 1992 in Europe.*

## 2.4 Health and environmental effects of emissions

Legislative limits are rare for the emissions species other than CO, HC, $NO_x$, and PM for the transport applications. However, a number of unregulated exhaust species are harmful to human health and to the environment, and some of them are also strong greenhouse gases (Table 3). Moreover, transformation of primary (tailpipe) emissions into secondary products is an important aspect when transport sector's emissions are assessed.

Air pollution is the world's largest single environmental health risk. WHO (2014) estimated that approximately 7 million premature deaths are a result of air pollution exposure. Air pollution also increases for example respiratory and cardiovascular diseases and cancer. This leads to substantial adverse economic impacts of air pollution (EEA 2015).

Air pollution affects vegetation, water, and soil. For example, ground-level ozone damages agricultural crops, forests, and plants. $NO_x$, $SO_2$, and $NH_3$ contribute to the acidification causing the loss of animal and plant life. $NH_3$ and $NO_x$ bring nutrients in land and water disrupting these ecosystems and leading to eutrophication and changes in species. Air pollution can damage materials and buildings by corrosion, biodegradation, and soiling caused by particles and by acidifying compounds ($SO_x$, $NO_x$, $CO_2$). (EEA 2015)

Methane, black carbon (BC, a constituent of PM) and tropospheric ozone are examples of air pollutants that are short-lived climate forcers contributing directly to global warming, while some of the PM components (organic carbon, ammonium, sulphate and nitrate) have a cooling effect on climate. Reducing BC, $CH_4$, and tropospheric $O_3$ will alleviate effects of emissions on health, ecosystem and global warming (EEA 2015).

*Table 3. Classification of emissions based on their effects on health, environment, and global warming.*

| | **Health effects** | **Environmental effects** | | | **Global warming** |
|---|---|---|---|---|---|
| | | Vege-tation | Acidifi-cation | Eutrophi-cation | |
| CO | x | x | | | |
| $NO_x/NO_2$ | x | x | x | x | |
| PM and SOA | x | | | | |
| PN | x | | | | |
| BC | x | | | | x |
| $SO_2$ | x | | x | | |
| Priority PAHs | x | | | | |
| Aldehydes: formaldehyde, acetaldehyde, acrolein | x | x | | | |
| 1,3-Butadiene | x | x | | | |
| Aromatics: benzenes, toluene, xylenes | x | x | | | |
| Methane | | | | | x |
| $NH_3$ | x | | x | x | |
| $N_2O$ | | | | | x |
| Ozone, ground-level troposphere caused by VOCs[a], CO, $NO_x$ | x | x | | | x |
| Ozone depletion in stratosphere caused by $N_2O$ | x | | | | x |
| $CO_2$ | | | | | x |

[a] Light olefins, aromatics, aldehydes

There are several lists of "priority air toxics" that define the most harmful compounds to be taken into account when evaluating exhaust gases from transport sector. These lists have been defined from various starting points, and consequently, outcomes are not uniform.

The U.S. Environmental Protection Agency (EPA) has defined key mobile-source air toxics (MSATs). The US EPA MSAT[2] list from 2001 included 21 compounds, among them acetaldehyde, acrolein, benzene, 1,3-butadiene, dioxin/furans, diesel exhaust, ethylbenzene, formaldehyde, *n*-hexane, six metals, methyl tert-butyl ether (MTBE), naphthalene, styrene, toluene, and xylene. In the 2007 rule[3], *eight key MSATs* and *gasoline particulate matter*[4] are included (US EPA 2007):

[2] US EPA (2001), 40 CFR Parts 80 and 86, Control of Emissions of Hazardous Air Pollutants From Mobile Sources. Final Rule. 2001.

[3] US EPA (2007), 40 CFR Parts 59, 80, 85, and 86, Control of Hazardous Air Pollutants From Mobile Sources. Final Rule. 2007.

[4] Particulate matter emission from gasoline-fuelled cars.

- Benzene
- 1,3-Butadiene
- Formaldehyde
- Acetaldehyde
- Acrolein
- Polycyclic organic matter
- Naphthalene
- Diesel exhaust
- Gasoline PM

The Health Effects Institute (HEI 2007) concluded that from the US EPA MSAT, the contribution of mobile sources is greatest for *1,3-butadiene,* followed by *benzene, formaldehyde, acetaldehyde, and acrolein.*

Diesel engine exhaust has been classified as carcinogenic to humans, Group 1, while gasoline engine exhaust is classified as possibly carcinogenic to humans, Group 2B (IARC, 2013).

## 2.5 Carbon monoxide (CO)

CO is a colorless, odorless gas, which reduces oxygen delivery to the body's tissues by binding and interfering with heme proteins. The health threat from lower levels of CO is most serious for e.g. persons with impaired cardiovascular systems. Potential effects include damage to the central nervous system, reproduction, and prenatal development, and to the respiratory system. At sufficient levels, CO is poisonous and can be fatal. (Vallero 2014)

CO contributes to the formation of ground-level ozone, which is harmful to human health and environment.

## 2.6 Nitrogen oxides ($NO_x$)

The sum of nitric oxide (NO) and nitrogen dioxide ($NO_2$), both calculated as $NO_2$, is called nitrogen oxides ($NO_x$). NO is reactive compound, which oxidizes to $NO_2$ in atmosphere. Rate of oxidation depends on the conditions and on the other compounds present.

*Health* – $NO_2$ can irritate the lungs and is addressed with adverse respiratory effects including airway inflammation and increased number and severity of asthma episodes. Inhalation of elevated short-term $NO_2$ concentrations has been associated with increased hospital emergency room visits for respiratory distress (Vallero, 2014). $NO_x$ reacts in the atmosphere with various compounds to form toxic products, for example, organic nitrates, nitroarenes, nitrosamines, and peroxyacetyl nitrate (PAN, a phytotoxicant and mutagen).

*Ozone* – $NO_x$ contribute to formation of ground-level ozone when $NO_x$ and VOCs react in the presence of heat and sunlight (see Chapter 3.13).

*Acidification, eutrophication* – $NO_x$ can have adverse effects on terrestrial and aquatic ecosystems through acid rain and eutrophication of waters due to increase in nitrogen containing nutrients. $NO_2$ is a strong oxidizing agent that can form nitric acid ($HNO_3$), which falls to earth as acid rain. This leads also to deteriorating materials, such as, historical buildings and monuments.

*PM* – $NO_x$ and its oxidation products can form small particles in reactions with ammonia, moisture, and other compounds (see PM).

*Visibility Impairment* – $NO_2$ and nitrate particles can reduce visibility.

(US EPA websites and http://www.extraordinaryroadtrip.org/research-library/air-pollution/understanding-air-pollution/nitrogen-dioxide/health.asp, accessed July 2016)

## 2.7 Nitrous oxide ($N_2O$)

$N_2O$ is a strong greenhouse gas with a global warming potential of 265 (GWP, 100-year) relative to $CO_2$. Lifetime of $N_2O$ is 121 years. (Myhre et al. 2013).

$N_2O$ is a nonflammable, colorless gas commonly called "laughing gas". $N_2O$ is used, for example, as an anesthetic agent. Adverse effects, such as, breathing difficulty are associated with $N_2O$ abuse.

The $N_2O$ probably plays the dominant role in the depletion of stratospheric ozone layer when concentrations of halocarbons reach the pre-industrial concentrations. (Portmann 2012).

## 2.8 Ammonia ($NH_3$)

Ammonia is associated with harmful effects on health and vegetation, and can form ammonium aerosols that affect climate, and visibility. Ammonia is corrosive and can cause permanent injury in the eye. Dermal exposure to ammonia or its solutions may result in irritation and alkali burns at sufficient concentrations. Ingestion of ammonia solution causes rapid signs and symptoms and extensive alkali burns to the aerodigestive tract. Aspiration of ammonia following ingestion may also lead to respiratory complications. Chronic oral exposure to ammonia may lead to osteoporosis secondary to chronic metabolic acidosis. Exposure to a massive concentration of ammonia gas may be fatal within minutes. (Public Health England 2015).

## 2.9 Sulphur dioxide ($SO_2$)

$SO_2$ is a precursor for compounds that are harmful to people and the environment. $SO_2$ is a respiratory irritant, damages crops, and causes visibility problems. $SO_2$ and other sulphur oxides form acids in the atmosphere, particularly sulphuric acid ($H_2SO_4$), a key component of acid rain. $SO_2$ causes crop and material damage when acidic liquid and solid aerosols are deposited. (Vallero 2014)

## 2.10 Volatile organic compounds (VOCs)

In Europe, VOCs are defined as organic compounds having an initial boiling point less than or equal to 250°C at 101.3 kPa (Directive 2004/42/CE). Examples of VOCs are hydrocarbons, alcohols, ethers, esters, and aldehydes. Some of the VOCs are toxic and some contribute to the ozone formation (see Chapter 3.13). Adverse health effects are identified, for example, for the following mobile-source VOCs:

- Benzene increases the risks of acute myeloid leukemia. (HEI 2007). IARC (2012) has defined benzene as carcinogenic to humans, Group 1.

- 1,3-Butadiene has a short lifetime, and it is a reactive compound forming other MSATs, such as formaldehyde, acetaldehyde, and acrolein. 1,3-Butadiene may cause lymphohaematopoietic cancers in high-exposures. (HEI 2007). IARC (2012) has

defined 1,3-butadiene as carcinogenic to humans, Group 1. Concentrations of 1,3-butadiene may be elevated in the tobacco smoke.

- Formaldehyde is an irritant to the eyes, skin, and respiratory tract in humans with possible increase in asthma. (HEI 2007). IARC (2012) has defined formaldehyde as carcinogenic to humans, Group 1. Formaldehyde is present predominantly indoors, but transport is a source of ambient concentrations, both directly and through photochemical activity. In Brazil, ambient formaldehyde concentrations increased along with increased use of natural gas vehicles.

- Acetaldehyde causes irritation to the eyes, skin and respiratory tract and induces cellular inflammation. Acetaldehyde is a carcinogen in rodents, but the data on its carcinogenicity in humans are inadequate. (HEI 2007). IARC has defined acetaldehyde as Group 1 carcinogen when associated with consumption of alcoholic beverages (IARC 2012). Indirect effect of acetaldehyde is through reaction with $NO_x$ in the atmospheric photochemical system producing peroxyacetyl nitrate (PAN), which is a phytotoxicant and mutagen. Acetaldehyde is present in, for example, in some foods, but it originates also from mobile sources. The use of ethanol as fuel may increase acetaldehyde emissions in air.

- Acrolein is irritant to the respiratory tract. Chronic inhalation results in inflammation. (HEI 2007). IARC (1995) defined acrolein as “not classifiable as to its carcinogenicity to humans (Group 3 carcinogen). Acrolein is formed from 1,3-butadiene in atmosphere in addition to the direct sources, such as, tobacco smoke.

## 2.11 Particulate mass (PM) and number (PN), black carbon (BC)

Particulate matter from internal combustion engines consists of elemental carbon, organic compounds, metals, sulphates, nitrates, and other constituents originating from fuel and lube oil in the combustion process and in the after treatment devices. Primary PM forms secondary organic aerosols (SOA) in the atmospheric reactions. Outdoor PM consists also of other species, including dust and dirt.

Human health concerns of PM include for example effects on breathing and the respiratory system, damage to lung tissue, and premature death. BC associated in particles increase the global warming, while other constituents of PM have a cooling effect on climate.

Effects of particles on human health depend on their size and composition. The primary mechanisms for deposition of particles in the respiratory tract are sedimentation, impaction, and diffusion, which depend on the diameter of the particle. Coarse particles are removed e.g. by swallowing or coughing (Figure 4). Particles below 0.1 µm can reach the surface of the lung. These particles can be removed by scavenging cells (macrophages), but they may also drift into lymphatic vessels, and possibly further into the blood. (DEFRA 2001). Small particles penetrate deeply into the lungs and can cause or worsen respiratory disease, such as, emphysema and bronchitis, and aggravate existing heart disease.

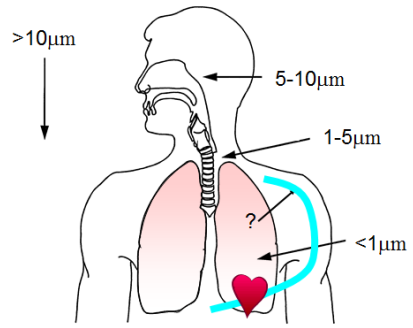



*Figure 4. Deposition of particles into human body (Altshuler 2002).*

More than 90% of diesel particles are in the size class

below 0.1 µm (ultrafine particles, UPs). Depending on technology, nanoparticles below 50 nm may be present at high concentrations (Figure 5). Diesel particles have a large surface area, which may adsorb various compounds that can be toxic, mutagenic, and carcinogenic, e.g., PAHs. (HEI 2002, Kittelson 2002, IARC vol 109, 2016).

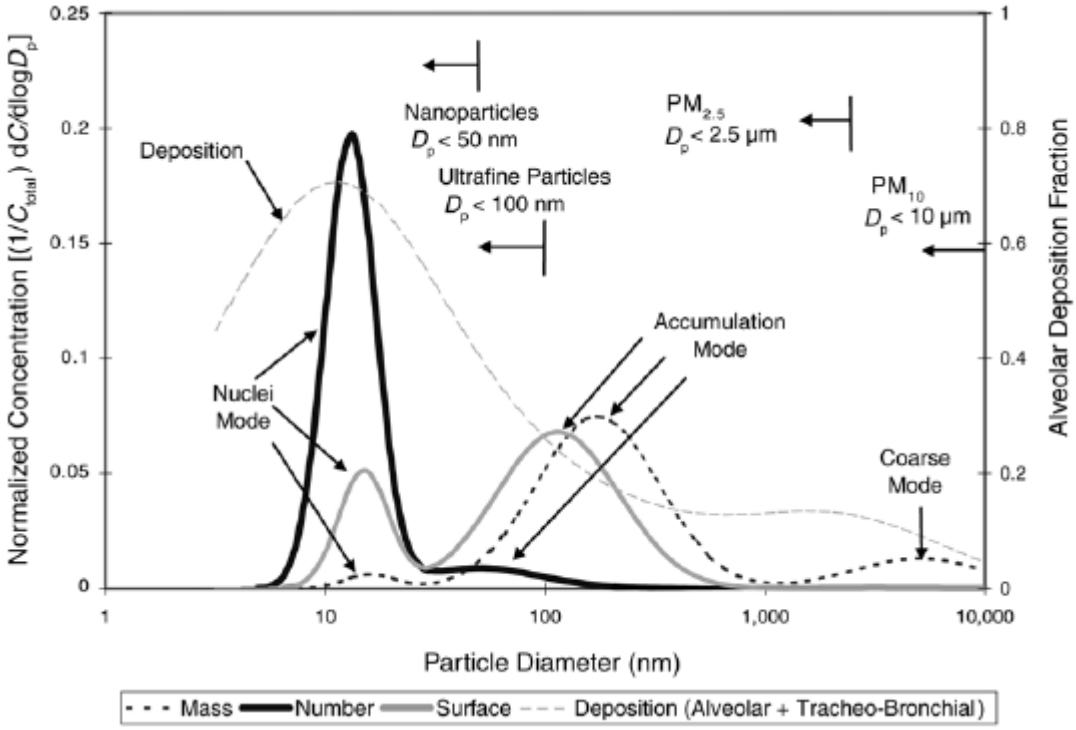



*Figure 5. Major features of atmospheric particle mass, number and surface distribution (HEI 2002).*

Li et al. (2016) found that UPs have detrimental effects on both the cardiovascular and respiratory systems, including a higher incidence of atherosclerosis and exacerbation rate of asthma. UPs can also play a role in allergen sensitization. The inflammatory properties of UPs can be mediated by reactive oxygen species, leading to the generation of proinflammatory cytokines and airway inflammation. In addition, UPs might be able to alter cellular function, penetrate intracellularly and potentially cause DNA damage. (Li et al. 2016).

IARC (Vol 109, 2016) has defined particulate matter of outdoor air pollution as carcinogenic to humans, Group 1.

## 2.12 Polyaromatic hydrocarbons (PAHs), and their derivatives

Polycyclic organic matter (POM) defined by the US EPA as “Priority Air Toxic”, consists of hundreds of different compounds, for example, PAHs with and without heteroatoms (N, S, O). PAHs are neutral, nonpolar aromatic molecules and are found in e.g. fossil fuels and are produced, generally, when insufficient oxygen or other factors result in incomplete combustion of organic matter (e.g., in engines). Mobile sources may be significant contributors to ambient PAH concentrations in urban areas. Diesel vehicles are known PAHs emitters, however, gasoline vehicles may also emit high PAH concentrations at cold temperatures (Aakko-Saksa et al. 2014b). Tobacco smoke and food-derived sources may lead to exposure to PAHs. (HEI 2007).

Many PAHs have been identified as carcinogenic and mutagenic, for example, benzo(*a*)pyrene is a PAH compound whose metabolites are mutagenic and highly carcinogenic. PAHs are of concern for their potency of potential health impacts. In addition to PAHs, substituted nitro-PAHs and oxy-PAHs may be present in the exhaust gases.The IARC classification for 2-nitropyrene is Group 2A and for 1,8-dinitropyrene Group 2B.

Naphthalene is the most abundant PAH in ambient air. There is evidence in rodents that exposure to naphthalene leads to inflammation of the nasal tract and tumors of the nasal epithelium. However, there are no data on carcinogenicity of naphthalene in humans. Case reports suggest that exposure to naphthalene may cause effects in blood cells, such as haemolysis and haemolytic anemia. (HEI 2007).

The US EPA (1998) defined 16 priority PAHs, many of these are classified as carcinogenic, Group 1, probably carcinogenic, Group 2A or possibly carcinogenic, Group 2B, according to the IARC classification (IARC 2008, 2011). In a list of mobile-source air toxics defined by the US EPA (2007), seven priority PAHs are included. European directive 2004/107/EC relating to arsenic, cadmium, mercury, nickel, and polycyclic aromatic hydrocarbons in ambient air, defines seven priority PAHs that are classified in Groups 2A and 2B by IARC. In addition to these definitions, there are several other lists of "Priority PAHs" to describe the cancer-related risks of substances. For example, (Kokko et al. 2000) presented a sum of 14 PAHs based on the US EPA priority list of 16 PAHs, from which naphthalene, acenaphthene, and acenaphthylene were excluded, because these low-molecular weight PAHs significantly decrease the repeatability of the results. On the other hand, benzo(e)pyrene was included as it is listed by NIOSH and VDI 3872. Table 4 summarizes the selected lists for priority PAHs.

*Table 4.* ***a)*** *16 PAHs[5] defined by the US EPA (1998)* ***b)*** *14 PAHs reported e.g. by Kokko et al. (2000).* ***c)*** *7 PAHs defined by the US EPA (2007) and* ***d)*** *7 PAHs defined in European Directive 2004/107/EC.*

| | N | Ace | Acy | Flu | Phe | An | F | P | BaA | DMBA | Chr | BbF | BjF | BkF | BaP | BeP | IP | DBahA | BghiP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| IARC[6] | 2B | 3 | | 3 | 3 | 3 | 3 | 3 | 2B | | 2B | 2B | 2B | 2B | 1 | 3 | 2B | 2A | 3 |
| Ring [a] | 2/2 | 3/2 | 3/2 | 3/2 | 3/3 | 3/3 | 4/3 | 4/4 | 4/4 | 4/4 | 4/4 | 5/4 | 5/4 | 5/4 | 5/5 | 5/5 | 6/5 | 5/5 | 6/5 |
| TEF EU (2001) | | | | 0.001[b] | 0.0005 –0.01 | 0– 0.01 | 0– 0.06 | 0– 0.081 | 0.005– 0.145 | (10[b]) | 0.001– 0.89 | 0.06– 0.14 | 0.045– 0.061 | 0.03– 0.1 | 1 | | 0– 0.232 | 0.69–5 | 0.01– 0.03 |
| a (16) | x | x | x | x | x | x | x | x | X | | X | X | | X | X | | X | X | x |
| b (14) | | | | x | x | x | x | x | X | | X | X | | X | X | x | X | X | x |
| c (US 7) | | | | | | | | | X | X | X | X | | X | X | | X | | |
| d (EU7) | | | | | | | | | X | | | X | X | X | X | | X | X | |

[a] No. of rings/aromatic rings [b] Collins et al. (1998)

A Working Group of the European Commission reviewed toxic equivalency factors (TEFs) of PAHs relative to benzo(*a*)pyrene (EU 2001). The review results with regard to 14 selected PAHs are summarized in Table 4. In addition, supplementary TEFs are shown for fluorene (Flu) and 7,12-dimethylbenz(*a*)anthracene (DMBA) (Collins et al. 1998).

[5] N = Naphthalene, Ace = Acenaphthene, Acy = Acenaphthylene, Flu = Fluorene, Phe = Phenanthrene, An = Anthracene, F = Fluoranthene, P = Pyrene, BaA = Benz[*a*]anthracene, DMBA = 7,12-dimethylbenz(*a*)anthracene, Chr = Chrysene, BbF = Benzo[*b*]fluoranthene, BkF = Benzo[*k*]fluoranthene, BjF = Benzo[*j*]fluoranthene, BaP = Benzo[*a*]pyrene, IP = Indeno[1,2,3-*cd*]pyrene, DBahA = Dibenz[*ah*]anthracene, BghiP = Benzo[*ghi*]perylene.

[6] Group 1: carcinogenic; Group 2A: probably carcinogenic; Group 2B: possibly carcinogenic; Group 3: not classifiable with regard to carcinogenicity; Group 4: probably non-carcinogenic.

A total cancer potency for PAHs can be evaluated by calculating the BaP equivalent using the equation (1):

$$BaP_{eq} = \sum (TEF_x * PAH_x) \qquad (1)$$

$BaP_{eq}$ = Benzo(*a*)pyrene equivalent (µg/km)
$TEF_x$ = Relative toxic equivalency factor for individual PAH compounds (Table 4)
$PAH_x$ = Mass emissions (µg/km) of PAH compound

## 2.13 Ozone – tropospheric and stratospheric

**Ground-level, tropospheric ozone**

Ground-level ozone ($O_3$) causes adverse health effects, for example, irritation of the respiratory system, coughing and reduction of lung function. Ozone may aggravate asthma. There is also evidence of the effect of ozone on, for example, cardiovascular-related morbidity. Potential interactions between ozone and PM have been suggested. Ozone contributes to damage to plants and ecosystems. The adverse effects of ozone on forest and other natural vegetation may lead to species shifts and loss from the affected ecosystems, resulting in the loss or reduction of related goods and services (US EPA 2007). The tropospheric ozone (lifetime ~12 years) increases global warming. Ozone is not an emitted as such, while it is formed by the precursor emissions of CO, VOCs, and $NO_x$ (Akimoto et al. 2011).

Formation of ozone

Ground-level tropospheric ozone is created in the presence of $NO_2$, VOCs, heat and sunlight via photochemical reactions. Ozone precursors arise from both natural and anthropogenic sources. Urban areas may have high ozone levels on warm, sunny days, but even rural areas may experience elevated ozone levels due to the transported emissions with the movement of an air mass from one region to another (Vallero 2014).

The formation of ozone in the troposphere is a complex process. The simplified summary is presented here based on (Drechsler 2004). Ozone is formed in the troposphere by addition of atomic oxygen to molecular oxygen (2).

$$O\cdot + O_2 \rightarrow O_3 \qquad (2)$$

The atomic oxygen needed for reaction (3) is produced from photolysis of $NO_2$ (2)

$$NO_2 \xrightarrow{h\nu} NO + O\cdot \qquad (3)$$

The reaction ends by reaction of ozone and NO back to $NO_2$ and $O_2$, forming a nitrogen cycle. When these reactions are in balance, the net ozone concentration does not change.

When ratio of the $NO_2$ to NO is low, ozone is not accumulated by the nitrogen cycle. Ozone accumulates only when excessive $NO_2$ is formed and when ozone is not destroyed. The photochemical oxidation of VOCs, such as hydrocarbons and aldehydes, provides the pathway to formation of excessive $NO_2$.

VOCs are oxidized in the atmosphere typically driven by hydroxyl radical (OH·) attack (4) to form peroxy radical. R can be hydrogen or any organic fragment. Hundreds of VOC species participate in similar reactions.

The key reaction in the VOC oxidation cycle is the conversion of NO to $NO_2$ by the radical transfer reaction (5). Production of $NO_2$ is necessary to generate atomic oxygen (3) and further ozone (2).

$$RH \xrightarrow{OH\cdot,\, O_2} RO_2\cdot + H_2O \qquad (4)$$

$$RO_2\cdot + NO \rightarrow RO\cdot + NO_2 \qquad (5)$$

Ozone is consumed in the presence of, for example, water vapor, nitrous acid (HONO) and hydrogen peroxide (formed by hydroxyl radical). Reaction of $NO_2$ with OH· produces nitric acid, $HNO_3$, which is a sink of $NO_2$ and radical thus inhibiting the net ozone formation. However, in some conditions $HNO_3$ may regenerate to $NO_2$. (Drechsler 2004).

In the early morning, the urban $NO_x$ is mainly in a form of NO, because free radicals are not sufficiently present to convert of NO to $NO_2$. When photolysis of VOCs starts, $NO_2$ becomes dominant and ozone builds up. VOC reactions are relatively slow and thus the highest ozone concentrations may be observed many kilometers from the emission sources. During the night, NO and ozone combine to form $NO_2$ and oxygen until either of the reactants is consumed. HONO may assists ozone formation when sunlight breaks it down to NO and OH·, which further reacts with VOCs (3, 4). (Drechsler 2004).

VOCs are necessary to generate high concentrations of ozone, but $NO_x$ emissions can be the limiting factor for the high ozone concentrations. When the $NO_x$ concentration is high and the VOC concentration low, $NO_x$ tends to inhibit ozone formation. When the VOC concentration is high relative to $NO_x$, ozone tends to be generated (Drechsler 2004).

Photochemical reactivity of VOCs

Photochemical reactivity describes a VOC's ability to participate in photochemical reactions to form ozone in the atmosphere. Examples of the reactive VOCs in California include propene, *m*-xylene, ethene, and formaldehyde. (Drechsler et al. 2004).

Individual VOC species contribute very differently to formation of oxidants and ozone. Carter and Atkinson (1987) developed a maximum incremental reactivity (MIR) scale to assess the ozone-forming potential (OFP) of any emitted molecule (6):

$$OFP = \Sigma (MIR \times mass\ emissions) \qquad (6)$$

The MIR values for selected individual hydrocarbons and oxygen-containing compounds are shown in Table 5 (Carter 2010).

*Table 5. Maximum incremental reactivity (MIR) values of selected compounds (Carter 2010).*

| | **MIR g ozone/g VOC** |
|---|---|
| carbon monoxide | 0.056 |
| methane | 0.0144 |
| ethane | 0.28 |
| ethene | 9.00 |
| propane | 0.49 |
| propene | 11.66 |
| acetylene | 0.95 |
| isobutene | 6.29 |
| 1,3-butadiene | 12.61 |
| benzene | 0.72 |
| toluene | 4.00 |
| ethylbenzene | 3.04 |
| *m*-xylene | 9.75 |
| *p*-xylene | 5.84 |
| *o*-xylene | 7.64 |

| | **MIR g ozone/g VOC** |
|---|---|
| ethanol | 1.53 |
| isobutanol | 2.51 |
| *n*-butanol | 2.88 |
| ETBE | 2.01 |
| formaldehyde | 9.46 |
| acetaldehyde | 6.54 |
| acrolein | 7.45 |
| propionaldehyde | 7.08 |
| crotonaldehyde | 9.39 |
| methacrolein | 6.01 |
| butyraldehyde | 5.97 |
| benzaldehyde | -0.67 |
| valeraldehyde | 5.08 |
| *m*-tolualdehyde | -0.59 |
| hexanal | 4.35 |

**Stratospheric ozone**

Stratospheric ozone approximately 10 to 30 miles above the earth's surface forms a layer that protects life on earth from the sun's harmful rays. The major losses of the stratospheric ozone have been due to the halocarbons gases, but as concentrations of halocarbons decrease, the role of $N_2O$ in the depletion of stratospheric ozone layer increases. (Portmann 2012).

## 2.14 Risk factors and external costs for emissions

Emissions impose indirect, external costs on society related to impacts in health and environment and climate change. The monetary values of these impacts evaluated can be used in determination of the lifetime costs of exhaust emissions from transport vehicles. Directive 2009/33/EC defines the following external costs for $CO_2$, NMHC, $NO_x$ and PM:

- $CO_2$ €30 – 40/tonne
- NMHC (without methane) €1000/tonne
- $NO_x$ €4400/tonne
- PM €87 000/tonne

CO and HC emissions are not included in 2009/33/EC, however, in Finland, Tiehallinto (2001) published external costs for CO and HC emissions in addition to those for $NO_x$, $PM_{2.5}$, and $CO_2$ emissions. National values in Finland for CO and HC emissions were defined as follows:

- CO €29/tonne
- HC (with methane) €62/tonne

Risk factors for calculating the cancer potency of exhaust gas, as defined by OEHHA (2009), US EPA IRIS (2010) and The Nordic Ecolablelling (2008), are shown in Table 6. OEHHA (2009) defines cancer unit risks and potency factors for 107 carcinogenic substances or groups of substances. The US EPA IRIS, Integrated Risk Information System, is a human health-assessment program that evaluates quantitative and qualitative risk information for effects that may result from exposure to environmental contaminants. The Nordic Swan labelling criteria for biofuels define substances, which are measured in accordance with a particular protocol, and calculate the cancer potency of exhaust gas using risk factors (Nordic Ecolabelling 2008).

The most significant differences in the risk factors defined by different organizations concern ethene and propene emissions, which are included in Nordic Ecolabelling, but not in the other definitions. Törnqvist et al. (1994) reported that ethene is metabolized in animals and in humans to a probable human carcinogen, ethylene oxide. Similarly, propene is metabolized to propylene oxide.

*Table 6. Substances and risk factors for calculating the cancer potency of exhaust gas according to OEHHA (2009), US EPA IRIS (2010) and Nordic Ecolabelling (2008).*

| Substance | Unit Risk Factor $(\mu g/m^3)^{-1}$ | | | Normalized[7] |
|---|---|---|---|---|
| | Nordic Ecolabelling | OEHHA 2009 | US EPA IRIS 2010 | |
| Particulate matter[8] | $7 \times 10^{-5}$ | $30 \times 10^{-5}$ | insuff. Data | 177 |
| Benzene | $0.8 \times 10^{-5}$ | $2.9 \times 10^{-5}$ | $(0.22\text{-}0.78) \times 10^{-5}$ | 17 |
| Formaldehyde | $10 \times 10^{-5}$ | $0.6 \times 10^{-5}$ | $1.3 \times 10^{-5}$ | 4 |
| Acetaldehyde | $0.2 \times 10^{-5}$ | $0.27 \times 10^{-5}$ | $0.22 \times 10^{-5}$ | 2 |
| Ethene | $5 \times 10^{-5}$ | | | 17 |
| Propene | $1 \times 10^{-5}$ | | | 3 |
| 1,3-Butadiene | $30 \times 10^{-5}$ | $17 \times 10^{-5}$ | $3 \times 10^{-5}$ | 100 |
| PAH (including benzo(a)pyrene) | $2800 \times 10^{-5}$ | | | 9333 |

## 2.15 Summary

Reduction of adverse health and environmental effects related to air quality has been the primary driving force for tightening the exhaust emission limits of transport sector.

Complete combustion of fuels produces only $CO_2$ and water, while constituents called traditionally “emissions” represent only a share of below 0.5% of the total exhaust gas. Most of the emission species are fuel- and engine-dependent, and some are formed in emission control devices. For natural gas or biomethane fueled vehicles, methane is emitted. Ethanol fueled cars emit, for example, ethanol and acetaldehyde. $N_2O$ and $NH_3$ are induced by the TWC catalyst, and $NH_3$ also by the SCR catalyst.

Spark-ignited cars equipped with a TWC catalyst are typically characterized by low CO, HC, and $NO_x$ emissions. In diesel combustion, complicated emission control systems consisting of e.g. SCR and DPF are required to achieve low $NO_x$ and PM emissions.

[7] In the normalization, 1,3-Butadiene = 100. OEHHA 2009 factors are used for substances other than ethene, propene and PAH, for which factors of Nordic Ecolabelling are used.

[8] OEHHA defines “Particulate Matter from Diesel-Fueled Engines”.

Hundreds of compounds are present in the exhaust gases, some of them toxic, for example, benzene and 1,3-butadiene, or greenhouse gases, such as, methane. Benzene, formaldehyde and 1,3-butadiene are classified as human carcinogens, while acetaldehyde has been classified as possible carcinogen. 1,3-Butadiene is reactive and form formaldehyde, acetaldehyde, and acrolein in atmospheric reactions. Acrolein is highly irritating, and long-term inhalation results in chronic inflammation. Polycyclic organic matter is found in the particle and semivolatile phase. Many PAHs, nitro-PAHs, and oxy-PAHs have been classified as proven, probable, or possible carcinogens to humans. Number of particles (PN), especially nanoparticles, is an important parameter when evaluating health impacts of the exhaust gas. In addition, the toxicological and epidemiological data suggest that the chemical composition of particles may be important contributor to the health effects. IARC classification of diesel engine exhaust is carcinogenic to humans (Group 1), and classification of gasoline exhaust is possibly carcinogenic to humans (Group 2B). Classification of diesel exhaust is based on the results with older diesel engines.

Ozone causes adverse health effects, such as, irritation of the respiratory system. Ozone also contributes to damage to plants and ecosystems. Formation of ground-level ozone is related to concentrations of $NO_x$, VOCs, and the presence of heat and sunlight in the atmosphere. $NH_3$ is also associated with harmful effects on health and vegetation. Besides $CO_2$, other transport-related GHG emissions are methane, black carbon, $N_2O$ and ozone precursors.

Risk factors for calculating the cancer potency of exhaust gases are defined by many organizations. There are also various methodologies for evaluation of risks related to ozone formation, acidification, photochemical oxidation, PM formation, and marine eutrophication, amongst others.

# 3. Emission measurement methods for alternative fuels at VTT

## 3.1 Overview

VTT's facilities include several chassis and engine dynamometers combined with analyzers for regulated gaseous emissions. Methods described here are limited to those used in testing of cars and vehicles on chassis dynamometers. Most of these methods can be used also in the engine test benches.

A schematic portfolio of VTT's emission measurements from cars and vehicles is illustrated in Figure 6 and listed below. Improved/developed methods within the 2GBIO_PILOT project are marked in bold and asterix.

- Gaseous emissions
  - CO, **THC***, $NO_x$, $CO_2$
  - C1-C8 individual hydrocarbons by GC-FID and the **total integrated sum*** for oxygen-containing fuels; a **microGC*** feasibility studied.
  - **Aldehydes***: $NO_2$ interference taken into account for the alcohol fuels.
  - Alcohol emissions can be analysed by GC-FID or FTIR.
  - **FTIR***: new methods developed for alternative fuels.
- PM collection with standard or high-capacity system.
- **Semivolatile*** SVOC sampling method developed.
- PM composition:
  - SOF, sulphates, nitrates, and metals.
  - **EC/OC*** analyses for on-road cars/vehicles fuels is applicable.
  - More detailed characteristics such as simulated distillation or fuel/lube.
- PM and SVOC:
  - **PAH*** analyses with simplified extraction procedure.
  - Ames test and a **microAmes*** test to indicate mutagenicity of small samples from low-emitting cars and vehicles.
  - An acellular chemical **DTT*** assay for oxidative potential in PM samples and SVOC samples was introduced.
  - A new **dosing*** principle was introduced basing on the exhaust volume instead of particulate mass.
  - New service providers were tested and evaluated for mutagenicity testing, oxidative potential testing, and PAH analyses.
- Particle number (solid PN and wet PN), size classification, and characterization are conducted with various methods at VTT.
- Special analytics, such as SEM, TEM and IR microscopy available at VTT.

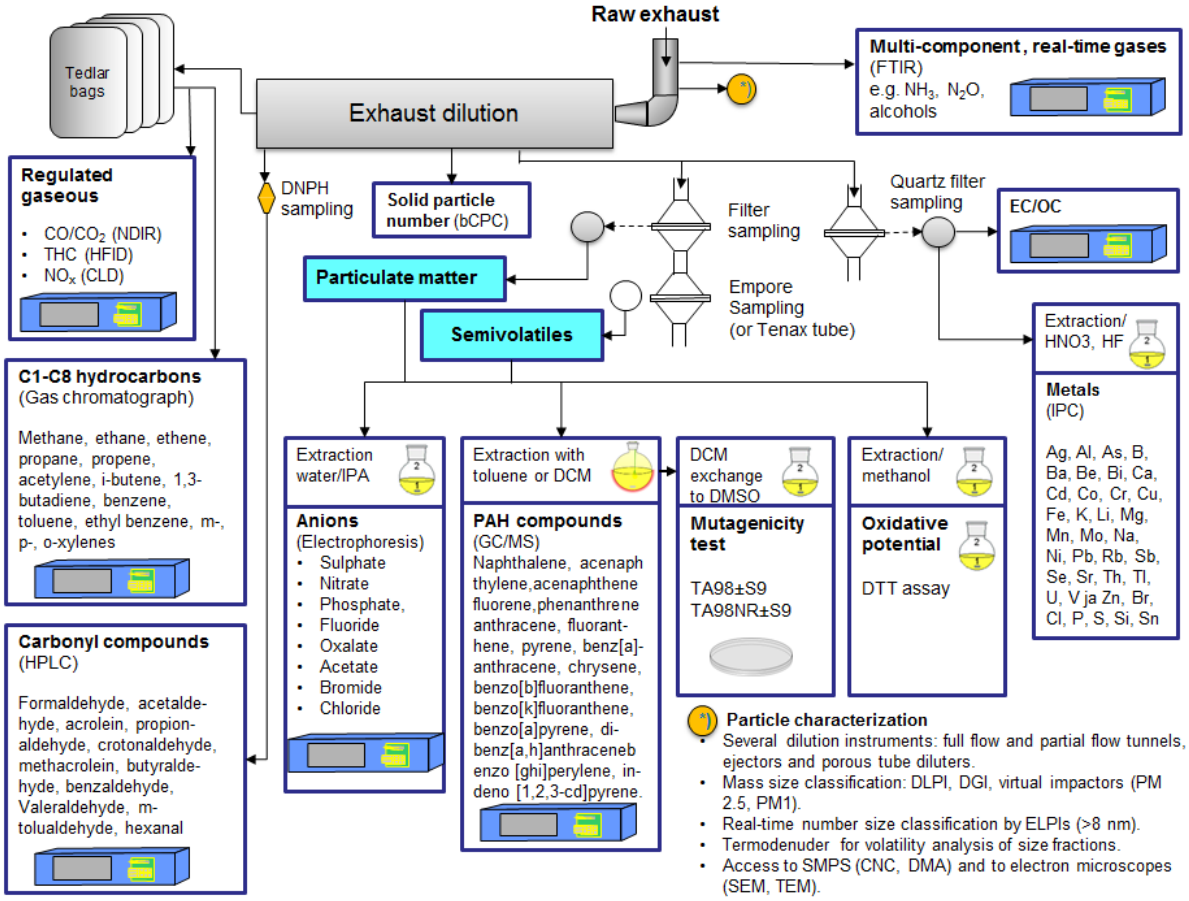



*Figure 6. A schematic portfolio of VTT's emission measurements from cars and vehicles.*

## 3.2 Sampling

### 3.2.1 Sampling options

Sampling options are:

**a)** Raw exhaust for multi-component analysis (FTIR)

**b)** Constant volume sampler (CVS) diluted exhaust in Tedlar bags

- CO (NDIR), THC (FID), $NO_x$ (CLD), C1 – C8 HCs (GC-FID)

**c)** CVS diluted exhaust through cartridges or impingers

- dinitro phenyl hydrazine (DNPH) cartridges for analysis of carbonyl compounds using high-performance liquid chromatography (HPLC)
- water impingers for analysis of alcohols (GC-FID)

**d)** CVS diluted exhaust through filters for PM analyses

- standard PM, high-capacity PM (different filter options)
- PM SOF, anions, metals, PAHs, Ames, DTT, EC/OC, other analyses such as fuel/lube, simulated distillation, GC-MS

**e)** CVS diluted exhaust through Empore disk or Tenax-tubes for SVOC collection

- PAHs, Ames, DTT, other analyses such as fuel/lube, simulated distillation, GC-MS

**f)** Special dilution systems such as porous tube and ejector diluters. Measurements for in-depth particle measurements including mass, size and number classifications as well as analyses with scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Sampling for regulated gaseous emissions and PM are described in this Chapter while sampling for the other analyses are described in the corresponding Chapters.

### 3.2.2 Sampling for PM and the gaseous regulated emissions

At VTT, gaseous emissions and PM are sampled in the measurements of cars and heavy-duty vehicles in the transient chassis dynamometers and from engines in the engine test cells. Sampling of the CVS diluted exhaust to the Tedlar bags is a standardized procedure for cars and heavy-duty vehicles. Test procedure for cars is defined for example in the UN Regulation No. 83. For the standard sampling to the Tedlar bags, it is noted that higher dilution ratios are needed to avoid condensation of water for vehicles using methane and ethanol than for vehicles using gasoline/diesel (differences in water concentrations in the exhaust gas).

Table 7 shows systems used in the measurements of light-duty and heavy-duty vehicles including the standard PM collection systems and dilution tunnels.

*Table 7. VTT's chassis dynamometers and analyzers for gaseous emissions in these test cells. Characteristics of VTT's standard particle sampling systems.*

| Light-duty vehicles | Heavy-duty vehicles |
|---|---|
| Chassis dynamometer: Froude Consine, 1,0 m, 100 kW/450-2750 kg<br>Constant volume sampler: AVL CVS i60 LD, Venturi-type<br>AVL AMA3, Pierburg GmbH: HC 0–10 000 ppm (HFID); $NO_x$ 0–10 000 ppm (chemiluminescence CLD); $CO/CO_2$ 0-3000 ppm/0-16 % (Laybold AG, NDIR)<br>Dil tunnel: Pierburg GmbH, 3-18 $m^3$/min, 400 cm, 27.3 cm i.d.;<br>AVL CVS i60 LD Venturi-type<br>Steel duct: from car to CVS insulated 4.0 m, i.d. 8.3 cm; from car to dil tunnel partly insulated 7.5 m, i.d. 8.3 cm<br>PM AVL AMA i60 sampling, probe i.d. 12 mm, 20 – 100 $dm^3$/min.<br>PN Butanol CPC: Airmodus A23, probe i.d. 12 mm<br>Balance: Sartorius SE2-F, 2.1 g, readability 0.1 µg | Chassis dynamometer: Froude Consine, UK, 300 kW (54 –110 km/h); 20 000 N (0 – 54 km/h); 2 500–60 000 kg; Roll diameter 2 500 mm, roll weight 20 000 kg<br>Constant volume sampler: CVS-120-WT, Multiple (3) CFV venturi, 120 $m^3$/min<br>AVL AMA 4000: HC 0 – 1000 ppm (HFID); $CH_4$ 0 – 3000 ppm (HFID); $NO_x$ 0 – 10 000 ppm (2 units, HCLD); CO 0 – 2500 ppm (NDIR), $CO_2$ and tracer 0 - 20 % NDIR<br>Pierburg GmbH, CVS-120-WT: Multiple (3) CFV-venturi system, max. flow 120 $m^3$/min<br>Tunnel: 8000 x 450 mm, secondary tunnel VT-458<br>PM collector PS2000 C, probe, i.d. 14 mm, 0-100 $dm^3$/min (typically 50 $dm^3$/min.) |

**PM mass emission – high-capacity sampling**

Particulate matter is a complex mixture of extremely small particles and liquid droplets. PM is made up of a number of components, including elementary carbon, organic compounds, acids and salts (such as nitrates and sulfates) and metals. PM mass emission is determined by weighing the particle filters before and after collection of particle mass according to the

procedures defined in the emission regulations (see Table 7). Depending on the test cell, a full-flow CVS system or partial flow dilution systems are used.

For low-emitting cars and vehicles, a high-capacity PM sampling system can be used. In this project, requirements and recommendations for PM collection with high-capacity sampling system were defined. The high-capacity PM sampling system for low-emitting cars and for special analyses was developed in early 90's at VTT (Rantanen et al. 1996&2005, Kokko 2000, Perander 2001, Aakko 2002). Further development of the high-capacity PM collection system has taken place over the past years by introducing a set of portable instruments to expand possibilities for PM collections in different test locations. Set-up needs to be considered case-specifically to fulfil requirements and recommendations in each project.

In the high-capacity system, theoretically up to 2000 L/min flow of diluted exhaust gas can be used with many options of probes and filter holders (Figure 7). However, the maximum flow rate is practically restricted to below 1500 L/min with currently used filter type even if two filter holders are used in parallel. The filter type used today in the high-capacity PM collections is Fluoropore 3.0 µm FSLW (o.d. 142 mm), which is a hydrophobic membrane filter with a pore size of 3.0 µm, an air flow rate of 20 L/min/cm$^2$, an operating temperature of 130 °C and a porosity of 85%. Pallflex T60A filters (o.d. 142 mm) allow using higher flow rates than Fluoropore 3.0 µm FSLW, however, Pallflex T60A filters easily break in bending required by Sartorius SE2-F micro balance.

Pre-tests are recommended for new vehicle/engine types to define the best set-up for each measurement campaign. Configuration is documented within the research projects.

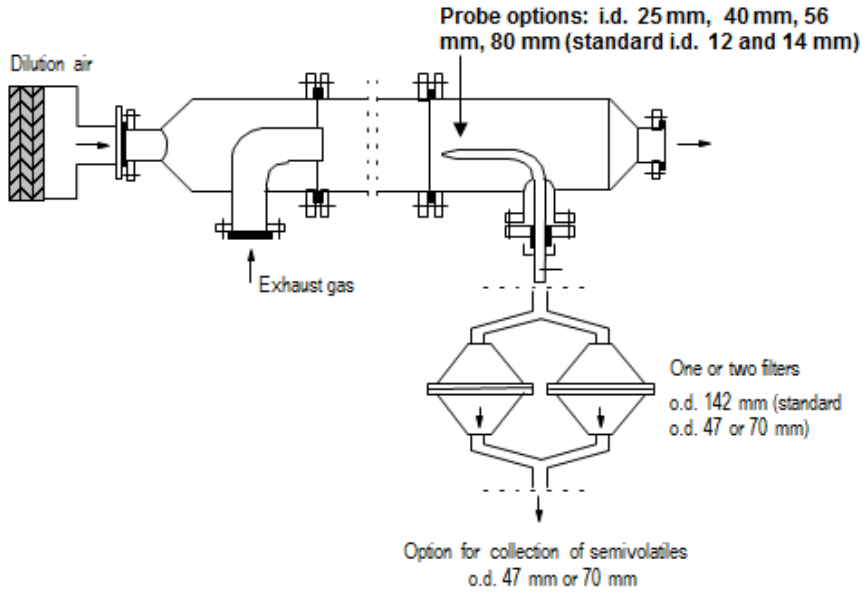



*Figure 7. Schematic configuration of high-capacity sampling system at VTT.*

Two high-capacity sampling systems are available at VTT. Examples of the options available for configurations are as follows:

- Probes in different sizes: i.d. 12, 14, 40, 56, and 80 mm. In the light-duty dilution tunnel, a probe of 56 mm is installed for high-capacity PM measurements
- One filter holder or two filter holders in parallel, o.d. 142 mm filters
- Blower Siemens ELMO-G, 2BH1 810-1HC36, 11 kW

- Flow meter Bronkhorst F-106C1-HD-V-12
- Controller Stafsjö MV-E-80-P-TY-AC100-PN10

The high capacity sampling system has been compared with the standard sampling system for example by Murtonen and Aakko-Saksa (2011). In Figure 8, correlation of the PM results using the standard and high-capacity collection systems was good in most cases. The results differed from each other on average by 4% and at the most by 13%.

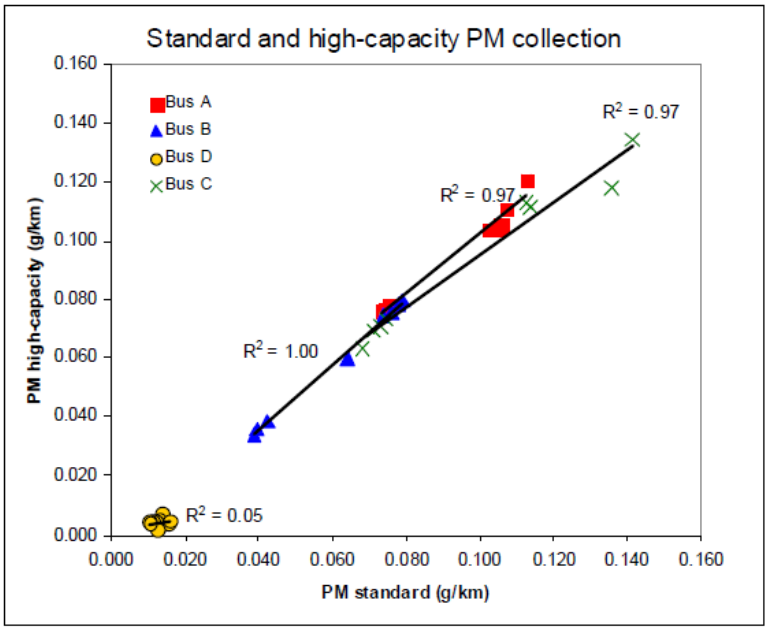



*Figure 8. Comparison of the results obtained with two sampling systems (Murtonen and Aakko-Saksa 2011).*

Comparison of the PM results collected in this project is shown in Figure 9 (see also Chapter 4.4.2). The PM emissions were collected using Fluoropore PTFE, Pallflex TX40 and quarz filters at different flows through filters depending on the requirements of special analyses. Face velocities on filters were as follows:

- Millipore Fluoropore 3.0 FSLW Ø 142 mm, PTFE membrane bonded to a high density polyethylene support: face velocity for DI-E2 13 cm/s and for the other cars 75-94 m/s. Fluoropore filters were used in the high-capacity sampling system to collect as much PM as possible for biological analyses.

- Pallflex TX40HI20WW Ø 47 mm, borosilicate glass microfibers reinforced with woven glass cloth and bonded with PTFE: face velocity 30 cm/s. Flow through these primary filters were limited due to SVOC sampling with the back-up filters.

- Munktell MK360 Ø 47 mm, micro-quartz fibres without glass fibres and binder: face velocity 30 cm/s, in one case 13 cm/s. Low flow rate was used for the quarz filters to avoid too dark samples for the EC/OC analysis.

PM emissions using high-capacity sampling system with Fluoropore filters were higher than those using standard sampling system and TX40 filters. This difference is most likely due to the missing back-up filters in the TX40 collections as Empore filters (SVOC sampling) were used in the place of back-up filters. The PM results obtained with quartz filters (standards

sampling) are only indicative, as very low masses were collected on purpose to avoid too dark filters for the EC/OC analyses.

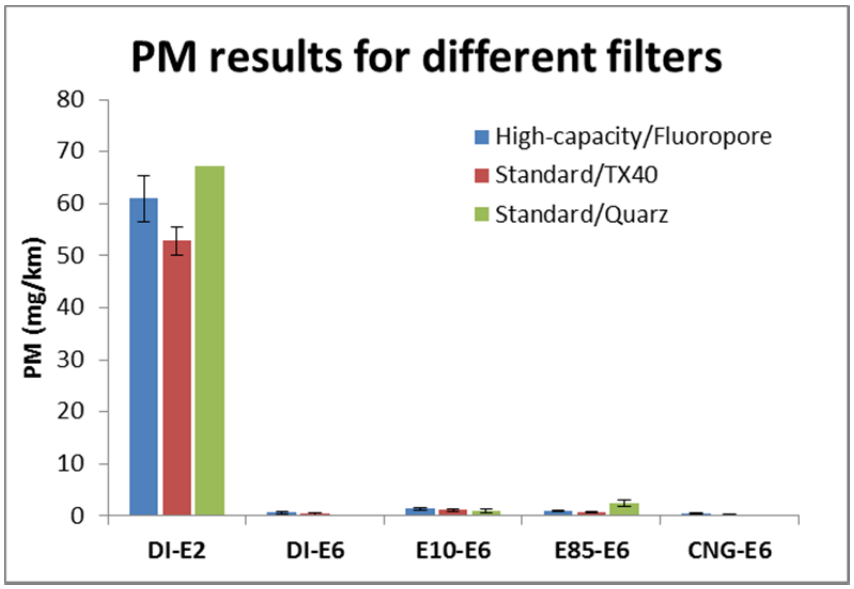



*Figure 9. Comparison of the PM results obtained using different filter materials and test conditions. Cars tested are described in Chapter 4.*

Sampling principles

The following limitations and/or recommendations are followed when particle sampling is designed:

1) Face velocity on the filter is in a range of 35–100 cm/s. [8,9]
2) Temperature on filter is less than or equal to 52 °C[9] and greater than 42 °C.[10]
3) Recommended velocity in the probe is higher than in the tunnel/exhaust duct.
4) Other recommendations: sharp edge on the sampling inlet (15 °); sampling inlet faces directly in to the exhaust stream; short sampling tube; sufficient distance (e.g. 50 mm) between probes; equal distance of the probes from the centre of tunnel/exhaust duct.
5) Two dilution tunnels are used for cars: "normal" for modern cars, another tunnel for high-emitters. In the heavy-duty tests, standard dilution tunnel is used for other vehicles than NGVs, for which a separate dilution tunnel is reserved.

Table 8 summarizes the recommended flow rates for different probes and permitted filter sizes to respect legislative limits for face velocity on filter (35–100 cm/s). For an example, in the tests of light-duty vehicles, tunnel flow velocity is typically max. 2.4 m/s and probe is i.d. 56 mm → can be combined with two parallel o.d. 142 mm filters at flow rate of over 560 L/min. For a heavy-duty vehicle/engine at tunnel flow velocity >3.9 m/s, probe i.d. 40 mm is acceptable in many cases. In each project, sampling details are decided depending on vehicle characteristics and on the analysis matrix.

[9] ECE Regulation No. 83, 1999/96/EC and other amendments to directive 88/77/EEC, ISO 8178
[10] ISO 8178

*Table 8. Recommended flow rates for different probes and permitted filter sizes and combinations. Allowed combinations on white background.*

| | Tunnel | | | | |
|---|---|---|---|---|---|
| | i.d. | Flow | | Velocity | |
| | | min | max | min | max |
| | mm | $Nm^3/min$ | $Nm^3/min$ | m/s | m/s |
| LD chassis | 265 | 3,5 | 8,0 | 1,1 | **2,4** |
| HD chassis | 450 | 37,0 | 75,0 | 3,9 | **7,9** |
| HD "NG" | 318 | 37,0 | 75,0 | 7,8 | **15,7** |

| Flow | Probe, mm | | | | | | Filter face velocity [a] | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 12 | 14 | 25 | 40 | 56 | 80 | | | | |
| rate | Velocity in probe [b] | | | | | | 35 mm [c] | 63 mm [c] | 1x130 [c] | 2x130 [c] |
| $Ndm^3/min$ | m/s | m/s | m/s | m/s | m/s | m/s | cm/s | cm/s | cm/s | cm/s |
| 20 | 2,9 | 2,2 | 0,7 | 0,3 | 0,1 | 0,1 | 35 | 10,7 | 3 | 1,3 |
| 57 | 8,4 | 6,2 | 1,9 | 0,8 | 0,4 | 0,2 | 99 | 30,5 | 7 | 3,6 |
| 66 | 9,7 | 7,1 | 2,2 | 0,9 | 0,4 | 0,2 | 114 | 35,3 | 8 | 4,1 |
| 187 | 27,6 | 20,2 | 6,3 | 2,5 | 1,3 | 0,6 | 324 | 100,0 | 23 | 11,7 |
| 280 | 41,3 | 30,3 | 9,5 | 3,7 | 1,9 | 0,9 | 485 | 149,7 | 35 | 17,6 |
| 465 | 68,5 | 50,3 | 15,8 | 6,2 | 3,1 | 1,5 | 806 | 248,6 | 58 | 29,2 |
| 560 | 82,5 | 60,6 | 19,0 | 7,4 | 3,8 | 1,9 | 970 | 299,4 | 70 | 35,2 |
| 730 | 107,6 | 79,0 | 24,8 | 9,7 | 4,9 | 2,4 | | | 92 | 45,8 |
| 800 | 117,9 | 86,6 | 27,2 | 10,6 | 5,4 | 2,7 | 1386 | 427,7 | 100 | 50,2 |
| 1170 | 172,4 | 126,7 | 39,7 | 15,5 | 7,9 | 3,9 | 2027 | 625,6 | 147 | 73,5 |
| 1590 | 234,3 | 172,1 | 54,0 | 21,1 | 10,8 | 5,3 | 2754 | 850,1 | 200 | 99,8 |
| 2000 | 294,7 | 216,5 | 67,9 | 26,5 | 13,5 | 6,6 | 3465 | 1069,3 | 251 | 125,6 |

[a] Face velocity on filter: 35-100 cm/s

[b] Higher celocity in probe than in tunnel recommended.

[c] Effective diameters for 47 mm, 70 mm and 142 mm filters

Isokinetic sampling is not required for the collection of submicron particles. However, flows higher (or close to) isokinetic sampling are recommended. Lower velocity in probe than in the main stream may lead to excessive collection of large particles as the large particles in the stream enter the probe due to their greater inertia while small particles follow the gas flow (Figure 10). At higher velocity in the probe than in the tunnel/exhaust duct, less large particles enter in the probe than in the isokinetic sampling. (Wilcox 1956). Large particles, above 1 µm, are mostly artefacts, such as particles falling off from walls of tunnel/exhaust duct in the exhaust measurements. Each of the standard PM collection probes at VTT is attached with a "hat" to avoid collection of these supermicron particles. However, in-house probes can be installed also without "hats". Anisokinetic mass bias has been observed for particles even at 500 nm size class (Eastwood 2007), but even that is above the size class of particles from vehicles.

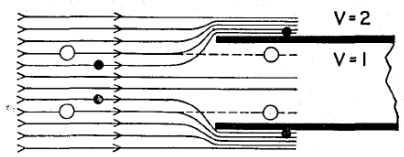



*Figure 10. When the sampling velocity is too low, collection of large particles is biased due to their high inertia (Wilcox 1956).*

### 3.2.3 Semivolatile organic compounds (SVOCs)

SVOCs are compounds sufficiently volatile to exist in vapor form in the engine exhaust, but capable to condensate under atmospheric conditions. Most SVOC molecules have at least 14 carbon atoms and boiling points from 240 to 400 °C. SVOCs may contain, for example, PAHs, dioxins and nitro-PAHs (US EPA 40 CFR 1065.1103–1111). Phase partitioning of semivolatile organic compounds vary depending on their concentration and saturation pressure, and on the other constituents of particulate matter. This will lead to differences in the SVOC results depending on the collection principles selected.

In the exhaust measurements, SVOCs are collected from the diluted exhaust gas after PM filters. US EPA 40 CFR 1065.1103–1111 gives guidelines for SVOC measurement along with PM using XAD-2 or XAD-4 (a hydrophobic cross-linked polystyrene copolymer resin adsorbent) or with PUF plugs (polyurethane foam). Pre-cleaning of PUF and XAD includes a series of Soxhlet extractions: 8 hours with water, 22 hours with methanol, 22 hours with methylene chloride, and 22 hours with toluene, followed by drying with nitrogen.

Semivolatiles were collected at VTT using PUF samplers until early 2000's when availability suitable PUF material diminished (former supplier Special Plast). In addition, pre-cleaning of PUF material was time-demanding and expensive including several washings (water, acetone) and Soxhlet extractions (toluene 12 h, acetone 12 h), drying and validation of purity by analysis of PAHs from the last extract. PUFs were stored in freezer until analysis. PAH results from samples collected using PUFs are reported, for example, by Aakko et al. (2000).

In this project, a robust collection method for semivolatiles was sought for. Sampling method without need for extensive pre-cleaning procedure was desired. Therefore, both XAD and PUF materials were excluded. Two sampling methods for SVOCs were tested:

- Empore disks (back-up position in the standard sampling system)
- Tenax TA Carbopack B-adsorbents (connected in the high-capacity sampling system)

The test set-up is shown in Figure 11. Flow through Empore disk was only 17.5 L/min due to its high back-pressure. Filter face velocity, 30 cm/s, was slightly lower than the recommended minimum velocity (35 cm/s). This may lead to decreased SVOC/PM ratio as a part of SVOCs is collected by the primary filter. For the high-capacity system using two parallel o.d. 142 mm filters, flow rates were lower (560-1590 L/min) than recommended for Euro 6 cars and even lower for the Euro 2 diesel (Scudo).

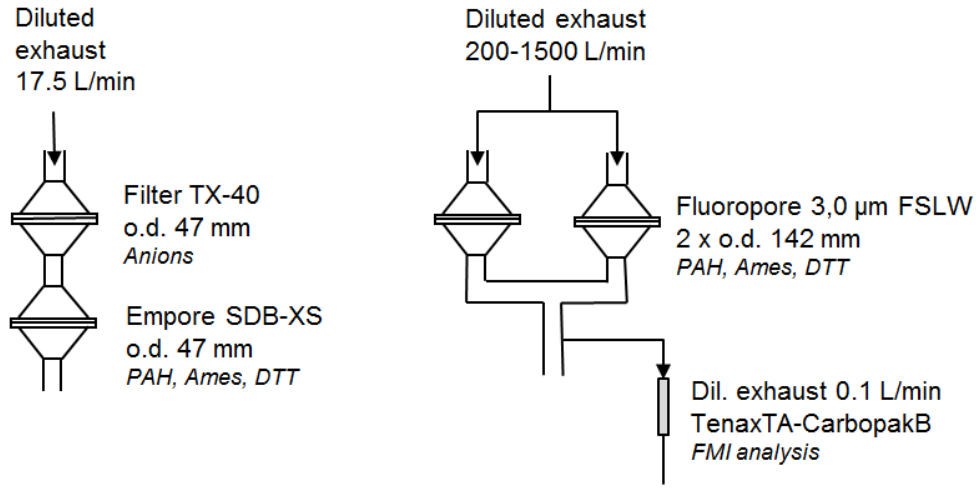



*Figure 11. Set-up of SVOC sampling with Empore disks and Tenax tubes.*

Empore disks

Collection of semivolatile organic compounds, SVOCs, using Empore disks was evaluated at VTT by Lappi et al. (1998) inspired by John Storey, ORNL within the IEA-AMF Annex 13 cooperation. Now a new type of material, Empore SDB-XC, was selected for the SVOCs collection.

Solid phase extraction (SPE) is commonly used for the extraction of liquid samples, but it can be used also in air sampling. The Empore SPE membrane consists of polytetrafluoroethylene (PTFE) fibrils impregnated with small particles of a solid sorbent e.g. C8. Airborne analytes are absorbed in the C8 phase and thus trapped, giving the membrane a high sampling capacity and simplifying the storage of the samples. The filtering efficiency of Empore membranes, which have 0.5 µm pores, demonstrated that even particles as small as 8 nm are retained in the membrane at pumping rates of up to 20 l/min. (Tollbäck et al. 2006).

Empore SDB-XC disks (∅ 47 mm) selected for semivolatile sampling in this project, is a poly(styrenedivinylbenzene) copolymer. Empore disks were located as back-up filters in a standard PM sampler after TX-40 filters. Diluted exhaust gas was drawn through PM filter and SVOC disk at flow rate of 17.5 L/min. The SVOC mass emission was defined by weighing the Empore disks before and after the emission test. The extracts of Empore disks were analysed for PAHs, mutagenicity and oxidative potential (DTT) (Chapter 4). In addition, samples were delivered to University of Eastern Finland for analysis of oxidative stress[11].

Empore sampling was accepted for SVOC sampling in the future projects at VTT.

Tenax-tubes sampling

In this work, Tenax TA Carbopak B-tubes were borrowed from the Finnish Meteorological Institute (FMI). Analysis method has originally been developed for ambient air samples. The Tenax TA Carbopack B-tubes were located in the high-capacity sampling after PM collection (Fluoropore filters). Flow rate was approximately 100 mL/min through tubes. Ten SVOC samples and one background sample were collected with Tenax-tubes (see Chapter 4).

The samples were analysed by Heidi Hellén (FMI) using thermal desorption and GC-MS technique. Analysing method is described in (Hellén 2006). The analysed compounds were as follows: *benzene, toluene, ethylbenzene, p/m-xylene, styrene, o-xylene, propylbenzene, 3-ethyltoluene, 4-ethyltoluene, 1,3,5-trimethylbenzene, 2-ethyltoluene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, carbon tetrachloride, heptane, octane, decane, nonane, isoprene, 2-methyl-3-butenol, α-pinene, camphene, β-pinene, carene, p-cymene, 1,8-cineol, limonene, terpinolene, linalool, myrcene, 4-acetyl-1-methylcyclohexene, nopinone, bornylacetate, geranylacetate, longicyclene, iso-longifolene, β-caryophyllene, aromadendrene, α-humulene, and 4-allylanisole.*

The results for benzene and toluene compared relatively well with those obtained using GC-FID (Figure 12) for other fuels than for **E85**. The analysed concentrations in the Tenax-tubes were very low for **E85**, and it is not known if the collection of samples had failed or if the alcohol containing exhaust gas did not suite for this type of Tenax-tubes.

[11] Oxidative stress measurements do not belong to this project and will be reported separately by UEF.

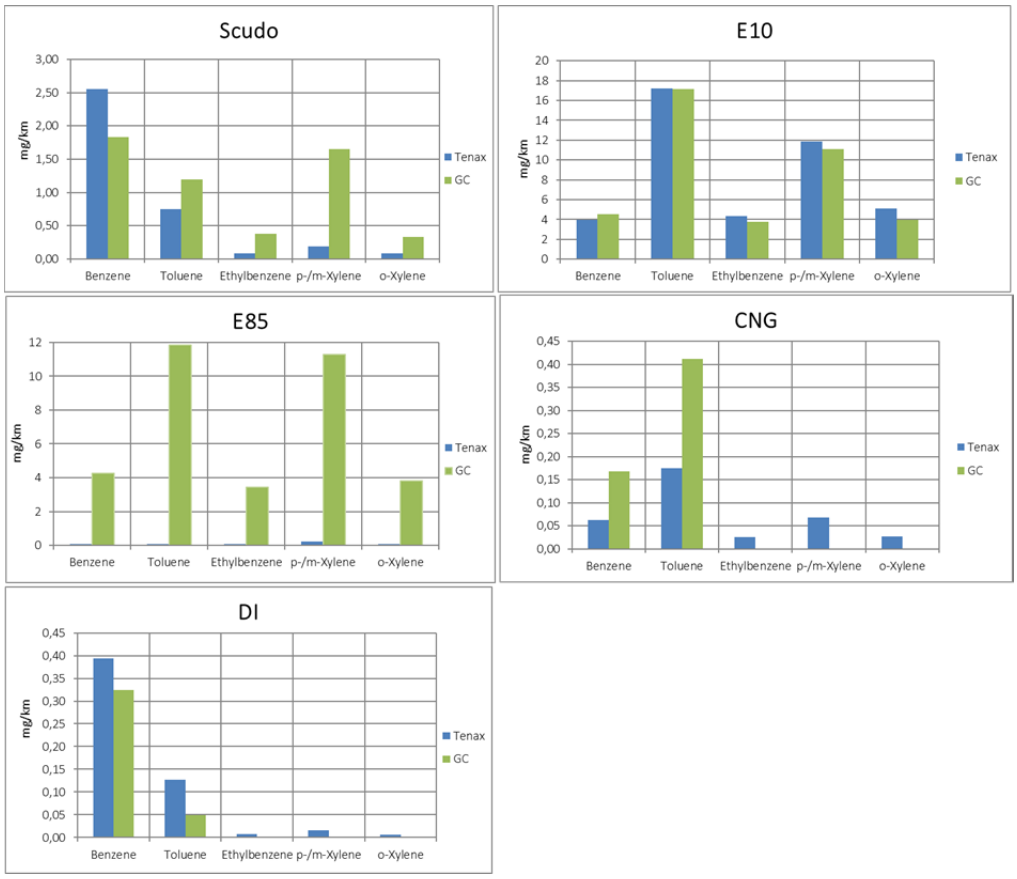



*Figure 12. Tenax-tube analysis results compared to GC-FID results for BTEX-compounds.*

## 3.3 Gaseous emissions

### 3.3.1 CO, $CO_2$ and $NO_x$ measurements (including $NO_2/NO_x$ ratio)

CO and $CO_2$ are analysed using NDIR principle. Nitrogen oxides are typically analysed by chemiluminescent principle (CLD), though the UN Regulation No. 83 also accepts the Non-Dispersive Ultra-Violet Resonance Absorption (NDUVR) type $NO_x$ analyzers. CLD is a proven and accepted method for measurement of "traditional" exhaust gas. However, in the presence of high concentrations of $NH_3$ or alcohols, aldehydes, water, and carbon dioxide, the $NO_x$ results obtained by CLD deserves consideration.

The $NO_x$ emission means a sum of exhaust NO and $NO_2$ calculated as $NO_2$. In the CLD measurement, exhaust $NO_2$ is first converted to NO and then the reaction between NO and $O_3$ (ozone) produces photons, which are detected.

Negative bias in $NO_x$ may occur, if exhaust $NO_2$ adsorbs on surfaces in the sampling system and dissolves in the condensed water. In the presence of $NH_3$ ammonium nitrate may be formed at sufficiently low temperatures, or $NH_3$ may react with $NO_x$ to $N_2$ (similarly as in SCR). (Hoard et al. 2007). In these cases, $NO_x$ is underestimated. If temperature in converter is sufficient, $NH_3$ may be converted to NO leading to overestimated $NO_x$. Ammonia could also cause loss of conversion efficiency of the $NO_x$ converter, but this would be revealed in routine calibrations. Hoard et al. (2007) compared FTIR, CLD and chemical ionization mass spectrometer (CIMS) for $NO_x$ emissions (Figure 13), and found the CLD analyser (Horiba) sensitive towards $NH_3$ concentrations.

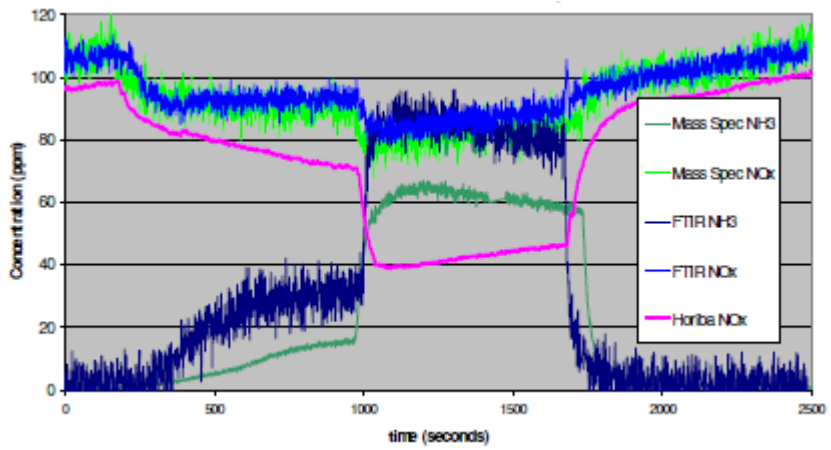



*Figure 13. Example of the $NO_x$ results obtained with different analyzers in the presence of ammonia (Hoard et al. 2007).*

In a study by Khalek et al. (2011) AVL's vacuum type CLD resulted in only 5% lower $NO_x$ results in the presence of 120 ppm $NH_3$, while atmospheric CLDs showed 21% lower $NO_x$ results in the same conditions, both analysers without scrubber. Ammonia scrubbers have been integrated into sampling systems to avoid this problem with CLD analysers in the presence of $NH_3$ (Shah et al. 2007).

In VTT's light-duty and heavy-duty measurements, vacuum type CLDs are in-use. Lower $NO_x$ was observed using old CLD than when using FTIR for the ammonia producing TWC equipped cars over the transient emission test (Figure 14) (Aakko-Saksa et al. 2011). However, for the new CLD at VTT, the $NO_x$ results obtained with CLD correlated relatively well with those obtained with FTIR (measurements of this project, Figure 15). Same humidity correction factor was used in the calculation of the regulated $NO_x$ results and the FTIR results.

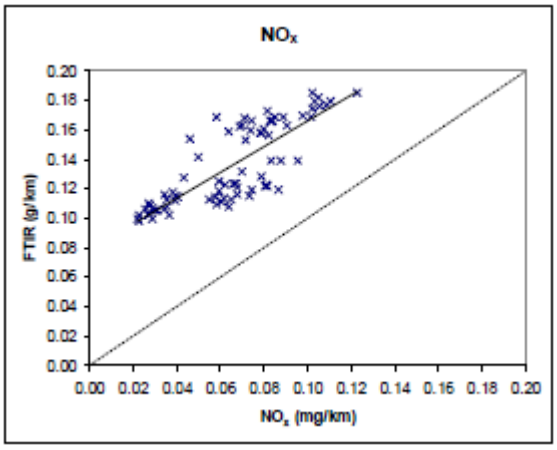



*Figure 14. The $NO_x$ results obtained with the traditional CLD are lower than those obtained by FTIR for TWC equipped cars (Aakko et al. 2011).*

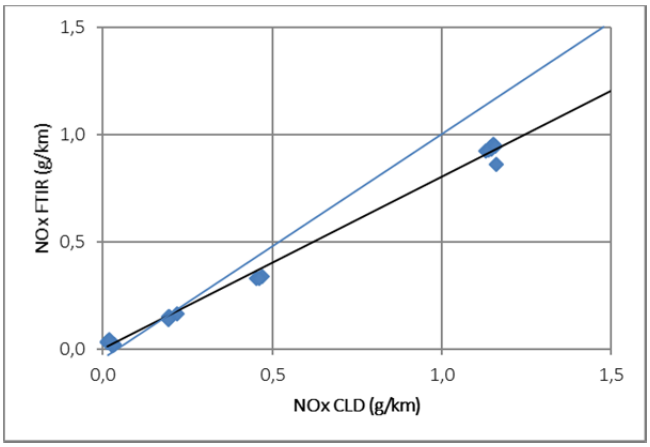



*Figure 15. $NO_x$ results obtained during the measurement campaign with traditional CLD compared to FTIR results.*

Presence of ammonia in the exhaust

Concern of traffic sources of ammonia ($NH_3$) has increased with the use of urea-based SCR systems for $NO_x$ control for diesel engines. However, 10 ppm limit for $NH_3$ applies to Euro VI heavy-duty diesel and gas engines, while ammonia emissions from cars are not limited.

High ammonia concentrations are common for TWC equipped cars. Figure 16 shows ammonia peak concentrations in the range of 300–500 ppm for model year 2011 TWC equipped car (Aakko-Saksa et al. 2015). Also in 90's, random ammonia peaks, for example 400 ppm, were observed with cars even when using high-sulphur gasoline (Aakko and Pentikäinen 1998). Ammonia (and as nitrous oxide) emissions from TWC equipped cars tend to increase with decreasing fuel sulphur content (Mejia-Centeno et al. 2007).

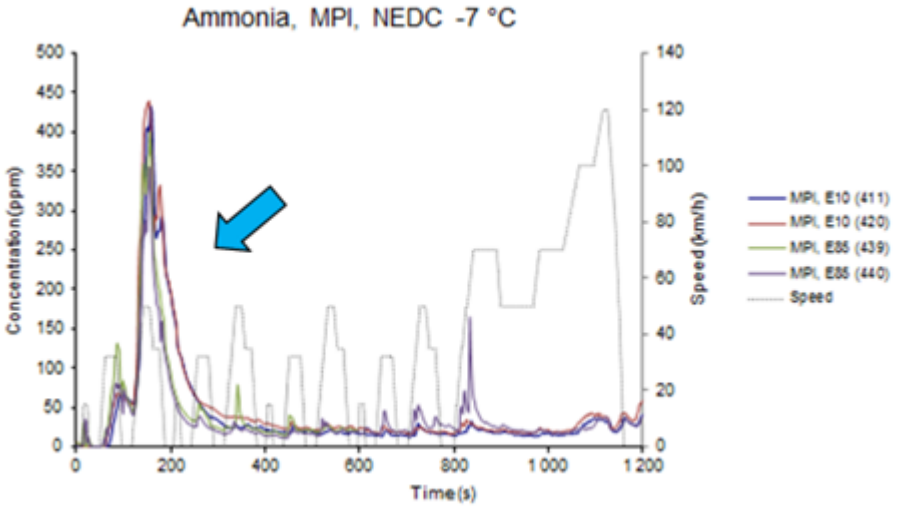



*Figure 16. Ammonia emissions over transient emission test with gasoline fueled TWC equipped cars, model year 2011 (Aakko-Saksa et al. 2015).*

At VTT, the $NO_x$ results from CLD are often compared to those from FTIR to reveal possible interferences with ammonia, alcohols or aldehydes that could bias the $NO_x$ results.

$NO_2/NO_x$ ratio

$NO_2/NO_x$ ratio can be calculated by using either mass emissions or concentrations (both give the same ratio).[12]

Some exhaust aftertreatment devices, especially DOCs and DPFs, tend to increase the $NO_2/NO_x$ ratio in the exhaust gases. Since January 2009, the US EPA has limited $NO_2$ emission from diesel retrofit technologies: $NO_2$ emissions from retrofitted engines must not be greater than 20% above baseline (b) engine levels. Determination of the $NO_2$ increase is based on mass emissions of $NO_2$ and $NO_x$ according to the procedure described by ARB (2011). Simplified equation for calculation procedure is presented in (7).

$$NO_2\ (increase - \%) = \frac{(NO_2 - NO_2^b)}{NO_x}\ x\ 100 \qquad (7)$$

### 3.3.2 Total hydrocarbons with oxygen containing fuels

A special issue concerns the total hydrocarbon emissions measured with a flame ionization detector (FID). In addition to hydrocarbons, all carbon-containing compounds, also oxygenates, give a response with an FID. This matter is discussed by Sandström-Dahl et al. (2010) and Aakko-Saksa et al. (2011). In the US, the Federal Test Procedure (FTP) emissions

[12] $NO_x$ is calculated as $NO_2$ and thus the same molecular weight is used in the calculation for NO and $NO_2$. In the case that NO emission is reported separately, its calculation principle should be visible.

measurement procedure takes into account the response of oxygenates with an FID by subtracting methane and alcohol (ROH) emissions multiplied by their respective response factors from hydrocarbon emissions measured with FID. In this way, so-called non-methane hydrocarbon emissions (NMHC) are obtained (8). Non-methane organic gases (NMOG) are calculated by adding alcohols and aldehydes (RHO) to NMHC (9). HC density used for calculations is 0.619 g/dm$^3$ at 273 K (0.5768 g/dm$^3$, 16.33 g/ft$^3$ at 293 K).

$$NMHC = HC_{FID} - 1.04*CH_4 - 0.66*ROH \quad (8)$$

$$NMOG = \Sigma NMHC + \Sigma ROH + \Sigma RHO \quad (9)$$

In the European emissions regulations (UN Regulation No. 83), calculation of the HC emissions uses a density of 0.619 g/dm$^3$ for gasoline ($C_1H_{1.85}$), 0.932 g/dm$^3$ for E85 ($C_1H_{2.74}O_{0.385}$) and 0.886 g/ dm$^3$ for E75 ($C_1H_{2.61}O_{0.329}$). Consequently, the result for the E85 and E75 fuels includes not only hydrocarbons, but also oxygen containing compounds, such as alcohols and aldehydes.

The effects of different calculation methods on the results are given for the FFV car using E85 fuel from study by Aakko-Saksa (2011) (Table 9). Hydrocarbon emissions achieved using the European calculation method for E85 fuel are at the same level as the US NMOG emissions. The regulated HC emission results in the European procedure represent all organic gases rather than the hydrocarbon emissions. Therefore, the total C1–C8 hydrocarbons (the total integration of GC-FID analysis) is recommended to be reported in addition to THC for the E85 and E75 fuels at VTT.

*Table 9. HC emissions from FFV car using E85 fuel with different calculation methods (Aakko-Saksa 2011).*

| | **HC emissions (g/km)** |
|---|---|
| European [a], density 0.619 g/dm$^3$ | 2.4 |
| European [b], density 0.932 g/dm$^3$ | 3.6 |
| NMOG (US) | 3.4 |

[a] UN regulation No. 83, HC density for gasoline [b] UN regulation No. 83, HC density for E85.

### 3.3.3 Individual hydrocarbons

Exhaust gases from gasoline and diesel fueled vehicles contain hundreds of compounds. Gaseous regulated emissions are collected in the Tedlar bags, where hydrocarbon losses are possible due to adsorption to the walls of bags or through chemical reactions. Lipari et al. (1990) analysed 103 individual hydrocarbons up to C12 from Tedlar bags. Most of the alkanes and olefins were stable in the Tedlar bag over a 48 hours period after sampling (e.g. ethylbenzene and xylenes varied by 10.5–13.3%), while concentration of 1,3-butadiene continually decreased (over 25% in 24 h and 70% in 48 h). The total integrated HCs did not vary more 5% in 24 hours. (Lipari 1990). The loss of 1,3-butadiene is likely due to its reactions with other exhaust species, such as $NO_2$.

Heavier C12–C24 hydrocarbons cannot be sampled from Tedlar bags due to their tendency for condensation under ambient temperature and pressure. Most typically, these hydrocarbons are collected using sorbents (see Chapter 4.2). (Natti 2007)

GC-FID method at VTT

Individual C1–C8 hydrocarbons have been analysed at VTT since early 90's by the GC-FID method (internal method 20.01). The diluted exhaust gas collected from the same Tedlar bags that are used for the measurement of the regulated emissions is fed through direct lines to the gas chromatograph, (HP 5890 Series II, $Al_2O_3$, KCl/PLOT column, FID detector, an external standard method). The hydrocarbons analysed are *methane, ethane, ethene, propane, propene, acetylene, isobutene, 1,3-butadiene, benzene, toluene, ethyl benzene and m-, p-, and o-xylenes.* Calibration gas contains all of the listed hydrocarbons. Methane is calibrated at 5–10 ppm concentration, 1,3-butadiene at below 1 ppm concentration and other compounds at concentrations below 5 ppm. The detection limit of the GC-FID method at VTT is 0.02 mol-ppm, which corresponds to approximately 0.1 mg/km for methane, 0.5 mg/km for 1,3-butadiene and 0.7 mg/km for benzene in the European emission test with cars. In addition, it is possible to integrate the total mass emissions of C1–C8 hydrocarbons including also those not calibrated in the method. Propane is used for calibration of total C1–C8 hydrocarbons. This is particularly suitable for alcohol fuels for which regulated total HC contains oxygenated compounds.

MicroGC method at VTT

To extend capacity to analyze individual hydrocarbons, a microGC analysis method is used at VTT in the measurements of large engines. The MicroGC is (semi) on-line with approximately 2 min time per sample. Feasibility of a microCG in addition to the GC-FID method for vehicle measurements was studied in this project. The microGC used was Agilent 490 MicroGC with the columns:

1) Molsieve, 10 m, Backflush, designed to separate hydrogen, CO, $CH_4$, $N_2$, $O_2$, and some noble gases
2) PoraPlot (PPU) 10 m, Backflush designed to separate ethane, propane, *i*-butane, and *n*-butane
3) $Al_2O_3$/KCl, Backflush designed to separate ethane, propane, *i*-butane, and *n*-butane
4) CP-Sil-5CB (8 m) designed to separate natural gas components. $N_2$, $CH_4$, $CO_2$, and ethane are not separated.

Calibration of the instrument was performed every day before the measurements. A span gas mixture contained propane (19.20 ppm), methane (246.30 ppm), ethane (19.50 ppm), and ethane (19.40 ppm). Detection limit of microGC is approximately 2 ppm for ethane, ethene, and propane and 10 ppm for methane.

The results obtained with traditional GC-FID method and with microGC were compared with each other over the phase I of the test cycle. The analyses were conducted from Phase I of the test cycle, after the cold start, in which the hydrocarbon emissions are at the highest. Samples for GC-FID and microGC were taken from the same CVS Tedlar bags.

For the E10 fuel concentrations of methane, ethane, and propane in the diluted exhaust gas were below the detection limit of microGC. However, the results of methane, ethane, ethene, and propane, analysed with GC-FID and with microGC correlated relatively well with each other when the concentrations were sufficient (Figure 17).

Detection limits of MicroGC were deemed to be too high for accurate analysis of hydrocarbon emissions from vehicles. In addition, MicroGC measures only C1-C3 hydrocarbons with this configuration. In some cases, the MicroGC would be useful for vehicle measurements at VTT.

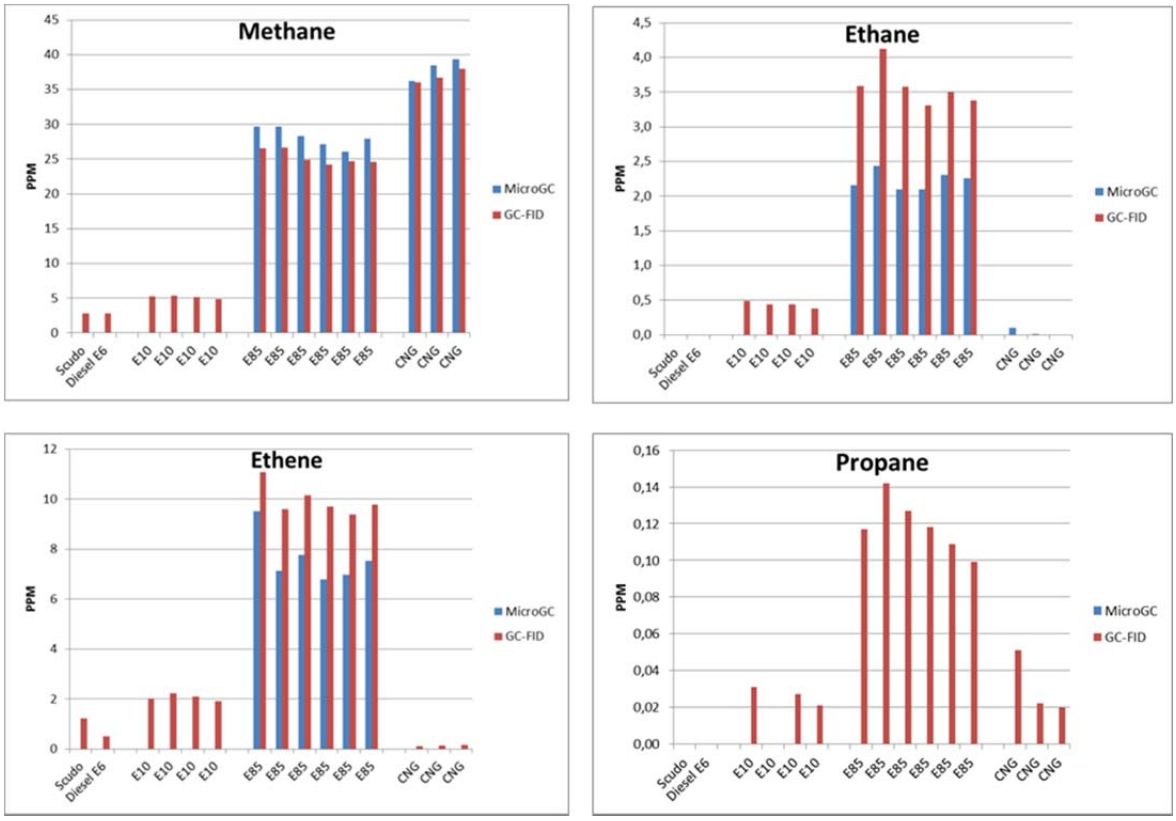



*Figure 17. Comparison of the results of methane, ethane, ethene, and propane obtained with GC-FID and with microGC.*

### 3.3.4 Carbonyl compounds using DNPH collection and HPLC analysis

Carbonyl compounds, i.e. aldehydes and ketones, are most commonly collected from the diluted exhaust gas using the cartridges, in which acidified 2,4-dinitrophenylhydrazine (DNPH) forms stable hydrazine derivatives from carbonyl compounds (Figure 18). In the US, formaldehyde emissions from cars are limited in regulation 40 CFR 86 (US EPA 2010), which includes also measurement method for formaldehyde emission. According to this regulation, the carbonyl collection sample lines needs to be heated to prevent condensation (3 °C above the maximum dew point of the sample, but below 121 °C). (40 CFR 86). Hydrazine derivatives are eluted by acetonitrile and analysed by HPLC.

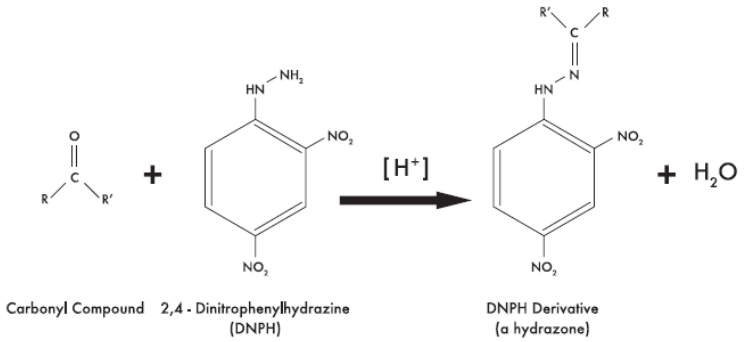



*Figure 18. Acidified 2,4-dinitrophenylhydrazine forms stable hydrazine derivatives from carbonyl compounds (Waters).*

**Analysis of aldehydes at VTT**

Aldehydes have been analysed at VTT using a DNPH/HPLC-UV or FTIR methods since early 90's (internal method M21.01). DNPH/HPLC-UV method is described in this Chapter and the FTIR method in Chapter 4.3.7.

In the DNPH/HPLC-UV method at VTT, aldehydes are collected from the CVS diluted exhaust gas (113 ± 8 °C) using 2,4-dinitrophenylhydrazine (DNPH) cartridges either in different test phases or over the emission test. The DNPH derivatives are extracted with an acetonitrile, diluted with water (1:1) and analysed using HPLC technology (Agilent 1260, UV detector, Nova-Pak C18 column). Aldehydes reported are *formaldehyde (FA), acetaldehyde (AA), acrolein (Acro), propionaldehyde (PrA), crotonaldehyde (CrA), methacrolein (MeAc), butyraldehyde (BuA), benzaldehyde (BzA)), valeraldehyde (VA), m-tolualdehyde (mTol), and hexanal (HexA).* Acetone and methyl ethyl ketone are included in the analysis, but they are not reported due to the high risk of contamination with the common laboratory chemicals. Detection limit for formaldehyde is 0.015 ppm in the DNPH/HPLC-UV method.

In 2011, VTT's PDP system was changed to critical flow venturi system (CFV-CVS) and aldehyde sampling was updated consequently to correspond recommendation by US EPA (2010) (Figure 19).

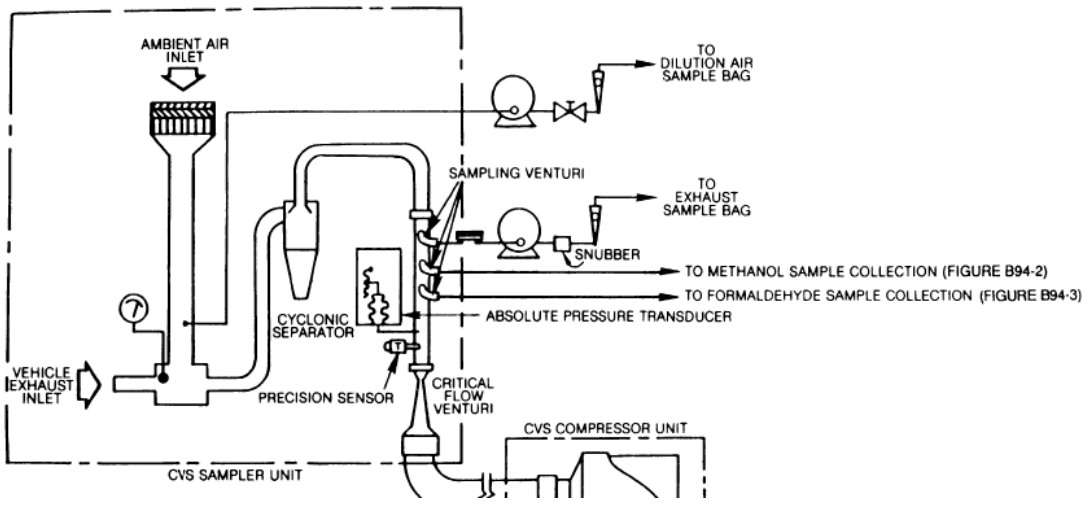



*Figure 19. Sampling of carbonyl compounds from exhaust gas sampling system (US EPA 2010).*

For the DNPH cartridges (Sep-Pak, Waters), a flow rate of 0.1−1.5 L/min through a DNPH cartridge is recommended by manufacturer. Collection efficiency is 95% at flow rates up to 1.5 L/min. Breakthrough of sampler may exhibit, if sampling flow is over 1.5 L/min or if the amount of sample collected is more than 50% of the amount of DNPH (Waters).

Some of the new alternative fuels, engines, and aftertreatment systems emit a large amount of $NO_2$ interfering with the analysis of the carbonyl compounds. In addition to the carbonyl compounds, $NO_2$ reacts with DNPH derivatives and consumes the DNPH reagent in the cartridges. For high carbonyl concentrations and/or high $NO_2$ emission level, a combination of a ”long-body” DNPH cartridge having larger capacity and “XpoSure” cartridge as a backup is used. Lower flowrate through DNPH-cartridges can also be applied. The $NO_2$ output of cars is checked during the preparation tests to enable design of a proper test set-up.

### 3.3.5 Alcohols

In the US, methanol emission measurement from cars is described in regulation 40 CFR 86 (US EPA 2010). According to the 40 CFR 86 rule, the collection using impingers charged with pure deionized water shall be placed in the methanol sampling system (Figure 19 for critical flow venturi system). Sample line needs to be heated to prevent condensation using temperature below 121 °C, but 3 °C above the maximum dew point of the sample (40 CFR 86).

At VTT, alcohols from exhaust gases are typically analysed using FTIR (Chapter 4.3.7). However, in some cases alcohols are collected also in water (deionized, 25 mL) impingers on ice bath through heated lines (113 ± 8 °C) at flow rate of 1-1.58 L/min. Alcohols are analysed by gas chromatograph using Carbowax 20M or FFAP columns and propanol as an internal standard. Detection limit of impinger method is 1 ppm. (Lappi and Rihko 1996).

### 3.3.6 FTIR – multicomponent analysis: $NH_3$, $N_2O$, alcohols, aldehydes, and ethers

#### 3.3.6.1 General

Fourier transformation infra-red (FTIR) technique is an effective tool for fast on-line measurements. IR radiation absorbed by molecule at characteristic frequencies leads to “higher” energy state in the form of vibrations and rotations. This changes the dipole moment of the molecule. Almost all compounds absorb IR radiation, except homonuclear dimolecular gases, such as oxygen, nitrogen, and hydrogen, and noble gases, such as, helium, neon, and argon.

IR techniques are, amongst others, non-dispersive infrared (NDIR), dispersive infrared and Fourier Transform Infrared (FTIR) spectroscopy. By NDIR, one compound at time can be analysed. Dispersive IR scans narrow wavelength area at time ending up to whole spectrum. FTIR results in whole spectrum similarly to dispersive IR, but technique is different. For FTIR, the interferometer divides a beam of radiation: half of the beam goes to a fixed mirror and another half to a moving mirror. Both beams are returned to the beam splitter and combined beams are directed through sample to detectors. The interferogram is Fourier transformed to the frequency spectrum. Background spectrum is reduced from sample spectrum. An example of spectrum from diesel exhaust gas measured with Gasmet Cr-2000 is shown in Figure 20. Usual range of infrared spectrum is from 600 $cm^{-1}$ to 4000 $cm^{-1}$.

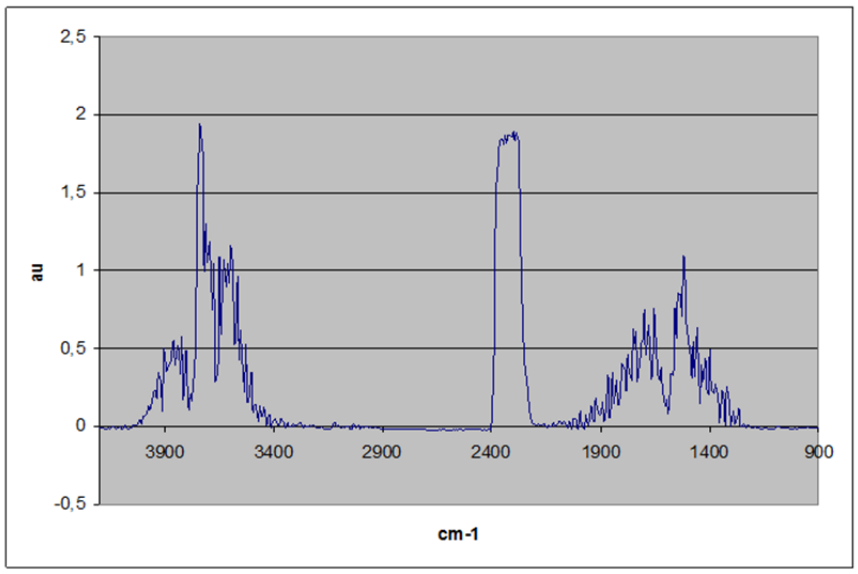



*Figure 20. Spectrum from diesel exhaust gas measured with Gasmet Cr-2000 at VTT (Ahonen 2006).*

Sufficient resolution of FTIR is required to identify compounds from mixtures with overlapping absorption bands. Resolution is improved by the design of the interferometer (longer optical path). Resolution, noise to signal ratio (SNR) and measurement time can be optimized when equipment is designed for purpose.

For identification and quantification of compounds from the FTIR spectrum of unknown mixture of compounds, multicomponent analysis is needed. Analysis is demanding, if sample contains many compounds with overlapping absorption bands. For example, water and carbon dioxide show broad, strong absorption bands. Library spectra of pure compounds are basis for the calculation of the best fit spectrum with the spectrum of sample. The difference between calculated and measured spectrum is a measure of success of analysis. (Ahonen 2006).

#### 3.3.6.2 FTIR analysis at VTT

VTT has over 20 years experience in using the FTIR technology in the exhaust gas measurements, at first with SESAM II (Fast) in the beginning of 90's (Aakko *et al*. 1994). Today, by using Gasmet Cr-2000 equipment, typically more than 10 compounds are measured simultaneously at two-second intervals from vehicle exhaust gases, and up to 50 different compounds could be measured according to manufacturer. Gasmet Cr-2000 analyzer is designed especially for the vehicle exhaust measurements.

In this project, FTIR methods for Gasmet Cr-2000 were reviewed and updated to reflect alternative fuels, engines, and vehicle of today. Calculation procedures of the FTIR-results were updated to perform with various driving cycles and to correspond better with the calculation methods of regulated emissions.

In 2015, VTT purchased a new FTIR instrument from Rowaco. The basic characteristics of the new instrument are also described in this Chapter.

#### 3.3.6.3 Gasmet Cr-2000 FTIR at VTT

The Gasmet Cr-2000 incorporates a FTIR spectrometer, a temperature controlled sample cell, and signal processing electronics (Table 10). Detector is liquid nitrogen cooled MCT (HgCdTe) detector. Raw exhaust gas (filtered) is introduced to Gasmet at flow rate of 4-5

liters per minute (L/min). Measurement is conducted at temperature of 180 °C, which is high enough to prevent condensation. Temet Carousel Interferometer of Gasmet is designed for portable equipment. Gasmet measures 10 scans (interferograms) in second. The exhaust gas flow through cell is changed in approximately three seconds. Successful multicomponent analysis requires that reference (library) spectra of all compounds present in sample mixture are taken into account in the methods.

*Table 10. Technical data of Gasmet Cr-2000.*

| | | |
|---|---|---|
| Spectrometer | • IR source: | SiC |
| | • Resolution: | 8 $cm^{-1}$ |
| | • Spectrum range: | 600-4200 cm-1 |
| | • Detector: | MCT, liquid $N_2$ cooled |
| | • Interferometer: | Temet Carousel |
| Cell and sample | • Path length: | fixed 2.0 m |
| | • Cell temperature: | 180 °C |
| | • Sample cell volume: | 0,22 l |
| | • Sample: | raw exhaust gas, filtered (2 µm) |
| | • Sample flow: | 2 – 10 liters per minute |
| | • Purging gas: | nitrogen |

## Calibrations

Gasmet is calibrated with single-component gases. Water calibration is done twice a year, and zero calibration with nitrogen before every measurement. The frequency of water calibrations has been found essential for e.g. $NO_x$ analysis repeatability. The water calibrations are stored for (post-)processing of data.

## Detection limits

The concentrations of many compounds are low in the exhaust gas of cars and vehicles. Detection limits[13] based on manufacturers' reference spectra for pure/interference free components in nitrogen are summarized in Table 11.

[13] Detection limits are calculated as 3*STDEV/A*e, where STDEV is standard deviation of noise (nitrogen), A is the peak absorbance, e is concentration. (reference spectrum, the lowest concentration).

*Table 11. Detection limits of Gasmet Cr-2000 determined from manufacturer's reference spectra at one-second intervals as concentrations.*

| | Detection limit at 1-second intervals (ppm) |
|---|---|
| Carbon monoxide (CO) | 7 |
| Nitric oxide (NO) | 13 |
| Nitrogen dioxide ($NO_2$) | 2 |
| Nitrous oxide ($N_2O$) | 4 |
| Ammonia | 2 |
| Methane | 2 |
| Ethanol | 4 |
| Isobutanol | 3 |
| *n*-Butanol | 5 |
| ETBE | 2 |
| Formaldehyde | 5 |
| Acetaldehyde | 5 |
| Water vapor H2O | 1400 |
| Carbon dioxide CO2 | 600 |
| Sulfur dioxide SO2 | 2 |
| Ethane C2H6 | 4 |
| Ethylene C2H4 | 3 |
| Acetylene C2H2 | 6 |
| Propane C3H8 | 2 |
| Propylene C3H6 | 9 |
| Butane C4H10 | 2 |
| 1.3-Butadiene C4H6 | 4 |
| Benzene C6H6 | 5 |
| Toluene C7H8 | 4 |
| Methanol CH4O | 4 |
| MTBE | 3 |
| TAME | 2 |
| Acetic acid C2H4O2 | 3 |
| Dodecane C12H26 | 1 |
| Isocyanic acid HNCO | 15 |
| Hydrogen cyanide HCN | 8 |

**Correlation between FTIR and traditional analyses**

The results obtained by FTIR at VTT have been compared with those from the traditional measurement methods for example in Aakko-Saksa et al. (1994, 2011) and for the results obtained in this project (Figure 21). For some exhaust species, the correlation between FTIR and the traditional method is good, whereas FTIR is not applicable for monitoring small changes in, for example, hydrocarbons. For the discussion on the $NO_x$ emissions, see Chapter 3.3.1.

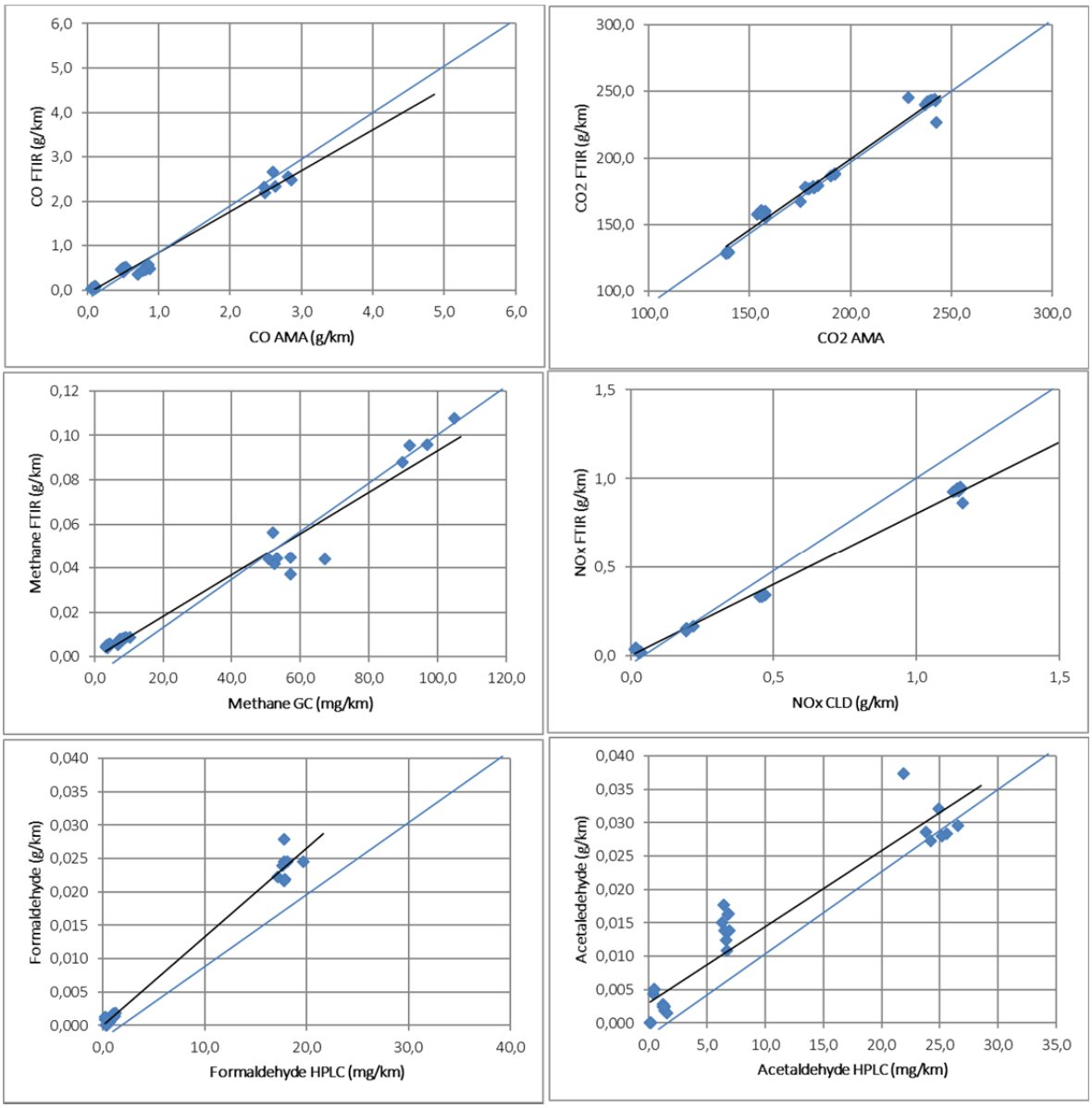



*Figure 21. Correlation between the results obtained with FTIR and with traditional measurement methods from the measurement campaign in this project (Chapter 4).*

**Methods for alternative fuels**

IR spectrum is a sum of the spectra of all individual compounds of the exhaust sample. Quantitative analysis of a compound requires that there is at least one wavelength region without overlapping of the other compounds. Each significant compound existing in the exhaust gas needs to be calibrated in several concentrations up to the highest concentration of the sample. The regions used in the measurement and the regions with interfering signals need to be defined. For gasoline and diesel, exhaust gases contain numerous compounds, and specific regions for each individual exhaust species do not exist. For example, aromatic compounds can be analysed as a sum of aromatics rather than separately as benzene, toluene, and xylenes due to overlapping signals of these compounds. Exhaust gases contain also high content of water and carbon dioxide covering a wide range of the IR spectrum, which complicates analysis of the individual compounds of the exhaust gases (Aakko et al. 1994).

In Figure 22 absorbances of CO, NO, $NO_2$, $N_2O$, and benzene are shown.

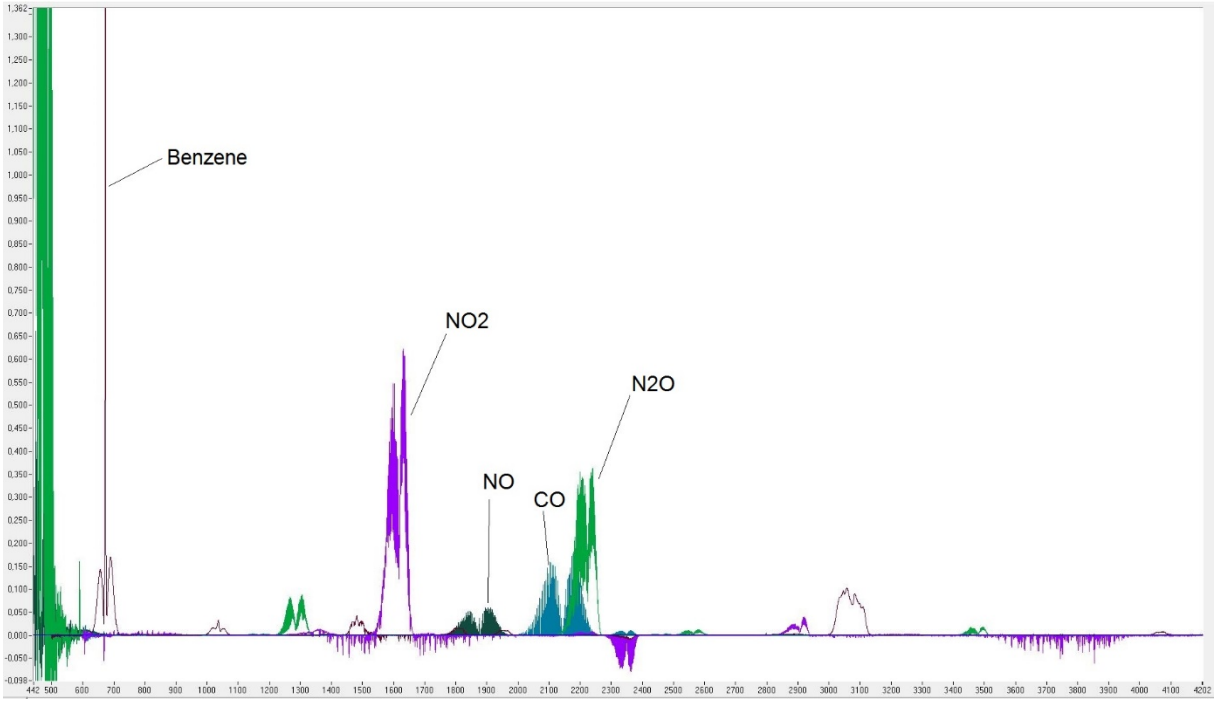



*Figure 22. Absorbances of CO, NO, $NO_2$, $N_2O$, and benzene (Rowaco FTIR calibration gas database).*

In past, only traditional hydrocarbonaceous gasoline and diesel were used as fuels and cars were equipped only with the TWCs or oxidation catalysts. Today, gasoline may contain alcohols and ethers, and diesel cars are equipped with complex exhaust after treatment technologies. Various alternative fuels, vehicles and emission control technologies are in the market, and development of these technologies are progressing all along. Eerroneous results may be obtained particularly when missing relevant compounds from the FTIR methods. Thus adjusted methods are needed for the FTIR analyses of different exhaust gases. The FTIR methods at VTT were updated:

- Method for the gasoline was enlarged to consider various alcohols and ethers present in the exhaust gas: *methanol, ethanol, propanol, butanol, MTBE, ETBE, and TAME*.
- Separate methods have been used for *diesel and for the SCR equipped* diesel applications. Today, many of the diesel applications are equipped with SCR and thereby diesel method was enlarged to apply to SCR, too.
- FFV cars can use gasoline containing *high concentration alcohols*. So called E85 fuel contains up to 85% ethanol blended with gasoline. Exhaust constituents relevant for the gasoline method were updated in the FFV method.
- *The ED95 concept* means using high concentration ethanol with ignition improver and other additives in Scania's alcohol engine (compression ignition)[14]. The ED95 fuel used in Sweden is called Etamax D, which contains 92% (m/m) of hydrated ethanol (grade 95%), 5.0% (m/m) ignition improver, 2.8% (m/m) denaturants, (2.3% (m/m) MTBE and 0.5% (m/m) isobutanol) and corrosion inhibitor additive. (Westman 2008).

[14] The ED95 fuel is used in Sweden and some other countries in buses and trucks manufactured by Scania.

These constituents of the ED95 fuel were taken into account for the FTIR method. In addition, methanol was also added in the method to apply to the MD95 concept.

- Development of the FTIR method for *natural gas (NG)* is challenging due to various engine technology options feasible for methane use. In addition, the quality of methane itself varies leading to differences in the exhaust gases. For example, Russian natural gas has a high content of methane, while NG from many other sources may contain substantial concentrations of $C_2$+ hydrocarbons and traces of $H_2S$. Methane originating from biogas may contain traces of siloxanes or $H_2S$ depending on the source and purification technology used.

  Traditionally the main engine technology for NG has been the spark-ignition (Otto) engine, either stoichiometric or lean-burn. In addition, dual-fuel engines based on compression-ignition engines have been developed:

  - Dedicated stoichiometric spark-ignition TWC equipped NGVs for methane only (mono-fuel). Meets the most stringent emission legislation.
  - Bi-fuel stoichiometric spark-ignition NGVs using either gasoline or natural gas, typically equipped with a TWC. Possible gasoline start may increase emissions before TWC has reached its operating temperature.
  - Lean-burn spark-ignition NG engines using indirect or direct fuel injection and excess oxygen. Typically equipped with an oxidation catalyst to reduce the CO and HC emission (no influence on $NO_x$).
  - Dual-fuel compression-ignition NG/diesel engines. Diesel pilot is used as the ignition source for the natural gas-air mixture. Diesel substitution ratios vary depending on the dual-fuel engine technology. For the dual-fuel engine, meeting the most stringent emission legislations using similar after-treatment technology as for diesel engines is required (SCR, oxidation catalyst, DPF).

  Due to the many different technologies available for methane use, an extensive selection of compounds was added in the FTIR analysis method for CNG.

- *Hydrogen cyanide* (HCN) could be formed when exhaust gases contain ammonia and hydrocarbons, and thus HCN was added in the FTIR methods.

The updated methods for Gasmet Cr-2000 at VTT for vehicle tests cover diesel, gasoline, E85/FFV, ED95 (also for MD95) and CNG. The new FTIR methods were studied using cross-analysis: spectra from different fuels/vehicles were analysed with different FTIR methods (Table 12). Gasoline method showed good results for diesel spectrum, E85 / FFV spectrum and CNG spectrum. Gasoline and diesel methods resulted in comparable results for the SCR spectrum. Results for an E85/FFV spectrum analysed using the FFV method and the gasoline method corresponded each other. The ED95 method gave different NO, ethylene and CO results when compared to the other methods in some cases. The results for a CNG spectrum analysed by the CNG, gasoline and diesel methods compared relatively well with each other.

Cross-analysis (sensitivity analysis) showed that in some cases the differences in the results were surprisingly small. For example, updated extensive gasoline method gave good results for gasoline, diesel, E85(FFV) and CNG spectra.

*Table 12.Cross-analysis of exhaust from diesel, gasoline and SCR equipped diesel vehicles using methods developed at VTT for the Gasmet Cr-2000 instrument.***

| | | Detection limit | Diesel spectrum | Max diff. btw method | Gasoline spectrum | Max diff. btw metho | FFV spectrum | Max diff. btw metho | ED95 spectrum | Max diff. btw method | MD95 spectrum | Max diff. btw method | CNG spectrum | Max diff. btw metho |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Water vapor H2O | % | 0,14 | 5,7 | 0,0 | 10,5 | 0,0 | 15,2 | 0,0 | 12,0 | 0,0 | 7,9 | 0,0 | 18,2 | 0,0 |
| Carbon dioxide CC | % | 0,06 | 5,7 | 0,2 | 12,8 | 0,7 | 13,6 | 1,0 | 8,6 | 0,6 | 4,3 | 0,3 | 11,0 | 0,5 |
| Carbon monoxide | ppm | 7 | 577,6 | 29,9 | 595,4 | 20,9 | 1139,6 | 100,6 | 104,0 | 15,8 | 74,4 | 10,9 | 39,0 | 14,0 |
| Nitric oxide NO | ppm | 13 | 26,2 | 0,7 | 24,5 | 2,2 | 94,6 | 6,5 | 189,4 | 1,9 | 132,7 | 0,3 | 6,6 | 0,0 |
| Nitrogen dioxide N | ppm | 2 | 0,6 | 0,0 | 0,0 | 0,1 | 1,0 | 0,1 | 15,6 | 1,9 | 27,0 | 0,3 | 0,3 | 0,1 |
| Nitrous oxide N2O | ppm | 4 | 3,8 | 1,6 | 0,6 | 0,5 | 0,5 | 0,9 | 0,0 | 0,0 | 0,0 | 0,3 | 0,0 | 0,1 |
| Ammonia NH3 | ppm | 2 | 0,7 | 0,2 | 36,0 | 0,1 | 15,5 | 0,8 | 11,4 | 0,6 | 0,0 | 0,0 | 2,0 | 0,2 |
| Sulfur dioxide SO2 | ppm | 2 | 0,9 | 0,3 | 0,8 | 0,7 | 0,3 | 1,9 | 1,4 | 0,8 | 0,0 | 0,0 | 1,2 | 5,7 |
| Methane CH4 | ppm | 2 | 15,4 | 0,9 | 11,9 | 0,8 | 34,3 | 4,9 | 0,0 | 1,1 | 0,1 | 0,3 | 3,1 | 1,5 |
| Ethane C2H6 | ppm | 4 | 1,1 | 0,5 | 1,0 | 0,3 | 4,3 | 52,1 | 4,5 | 23,6 | 0,0 | 0,0 | 0,2 | 1,3 |
| Ethylene C2H4 | ppm | 3 | 18,2 | 11,8 | 5,4 | 2,4 | 12,0 | 3,0 | 15,7 | 15,7 | 6,6 | 6,6 | 1,7 | 1,2 |
| Acetylene C2H2 | ppm | 6 | 0,8 | 0,8 | 1,8 | 1,0 | 1,5 | 0,6 | 0,6 | 11,0 | 0,0 | 0,0 | 0,0 | 0,0 |
| Propane C3H8 | ppm | 2 | 0,2 | 1,3 | 4,1 | 3,9 | 1,2 | 10,8 | 2,4 | 5,1 | 0,0 | 0,0 | 0,2 | 1,5 |
| Propylene C3H6 | ppm | 9 | 8,7 | 7,4 | 13,2 | 7,9 | 11,4 | 6,8 | 0,7 | 0,7 | 0,4 | 0,9 | 6,5 | 4,3 |
| Butane C4H10 | ppm | 2 | 3,8 | 2,7 | 8,7 | 0,5 | 4,7 | 24,3 | 1,1 | 7,4 | 0,0 | 0,0 | 0,6 | 0,3 |
| 1.3-Butadiene C4H | ppm | 4 | 0,8 | 0,6 | 1,3 | 1,7 | 1,4 | 8,4 | 0,0 | 0,0 | 0,0 | 0,0 | 0,1 | 1,7 |
| Benzene C6H6 | ppm | 5 | 2,7 | 0,9 | 6,2 | 1,2 | 6,0 | 1,4 | 1,7 | 1,7 | 2,8 | 1,2 | 4,4 | 2,7 |
| Toluene C7H8 | ppm | 4 | 1,6 | 1,6 | 2,0 | 5,5 | 1,1 | 3,3 | 0,0 | 1,3 | 0,6 | 0,2 | 13,2 | 3,1 |
| Formaldehyde CH2 | ppm | 5 | 13,9 | 1,7 | 0,2 | 0,2 | 1,5 | 1,9 | 0,4 | 2,7 | 1,9 | 2,7 | 0,0 | 0,0 |
| Acetaldehyde C2H4 | ppm | 5 | 5,4 | 3,5 | 0,0 | 2,1 | 9,9 | 3,8 | 0,9 | 2,2 | 0,0 | 0,0 | 1,9 | 0,5 |
| Ethanol C2H6O | ppm | 4 | * | *2,6* | 0,1 | 5,2 | 135,7 | 10,5 | 66,3 | 5,6 | 1,2 | 0,2 | 0,3 | 0,0 |
| Methanol CH4O | ppm | 4 | * | *3,2* | 1,7 | 3,6 | 4,6 | 1,1 | 0,3 | 0,4 | 146,7 | 1,4 | 4,0 | 0,0 |
| Propanol C3H8O | ppm | | * | * | * | * | * | * | * | * | * | * | * | 0,0 |
| 1-Butanol | ppm | 5 | * | *0,2* | 0,1 | 0,2 | 2,9 | 1,6 | 0,9 | 0,8 | 0,0 | 0,0 | 2,4 | 0,0 |
| MTBE | ppm | 3 | * | *0,4* | 0,1 | 0,0 | 0,4 | 0,0 | 0,0 | 0,0 | 0,3 | 0,3 | 0,0 | 0,0 |
| ETBE | ppm | 2 | * | *2,5* | 0,0 | 1,6 | 4,0 | 4,0 | 2,6 | 2,6 | 1,7 | 0,5 | 0,0 | 0,0 |
| TAME | ppm | 2 | * | *0,1* | 0,0 | 0,0 | 0,0 | 0,0 | 0,0 | 0,1 | 0,0 | 0,0 | 0,0 | 0,0 |
| Acetic acid C2H4O | ppm | 3 | 7,5 | 0,0 | * | *0,9* | * | *0,9* | * | 0,0 | * | 0,0 | * | 0,3 |
| Dodecane C12H26 | ppm | 1 | 1,7 | 0,1 | 0,3 | 0,0 | 0,2 | 0,2 | 1,0 | 0,5 | 0,5 | 0,2 | 0,1 | 0,1 |
| Isocyanic acid HN | ppm | 15 | 0,0 | 0,0 | * | *0,0* | * | *0,0* | * | 0,0 | * | 0,0 | * | 26,5 |
| HCN | ppm | 8 | 0,5 | 0,1 | 2,3 | 0,1 | 0,4 | 0,3 | 5,9 | 2,3 | 1,2 | 1,2 | 0,0 | 0,0 |
| NOx | ppm (calc.) | | 26,8 | 0,7 | 24,6 | 2,2 | 95,5 | 6,5 | 205,0 | 0,7 | 159,7 | 0,6 | 6,9 | 0,1 |
| Spectrum id/no of methods | | | 13291ED | 5 | 13423EB | 2 | 13429EA | 5 | 14007ag4 | 5 | 14172ag4 | 2 | 14R407 | 3 |

*) compound does not belong to the method. **) Grey numbers are below the detection limit.

## Note on the exhaust flow needed for the calculation of the FTIR results

Calculation of the mass-based FTIR results requires the volumetric flow of the raw exhaust gas in one second time intervals. This is calculated based on the constant CVS flow of the diluted exhaust gas and dilution ratio (DR) in one second time intervals. This is a substantial source of uncertainty in the results.

At VTT, DR is calculated based on modal analyses of $CO_2$ concentrations from diluted and raw exhaust gas (10). It should be noted that so called dilution factor (DF) of ECE R83 is based on the stoichiometric combustion, and it is not true DR for vehicles using lean combustion principle, such as diesel vehicles.

$$DR = \frac{c_{raw\_wet} - c_{background}}{c_{dil\_wet} - c_{background}} \qquad (10)$$

$c_{raw\_wet}$ = concentration in raw exhaust gas
$c_{dil\_wet}$ = concentration in the diluted exhaust gas
$c_{background}$ = background concentration

All concentrations in equation (10) need to be either dry or wet (not mixed). At VTT, diluted exhaust gas is dry, while raw exhaust gas is (semi)wet in the $CO_2$ analysers. Therefore wet/dry conversions are needed for calculation of DR (equation 11).

$$C\ wet\ =\ C\ dry\ *\ (1-w) \qquad (11)$$

w = water fraction, for example 0.1 represents 10% of water (at 3 °C 0.754 %(V/V) water is present in dry exhaust)

Due to high uncertainties related to the volumetric flow of the raw exhaust gas, the $CO_2$ mass emission results obtained by FTIR are compared to the $CO_2$ results obtained by NDIR from regulated Tedlar bag samples to verify that the calculations.

#### 3.3.6.4 Rowaco FTIR at VTT

The Rowaco MKS MiniMega 2030 incorporates a FTIR spectrometer, a temperature controlled sample cell, and signal processing electronics (Table 13). Detector is liquid nitrogen cooled MCT (HgCdTe) detector. Raw exhaust gas (filtered) is introduced to Rowaco at flow rate of 12 liters per minute. Measurement is conducted at temperature of 191 °C. Very low resolution of 0.5 $cm^{-1}$ enables good quantitative analysis. Sampling frequency of Rowaco is 1 Hz and data saving interval 1 s.

*Table 13. Technical data of Rowaco MKS MiniMega 2030.*

| | | |
|---|---|---|
| Spectrometer | • Window: | ZnSe |
| | • Mirrors: | Au |
| | • Resolution: | 0,5 $cm^{-1}$ |
| | • Spectrum range: | 400 – 4000 cm-1 |
| | • Detector: | MCT, liquid $N_2$ cooled |
| Cell and sample | • Path length: | 5.11 m |
| | • Cell temperature: | 191 °C |
| | • Sample cell volume: | 200 mL |
| | • Sample: | raw exhaust gas, filtered (2 µm) |
| | • Sample flow: | 12 lpm possibility to 0 – 18 lpm |
| | • Purging gas: | nitrogen |

Rowaco is calibrated with single-component gases. Zero calibration with nitrogen (background) is done before every measurement. Detection limits and ranges given by the manufacturer are summarized in Table 14.

*Table 14. Detection limits and ranges given by the manufacturer, Rowaco.*

| | MDL* | Range |
|---|---|---|
| Carbon monoxide (CO) | 0,75% | - |
| Nitric oxide (NO) | 1 ppm | 3000 ppm |
| Nitrogen dioxide ($NO_2$) | 0.6 ppm | 2000 ppm |
| Nitrous oxide ($N_2O$) | 0.4 ppm | 300 ppm |
| Ammonia | 0.4 ppm | 3000 ppm |
| Methane | 0.6 ppm | 3000 ppm |
| Ethanol | 2.5 ppm | 1 % |
| Isobutanol | Estimated 1 - 2 ppm | 280 ppm |
| *n*-Butanol | Estimated 1 - 2 ppm | 930 ppm |
| ETBE | 1 - 2 ppm | 1000 ppm |
| Formaldehyde | 0.75 ppm | 70 ppm |
| Acetaldehyde | 3 ppm | 1000 ppm |

*Detection limit: 3 x Std dev of measured values in 10% $H_2O$ and 10% $CO_2$ for 1 Hz analysis

## 3.4 PM and SVOC characteristics

### 3.4.1 PM

For PM mass emissions from road-transport applications, composition of PM can be analysed. However, more and more emphasis is given to the comprehensive analyses, such as biological tests.

### 3.4.2 Soluble organic fraction (SOF)

Soluble organic fraction is determined by weighing the PM filters before and after the extraction with toluene or dichloromethane (internal method M22.01). This is often combined with the extraction of samples for PAH analysis and mutagenicity testing (see Chapter 4.6).

Deviation of the SOF results have been generally below 10% of the result at sufficient PM mass and when using filters of the standard PM sampling procedure, namely glass microfibers reinforced borosilicate filters or filters with pure borosilicate glass fibers with fluorocarbon coating. In the high-capacity PM sampling system, filter type is a hydrophobic Fluoropore PTFE membrane bonded to a high density polyethylene support (FSLW) to allow bending of the filters for weighing by a micro balance (standard filters break easily). However, these Fluoropore filters loose substantial amount (approximately 1% (m/m) = ~5 mg) of material in the SOF extraction leading to only indicative SOF results.

### 3.4.3 Anions: sulphates and nitrates

Analysis of anions from exhaust particles at VTT by internal method (23.01) is based on the SAEJ1936 and IP 416 guidelines. Analysis is conducted by capillary electrophoresis (CE) or by ion chromatography (IC). In addition to sulphates, a method to analyze nitrate, phosphate, fluoride, oxalate, acetate, bromide, and chloride is available. Round-robin tests of anion analyses have shown good correlations between laboratories (Aakko et al. 2000, Lappi et al. MOBILE 232T-2).

**Extraction of samples**

PM samples collected on filters are extracted at VTT according to the IP 416 standard using 10% isopropanol (IPA) in water. In principle, the anions could be determined from the same filters that have been extracted for PAH analysis. However, due to risk of losses of sulphates, particularly when sulphuric acid is present, separate samples are reserved for anion analysis. Particulate filters are placed in Erlenmeyer and 10% IPA/water is pipetted 50 mL or other volume depending on the size of filters and on the expected sulphate concentration. Erlenmeyer is shaken carefully and treated in the ultrasonic bath for 60 min (20 min in the IP 416 standard). Samples are left at room temperature for overnight.

*Hydrogen peroxide ($H_2O_2$) treatment* – Addition of three drops of $H_2O_2$ can be used to convert sulphides and other such compounds to sulphates. In a study by Koponen et al. (2006), $H_2O_2$ treated sample gave approximately 25% lower result than the untreated samples (approximately 370 vs 450 µg/mg and 327 vs. 433 µg/mg). Consequently, the $H_2O_2$ treatment is not used at VTT.

*Ammonia treatment* – Ammonia pre-treatment for the particulate filters is needed, if anions are analysed from the filters already extracted with organic solvent for SOF analysis and when high sulphate concentrations are expected. Inorganic sulphates are not soluble in organic solvents, while sulphuric acid can be partly transferred to organic solvent. Sulphuric acid can be converted to ammonium sulphate ($(NH4)_2SO_4$) with ammonia treatment.

Pre-treatment of PM samples with ammonia at VTT is based on communications[15]. Ammonia treatment was studied by Koponen et al. (2006). Strong ammonia/water solution was added in exsiccator, where filters were treated for two hours (1 h in SAEJ1936). Samples were stabilized at 50% relative humidity and 21 °C. Samples were extracted with toluene and then with 10% IPA/water. The extracts were analysed by CE. The results showed that the ammonia treatment is necessary, if SOF extraction is conducted before the anion analysis. However, at VTT anion analysis is always carried out from native particulate samples.

When ammonia pre-treatment is used, combined water correction is based on stabilized water content of 1 mol of water per one mole of sulphate.

**Analysis with capillary electrophoresis (CE)**

CE uses electrical field to separate the components of a mixture based on the difference in charge to size ratio and viscosity. A capillary is filled with a conductive fluid at a certain pH value (the buffer solution for separation). A high voltage is generated over the capillary and due to this electric field, up to more than 300 V/cm, the sample components move through the capillary at different speeds. Positive components migrate to the negative electrode and negative components migrate to the positive electrode. If two ions are the same size, the one with greater charge will move the fastest. For ions of the same charge, the smaller particle has less friction and overall faster migration rate. CE gives fast results and provides high resolution separation. The column is typically a fused-silica capillary. Most small ions do not absorb in the ultraviolet (UV) or visible regions of the spectrum, and thus the detection is conducted using indirect photometric detection. (“Capillary Electrophoresis,” n.d.; “Introduction to Capillary Electrophoresis,” n.d.).

[15] E-mail Michel Pasquereau, IFP / Päivi Aakko, VTT, 6.4.1998.

At VTT, anions are analysed with CE according to the modified internal method RO22/MK/130. Waters Capillary Ion Analyzer CIA 4100, IonSelect High Mobility Anion electrolyte, 75µm × 375 µm × 60 cm capillary column.

Uncertainty of the anion analysis by CE at VTT based on repeatability and accuracy of the instruments is estimated to be around ± 5% of the result for high concentrations of anions, and ± 20 % for low concentrations of anions. Higher uncertainty is related to anions, which are hardly soluble in IPA and water.

**Ion chromatography (IC) and acid extraction**

Ion chromatography is a chromatography process that separates ions and polar molecules based on their affinity to the ion exchanger. Ion chromatographs are able to measure concentrations of major anions, such as fluoride, chloride, nitrate, nitrite, and sulfate, as well as, major cations such as Li, Na, ammonium, K, Ca, and Mg at ppb range. Concentrations of organic acids can also be measured through ion chromatography. The water-soluble and charged molecules bind to moieties, which are oppositely charged by forming covalent bonds to the insoluble stationary phase. The equilibrated stationary phase consists of an ionizable functional group where the targeted molecules of a sample to be separated and quantified can bind while passing through the column. Cation exchange chromatography is used when the desired molecules to separate are cations, and an anion exchange chromatography is to separate anions. With anion exchange the beads in the column contain positively charged functional groups to attract the anions and with cation exchange the beads in the column are negatively charged. The bound molecules then are eluted from the column using an eluent which contains anions and cations by running higher concentration of ions through the column or changing pH of the column. The retention time of different species determines the ionic concentrations in the sample.(“Ion Chromatography,” n.d.; “Ion Chromatography,” n.d.)

At VTT, in addition to CE, an alternative method for extraction of anions from PM is acid extraction and analysis by IC. Procedure according to SFS 5789 was studied by Koponen et al. (2006). PM filters were placed in the decanter and 5 mol/L HCl was added to sufficient quantity to cover filters. Solution was mixed for 10 min at room temperature and then for 15 min at 40–50 ºC. Solution was left at room temperature for overnight. Solution was filtered and water was added to match 100 mL. The result with 10% IPA/water extraction and CE analysis gave 450 and 420 µg/mg of sulphates, while acid extraction and IC gave 385 µg/mg. (Koponen et al. 2006).

**Combined water**

“Sulphates” analysed from PM can be in a form of sulphuric acid, organic sulphates, ammonium sulphate, or inorganic sulphates. All of these have different capability to combine water. For sulphuric acid, the amount of combined water depends on the humidity of weighting chamber. At 50% relative humidity, the amount of “combined water” is assumed as 1.32 × sulphates (sulphuric acid) according to SAEJ1936 (Figure 23). For ammonium sulphate the respective factor is only 0.19, and, for example, for dihydrate $CaSO_4(H_2O)_2$, the factor is 0.38, for tetrahydrate 0.75 and for pentahydrate 0.94. When minerals, metals, or ammonia is present in the exhaust gas, the factor for “combined water” can be lower than that defined for sulphuric acid (1.32 at 50% relative humidity). Water content of PM can be analysed by weighting the particulate filters at defined humidity and after stabilization in an exsiccator.

High uncertainty is addressed with the calculated amount of water in PM. Therefore "combined water" is often included in the "others" or in the "undefined" portion of PM at VTT.

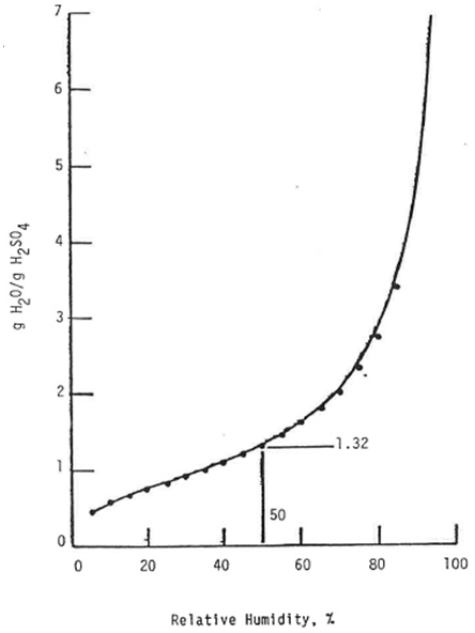



*Figure 23. Mass of water associated with sulphuric acid in an aqueous solution (SAE J1936).*

### 3.4.4 Elemental and organic carbon (EC and OC)

Elemental carbon (EC) and organic carbon (OC) analysis method has been applied so far for PM from medium-speed engines at VTT. However, there is need for information on the BC emissions from on-road transport applications, particularly when using alternative fuels. EC/OC method is based on a thermal-optical analysis technique, while BC is measured with optical methods and thus they are not commensurable with each other (Bauer 2009).

In the EC/OC method, temperature and gas atmosphere is adjusted while continuously measuring the transmission of a laser through the sample matrix. In the second phase, sample is cooled, $O_2$/He is introduced and temperature is raised again. Carbon is oxidized to $CO_2$, which is then converted to methane and detected by the FID. The organic compounds pyrolytically converted to EC are compensated by continuous measurement of the transmission of a laser. Based on the FID response and laser transmission data, the quantities of OC and EC in the sample are calculated. Methane and saccharose are used for calibration.

Different temperature programs can be used in the EC/OC analysis. In the NIOSH 5040 program, the sample is heated in steps up to 850–900 °C in Helium (He) atmosphere to remove OC, or lower peak temperature is used if EC loss is evident. EUSAAR2 protocol (prEN 16909) uses a peak temperature of 650 °C in He phase to decrease risk for premature evolution of EC. This peak temperature and prolonged temperature steps are normally sufficient to minimize the effect of pyrolysis. EC/OC analysis is sensitive towards PM constituents, such as sulphates, metals and OC, which are challenging for the thermal-optical determination of the EC/OC split. (Panteliadis et al. 2015, Jung et al. 2011, Karanasiou 2011).

For some samples the EC/OC split may occur in the middle of the large FID peak where slight changes in the laser performance leads to substantial differences in the EC results.

EC/OC is analysed at VTT using Sunset Laboratories Inc.'s analyzer model 4L (internal method 25.01). Samples for EC/OC analysis are collected by drawing diluted exhaust through quartz (for example Pallflex Tissuquartz or Munktell MK360 or) located in the standard or special PM sampling systems. Preliminary tests with the EC/OC analysis from cars showed challenges in adjusting suitable collection times to achieve optimal darkness of samples (Chapter 4). However, no changes in the actual procedure of the EC/OC analyses were required for cars running on alternative fuels.

### 3.4.5 Fuel/lube, simulated distillation and other special analyses

The fuel/lube analysis has been developed to screen, which part of the diesel particulate hydrocarbons originates from the lube oil and which part from the fuel. Procedure for the fuel lube analysis by gas chromatography is defined in for example in SAE (1990) and in IP 442/99 standard (Analysis of fuel- and oil-derived hydrocarbons in diesel particulates on filters – Gas chromatography method). In a study by (Aakko et al. 2000) fuel/lube analysis from particulate samples were carried out with GC/solid injection method by Neste (at that time Fortum Oil and Gas). The analysis is based on the standard chromatograms of lube oil and 10% distillation residue of the fuel and respective chromatogram of the particulate sample. For gasoline, fuel standard cannot be obtained similarly as for the diesel fuel due to the lower final boiling point of gasoline (about 200 °C). For gasoline PM, it is assumed that compounds other than those found in the boiling area of the lube standard originate from the fuel. (Aakko et al. 2000).

GC/solid injection method for fuel/lube analysis was not available in the laboratories in Finland at the time of report, while it could be available, for example, in Ricardo, UK (discussions). Role of lube in PM could be evaluated basing on the metal analysis of PM, fuel and lube. This procedure was used by Aakko-Saksa (2016) for ship PM. Calcium (Ca) proved to be the best fingerprint element for lube in those measurements. The Finnish Meteorological Institute (FMI) is developing a method to characterize role of fuel and lube in exhaust aerosols basing on analysis by SP-AMS.[16]

**Simulated distillation**

Particulate samples can be extracted for example with dichloromethane and analysed with GC. Temperature calibration of GC can be performed with a standard that contain paraffins from for example C5 to C40. This methodology was used in a study reported by Aakko (2000).

### 3.4.6 Metals

Metals in PM originate from fuel, lube or engine wear in the PM. Calcium and zinc are typical in oil additives of road-transport applications, as well as, trace elements magnesium and manganese. Engine wear elements are iron and aluminum, and also some trace elements such as chromium, nickel, and copper, amongst others.

In a study by Aakko (2016), metals from PM samples collected on Munktell MK360 quartz filters were analysed by Labtium. Filters were extracted in micro oven by using nitric acid ($HNO_3$) and hydrofluoric acid (HF) (EN 14385). Analysis was carried out by using

[16] Discussions Timonen, FMI/Aakko-Saksa, VTT July 2016

inductively coupled plasma mass spectrometry (ICP-MS). Elements analysed included Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Sr, Th, Tl, U, V, Zn, Br, Cl, P, S, Si, and Sn. Reference filters analysed contained relatively high concentrations of some elements, such as Al, Ca, Na, and Fe (manufacturers information in Table 15). Later on, quarz filter material used at VTT for the EC/OC and metal analyses is Pallflex Tissuquartz 2500QAT-UP filters, which are ultra-pure and heat-treated for reduction of trace organics. Tissuquartz are designed for temperatures up to 1093°C and for aggressive atmospheres.

*Table 15. Trace elements in the Munktell MK360 filters (information from manufacturer).*

| Typical Levels of Trace Elements in MK 360 and T 293 – ppm | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | Ba | Ca | Cd | Co | Cr | Cu | Fe | Mg | Mn | Na | Ni | Pb | Sr | Ti | V | Zn |
| 300 | 10 | 250 | 0.002 | <0.5 | 2 | 2 | 50 | 25 | 2 | 100 | 2 | <1 | 3 | <1 | <5 | 6 |

At VTT, metal analyses of the PM samples have been carried out also in cooperation with other research organizations or by service providers. In a study by Aakko (2000) metal analysis of PM was carried out by Gent University (Belgium) with INAA and Particle-induced X-ray (PIXE) methods. PIXE method requires polycarbonate filters for collecting the PM samples. Back-pressure of polycarbonate filter is high and thus flow rate of diluted exhaust gas through filter was low (around 15 L/min). Another filter material, Gellman Teflo R2PJ047, applicable to INAA, was also used for the collection of metal samples. Gent University found good correlation between the results obtained with polycarbonte/INAA+PIXE and Teflo/INAA methods for e.g. K, Ca, V, Mn, Fe, Cu, Zn, and In. The levels of the most metals in the samples were very low. (Aakko et al. 2000).

## 3.5 Carcinogenicity, mutagenicity, and toxicity of PM and SVOC

### 3.5.1 Polycyclic aromatic hydrocarbons (PAHs)

PAH compounds in the exhaust gases are analysed from particulate matter and/or semivolatiles collected to filters or adsorbent materials. A set of PAHs (Table 16) from the Soxhlet extracted PM and SVOC samples have been analysed until early 2000's by VTT and then by NabLabs. From all PAH compounds analysed, sums of 7, 14, or 16 priority PAHs are reported at VTT (see Chapter 3.12).

*Table 16. The 30 PAH compounds analysed by NabLabs. PAH16 marked with boldface.*

| | | |
|---|---|---|
| **naphthalene** [a] | **anthracene** [a] | benzo(*j*)fluoranthene |
| 2-methylnaphthalene [a] | 1-methylanthracene | **7,12-dimethylbenz(*a*)anthracene** [b] |
| 1- methylnaphthalene [a] | 2-phenylnaphthalene | benzo(*e*)pyrene |
| 1,1-biphenyl [a] | **fluoranthene** [a] | **benzo(*a*)pyrene** [a, b] |
| **acenaphthylene** [a] | **pyrene** [a] | perylene [a] |
| **acenaphthene** [a] | benzo(*a*)fluorene | **indeno(1,2,3-*cd*)pyrene** [a, b] |
| dibenzofuran | benzo(*b*)fluorene | **dibenzo(*a,h*)anthracene** [a] |
| **fluorene** [a] | **benz(*a*)anthracene** [a, b] | **benzo(*g,h,i* )perylene** [a] |
| dibenzothiophene | **chrysene** [a, b] | coronene |
| **phenanthrene** [a] | **benzo(*b*)fluoranthene** [a, b] | |
| 2-methylanthracene | **benzo(*k*)fluoranthene** [a, b] | |

[a] PAHs analysed by MetropoliLab. In addition, MetropoliLab analysed also 2,6-dimethylnaphthalene, 2,3,5-trimethylnaphthalene and 1-methylphenanthrene.
[b] PAHs belonging to sum of PAH7 defined by US EPA (see Chapter 3.12).

At NabLabs and VTT Expert Services, PM samples are Soxhlet extracted using toluene for PAH, or in the case of combined PAH and mutagenicity test, using dichloromethane. PAH analyses at NabLabs are performed by GC/SIM-MS following purification of the extract by liquid chromatography. EPA 610 PAH mixture from Supelco and PAH-MIX 63 from Ehrensdorf have been used to check the calibration standard. The calibration standard has been made from pure solid substances of each PAH compound determined. Detection limits have been at NabLabs 0.1 µg compound/sample, which represents approximately 0.04–0.08 µg/km for the cars over the European emission test.

Repeatability of sample collection, extraction and PAH analysis at NabLabs has been reported by Aakko-Saksa (2011) (Figure 24). The standard deviations of the PAH results were below 6%, except in one case (13%). Repeatability was excellent, taking into consideration that the samples originated from different exhaust emissions test runs and from different Soxhlet extractions.

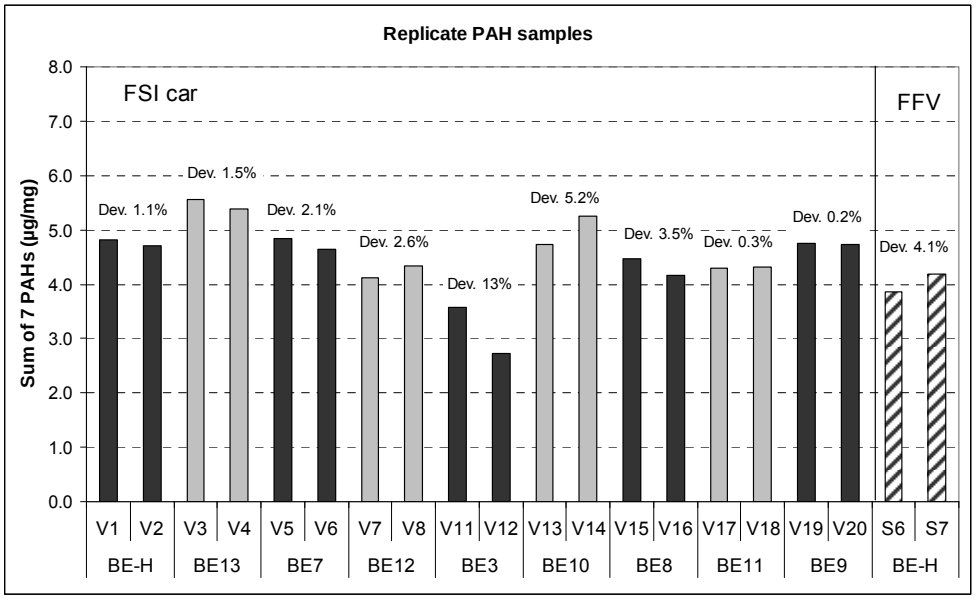


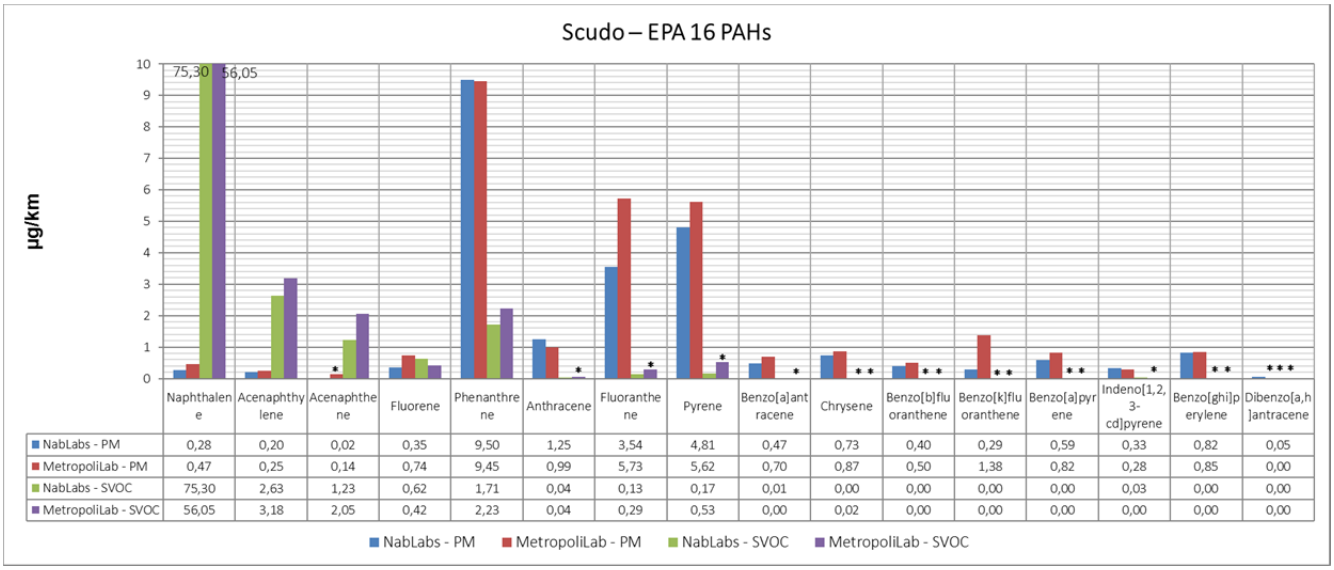

*Figure 24. PAH results from the replicate European test runs with different car and fuel combinations. Standard deviations are shown as percentages.*

Another subcontractor for PAH analyses is MetropoliLab, analyzing a total of 24 individual PAH compounds according to ISO 16000 and EN 14662 analysis methods. Samples are extracted with toluene in ultasonic bath. Detection limits of the PAH analysis at MetropoliLab are 10–30 ng per compound per sample (1 µg/m$^3$) and measurement uncertainty is 30%. The analysis method has been developed for ambient air samples in filters or/and in XAD-2 adsorbent.

In the evaluation of the MetropoliLab procedure, PM filter samples and SVOC samples (Empore disks) of Euro 2 diesel car (see Chapter 4) were extracted and analysed. PM filter samples were so dark/black that they were extracted twice with toluene in ultrasonic bath. It was also noticed that after toluene extraction of the Empore disks the solution was cloudy (milky) and deposit fell down to the bottom of the vial prior the analysis. This would imply that Empore disks are partly degraded during the toluene extraction of the disks in ultrasonic bath. However, the deposit did not disturb the PAH analyses.

PAH analyses carried out by NabLabs and MetropoliLab were compared with each other in this project (16 EPA PAHs in Figure 25). The PAH results for two different extraction methods (Soxhlet and ultrsonic extractions) and analysis methods in two different laboratories

(NabLabs and MetropoliLab) correlated well for both PM and SVOC phases. Ultrasonic extraction technique for sample preparation is simpler than Soxhlet extraction. This alternative procedure for PAH analysis was approved for future projects at VTT.




| | Naphthalene | Acenaphthylene | Acenaphthene | Fluorene | Phenanthrene | Anthracene | Fluoranthene | Pyrene | Benzo[a]anthracene | Chrysene | Benzo[b]fluoranthene | Benzo[k]fluoranthene | Benzo[a]pyrene | Indeno[1,2,3-cd]pyrene | Benzo[ghi]perylene | Dibenzo[a,h]antracene |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NabLabs - PM | 0,28 | 0,20 | 0,02 | 0,35 | 9,50 | 1,25 | 3,54 | 4,81 | 0,47 | 0,73 | 0,40 | 0,29 | 0,59 | 0,33 | 0,82 | 0,05 |
| MetropoliLab - PM | 0,47 | 0,25 | 0,14 | 0,74 | 9,45 | 0,99 | 5,73 | 5,62 | 0,70 | 0,87 | 0,50 | 1,38 | 0,82 | 0,28 | 0,85 | 0,00 |
| NabLabs - SVOC | 75,30 | 2,63 | 1,23 | 0,62 | 1,71 | 0,04 | 0,13 | 0,17 | 0,01 | 0,00 | 0,00 | 0,00 | 0,00 | 0,03 | 0,00 | 0,00 |
| MetropoliLab - SVOC | 56,05 | 3,18 | 2,05 | 0,42 | 2,23 | 0,04 | 0,29 | 0,53 | 0,00 | 0,02 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 | 0,00 |

* = < DL

*Figure 25. EPA 16 PAHs for PM and SVOC exhaust gas emission phases, Euro 2 diesel described in Chapter 4.*

### 3.5.2 Ames mutagenicity

#### 3.5.2.1 General

Ames tests are widely employed methods that use bacteria to test the mutagenicity of a given compound/chemical to the DNA of the test organism. It is a biological assay to assess the mutagenic potential of chemical compounds. The test is a quick and convenient to estimate the carcinogenic potential of a compound as the standard carcinogen assays on mice and rats are time-consuming and very expensive. The tester strains are specially constructed to detect either frameshift or point mutations, so that mutagens acting via different mechanisms may be identified. To enable indirect mutagens, which are mutagenic in mammals only after metabolic activation, also to be detected, a metabolic activation system has been incorporated in the test procedure. The enzyme system used is isolated from rat livers after a specific induction treatment, and is a simplified simulation of mammalian metabolism. Some compounds, like benzo(a)pyrene, are not mutagenic themselves but their metabolic products are.

The Ames test was originally developed for screening individual, pure chemicals for mutagenicity, and potential carcinogenicity in mammals (Ames et al. 1973a, 1973b, 1975). The short-term in vitro assay is capable of detecting compounds causing either base-pair substitution or frameshift mutations in DNA. The tester strains, specially tailored Salmonella mutants, have been made sensitive to chemical attacks, for example, by increasing the permeability of the cell wall to large molecules such as PAHs. In the early 1970s, the correlation between carcinogenicity and mutagenicity detected by the Ames assay was estimated to be nearly 90% (Ames and McCann 1981). However, validation studies suggest the correlation rate is most probably much lower. Of 301 chemicals demonstrated to be

carcinogenic in mice and rats, only 56% exhibited mutagenicity in the Ames reversion assay (ETAD 1998).

In addition to its use with single chemicals, the Ames test has been used for a long time to assess the mutagenicity of a wide variety of complex samples. A number of studies have been published on the assessment of the mutagenicity of for example diesel exhausts and air pollution. Certain limitations of the test method must be taken into account in these kinds of applications. The test organisms are sensitive to any kind of chemical attack. Toxic components may interfere with the target organisms and inhibit some vital metabolic reactions of the tester strain, interfere with transport processes in the cell, or cause fatal shock reactions. Toxicity may be due to a single toxic component or the cumulative effect of several components. If the mixture contains any component acutely toxic to the test organism, the mutagenicity of the sample may be masked. The test results are therefore only reliable within a non-toxic concentration range. To avoid interference from toxic components, it may be necessary to fractionate the original complex sample into chemical subfractions. Another potential source of error in the assessment of complex samples may be attributable to the metabolic activation system applied. It consists of a range of enzymes responsible not only for metabolic activation but also for a range of deactivation reactions in mammals. Full control of these enzymatic reactions is not possible under the test conditions.

The Ames test provides one of the most widely used short-term mutagenicity assays, and is widely applied as a preliminary screening tool for chemicals with potential genotoxic activity. A positive result from the Ames test provides an indication of genotoxic potential that must always be confirmed by some other method capable of predicting more accurately the risk of carcinogenicity in mammals.

#### 3.5.2.2 Ames test method at VTT

The PM filters and SVOC discs are wrapped in aluminum foil and kept in a freezer before the Soxhlet extraction of samples with dichloromethane. During all handling phases the filters and during extraction, samples are protected from light to avoid changes that could affect the mutagenicity results for the samples. Because dichloromethane is toxic to the Ames tester strains, the solvent is replaced by dimethyl sulphoxide (DMSO). Samples are extracted at VTT Expert Services or NabLabs and Ames tests are conducted by VTT or BioSafe Biological Safety Solutions.

At VTT, the mutagenicity of the extracts is assessed by the Ames test using histidine auxotrophic *Salmonella typhimurium* tester strains originating from B.N. Ames, University of Berkeley, California, USA. The method applied (VTT-4352-91) is based on the original reference method by Maron et al. (1983) and the recommendations of the OECD (1997).

Different tester strains can be used in the Ames test. The tester strain TA98 used is sensitive to frameshift-type mutagens. Samples can be tested both for direct (without metabolic activation) and indirect (with metabolic activation) mutagenicity. PAHs show indirect mutagenicity, i.e. only after metabolic activation (+S9 mix), whereas nitro-PAHs are direct-acting mutagens. The contribution of nitro-PAH-type compounds to mutagenicity can be studied using tester strains TA98 and the nitroreductase-deficient TA98NR in parallel. Provided the sample exhibits direct mutagenicity in TA98 but not in TA98NR, the presence of nitro-PAHs is likely. Other tester strains are also available.

Tester strain is typically used at five dose levels corresponding to particle masses of 0.1, 0.2, 0.4, 0.6, and 0.8 mg/plate. For metabolic activation a S9 homogenate prepared from rat livers induced with phenobarbital and β-naphtoflavone can be used. The tests are carried out using

three replicate plates for each dose level. 2-Aminoanthracene is used as the positive control for indirect mutagenicity. DMSO is used as the solvent control.

The mutagenic dose response of each sample is calculated by linear regression analysis. The slope (b) within the linear part of regression line (y = bx + a) describes the magnitude of mutagenic activity, and is expressed as revertants/mg of sample. Only the responses obtained at those concentration levels not toxic are included in the calculations. For a sample to be classified mutagenic it must cause a dose-related, more than two-fold, increase in the number of revertants compared with the solvent control.

Repeatability of the Ames test results has been studied for example by Aakko-Saksa (2011) (Figure 26). The standard deviation of the Ames results from replicate European emissions test runs was below 25%. The replicate samples originated from different emissions test runs, and from different Soxhlet extractions.

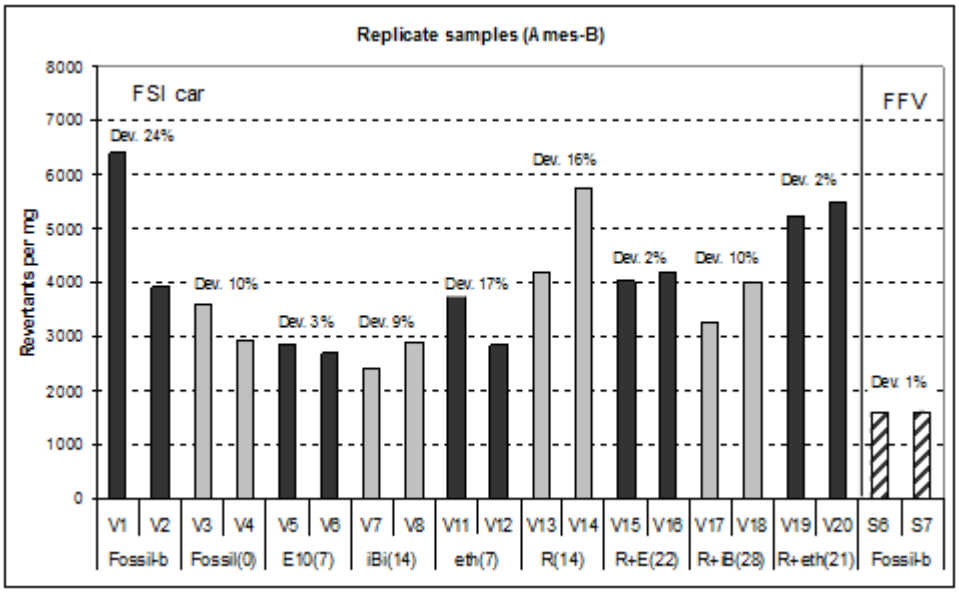



*Figure 26. Ames results from replicate European test runs with different car/fuel combinations. Standard deviations are shown as percentages.*

### 3.5.2.3 MicroAmes test method

Particulate masses from new and alternative fueled vehicles are often lower than that required for the traditional Ames test (6.3 mg). For microAmes test (miniaturized version of the standard Ames test), 1 mg of sample is sufficient for testing with six doses and three replicates with and without metabolic activation (+/- S9 mix). The microAmes test is a 24-well-plate version of the Bacterial Reverse Mutation Test, and it was designed to predict the results of the regulatory Ames assay (OECD 471). It has been showed that the performance of the 24-well assay is equivalent to the standard Ames assay. In addition, 24-well assay has showed sensitivity similar to the standard Ames assay (Pant *et al.* 2016).

MicroAmes *Salmonella typhimurium* reverse mutation test measures the mutations in histidine utilization capability (his- → his+). In the traditional test the reversion is detected by calculating the revertant colonies on minimal histidine agar, while microAmes test reversion is detected in 384-well plate as color change in wells. A positive result is indicated where the compound causes a substantial dose-related increase in colony counts (at least two- or three-

fold greater than the spontaneous rate, with colony counts outside the historical control range). MicroAmes can be conducted with and without metabolic activation (rat liver fraction S9). (“Early Stage Genetic Assays with Low Compound Requirements,” n.d.; “Genetic Toxicology Screening Tests,” n.d.)

Ames and microAmes tests were compared from samples from Euro 2 diesel car described in Chapter 4. NabLabs and VTT Expert Services Ltd. extracted samples, Ames and microAmes tests were carried out at BioSafe. Unfortunately, most of the Ames test sample plates dried during the incubation period and therefore, only microAmes results are available.

Soxhlet extraction was performed with dichloromethane (DCM) for the Fluoropore filters and Empore disks. Several filters were combined for each extraction batch, and an equivalent number of filters for the blank control sample. Filters were protected from light during and after the Soxhlet treatment to avoid unwanted changes in the samples. The Soxhlet apparatus was cleaned by solvent extraction (6 hours). An internal standard was added, and samples were Soxhlet extracted for 16 hours. The volume of extract was reduced by evaporating the solvent, and the concentrates were divided for the PAH analyses and microAmes tests. For the microAmes test, the DCM solvent was replaced by DMSO, which is better tolerated by the test organisms used in the Ames assays. MicroAmes tests were performed with Salmonella typhimurium strain TA98 ±S9. DMSO was used as solvent control. 4-Nitroquinoline 1-oxide (4-NQO) and 2-amino anthracene were used as positive control without and with S9 mix, respectively.

In microAmes assay the culture of tester strain TA98 was grown in Nutrient Broth #2 supplemented with 10 mg/mL ampicillin at +37 °C for 16 h in shaking water bath. 9 µL of this overnight culture, as well as, the appropriate volume of sample and the metabolic activation system or buffer were added into minimum glucose medium on a 24 well plate and the plate was incubated at +37 °C for 2 hours. After the incubation, the content of one well was transferred into 48 wells (50 µL per each well) of a 384 well plate. The 384 well plates were incubated in an air tight plastic bag at +37 °C for 72 hours. The mutations are detected as a color change from purple to yellow due to pH change caused by the growth of tester strain. The results are considered as positive when number of yellow wells is at least twice the number observed with the bacterial control

With microAmes assay the PM samples **1a**, **1b**, and **1c** were *slightly mutagenic with mutagenic activation (S9 mix)* (Table 17), but not without metabolic activation. Combined PM + SVOC sample **7** showed mutagenic activity with and without mutagenic activation at concentration 21 µg/mL. Reference diesel particulate mass, **SRM2975**, was extremely mutagenic at concentrations 2 µg/mL and 10 µg/mL. Reference filter samples (blanks) were not mutagenic.

MicroAmes test was deemed to be feasible for mutagenicity tests for low-emitting cars using alternative fuels at VTT.

*Table 17. The samples from diesel car (**Scudo**) and reference diesel particulate mass for microAmes tests.*

| Sample | PM mg | Dil. exh. L | TA98-S9 Mutagenicity | TA98+S9 Mutagenicity |
|---|---|---|---|---|
| **PM (1a–1c) [a]** | 22.2 | 4400 | No | Slightly |
| **PM [a] + SVOC [b] (7)** | 1.4 + 2.6 | 250 + 100 | Mutagenic | Mutagenic |
| **SVOC (11) [b]** | 4.3 | 170 | No | No |
| **SRM2975** | 100.0 | - | Extreme | Extreme |
| **Blanks (2 [a], 8 [a, b], 12 [b]** | - | - | No | No |

[a] Fluoropore [b] Empore

### 3.5.3 Oxidative potential (OP)

The exhaust gases from diesel engines have been classified as group 1 carcinogens (IARC 2012, Silverman et al. 2012 and Benbrahim-Tallaa et al. 2012). Usually only the (organic) extracts and not "the whole" exhaust gases are tested for possible health impacts such as genotoxicity or mutagenicity (Steiner et al. 2014). Though, for example, PAHs have also been detected in filtered exhaust gases indicating that they are volatile enough to penetrate through the particulate filters and stay in gaseous or liquid form form (Steiner et al. 2014 and Portet-Koltalo, Preterre, and Dionnet 2011). The efficiency of after treatment devices for semivolatiles present in the exhaust gases may be weak (Biswas et al. 2009).

The composition of diesel exhaust particles changes significantly as they are diluted in the atmosphere and therefore also their toxicological behavior/characteristics can change (Li, Wyatt, and Kamens 2009). Introduction of DFP to the diesel cars did not change the genotoxicity of diesel exhaust gas, which suggests that the gas phase of the exhaust gas has a significant part in mutagenicity (Fall et al. 2011). The complexity and diversity of the exhaust gases and air pollutions in general (thousands of gaseous compounds and/or particles) makes the evaluation and estimation of their health impacts challenging (Fall et al. 2011; Steiner, Czerwinski, Comte, Müller, et al. 2013).

It would be relevant to determine the relationship between the toxicity and the composition of the exhaust gases, only this would give a possibility to develop and design suitable emission reduction technologies/methods (Cheung et al. 2009). For example, although using fatty acid methyl ester (FAME) as fuel reduces the PM emissions, it does not necessarily reduce the dangerousness of the remaining particulate emissions (Gerlofs-Nijland et al. 2013; Steiner, Czerwinski, Comte, Popovicheva, et al. 2013). It would be essential to, for example, determine the biological effects of different after treatment systems.

Several studies have verified that <10 µm particulates are toxic for lung cells and in epidemiological researches the connection between PM10 exposure and lung-, heart-, and vascular diseases has been detected (Bates et al. 2015). Oxidative stress and (pro)inflammatory reactions are critical/crucial for the development of these diseases (Müller et al. 2010). In addition, a connection between diesel soot and lung cancer has been detected (Silverman et al. 2012; Benbrahim-Tallaa et al. 2012).

One generally used method for determination of the mutagenicity of the exhaust gases is the Ames test. In general, Ames tests vary in mutagenicity results when the results are compared to the cell tests and different bacterial strains used in Ames tests react very differently.

Therefore, Ames tests should be carried out with several bacterial strains and/or employ more complex eukaryotic cell systems in the tests. In addition, the mutagenicity of exhaust gas may be different from the mutagenicity of particles, as has been indicated in many studies (Steiner et al. 2014).

Many different components have an effect on oxidative potential of the exhaust gases, for example, fuels, engines, aftertreatment devices, and the oxidative potential analysis method (Jalava et al. 2012). No quantitative comparisons between oxidative potentials measured in different research projects can be made. (Gerlofs-Nijland et al. 2013).

In addition to oxidative potential, also oxidative stress can be studied/analysed. Oxidative stress is associated with inflammation and tissue damage in the cells and lungs. Aerosol samples' oxidative potential can be studied with acellular assays from which dithiothreitol (DTT) assay is one of the most commonly used. The oxidative potential may then lead to oxidative stress in the cells and the oxidative stress can be analysed by studying the oxidative and inflammatory responses seen in cell cultures. Oxidative stress in the cells can be analysed as oxidation of fluorescent DCF-DA probe, as well as, by analyzing e.g. reduced glutathione and thiols in the cells. Inflammation can be analysed as production of proinflammatory cytokines. Testing oxidative stress is though expensive and more time consuming than the acellular tests, for example, DTT assay for oxidative potential.

**Test methods for oxidative potential**

Many reactive oxygen- and nitrogen compounds found in air pollutions have been detected to correlate with mechanisms causing health hazards. Oxidative stress can cause inflammation and e.g. tissue damage in lungs and in cells in respiratory tract. As the biological oxidative stress testing methods are very expensive, acellular chemical fast and not expensive testing methods for oxidative potential of e.g. particulates are performed.

Several different chemical, acellular, methods for determining the oxidative potential of e.g. particulate samples exist and the most commons are dithiothreitol (DTT)-, ascorbic acid (AA)-, and dihydroxybenzoate (DHBA)-assays. (Biswas et al. 2009; Gerlofs-Nijland et al. 2013; Daher et al. 2011; Cho et al. 2005; Geller et al. 2006; Janssen et al. 2014; Sauvain, Rossi, and Riediker 2013; Hedayat et al. 2015; Yang et al. 2014). Also online measurements for oxidative potential have been developed utilizing e.g. Versatile Aerosol Concentration Enrichment System (VACES) and particle-into-liquid-sampler with microfluidic-electrochemical detection. (Sameenoi et al. 2013; Koehler et al. 2014; Sameenoi et al. 2012; Shapiro 2012; Kim, Jaques, Chang, Froines, et al. 2001; Kim, Jaques, Chang, Barone, et al. 2001; Orsini et al. 2003; Weber et al. 2001). These online systems are not yet commercially available.

**Oxidative potential testing at VTT**

When comparing the different assays described in the literature, it was concluded that currently the most practical method for assessment of the oxidative potential of the samples collected during our measurement campaign in this project, would be the DTT assay. DTT assay is based on the capability of the sample to receive electrons from DTT and transfer them to oxygen. DTT assay as a test is simple and not expensive, when compared to the biological tests for oxidative stress.

Dithiothreitol (DTT = $HSCH_2(CH(OH))_2CH_2SH$) is commonly used as a cell-free measure of the oxidative potential of particles. In this assay, redox-active chemicals in e.g. particulate

matter (PM) oxidize added DTT to its disulfide form and the linear rate of DTT loss is used as a measure of the oxidative capacity of the PM.

Development of method and all oxidative potential DTT tests in this project were performed at Biosafe Biological Safety Solutions Ltd in Kuopio. PM samples from DI-E2 (Scudo) were used in the pre-tests to develop procedure for oxidative potential analysis (Table 18). The results from the pre-tests are shown in Chapter 4 together with the other results for the samples collected during the measurement campaign and also for one reference diesel particle sample (NIST SRM 2975). For Round Robin type testing and evaluation of the analysis results between different laboratories "NIST Standard Reference Material 2975 – Diesel particulate matter" is often used.

Samples were sent also to the analysis of oxidative stress in UEF. However, UEF's contribution belongs to another project, and those results will be published later on as articles.

*Table 18. The samples from diesel car (**Scudo**) and reference diesel particulate mass for DTT assays.*

| Sample | Sample type | PM mg/sample | Dil. exh. L/sample | µMDTTmin$^{-1}$ |
|---|---|---|---|---|
| **3 – 5** | PM [a] | 12.8 | 2500 | 0.21 |
| **9** | PM [a] + SVOC [b] | 1.5 + 2.5 | 250 + 100 | 0.41 |
| **11** | SVOC [b] | 2.1 | 171 | 0.08 |
| **SRM2975** | PM | 100.0 | - | 1.40 |
| **6 [a], 10 [a, b], 12 [b]** | Blanks | - | - | 0.12[a], 0.00[a,b], 0.01[b] |

[a] Fluoropore [b] Empore

## 3.6 Particle number, size classification, and characterization

Solid particle number emission (solid PN) is measured by apparatus and the procedure in compliance with the Particulate Measurement Programme (PMP) of the United Nations Economic Commission for Europe ('UN/ECE), and subsequently used in type approval tests for Euro VI (Regulation (EU) No 133/2014).

The instrument used is butanol Condensation Particle Counter (bCPC), Airmodus A23 (Figure 27):

- Particle size range: from 7 nm to 1 µm
- Particle concentration: 0–100 000 particles per cubic centimeter (cm$^3$)
- Response time: 3 s
- Inlet flow rate: 1 L/min

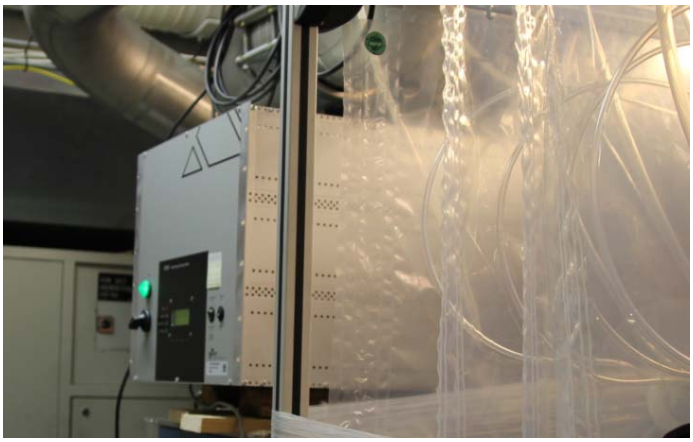


*Figure 27. Airmodus A23 butanol Condensation Particle Counter (bCPC).*

In addition to legislative solid PN method, VTT has a number of options for in-depth particle characterization:

- Several dilution instruments: full flow and partial flow tunnels, ejectors and porous tube diluters.
- Mass size classification: DLPI, DGI, virtual impactors (PM 2.5, PM1).
- Real-time number size classification by ELPIs (> 8 nm) (internal method 24.01).
- Thermodenuder for volatility analysis of size fractions.
- Access to electron microscopes (SEM, TEM).

These instruments have been used in a number of projects including alternative fuels, for example, by Nylund (2012), Thompson et al. (2004) and Aakko et al. (2003).

## 3.7 Summary

In summary, exhaust analysis from vehicles at VTT are shown in Figure 6. From these, the following analysis methods were improved, modified or developed during this project:

a) Analysis of hydrocarbons for oxygen-containing fuels, such as E85 and ED95.
   - Total hydrocarbons analysed with FID counts also oxygenates with variable response factors. Reporting of the total C1-C8 hydrocarbons integrated from the GC-FID analysis is recommended to be reported in addition to THC for the oxygenated fuels at VTT. GC, FTIR, and HPLC analyses give accurate information on the composition of gaseous emissions when using oxygenated fuels.
   - For individual hydrocarbons, a microGC method was studied in addition to the GC-FID method in-use. This method is capable for analysis in approximately 2 min. time intervals. Only small molecules can be analysed (methane, ethane, and

propane) and detection limits are high, and thus it is not suitable for low-emitting cars.

b) Carbonyl compounds.
   - Carbonyl compounds. For reliable measurements of carbonyl compounds at VTT, preliminary measurements of $NO_2$ during preparation of cars will be conducted to enable design of test set-up with sufficient collection capacity even when high concentration of $NO_2$ is present in the exhaust gas.

c) Real-time multi-component analysis with FTIR. Gasmet FTIR methods were reviewed and improved for more accurate analysis of exhaust when using alternative fuels. The FTIR-results calculation was updated.

d) Elemental and organic (EC/OC) composition of PM. EC/OC is a thermal-optical analysis, which has been used for PM from medium-speed, large engines at VTT. The EC/OC method was tested and approved for PM originating from on-road cars/vehicles using alternative fuels.

e) Semivolatile organic compounds. SVOC of exhaust gas in addition to VOCs and PM is important in the assessment of alternative fuels. Two methods to collect SVOCs were tested (Empore and Tenax-tubes). SVOC collection with Empore disks was approved for future use at VTT.

f) Toxicity, mutagenicity, and carcinogenicity for low-emitting cars and vehicles..
   - Collection of PM mass for biological tests is challenging even with high-capacity collection systems. Exhaust gas volume based dosing of PM and SVOC samples was designed instead of mass based dosing.
   - An acellular chemical DTT assay for oxidative potential in PM and SVOC samples was chosen and validated for future projects at VTT.
   - Carcinogenicity and mutagenicity of exhaust gases are evaluated also with PAH analyses and Ames tests at VTT. A microAmes test was introduced to indicate mutagenicity of small samples from low-emitting cars and vehicles.
   - New service providers evaluated for mutagenicity testing (Ames and microAmes), oxidative potential testing (DTT assay), and PAH analyses.

g) Validation.
   - Several methods were validated in the IEA AMF Annex 44" Unregulated Pollutants Emissions of Vehicles Fuelled with Alcohol Alternative Fuels" (Annex 44, Operating Agent CATARC, China). VTT studied emissions from two FFVs using three fuels (E10, E85, and E100) at +23 and -7 °C). (Aakko-Saksa 2014)
   - A measurement campaign with five passenger cars was carried out during the project in April 2015. New procedures and methods for alternative fuels were tested and validated (Chapter 4).

# 4. Measurement campaign

## 4.1 General

The aim of the two-week measurement campaign carried out in April 2015 was to test and evaluate the new and updated methods and procedures: microGC, microAmes, and oxidative potential (DTT assay). A campaign was conducted with new passenger cars using gasoline, diesel, and alternative fuels (E85, CNG). Based on the results of development work described in previous Chapter, new analysis methods were applied in the tests.

## 4.2 Fuels and cars

Test fuels matrix in the measurement campaign comprised of the following fuels:

- Commercial E10 gasoline: max. 10% ethanol containing gasoline
- Commercial E85 containing: 75% ethanol and 25% gasoline (winter grade) according to car, but according to analyses 83% ethanol (summer grade)
- Commercial diesel fuels: Neste Pro Diesel (winter grade) for Scudo and regular diesel for VW Passat
- Commercial CNG

The fuels were analysed at ASG Analytik-Service GmbH according to fuel standards for different fuel types (EN 228 for gasoline, EN 590 for diesel, DIN 51625 for E85). The analysed results for E10, E85, and diesel fuels are shown in Table 19. All the fuels fulfilled the standard quality specifications.

*Table 19. Selected properties of the test fuels.*

| Parameter | Gasoline E10 | Gasoline E85 | Pro Diesel | Diesel |
|---|---|---|---|---|
| Cetane number (DCN) | - | - | 69.9 | 66.3 |
| Cetane Index | - | - | 67.8 | 64.9 |
| Lead content, mg/kg | < 0.1 | - | - | - |
| Density 15 °C, kg/m$^3$ | 735.9 | 779.1 | 802.5 | 804.5 |
| Sulphur content, mg/kg | 8.1 | 1.2 | < 5 (2.6) | < 5 (3.5) |
| Manganese content, mg/L | < 0.5 | - | < 0.5 | < 0.5 |
| Water content, % (w/w) | - | 0.114 | < 30 (mg/kg) | < 30 (mg/kg) |
| Aromatic hydrocarbon content, % (V/V) | 26.72 | - | - | - |
| PAH content, % (w/w) | - | - | 1.2 | 1.3 |
| Ash content (775 °C), % (w/w) | - | - | < 0.005 | < 0.005 |
| Total contamination, mg/kg | - | - | 5 | < 1 |
| Carbon residue (10% Dist.), % (w/w) | - | - | < 0.10 | < 0.10 |
| Oxidation stability, min. | > 360 | > 360 | 35.7 (h) | 33.9 (h) |
| Gum content, mg/100 mL | < 4 | < 4 | - | - |
| Copper strip corrosion, Corr° | 1 | 1 | 1 | 1 |
| Electrical conductivity, µS/cm | - | 1.11 | - | - |
| $pH_E$ | - | 6.6 | - | - |
| Acidity (as acetic acid), % (w/w) | - | 0.003 | - | - |
| Total oxygen content, % (w/w) | 3.55 | - | - | - |
| Methanol, % (V/V) | < 0.1 | < 0.01 | - | - |
| FAME content, % (V/V) | - | - | < 0.1 | 0.2 |
| Ethanol, % (V/V) | 7.1 | - | - | - |
| Ethanol and higher alcohols, % (V/V) | - | 83.0 | - | - |

| | | | | |
|---|---|---|---|---|
| Unleaded gasoline content, % (V/V) | - | 17.6 | - | - |
| Ether (≥ 5 C-atoms), % (V/V) | 5.00 | 2.80 | - | - |
| Alcohols C3 - C5, % (V/V) | - | 0.56 | - | - |
| Other oxygenated compounds, % (V/V) | < 0.01 | - | - | - |
| Vapor pressure DVPE, kPa | 84.9 | 70.8 | - | - |
| Initial boiling point (IBP), °C | 31.8 | - | - | - |
| % (V/V) recovery at 250 °C, % (V/V) | - | - | 36.7 | 41.0 |
| % (V/V) recovery at 350 °C, % (V/V) | - | - | > 98 | > 98 |
| 95 % (V/V) recovery, °C | - | - | 296.0 | 320.5 |
| Final boiling point (FBP), °C | 180.5 | 82.1 | - | - |
| Flash point, °C | - | - | 64.5 | 62.5 |
| Distillation residue | 0.9 | 0.8 | - | - |
| HFRR (lubricity), µm | - | - | 341 | 365 |
| Kin. viscosity (40 °C), $mm^2/s$ | - | - | 2.3 | 2.3 |
| CFFP, °C | - | - | -48 | -41 |

In total five passenger cars (Figure 28 and Table 20) were tested during the measurement campaign. Four of the cars were rented (Europcar) and one was owned by VTT (DI-E2, **Scudo**).

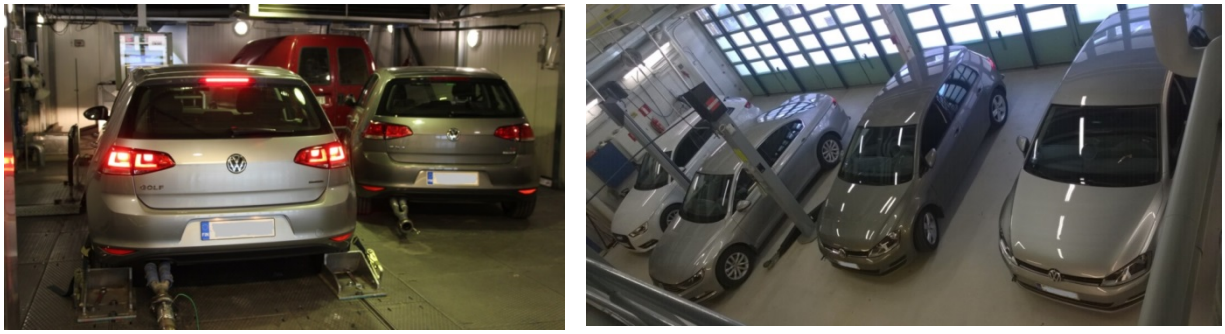


*Figure 28. The test cars stabilizing to -7 °C (left-hand side) and under preparation (right-hand side).*

*Table 20. Test cars and fuels.*

| Car | Year, type | Abbrev. | Fuel | After-treatment | Euro level | $CO_2$/km |
|---|---|---|---|---|---|---|
| **DI-E2** Fiat Scudo | 1999, 1.9 L 66 kW | Scudo | Diesel (Neste Pro Diesel) | | Euro 2 | - |
| **E10-E6** | 2015, 1.4 TSI 110 kW | E10 | E10 | TWC | Euro 6 | 112 |
| **E85-E6** | 2015, 1.4 TSI 92 kW | E85 | E85 | TWC | Euro 6 | 120 (gasoline) 116 (ethanol) |
| **DI-E6** | 2015, 1.6 TDI 88 kW | DI | Diesel (Regular diesel) | $NO_x$ adsorber catalyst, 2 × EGR | Euro 6 | 103 |
| **CNG-E6** | 2014, 1.4 TFSI 81 kW | CNG | CNG/ gasoline* | TWC | Euro 6 | 115 (gasoline) 88 (CNG) |

* The **CNG** car started at all the test driving cycles with CNG, no gasoline was used even at the start.

Three-way catalyst (TWC) technology introduced in the 1980s became mandatory for the gasoline fueled spark-ignited cars in EU. The TWC catalyst, operating on the principle of

non-selective catalytic reduction of $NO_x$ by CO, and HC, requires that the engine is operated at a nearly stoichiometric air-to-fuel (A/F) ratio. Modern catalyst systems for gasoline or natural gas engines include an oxygen sensor in front of the catalyst and a closed loop electronic control system to maintain the stoichiometric A/F ratio within a narrow range. ("Diesel Catalysts," n.d.).

In active $NO_x$ adsorbers, stored $NO_x$ is periodically released – with a typical frequency of about once per minute – during a short period of rich air-to-fuel ratio operation, called $NO_x$ adsorber regeneration. The released $NO_x$ is catalytically converted to nitrogen, in a process similar to that occurring over TWC. The catalyst washcoat combines three active components: (1) an oxidation catalyst, for example Pt, (2) an adsorbent, for example barium oxide (BaO), and (3) a reduction catalyst, for example Rh. ("NOx Adsorbers," n.d.).

EGR is a $NO_x$ emission reduction technology for diesel engines. EGR is a method by which a portion of an engine's exhaust gas is returned to its combustion chambers via the inlet system. EGR decreases the peak temperature of the diesel combustion flame. ("Exhaust Gas Recirculation," n.d.). One way to introduce EGR into the exhaust system is to extract a portion of the exhaust flow upstream of the exhaust gas turbine, cool it and then return it to the intake manifold after the intake air compressor through an electronically-controlled EGR valve. This approach is commonly referred to as high pressure loop (HPL) EGR or as short-route (SR) EGR. Another scheme for EGR implementation in (heavy-duty) diesel engines is the low pressure loop system (LPL EGR) – also known as long-route (LR) EGR. This system is often employed in conjunction with particulate filter-based aftertreatment systems, where several benefits may accrue. Rather than sourcing EGR from a pre-turbine location (as in the HPL EGR case), LPL EGR systems use exhaust that has been filtered through diesel particulate filters.

## 4.3 Test procedure and test matrix

Cars were tested on a chassis dynamometer in a climatic test cell at -7 °C according to the European exhaust emissions driving cycle (UN ECE R83) (Figure 29). Driving cycle, which totals 11.0 km, was divided into three test phases to study emissions behavior at cold start and with warmed-up engines. The first and second test phases each consisted of 2.026 km driving (ECE15), and the third test phase, the extra-urban driving cycle (EUDC), was 6.955 km. The basic equipment are dynamometer Froude Consine 1.0 m, DC, 100 kW, constant volume sampler (CVS) AVL CVS i60 LD, Venturi-type and Pierburg AMA 2000, triple bench for gaseous regulated emissions.

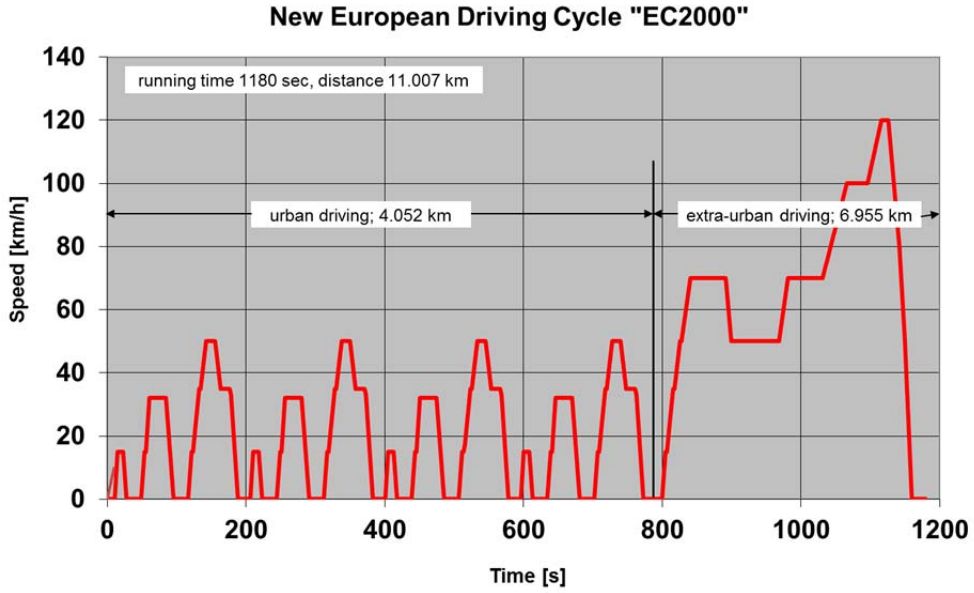



*Figure 29. European Driving Cycle according to the UN ECE R83 Regulation.*

Regulated and unregulated emissions were measured for all the cars at -7 °C (Table 21).

*Table 21. Test matrix.*

| | Regu-lated | Alde-hydes | C1–C8 | FTIR | PM: PAH, Ames, DTT | SVOCs (Tenax) | SVOC (Empore): PAH, microAmes, DTT | SPN (PMP) | EC/OC | Micro-GC |
|---|---|---|---|---|---|---|---|---|---|---|
| **DI-E2** | 8 | 8 | 8 | 8 | 8 | 3 | 6 | 8 | 2 | 2 |
| **E10-E6** | 7 | 7 | 7 | 7 | 7 | 2 | 5 | 7 | 2 | 2 |
| **E85-E6** | 7 | 7 | 7 | 7 | 7 | 2 | 5 | 7 | 2 | 3 |
| **DI-E6** | 4 | 4 | 4 | 4 | 4 | 1 | 4 | 4 | 0 | 1 |
| **CNG-E6** | 4 | 4 | 4 | 4 | 4 | 1 | 4 | 4 | 0 | 3 |

## 4.4 Analysis methods

### 4.4.1 Gaseous emissions

Equipment used in the measurement of the CO, HC, and $NO_x$ emissions conforms to the specifications of the UN ECE R83. The true oxygen contents and densities of the fuels were used in the calculation of the results. FID used for measurement of hydrocarbons detects all carbon-containing compounds, also oxygenates, which is discussed by Sandström-Dahl et al. (2010) and Aakko-Saksa et al. (2011). The calculation method chosen here uses the density of 0.619 g/dm$^3$, and for the **E85-E2** car density of 0.923 g/dm$^3$ according to the EC regulation 692/2008 method (see chapter 4.3.3).

Aldehydes were collected from the CVS diluted exhaust gas using 2,4-dinitrophenylhydrazine (DNPH) cartridges. The DNPH derivatives were extracted with acetonitrile and water and analysed using HPLC technology (Agilent 1260, UV detector, Nova-Pak C18 column). Aldehydes reported are *formaldehyde (FA), acetaldehyde (AA), acrolein (Acro), propionaldehyde (PrA), crotonaldehyde (CrA), methacrolein (MeAc), butyraldehyde (BuA), benzaldehyde (BzA)), valeraldehyde (VA), m-tolualdehyde (mTol), and hexanal (HexA).*

The diluted exhaust gas for analysis of C1–C8 hydrocarbons was collected from the same Tedlar bags that were used for the measurement of the regulated emissions, and fed to the gas chromatograph (HP 5890 Series II, $Al_2O_3$, KCl/PLOT column, FID-detector, an external standard method). The hydrocarbons analysed are *methane, ethane, ethene, propane, propene, acetylene, isobutene, 1,3-butadiene, benzene, toluene, ethyl benzene and m-, p-, and o-xylenes.*

A number of compounds, amongst others *ethanol ($CH_3CH_2OH$), ammonia ($NH_3$), sulphur dioxide ($SO_2$), acetic acid, and nitrous oxide ($N_2O$)*, were measured on-line at one-second intervals using Fourier Transformation Infra-Red (FTIR) equipment (Gasmet Cr-2000).

### 4.4.2 PM and SVOC sampling

**PM sampling with high-capacity collection system**

High capacity collection system was used for the PM emission measurement and collection of samples for PAH, micro-Ames and DTT analyses. A high-capacity sampler has been developed in 1990s for measurements of gasoline cars (Kokko et al. 2000), and many set-up options are available today at VTT. The high-capacity collection system here included a dilution tunnel (Ø 265 mm), a sample probe (Ø 80 mm), two filter holders in parallel (Ø 142 mm), a blower (Siemens ELMO-G, 2BH1 810-1HC36, 11 kW), a flow meter (Bronkhorst F-106C1-HD-V-12) and a controller (Stafsjö MV-E-80-P-TY-AC100-PN10).

The sample flow can be controlled up to 2000 L/min to obtain appropriate masses of particles. The filter type used was Fluoropore 3.0 µm FSLW (Figure 30). In these measurements, the flow was adjusted to 200 – 1500 L/min and two Ø 142 mm filters were used in parallel. A Sartorius SE2-F microbalance was used to weigh the filters. After the sampling the filters were weighed and then wrapped in aluminum foil to protect them from light, to avoid changes that could affect the mutagenicity results from the samples. Particulate filters were then stored in freezer, and sent for further analysis (PAH, micro-Ames, and DTT). The PM mass emissions (per km) were calculated based on the high-capacity collection system (Fluoropore filters).

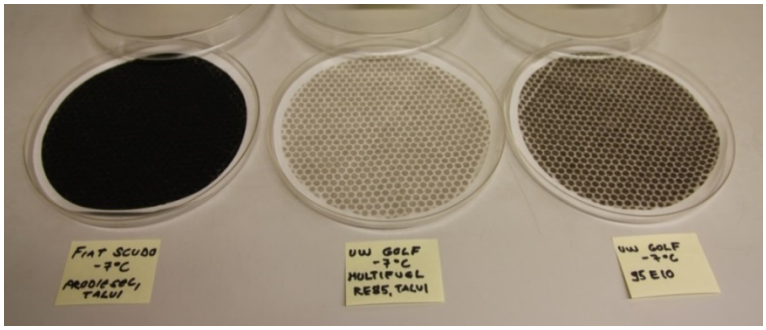



*Figure 30. Fluoropore filters after sample collection, from left:* ***DI-E2 (Scudo), E85-E6****, and* ***E10-E6****.*

For the **Scudo's** having high PM emission levels, the flow of high-capacity sampler was adjusted to 200 L/min and this part of the exhaust gas was not returned to the CVS system. This modification was taken into account in the calculations of the emission results for **Scudo**.

When collecting samples for **E85**, it was noticed that the filter holders of the high-capacity sampler became wet (Figure 31).

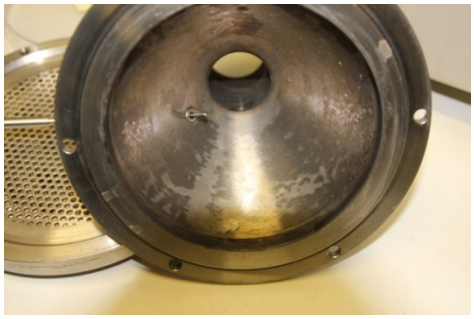


*Figure 31. The high-capacity sampler filter holders became wet when collecting samples from **E85**.*

**Sampling with the standard collection system: anions, EC/OC and SVOC using Empore disks**

Standard PM sampling system was used for samplings for anions, EC/OC and SVOC and EC/OC sampling.

Primary particle samples were collected with standard PM collection system using Pallflex® TX-40 filters (∅ 47 mm) (Figure 32). These Pallflex TX-40 filters were used for the anion analyses. EC/OC samples were collected in replicate tests with standard PM collection system by using Munktell MK 360 (∅ 47 mm) quartz filters as primary filters (in our future projects, Pallflex Tissuquarz 2500QAT-UP will be used for the EC/OC analyses).


*Figure 32. Standard particle collection system and primary Pallflex® TX-40 filter (∅47 mm) collected (from left): **DI-E2 (Scudo), E85-E6**, and **E10-E6**.*

Collection and analysis of semivolatile organic compounds, SVOCs, was tested and evaluated with Empore SDB-XC disks (∅ 47 mm). Instead of Pallflex TX-40 back-up filters, SVOC Empore disks were placed as back-up filters for SVOC sampling in the standard PM sampler (primary filters TX-40). Sample flow rate was 17.5 L/min in the standard PM sampling

system (Figure 33). The Empore disks were then sent for analyses of PAHs, oxidative potential (DTT), and mutagenicity (Ames/microAmes).


*Figure 33. Empore disks after sample collection, from left:* ***DI-E2 (Scudo), E85-E6****, and* ***E10-E6****.*

**SVOC sampling with Tenax tubes**

Volatile and partly semivolatile compounds were also collected to Tenax TA-Carbopack B tubes. The tubes were borrowed from Finnish Meteorological Institute and the results were also analysed there by Heidi Hellén by procedures described in (Hellén). Tenax tubes were located after the PM filters (Fluoropore) of high-capacity PM sampling system using a side-stream of diluted exhaust gas. Sample flow of ~0.1 L/min was drawn through Tenax TA-Carbopack B -tubes (Figure 34) with a separate pump during the whole driving cycle. One background Tenax-tube was collected. The analysed compounds were: *benzene, toluene, ethylbenzene, p/m-xylene, styrene, o-xylene, propylbenzene, 3-ethyltoluene, 4-ethyltoluene, 1,3,5-trimethylbenzene, 2-ethyltoluene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, carbon tetrachloride, heptane, octane, decane, nonane, isoprene, 2-methyl-3-butenol, α-pinene, camphene, β-pinene, carene, p-cymene, 1,8-cineol, limonene, terpinolene, linalool, myrcene, 4-acetyl-1-methylcyclohexene, nopinone, bornylacetate, geranylacetate, longicyclene, iso-longifolene, β-caryophyllene, aromadendrene, α-humulene, and 4-allylanisole.*

Ten SVOC samples were collected with Tenax-tubes. Three parallel tubes were collected for **DI-E2** (Scudo), two for **E85**, and **E10** and only one for **CNG** and **DI-E6**. The analysis method used has originally been developed for ambient (lower concentration) air samples.

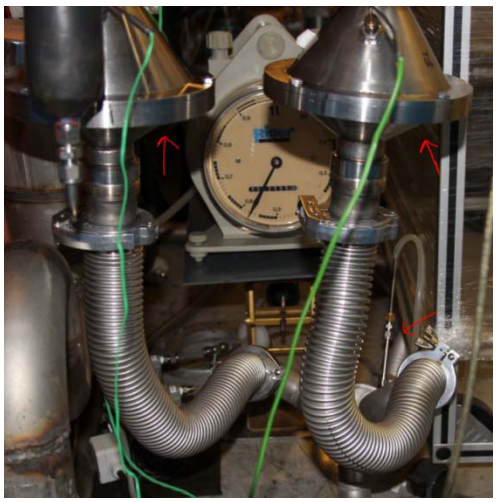


*Figure 34. Tenax-tube, Fluoropore filter holders, and gas meter for measurement of sample volumes in Tenax-tubes.*

Particulate (PM) and semivolatile (SVOC) sample collections and flows used are presented in Table 22. Face velocity on filters varied from ~13 to 99 cm/s (see Chapter 3.2). When the EC/OC samples were not collected, the Empore disk was used as a secondary filter after the TX-40 filters (see Test Matrix 5.5).

*Table 22. Particulate (PM) and semivolatile (SVOC) sampling flows.*

| | DI-E2 (Scudo) Sampling flow (L/min) | E10-E6 Sampling flow (L/min) | E85-E6 Sampling flow (L/min) | CNG-E6 Sampling flow (L/min) | DI-E6 Sampling flow (L/min) |
|---|---|---|---|---|---|
| PM – Fluoropore 3.0 FSLW Ø 142 mm, two in parallel | 200 | 1200 | 1350 | 1500 | 1500 |
| PM (anions) – Pallflex TX40HI20WW Ø 47 mm (primary) | 17.5 | 17.5 | 17.5 | 17.5 | 17.5 |
| SVOC** Empore Ø 47 mm (back-up) | 17.5 | 17.5 | 17.5 | 17.5 | 17.5 |
| PM (EC/OC) – Munktell MK 360 Quartz Ø 47 mm | 7.5 and 17.5* | 17.5 | 17.5 | - | - |
| VOC/SVOC – Tenax tubes | 0.12 | 0.07 | 0.09 | 0.08 | 0.10 |

*Sample too dark for EC/OC analysis ** In the standard sampling system, either the EC/OC samples were collected using primary Quarz filters or the SVOC samples were collected using Empore disks as secondary filters after the TX-40 filters (see Figure 11 and Table 21).

### 4.4.3 Solid particle number (SPN)

Solid particle number emission was measured by particle counter. This apparatus and the procedure are in compliance with the one determined by the Particulate Measurement Programme (PMP) of the United Nations Economic Commission for Europe (hereinafter 'UN/ECE') and subsequently used in type approval tests for Euro VI (Regulation (EU) No 133/2014).

The instrument (Figure 35) is butanol Condensation Particle Counter (bCPC): Airmodus A23

- Particle size range: from 7 nm to 1 µm
- Particle concentration: 0 – 100 000 particles per cubic centimeter ($cm^3$)
- Response time: 3 s
- Inlet flow rate: 1 L/min

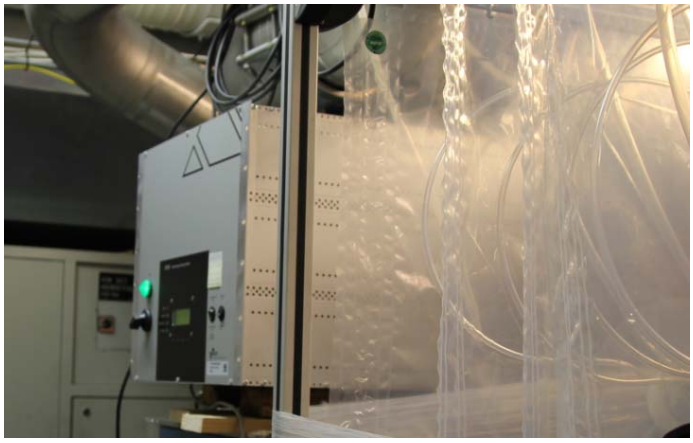


*Figure 35. The Airmodus A23 butanol Condensation Particle Counter in the middle.*

### 4.4.4 Anions and EC/OC

**Anion samples** were collected to standard Pallflex TX-40 filters (∅ 47 mm) which were used as primary filters when collecting SVOCs with Empore disks. The sample flow was adjusted to 17.5 L/min.

**EC/OC samples** were collected with standard particle collection system by using Munktell MK 360 (∅ 47 mm) quartz filters. The EC/OC samples were collected only for **DI-E2 Scudo, E10-E6**, and **E85-E6** cars. The particles were collected over the whole driving cycle to one filter for **E10-E6** and **E85-E6**, while for **DI-E2 Scudo** the samples were collected in three phases due to its high PM emission level. Sample flow of the system was adjusted to 17.5 L/min and once to 7.5 L/min for **Scudo** to obtain suitable darkness of samples for the EC/OC analysis. Munktell MK 360 (∅47 mm) quartz filters had been heated in an oven at 700 °C for 1 hour and stabilized prior sample collection. (In our future projects, Pallflex Tissuquarz 2500QAT-UP will be used for the EC/OC analyses.)

### 4.4.5 PAH, microAmes, and oxidative potential

The filter samples were sent to NabLabs laboratories and VTT Expert Services in which they were weighed and Soxhlet extraction (16 h, low level light was maintained during the extraction) was performed in dichloromethane, after which the solvent was changed into 1 mL DMSO for Ames- and microAmes samples.

**Polycyclic aromatic hydrocarbons (PAHs)**

At MetropoliLab a total of 24 individual PAH compounds were analysed from the Fluoropore filters and Empore disks according to ISO 16000-6:2011, EN 14662-4:2005 analysis method. The filters and disks were extracted with toluene in ultrasonic bath and then analysed. PM filter samples of **Scudo** were so dark/black that they were extracted twice with toluene in ultrasonic bath. It was also noticed that after toluene extraction of the Empore disks the solution was cloudy (milky) and deposit fell down to the bottom of the vial prior the analysis. This would imply that Empore disks are partly degraded during the toluene extraction of the disks in ultrasonic bath. Though the deposit did not disturb the PAH analyses. Detection limits were 10–30 ng (1 µg/m$^3$) per compound and measurement uncertainty 30%. The analysis method has been developed for ambient air samples in filters or/and in XAD-2 adsorbent.

**MicroAmes assays**

Genotoxicity of the samples was analysed microAmes *Salmonella typhimurium* reverse mutation test with and without metabolic activation (rat liver fraction S9). The reverse mutation tests measure the mutations in histidine utilization capability (his- → his+). The reversion is detected in 384-well plate as color change in wells. MicroAmes test was performed with *Salmonella typhimurium* strain TA98. DMSO was used as solvent control. 4-nitroquinoline 1-oxide (4-NQO) and 2-amino anthracene were used as positive control without and with S-9 mix, respectively.

The test concentrations were determined according to the amount of exhaust gas passed through the filter samples. For **Scudo**, two batches of samples were analysed.

**Oxidative potential (DTT assay)**

DTT assays for the PM (Fluoropore filter) samples, SVOC (Empore disk) samples and the combined sample of PM and SVOC for Euro 2 diesel (**Scudo**), were performed at Biosafe Biological Safety Solutions Ltd.

Sample treatment

The Fluoropore and Empore samples were cut into pieces with sterile scissors and transferred into sterile petri dish (diameter 9 cm) filtering side upwards. Six milliliter of methanol was added onto the filters and petri dish was covered with laboratory film. The samples were transferred into Branson 251OE sonicator to float on top of the water. Samples were sonicated 15 s and plate was carefully mixed and sonicated for another 15 s.

Methanol was transferred into 8 mL acid-washed amber sample vials. Sample vials were placed on +30 °C heating block and dried overnight under a constant flow of nitrogen. For **Scudo** the sample extracts were weighed and re-suspended in ultra-pure water (Millipore Direct Q 5UV-R) to a *fixed concentration of 500 µg/mL*. The reference control filter extracts were re-suspended into volume corresponding to the sample obtained from the same filter type with the lowest retained particulate mass. For other cars, the sample extracts were re-suspended in ultra-pure water (Millipore Direct Q 5UV-R) to a fixed concentration of *88 $m^3$ diluted exhaust gas /mL for Fluoropore* filter samples and 0.86 *$m^3$ diluted exhaust gas/mL for Empore* disk samples.

DTT assay - **Scudo**

The DTT assay was performed according to Charrier & Anastasio (2012) except that 200 µM DTT in Chelex treated 0.10 M phosphate buffer (77.8 mM $NaH_2PO_4$ and 22.2 mM $KHPO_4$) was used and OD 412 nm measurements were performed after 5, 10, 15, and 20 minutes. The DTT assay was performed with laboratory lights turned off and in subdued natural light. Chelex treated 0.1 M phosphate buffer was used as negative control and 9,10-phenanthrenequinone (30 µM) as positive control. The negative sample control (methanol) value was subtracted from the sample results. The analysis was repeated with three replicates. The positive control, 9,10- phenanthrenequinone (30 µM), resulted 3.5 times higher DTT loss (9.4 µM/min.) than the sample with highest oxidative potential (2.68 µM/min). Phosphate buffer DTT loss did not exceed the detection limit.

DTT assay testing of the samples started with **Scudo** samples, which were sent for DTT analysis as mass based (PM and SVOC mg/sample) and at the same time reference Fluoropore filter (PM) and reference Empore filter (SVOC) were tested. DTT samples of **E10**, **E85**, **CNG**, and **DI** were tested as volume based ($m^3$ exhaust gas/sample filter).

### 4.4.6 Analyses laboratories

External analysis laboratories utilized in the project:

- MetropoliLab Oy: PAHs from Fluoropore filters and Empore disks.
- NabLabs Oy: PAHs from the Soxhlet extracts of Fluoropore filters and Empore disks. Soxhlet extraction of **DI-E2 Scudo** Ames- and all the microAmes samples.

- Biosafe Biological Safety Solutions Ltd: Ames and microAmes tests and DTT assays from Fluoropore filters and Empore disks and their combined sample (**Scudo**). BioSafe used NabLabs (Jyväskylä) as a sub-contractor to extract the Ames samples.
- VTT Expert Services Ltd: Soxhlet extraction of PAH samples (analysed at NabLabs) and **DI-E2 Scudo** microAmes samples (analysed at BioSafe).
- Finnish Meteorological Institute: Tenax tubes and their analyses.
- ASG Analytik-Service Gesellschaft mbH: Fuel analyses.

## 4.5 Results

### 4.5.1 Regulated emissions

The measured regulated emissions and Euro 6 emission limits are presented in Table 23.

*Table 23. The regulated emissions at -7 °C for the test cars and Euro 6 limits at +23 °C for gasoline and diesel passenger cars for comparison.*

| | CO (mg/km) | HC (mg/km) | PM[a] (mg/km) | $NO_x$ (mg/km) | $CO_2$ (g/km) | $CO_2e$ (g/km) | PN (#/km ) |
|---|---|---|---|---|---|---|---|
| **DI-E2 (Scudo)** | 501 | 69 | 62.63 | 1148 | 239 | 242 | 1.28E+14 |
| **E10-E6** | 810 | 149 | 1.35 | 31 | 180 (112*) | 180 | 7.63E+11 |
| **E85-E6** | 2674 | 478 (0.619 g/dm$^3$)<br>720 (0.923 g/dm$^3$) | 0.92 | 16 | 157<br>(116* Ethanol<br>120* Gasoline) | 158 | 7.49E+11 |
| **CNG-E6** | 75 | 98 | 0.48 | 201 | 139<br>(88* CNG.<br>115* Gasoline) | 142 | 6.63E+10 |
| **DI-E6** | 97 | 15 | 0.64 | 463 | 191 (103*) | 196 | 5.62E+09 |
| **Euro 6 limit values** | | | | | | | |
| **Euro 6 – SI (Gasoline, +23 °C)** | 1000 | HC: 100 and NMHC: 68 | GDI: 4.5 [b] /5.0 | 60 | | | 6.0E+11 (6.0E+12 [c] ) |
| **Euro 6 – SI (Gasoline, E85, -7 °C)** | 15000 | 1800 | | | | | |
| **Euro 6 – CI (Diesel,+23 °C)** | 500 | - | 4.5 [b] /5.0 | 80 | | | $6.0 \times 10^{11}$ |

* Given in registration document, at +23 °C. a) PM calculated from high-capacity collection system (Fluoropore) as regular PM system was used for SVOC and EC/OC collections. b) PMP analysis method c) only GDI and until 09/2017

Carbon dioxide ($CO_2$) and carbon dioxide equivalent ($CO_2e$)[17] emissions were highest for **Scudo** (239 g/km and 242 $CO_2e$ g/km) and lowest for **CNG** (139 g/km) and 142 $CO_2e$ g/km) (Table 23 and Figure 36).

[17] Global warming potentials (GWP) used in $CO_2e$ calculations : $CO_2$=1 $CH_4$=25 $N_2O$=298

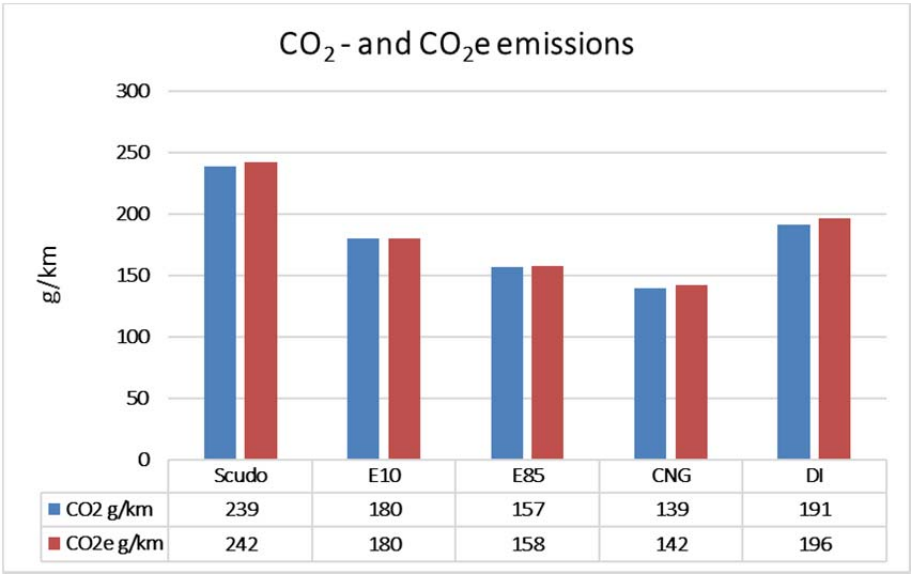



*Figure 36. Carbon dioxide $CO_2$ emissions (g/km) and $CO_2e$ emissions (g/km) for the test cars at -7 °C.*

Highest CO (2674 mg/km) and HC (478 mg/km) emissions were measured for **E85-E6**. The lowest CO (75 mg/km) was observed for **CNG-E6** and the lowest HC (15 mg/km) for **DI-E6** (Table 23 and Figure 37). The Euro 6 level limit for CO is 1000 mg/km and for HC 1000 mg/km at +23 °C for spark ignition cars.

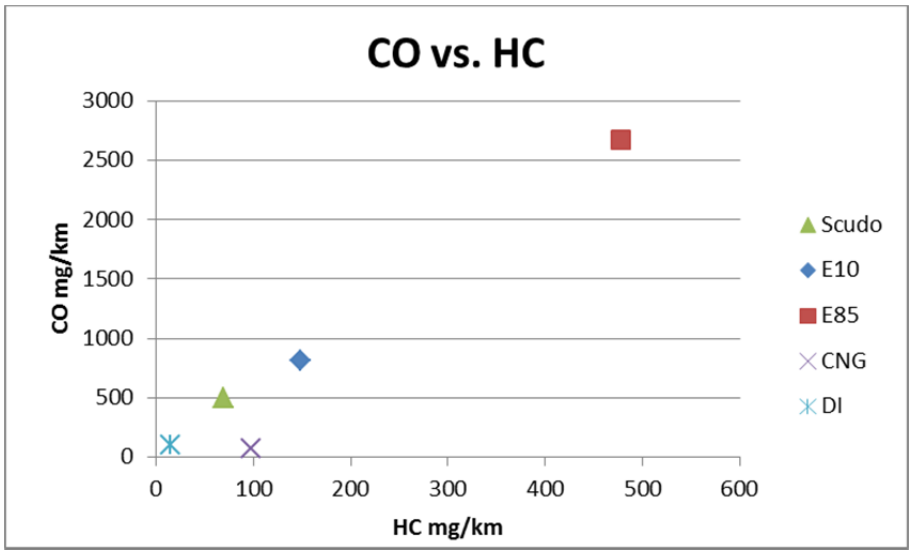



*Figure 37. CO and HC emissions (mg/km) over the European test cycle at -7 °C.*

As discussed in Chapter 3.3.2, measurement of the regulated HC emissions with an FID takes into account all carbon-containing compounds, also alcohols and aldehydes. Thus is represents rather "organic gases" than the HC emissions. Integration of the total hydrocarbons analysed by GC-FID (calibrated with propane) gives an overview of the the actual hydrocarbon emissions (Figure 38). Regulated HCs consist mostly of other compounds than hydrocarbons for the E85-E6 car.

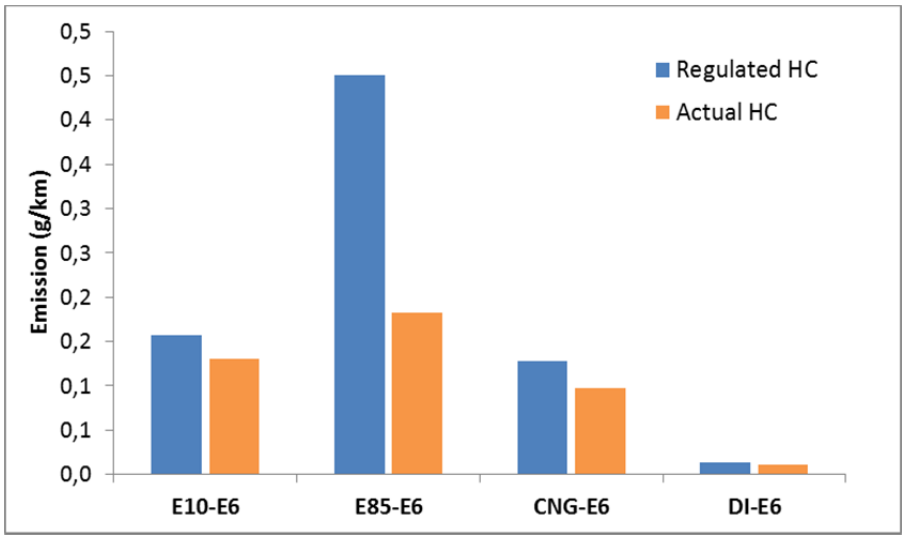



*Figure 38. Regulated HC emissions (FID) and actual HC emissions (integrated GC-FID). Euro 6 cars, the European test cycle at -7 °C.*

The highest PM (62.63 mg/km) and $NO_x$ (1148 mg/km) emissions were measured for **DI-E2 Scudo** (Table 23 and Figure 39). This was expected as **Scudo** did not have DPF or $NO_x$ reduction technology. The lowest PM (0.48 mg/km) was measured for **CNG-E6** and the lowest $NO_x$ 16 mg/km for **E85-E6**. The Euro 6 limit for PM is 5.0 mg/km (GDI and DI) and for $NO_x$ 80 mg/km (diesel) and 60 mg/km (gasoline) at +23 °C.

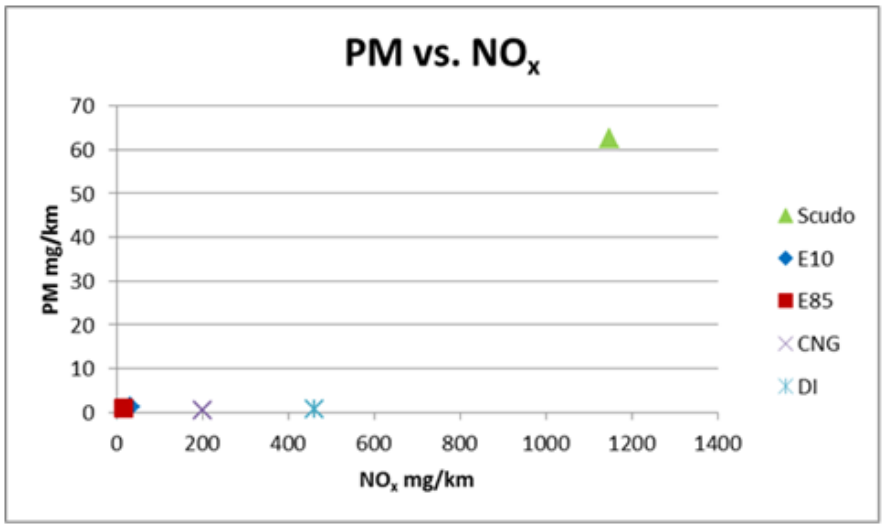



*Figure 39. PM and $NO_x$ emissions (mg/km) over the European test cycle at -7 °C. Euro 2 diesel car (Scudo) and four Euro 6 cars.*

Solid particle number emission was the highest for the Euro 2 diesel car **Scudo** (1.28E+14 #/km) and lowest for the new **DI-E6** car having DPF (5.62E+09 #/km). The next highest SPN emissions were observed for **E10-E6** (7.63E+11 #/km) and **E85-E6** (7.49E+11 #/km). The next lowest SPN was measured for **CNG** (6.63E+10 #/km). Euro 6 level limit for SPN is 6.0E+11 #/km at +23 °C, though until 09/2017 it is 6.0E+12 for direct injection gasoline cars (Table 23 and Figure 40).

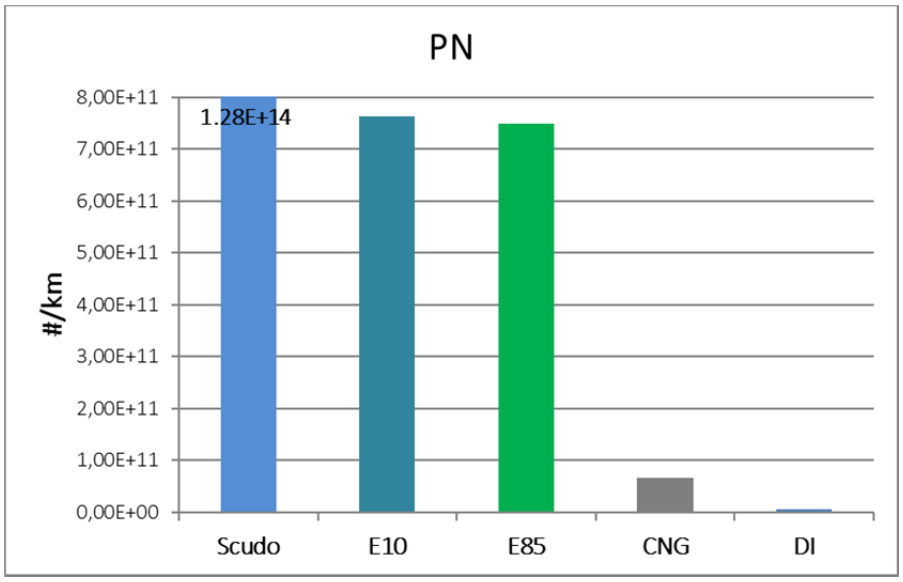
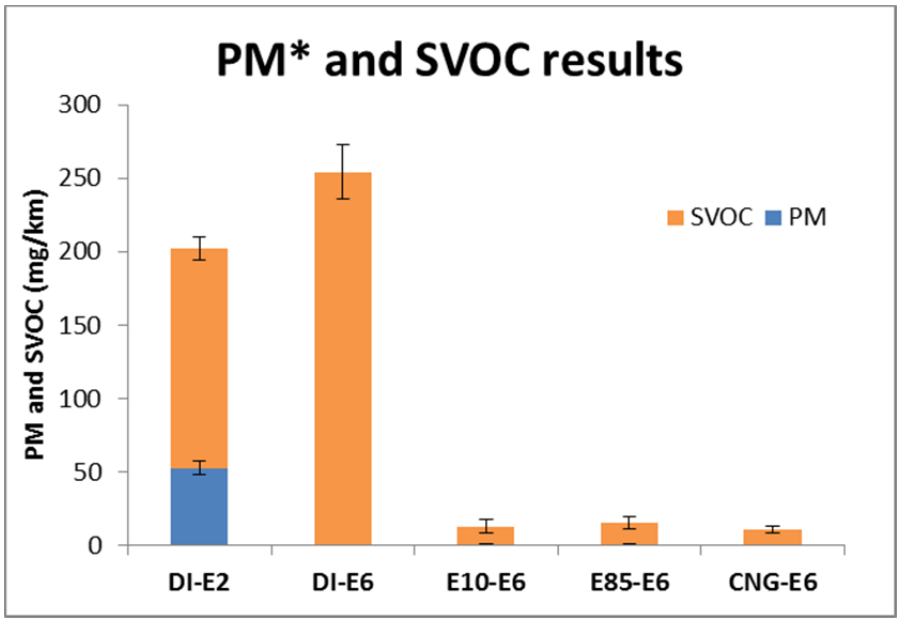



*Figure 40. Solid PN emissions (#/km) over the European test cycle at -7 °C. Euro 2 diesel car (Scudo) and four Euro 6 cars.*

### 4.5.2 PM and SVOC

Regulated PM emissions were shown in the previous Chapter. In Figure 41, both PM and SVOC emissions are shown. The magnitude of SVOC emissions depends on collection material and collection parameters, as explained in Chapter 3.2.

With the SVOC sampling system using Empore disks, the SVOC emissions were higher than the PM emissions for all cars. For **DI-E6** a considerably high amount of SVOC was observed in the Empore disks in the tests. The amount of sample as milligrams was 10–20 times higher than for the other new Euro 6 cars and double the amount collected for the old Euro 2 diesel **Scudo**. This was considered as surprising and more detailed analysis of the chemical composition of the SVOC sample for **DI-E6** would have been informative, but more detailed analysis of these samples was unfortunately not possible in this project. However, PAH compounds were analysed from the SVOC samples (4.5.8).




* PM and SVOC results using the standard collection system.

*Figure 41. PM and SVOC emissions (mg/km) over the European test cycle at -7 °C. Euro 2 diesel car (DI-E2) and four Euro 6 cars.*

### 4.5.3 Aldehydes

Overall highest total aldehyde emissions were measured for **DI-E2 Scudo** (41.2 mg/km). Due to high acetaldehyde emissions **E85-E6** had significantly higher overall aldehyde emissions (32.2 mg/km) than other Euro 6 level cars at -7 °C (0.8 – 4.1 mg/km ) (Figure 42).

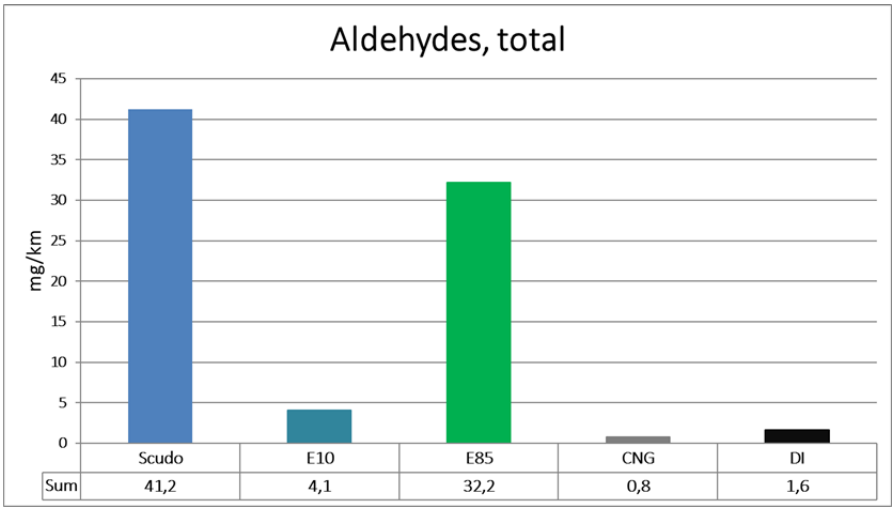



*Figure 42. Total aldehyde emissions (mg/km) for all the test cars over the European test cycle at -7 °C. Euro 2 diesel car (Scudo) and four Euro 6 cars.*

The highest formaldehyde emissions (18 mg/km) were measured for **DI-E2 Scudo** and lowest for **DI-E6** (0.3 mg/km) (Figure 43). The highest acetaldehyde emissions were detected for **E85-E6** (24.6 mg/km) and its acetaldehyde emissions were significantly higher than for other Euro 6 level cars and 4 times higher than for **Scudo**. The lowest acetaldehyde emissions were detected for **CNG**.

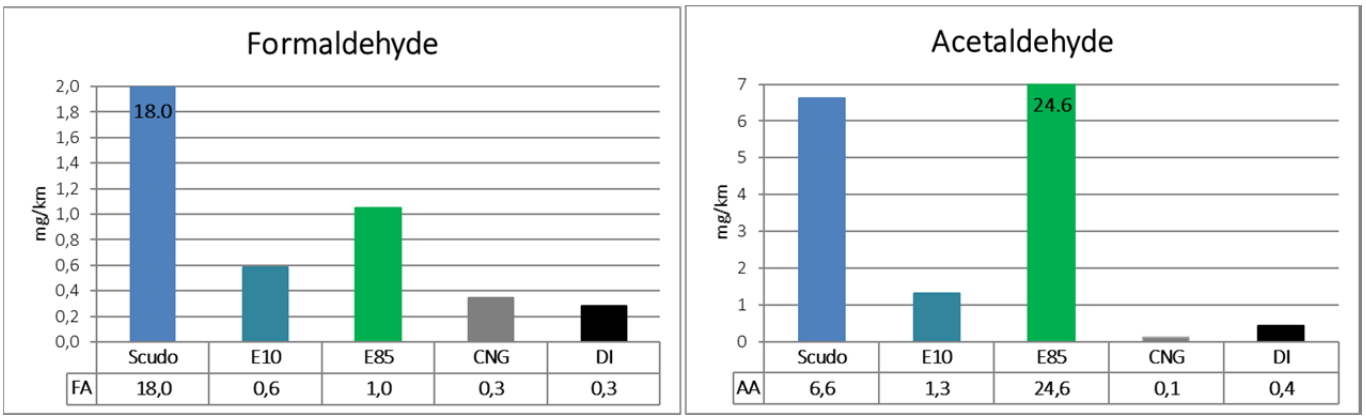



*Figure 43. Formaldehyde and acetaldehyde emissions (mg/km) for all the test cars over the European test cycle at -7 °C. Euro 2 diesel car (Scudo) and four Euro 6 cars.*

### 4.5.4 Individual hydrocarbons

With GC-FID, the highest C1–C8 emissions had **E85** and the highest methane emission had expectedly **CNG**. The lowest overall C1–C8 emissions had Euro 6 **DI** (Figure 44). C1–C8 emissions from **E85** composed mostly of methane (56 mg/km) and ethene (40 mg/km), when toluene (17.3 mg/km) and *m*-, *p*-xylenes (11.2 mg/km) were the main components for **E10**.

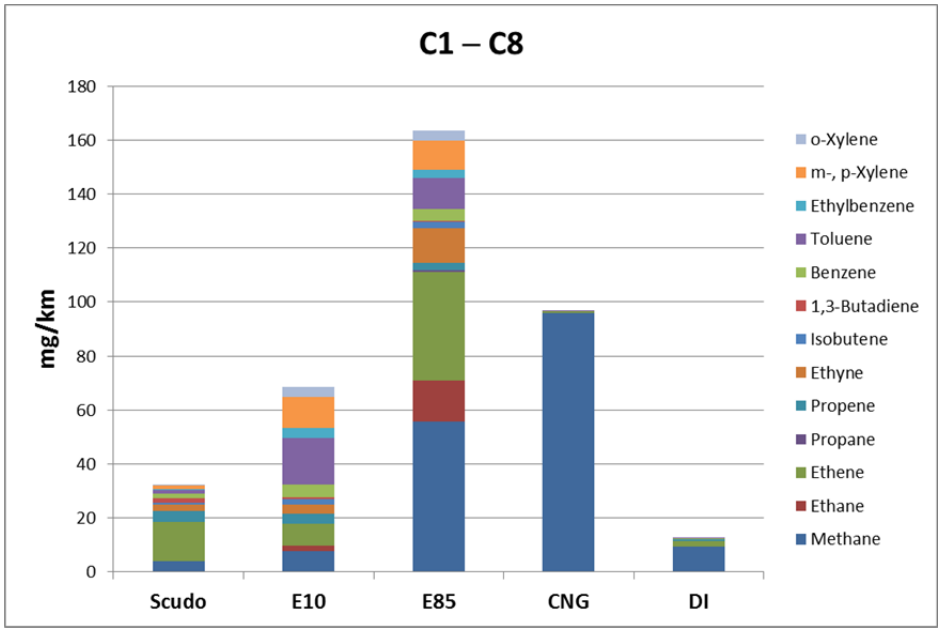



*Figure 44. Overall C1–C8 emissions (mg/km) for all test cars measured with GC-FID. The European test cycle at -7 °C. Euro 2 diesel car (Scudo) and four Euro 6 cars.*

The highest BTEX (benzene, toluene, ethylbenzene, and xylenes) emissions were measured for **E10-E6**, 41 mg/km. Both **CNG-E6** and **DI-E6** had very low levels of BTEX emissions, that is, 0.3 – 0.4 mg/km, which is ten times lower than for **E10-E6** (Figure 45).

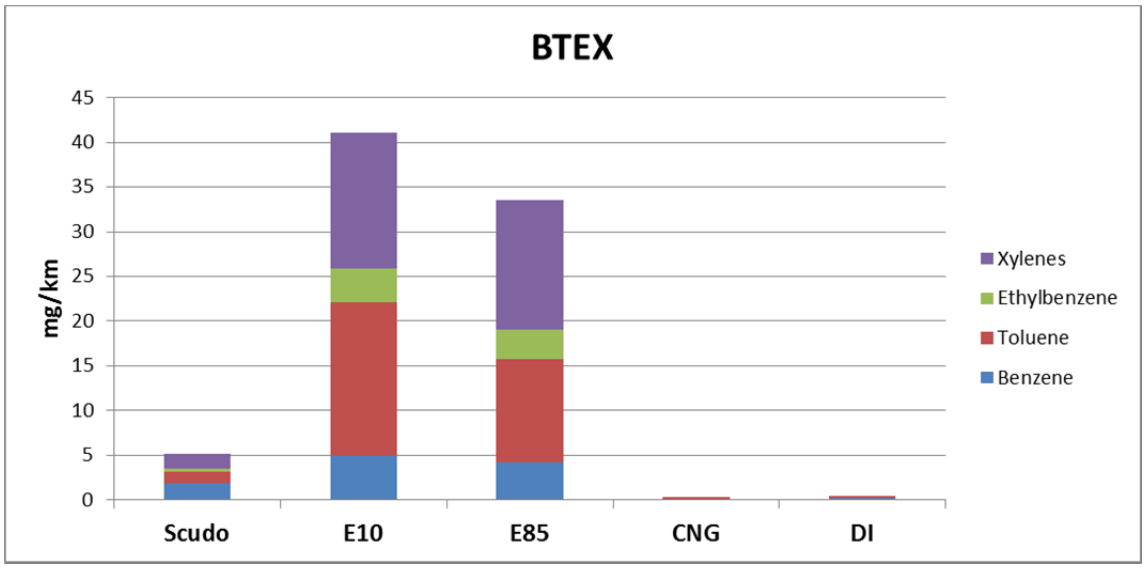



*Figure 45. BTEX levels (mg/km) for the test cars. The European test cycle at -7 °C. Euro 2 diesel car (Scudo) and four Euro 6 cars.*

The results from samples collected using Tenax TA-Carbopack B -tubes for different VOCs and SVOCs are shown in Figure 46 as mg/km. The results for **CNG-E6** and **DI-E6** are only indicative as no parallel analyses were performed (only one sample per car). The highest emissions were analysed for **E10-E6** and the lowest for **CNG-E6** and **DI-E6**. Two parallel analysis results for **E85-E6** differed considerably from each other and therefore the results given from only one tube are indicative. For Tenax-tube collections for **E85**, it is not known if the collection of samples failed or if the alcohol containing exhaust gas is not suitable for this type of Tenax-tubes.

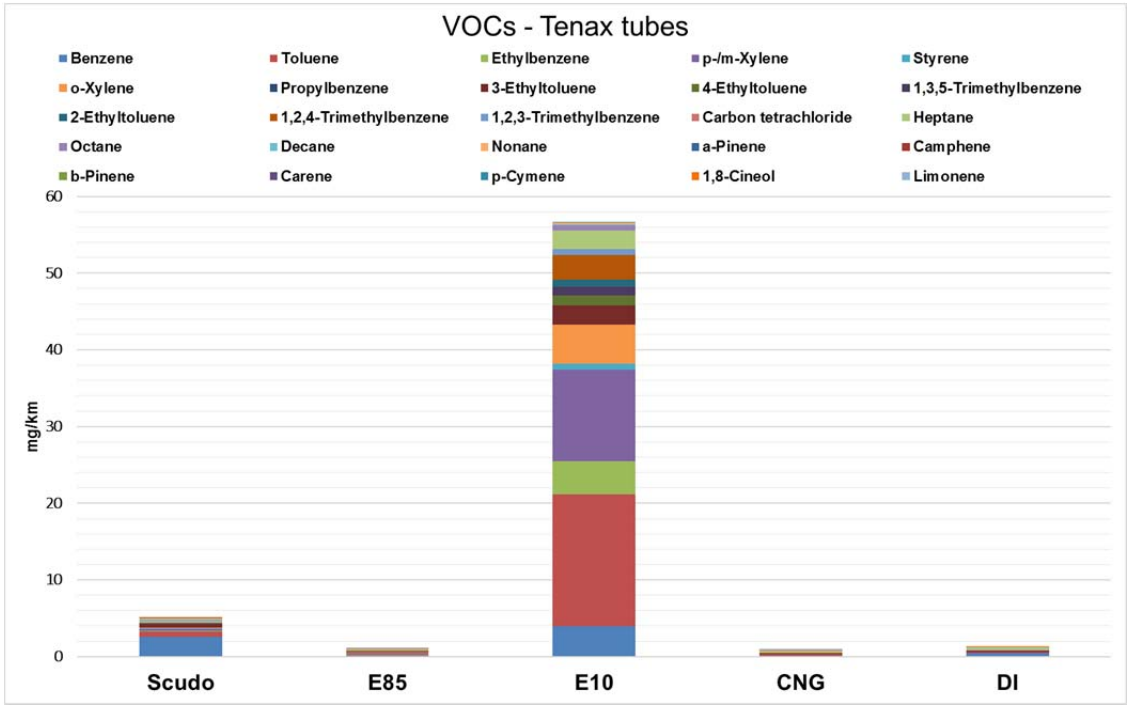



*Figure 46. Tenax tube VOC-analysis results for all cars as mg/km. The European test cycle at -7 °C. Euro 2 diesel car (Scudo) and four Euro 6 cars.*

### 4.5.5 Alcohols, ethers, ammonia, nitrous oxide, and other gaseous components

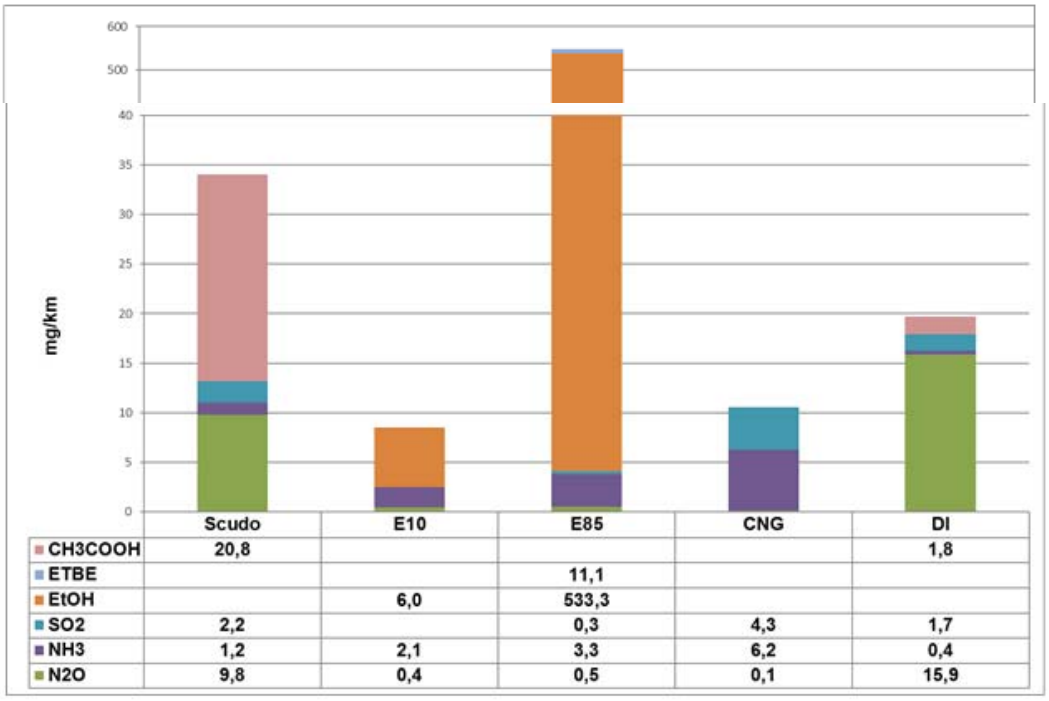
A number of compounds, amongst others ethanol (EtOH, $CH_3CH_2OH$), ammonia ($NH_3$), acetic acid ($CH_3COOH$), and nitrous oxide ($N_2O$), were measured on-line at one-second intervals using FTIR equipment (Gasmet Cr-2000). Results for nitrous oxide ($N_2O$), ammonia ($NH_3$), sulphur dioxide ($SO_2$), ethanol (EtOH), ETBE (ethyl *tert*-butyl ether), and acetic acid ($CH_3COOH$) are presented in Figure 47.

As expected the highest ethanol emissions were detected for **E85-E6** (533 mg/km) and **E85** had also highest ETBE emissions (11 mg/km). **E10-E6** had 6 mg/km ethanol emissions and not measurable amounts of ETBE emissions. Ethanol and ETBE were not measured for other cars.

Highest $N_2O$ emissions were detected for the new Euro 6 **DI-E6**, 16 mg/km, when the emissions for the old Euro 2 diesel car **DI-E6 Scudo** were 10 mg/km. All the other cars had nitrous oxide emissions between 0.1 and 0.5 mg/km.

Highest ammonia emissions were measured for **CNG-E6**, 6 mg/km, and the lowest for **DI-E6** (0.4 mg/km). Ammonia was also detected for **E10-E6** (2 mg/km) and **E85-E6** (3 mg/km), both having three way catalyst as **CNG-E6**.

Acetic acid emissions were for **DI-E2 Scudo** 21 mg/km and **DI-E6** 2 mg/km. Acetic acid was not measured for other cars.




| | Scudo | E10 | E85 | CNG | DI |
|---|---|---|---|---|---|
| CH3COOH | 20,8 | | | | 1,8 |
| ETBE | | | 11,1 | | |
| EtOH | | 6,0 | 533,3 | | |
| SO2 | 2,2 | | 0,3 | 4,3 | 1,7 |
| NH3 | 1,2 | 2,1 | 3,3 | 6,2 | 0,4 |
| N2O | 9,8 | 0,4 | 0,5 | 0,1 | 15,9 |

*Figure 47. FTIR analysis results for the selected gaseous emissions over the European test cycle at -7 °C. Euro 2 diesel car (Scudo) and four Euro 6 cars.*

### 4.5.6 EC/OC

EC, OC and total carbon (TC) for selected cars during the measurement campaign EC/OC quartz filters are shown in Table 24. Samples were collected for **DI-E2 Scudo** in three phases and for **E10-E6** and **E85-E6** in one phase over the whole NEDC driving cycle.

*Table 24. Organic Carbon (OC), Elemental Carbon (EC), and Total Carbon (TC) for selected cars during the measurement campaign.*

| Car | OC, % | EC, % | TC, % |
|---|---|---|---|
| **Scudo (NEDC Phase 1)** | 40 | 50 | 90 |
| **Scudo (NEDC Phase 2)** | 37 | 61 | 98 |
| **Scudo (NEDC Phase 3)** | 28 | 63 | 91 |
| **E10** | 50 | 50 | 100* |
| **E85 Average:** | 31 | 5 | 32 |

*) Analysed TC>100%, but particle mass too low for reliable TC analysis.

Only one sample (i.e. no parallel filters) was collected for **E10** and **E85**. **Scudo** had dark samples, which made reliable EC/OC analysis challenging. Indicatively, share of EC of total PM was 50–60% for diesel and E10 fueled cars, while it was below 5% for the **E85** fueled car. These EC/OC results are indicative due to lack of replicate analyses. However, the analysis method itself worked well with the samples collected from cars using alternative fuels.

### 4.5.7 Anions

Results of anions associated with PM are presented in Table 25. Mostly the results for the anions analysed were below the detection limits. **DI-E2 Scudo** had the highest $SO_4^{2-}$, $NO_3^-$ and $Cl^-$ levels.

*Table 25. Sulphates, nitrates and chlorides in PM (mg/km).*

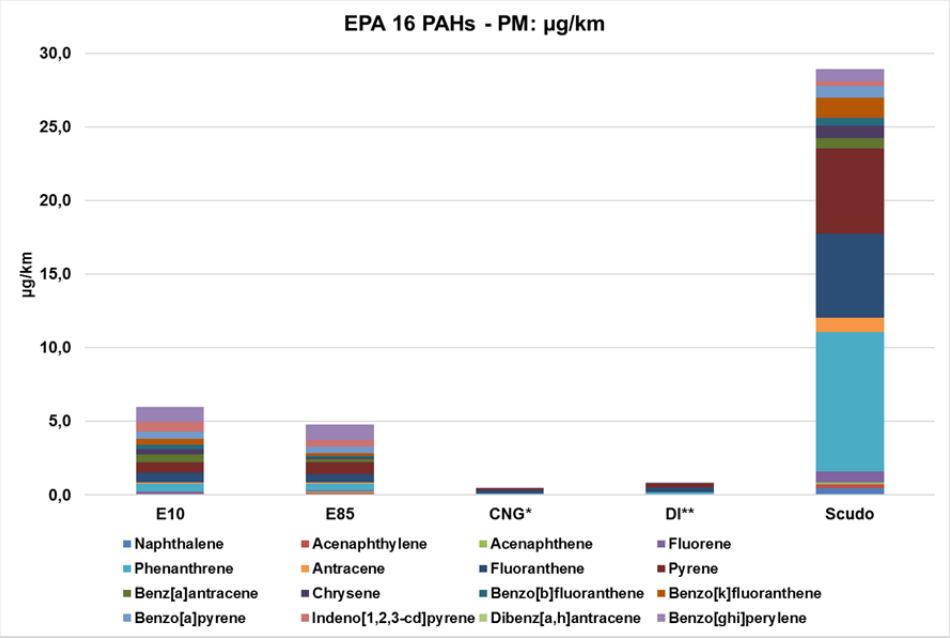
| Car | $SO_4^{2-}$ (mg/km) | $NO_3^-$ (mg/km) | $Cl^-$ (mg/km) |
|---|---|---|---|
| **Scudo** | 0,125 | 0,125 | 0,063 |
| **E10-E6** | < DL | < DL | < DL |
| **E85-E6** | < DL | < DL | < DL |
| **CNG-E6** | < DL | < DL | < DL |
| **DI-E6** | < DL | 0,053 | < DL (0,029) |

DL=detection limit

### 4.5.8 Polycyclic aromatic hydrocarbons (PAH)

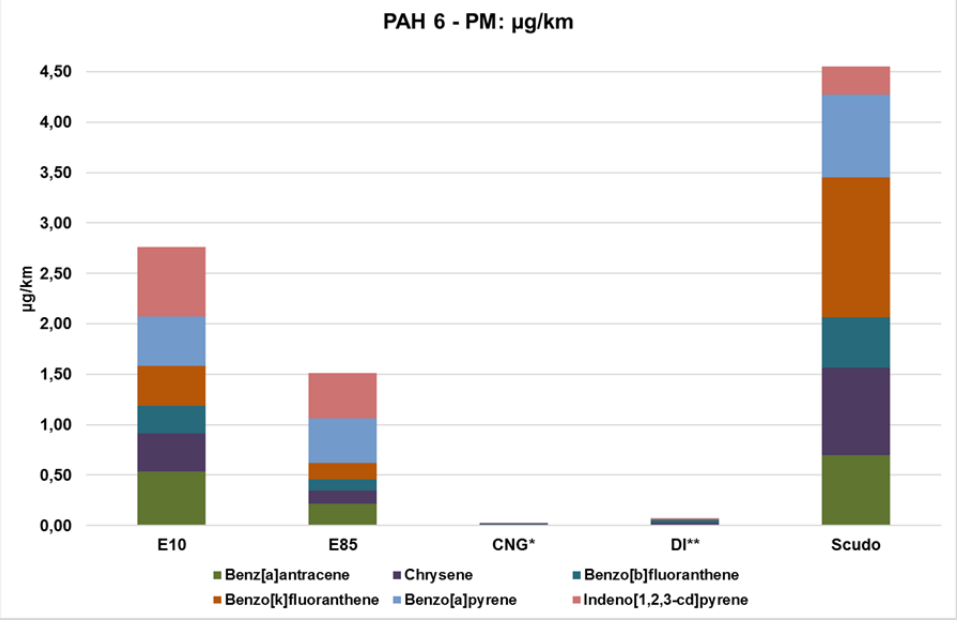
Particle-associated PAH emissions, namely sums of 16 PAHs and 6 PAHs, are shown for all test cars in Figure 48 and Figure 49. The PAH concentrations for many PAH compounds were below detection limits for all the cars. Overall, the highest particle-associated sum of 16 PAHs (mass per km) had **DI-E2 Scudo** (28 µg/km). The next highest sum of 16 PAHs had **E10-E6** (5.8 µg/km) and **E85-E6** (4.7 µg/km) and the lowest **CNG-E6** (0.4 µg/km) and **DI-E6** (0.8 µg/km).

For the **DI-E2 Scudo**, phenanthrene was the main PAH compound in PM (9.5 µg/km), and the next were pyrene (5.8 µg/km) and fluoranthene (5.7 µg/km). For **E10-E6** and **E85-E6**, the highest PAH emission levels were found for benzo(*ghi*)perylene (1.0 µg/km and 1.1 µg/km). The highest benzo(*a*)pyrene emission were detected for **DI-E2 Scudo** (0.8 µg/km) while that for for **E10-E6** was 0.5 µg/km, for **E85-E6** 0.4 µg/km, and for **DI-E6** 0.006 µg/km.




*CNG: 63% (10/16) compounds < DL; ** DI: 30% (5/16) compounds < DL

*Figure 48. Particle-associated (PM) EPA 16 PAH emissions. The European test cycle at -7 °C. Euro 2 diesel car (Scudo) and four Euro 6 cars.*

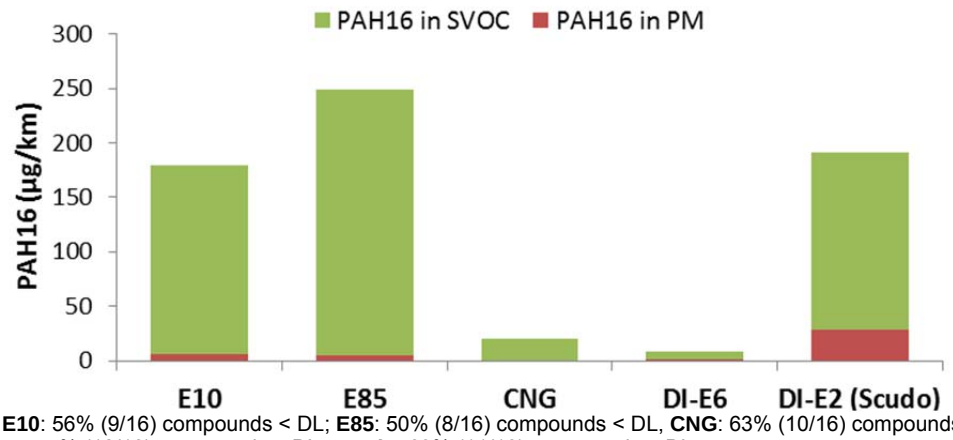



** CNG: Benz(a)antracene, benzo(k)fluoranthene, benzo(a)pyrene, and indeno(1,2,3-cd)pyrene < DL*
***DI: Benz(a)antracene and indeno(1,2,3-cd)pyrene < DL*

*Figure 49. Particle-associated PAH 6 emissions. The European test cycle at -7 °C. Euro 2 diesel car (Scudo) and four Euro 6 cars.*

Sum of 16 PAHs and sum of 6 PAHs in PM and SVOC fraction are shown in Figure 50 and Figure 51. The 16 PAHs associated in the SVOC were substantially higher than those associated in the PM. The overall highest SVOC associated EPA 16 PAH emissions had **E85-E6**, **E10-E6** and **DI-E2 (Scudo)**. **CNG** and **DI** had the smallest SVOC-associated sum of 16 PAH emissions.

SVOC associated 6 PAHs were under the detection limits for all the test cars, while PM associated 6 PAHs clearly exceeded the detection limit for **E10-E6**, **E85-E6** and **DI-E2 (Scudo)**. **DI-E2 Scudo** had the highest sum of 6 PAHs, and the next highest emission was observed for Euro 6 cars using **E10-E6** and **E85-E6**. **CNG-E6** and **DI-E6** had hardly detectable emissions of 6 PAHs.




**E10**: 56% (9/16) compounds < DL; **E85**: 50% (8/16) compounds < DL, **CNG**: 63% (10/16) compounds < DL; **DI**: 75% (12/16) compounds < DL; **Scudo**: 69% (11/16) compounds < DL

*Figure 50. Emissions of 16 PAHs associated in PM and in semivolatile organic fraction. The European test cycle at -7 °C. Euro 2 diesel car (Scudo) and four Euro 6 cars.*

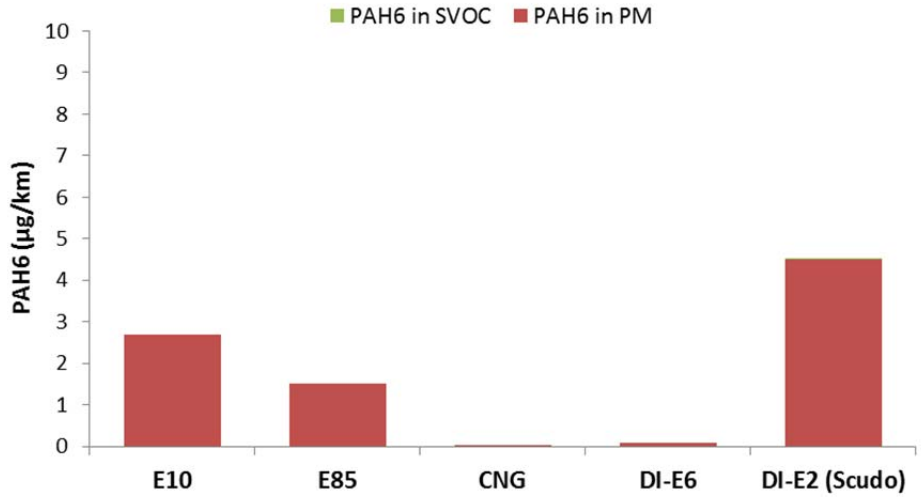



*Figure 51. Emissions of 6 PAHs associated in PM and in semivolatile organic fraction. The European test cycle at -7 °C. Euro 2 diesel car (Scudo) and four Euro 6 cars.*

PAH analyses revealed that different PAH compounds were present in PM phase (Figure 52) and in SVOC phase (Figure 53). For semivolatile phase naphthalene was the major compound present in the samples, while heavy PAHs were present in the PM phase.

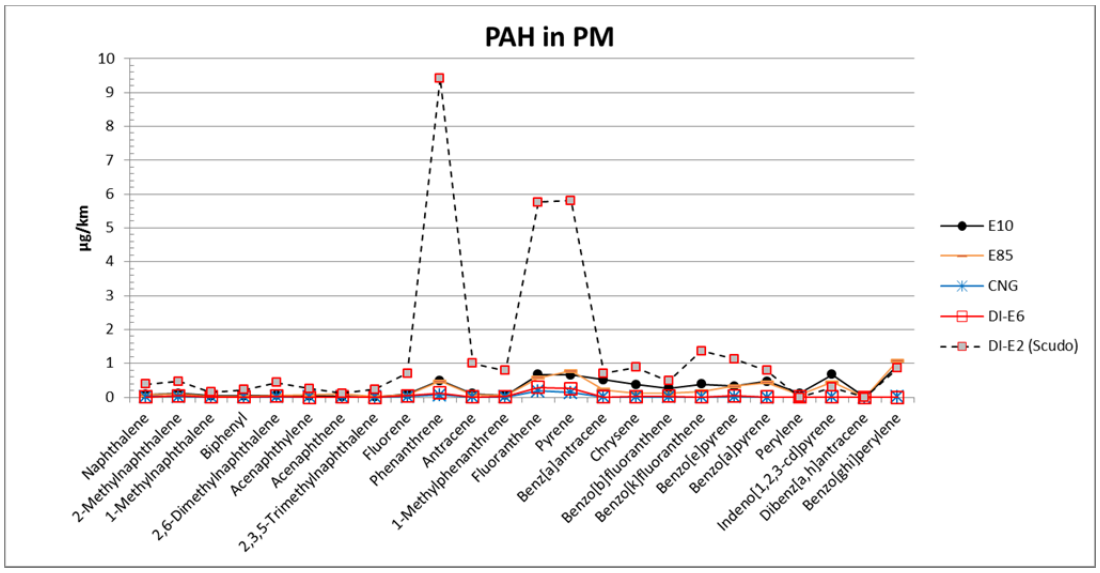



*Figure 52. PAH compounds found in PM samples.*

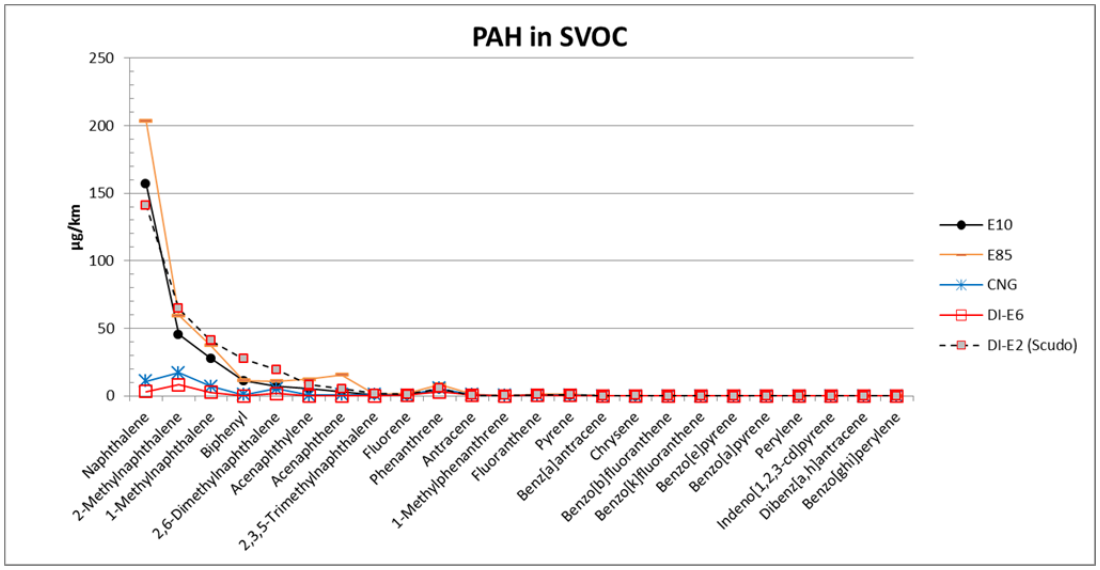



*Figure 53. PAH compounds found in SVOC samples. The European test cycle at -7 °C. Euro 2 diesel car (Scudo) and four Euro 6 cars.*

### 4.5.9 MicroAmes

MicroAmes assays showed that all PM samples (Table 26) were mutagenic at least at the concentration of 2.5 L diluted exhaust gas per test well. The samples **E85** and **DI** showed clear metabolic activation with S9 mix, while effect of activation in sample **E10** was more inconsistent.

The SVOC (Empore) samples were not mutagenic at tested concentrations, except the samples for **DI-E6** and **DI-E2 Scudo**, which showed mutagenic activity at the highest tested concentration. The low flow through filter during collection of the Empore samples prevented testing higher doses.

*Table 26. MicroAmes results (volume based) for Euro 2 diesel car (Scudo) and four Euro 6 cars..**

| Sample | Concentration of exhaust gas per well/liters | TA98 -S9 mix Average | TA98 -S9 mix SD | TA98 -S9 mix rev per L | TA98 +S9 Mix Average | TA98 +S9 Mix SD | TA98 +S9 Mix rev per L |
|---|---|---|---|---|---|---|---|
| **Scudo PM** | 2,5 | 3,00 | 1,73 | | 3,00 | 1,73 | |
| | 1,25 | 3,00 | 1,00 | | 6,00 | 5,29 | |
| | 0,625 | - | - | | 4,33 | 0,58 | |
| | 0,3125 | 1,00 | 1,00 | - | 5,67 | 3,06 | - |
| **E10 PM** | 40 | 23,67 | 3,21 | | 22,00 | 6,08 | |
| | 10 | 17,67 | 1,53 | | 21,67 | 2,08 | |
| | 2,5 | 5,67 | 3,21 | | 10,33 | 2,52 | |
| | 1,25 | 6,33 | 2,08 | | 4,33 | 3,21 | |
| | 0,625 | 3,00 | 1,73 | **1,47** | 1,33 | 1,53 | **2,01** |
| **E85 PM** | 40 | 11,67 | 1,53 | | 22,00 | 2,65 | |
| | 10 | 3,67 | 2,89 | | 14,33 | 5,13 | |
| | 2,5 | 3,00 | 2,65 | | 5,67 | 3,79 | |
| | 1,25 | 2,33 | 0,58 | | 4,33 | 1,53 | |
| | 0,625 | 1,67 | 1,53 | **0,24** | 1,67 | 1,53 | **1,25** |
| **CNG PM** | 20 | 7,67 | 4,16 | | 8,33 | 3,06 | |
| | 10 | 4,33 | 0,58 | | 7,00 | 1,73 | |
| | 2,5 | 3,00 | 1,73 | | 2,00 | 1,00 | |
| | 1,25 | 1,67 | 2,08 | | 3,33 | 3,21 | |
| | 0,625 | 1,33 | 1,53 | **0,31** | 2,00 | 2,00 | **0,34** |
| **DI PM** | 20 | 5,33 | 0,58 | | 12,67 | 4,51 | |
| | 10 | 9,33 | 2,31 | | 13,67 | 0,58 | |
| | 2,5 | 2,67 | 0,58 | | 4,67 | 1,15 | |
| | 1,25 | 3,00 | 2,00 | | 4,67 | 1,53 | |
| | 0,625 | 0,33 | 0,58 | **0,85** | 2,00 | 1,73 | **1,16** |
| **Scudo SVOC** | 0,625 | 6,67 | 4,04 | | 3,67 | 2,08 | |
| | 0,15625 | 1,33 | 0,58 | - | 0,67 | 1,15 | - |
| **E10 SVOC** | 0,625 | 0,67 | 1,15 | | 1,67 | 0,58 | |
| | 0,3125 | - | - | | 1,00 | 1,00 | |
| | 0,15625 | 0,67 | 0,58 | - | 1,33 | 0,58 | - |
| **E85 SVOC** | 0,625 | 1,00 | 1,00 | | 1,33 | 0,58 | |
| | 0,3125 | - | - | | 2,00 | 0,00 | |
| | 0,15625 | 0,33 | 0,58 | - | 1,33 | 1,15 | - |
| **CNG SVOC** | 0,3125 | 0,33 | 0,58 | | - | - | |
| | 0,15625 | 1,33 | 0,58 | - | 0,33 | 0,58 | - |
| **DI SVOC** | 0,3125 | - | - | | 2,67 | 1,15 | |
| | 0,15625 | 1,33 | 0,58 | - | 2,33 | 1,53 | - |
| | | | | = mutagenic concentration | | | |

*Note: no reference filter was analysed in this batch, but in the first analysis batch they were analysed not to be mutagenic.

The mutagenic dose response of samples was calculated by linear regression analysis. The slope (b) within the linear part of the regression line (y = bx + a) describes the magnitude of mutagenic activity, and is expressed as revertants/(ng or liter) of sample.

Results as krev/km were then calculated for the PM samples acquired from **E10-E6**, **E85-E6**, **CNG-E6**, and **DI-E6** (Figure 54).. In general, the overall highest mutagenicity as krev/km had **E10** and the lowest **CNG. E85** had the largest difference between the *TA98 without the mutagenic* (-S9 mix) activation and *with mutagenic activation* (+S9 mix). PAHs show indirect mutagenicity, i.e. only after metabolic activation (+S9 mix).

SRM2975 reference Diesel Particulate Matter was analysed as reference and verification and it was extremely mutagenic at concentrations 100 ng/well (2 µg/ml) and 500 ng/well (10 µg/ml).

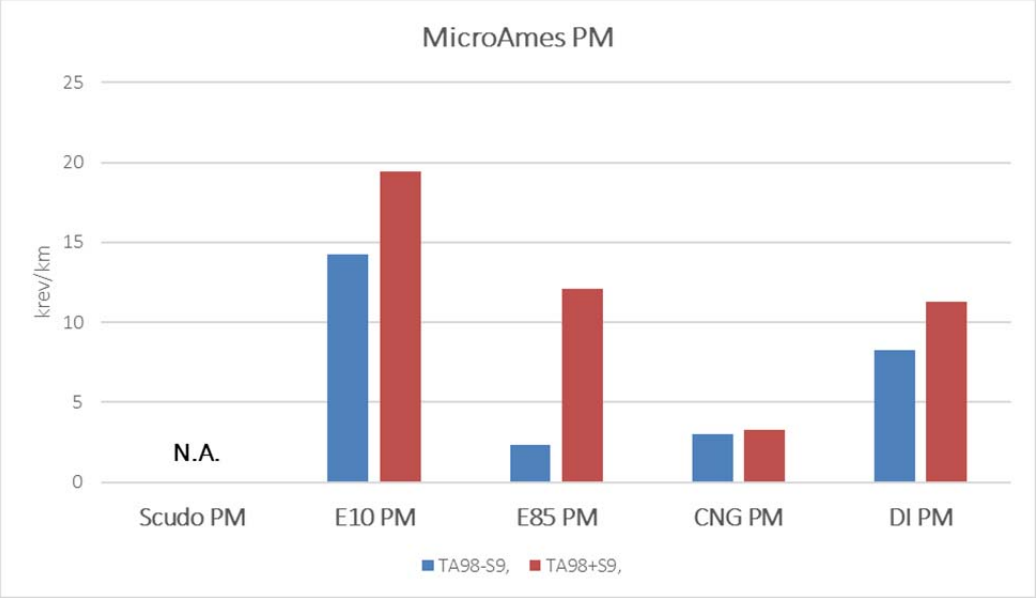



*Figure 54. MicroAmes results from PM samples as krev/km. The European test cycle at -7 °C. Euro 2 diesel car (Scudo) and four Euro 6 cars.*

### 4.5.10 Oxidative potential (DTT assay)

DTT assay testing of the samples started with **DI-E2 Scudo** samples, which were sent for DTT analysis as mass based (PM and SVOC mg/sample) and at the same time reference Fluoropore filter (PM) and reference Empore filter (SVOC) were tested. Also SRM2975 reference Diesel Particulate Matter was analysed. Later on, DTT samples of **E10**, **E85**, **CNG**, and **DI** were tested as volume based (per $m^3$ diluted exhaust gas).

The reference diesel particulate mass SRM2975 had clearly the highest oxidative potential per mg PM, 55.9 $\mu M min^{-1} mgPM^{-1}$, almost 7 times higher than the **DI-E2 Scudo** combined PM+SVOC sample.

The results for all DTT assay as µM DTT$min.^{-1}$ and µM DTT $min.^{-1}$(diluted $m^3)^{-1}$ are presented in Figure 55. No reference filters or reference particulate mass was analysed in this batch.

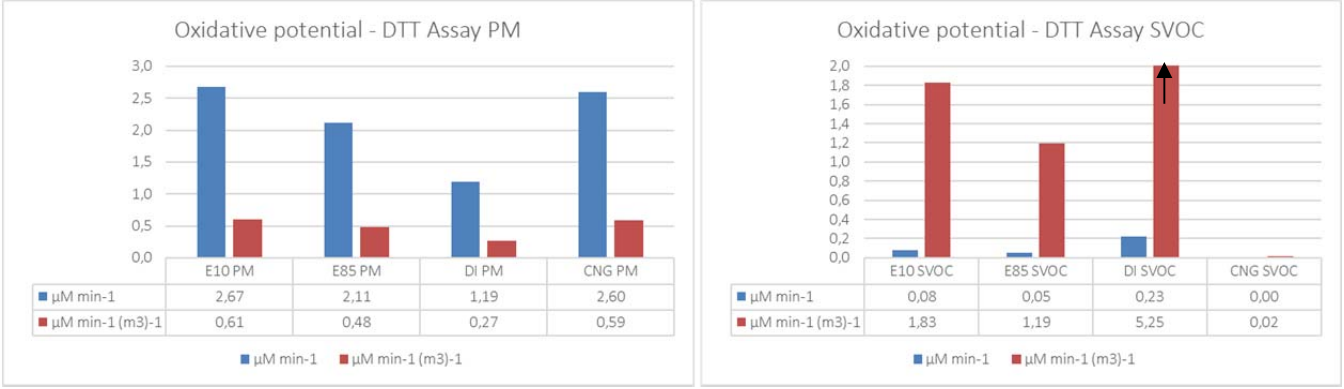



*Figure 55. Oxidative potentials for **E10-E6**, **E85-E6**, **CNG-E6**, and **DI-E6**. The European test cycle at -7 °C. Euro 2 diesel car (Scudo) and four Euro 6 cars.*

In Figure 56 the oxidative potentials are presented as $\mu Mmin^{-1}km^{-1}$. Overall**, DI-E2 Scudo** PM+SVOC sample had the highest oxidative potential of all the tested samples (per km). Oxidative potential for the SVOC sample from **DI-E6** was also notable, and the next highest oxidative potentials of SVOC were observed for **E10-E6** and **E85-E6**. Oxidative potential for **CNG-E6** was very low. For **E10-E6**, **E85-E6**, and **DI-E6** the oxidative potentials of SVOC were higher than the oxidative potentials of PM.

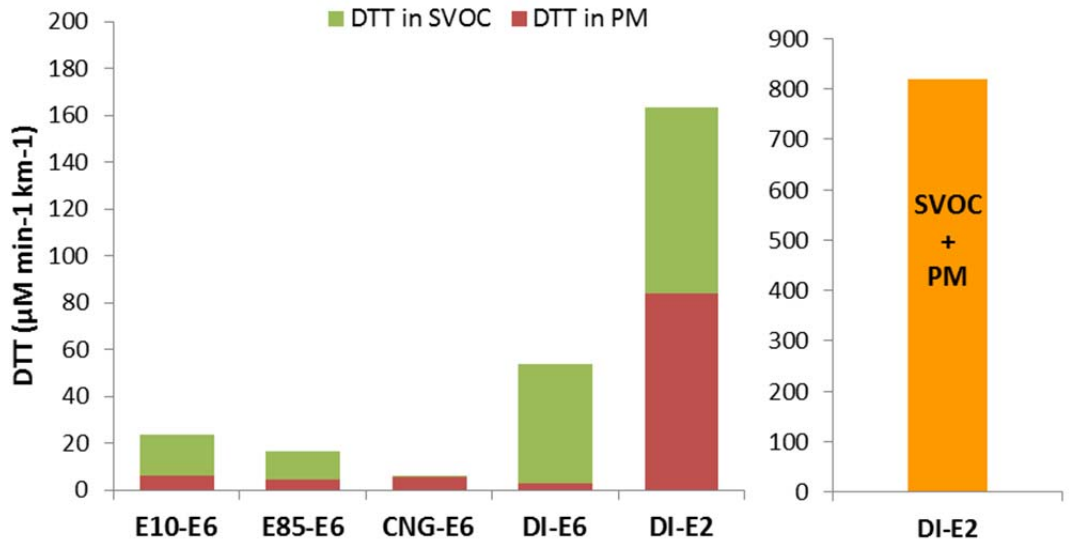



*Figure 56. Oxidative potential results from DTT assay (per km). The European test cycle at -7 °C. Euro 2 diesel car (Scudo) and four Euro 6 cars.*

# 5. Summary

Reduction of adverse health and environmental effects related to the air quality has been the primary driving force for tightening the exhaust emission limits of transport sector. Complete combustion of fuels produces only $CO_2$ and water. Constituents called traditionally "emissions" represent only below 0.5% of the total exhaust gas. Most of the emission species are fuel- and engine-dependent, while some are formed in emission control devices. Spark-ignited cars equipped with a TWC catalyst are typically characterized by low CO, HC, and $NO_x$ emissions. In diesel combustion, complicated emission control systems (e.g. SCR and DPF) are required to achieve low $NO_x$ and PM emissions. For (bio)methane fueled vehicles, methane is emitted. Ethanol fueled cars emit ethanol and acetaldehyde. $N_2O$ and $NH_3$ are induced by the TWC catalyst, and $NH_3$ also by the SCR catalyst.

Hundreds of different compounds are present in the exhaust gases, some of them are toxic, or greenhouse gases, and some are classified as human carcinogens or possible carcinogens. In addition, the toxicological and epidemiological data suggest that the chemical composition of particles in exhaust gases may be important contributor to the health effects. IARC classification of diesel engine exhaust is carcinogenic to humans, and classification of gasoline exhaust is possibly carcinogenic to humans.

Current emission measurement methods have been developed for traditional vehicles and fuels and therefore are not necessarily compatible with new technologies and different alternative fuel options. This applies to both regulated and unregulated emissions. New technologies and fuels can lead to alterations in the exhaust gas composition and to the formation of new emission species. Due to the tight emission regulations, the emissions have decreased and their quantitative analysis has become more challenging. Therefore, in addition to improving and developing of the traditional analysis methods, it has also become essential to find new comprehensive analysis and evaluation methods for the exhaust gas emissions.

The aim of this project was to review, improve, develop, and validate emission measurement methods for more comprehensive characterization and impact assessment of the exhaust gas emissions. The aim was also to take more into account the semivolatile organic fraction (SVOC) of the exhaust gas by developing a robust sampling system for SVOCs. Due to the limited amount of PM and SVOC from new low-emission cars using alternative fuels, exhaust gas emission volume-based sample approach was developed and it will be used for the PAH, microAmes, and oxidative potential samples in the future projects. Furthermore, new approach to extraction of samples was tested instead of time and solvent consuming Soxhlet-extraction ultrasonic extraction of filters for PAH analyses and biological tests. New analysis service providers were tested and evaluated. All of these development steps will improve flexibility and cost-effectiveness of the tests. The emission measurement portfolio for cars and vehicles at VTT is shown in Figure 57.

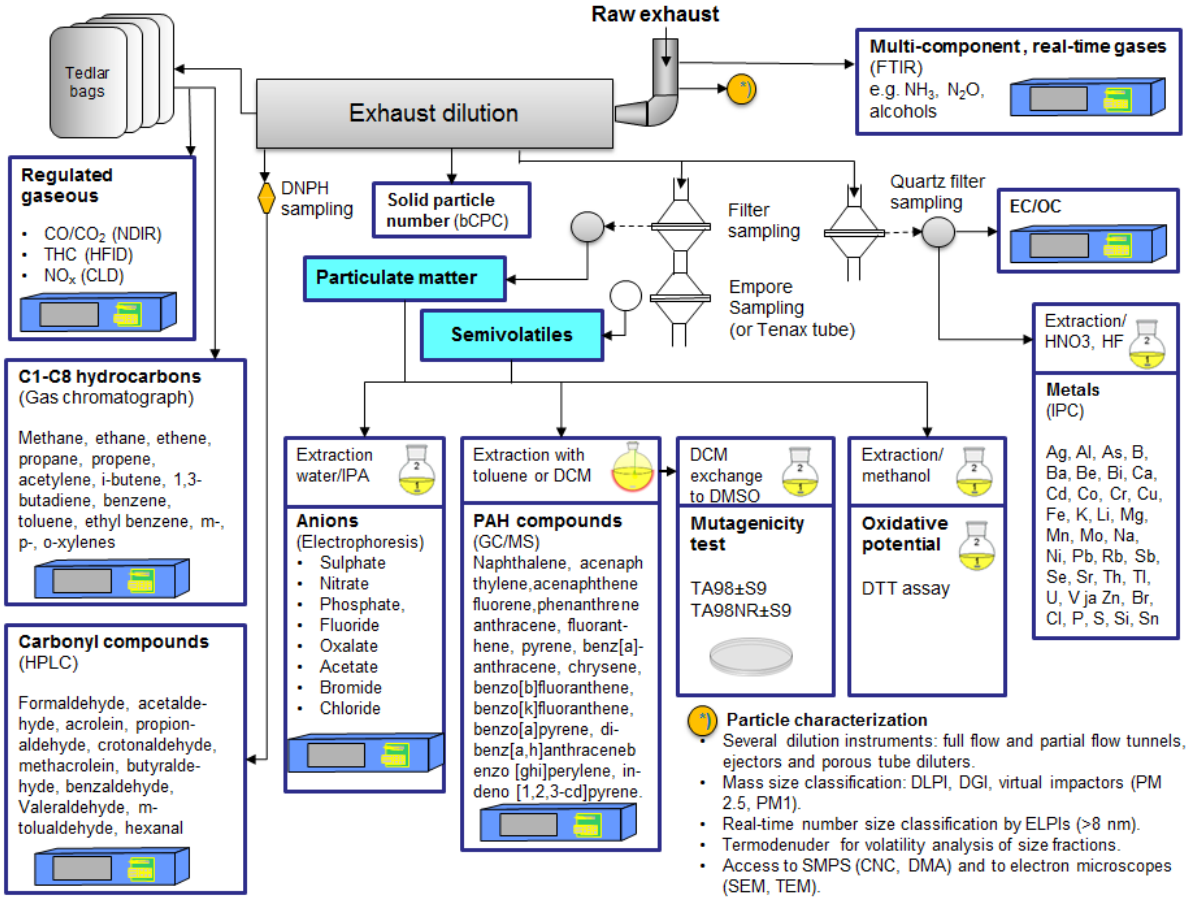



*Figure 57. A schematic portfolio of VTT's emission measurements from cars and vehicles.*

For validation of the different analysis methods two measurement campaigns were carried out during the project. In the IEA AMF Annex 44, VTT studied emissions from two FFVs using E10, E85, and E100 fuels at +23 and -7 °C (Aakko-Saksa et al. 2014). In the second measurement campaign, Euro 6 passenger cars using gasoline, diesel, E85 and CNG were studied, as well as a Euro 2 diesel car as a reference. The results presented here are from the second measurements campaign.

The highest $NO_x$ emissions were measured for the Euro 2 diesel car, which was not equipped with emission control systems. The lowest $NO_x$ was observed for the E85 fuelled Euro 6 FFV. The highest CO and HC emissions in the tests at -7 °C were measured for E85, while the lowest level was observed for the CNG and diesel cars. The highest methane emission had expectedly the CNG car. The hydrocarbon emissions from E85 fuelled car composed mostly of methane and ethene, while the aromatic compounds were mainly present for the E10 fuelled car. The highest aldehyde (particularly formaldehyde) emissions were measured for the Euro 2 diesel car, while the lowest aldehyde emissions were observed for the Euro 6 diesel car. E85 fuelled Euro 6 FFV had high acetaldehyde and ethanol emissions. The $N_2O$ emissions were low for other cars than diesel cars (Euro 6 and 2). Higher ammonia emissions were observed for TWC equipped E10, E85 and CNG fuelled cars than for the Euro 6 diesel car. Acetic acid was detected only for the diesel cars (Euro 6 and 2).

The highest PM and solid PN emissions were measured for the Euro 2 diesel car, which did not have DPF. The lowest PM was measured for the CNG fuelled car, and the lowest solid PN emission for the Euro 6 diesel car. Indicatively, share of EC of PM was 50–60% for the Euro 2 diesel and Euro 6 E10 fuelled cars, while that was below 5% of PM for the E85 fuelled

FFV. Mostly, the results for PM associated anions were below the detection limits. SVOC emissions were higher than the PM emissions for all cars, especially for the Euro 6 diesel car.

The PAH emissions were lowest for Euro 6 CNG and diesel cars. The 16 PAHs associated in SVOC were substantially higher than those associated in PM. For SVOC, naphthalene was the major compound present, while PM contained heavier PAHs. The sum of 6 priority PAHs was substantial for Euro 2 diesel car and for Euro 6 E10 and E85 fuelled cars, while Euro 6 CNG and diesel cars had hardly detectable emissions of these heavy PAHs.

In the microAmes test, all the PM samples were mutagenic. The highest PM associated mutagenicity had the Euro 6 E10 fuelled car, and the lowest had the CNG car. The SVOC samples were mutagenic at tested concentrations only for diesel cars.

For Euro 6 cars using E10, E85 and diesel fuels, the oxidative potentials were higher in the SVOC than in the PM phase. Considering both PM and SVOC phases, the Euro 2 diesel car had the highest oxidative potential in DTT assay test, and the Euro 6 diesel car the next highest. Oxidative potentials observed were lower for E10 and E85 than for diesel cars, while that for the CNG car was very low. Interesting was the Euro 6 diesel car, which showed high SVOC emission, and also notable oxidative potential of the SVOC sample. In addition, this was the only new car showing mutagenic SVOC phase. This result for the new Euro 6 diesel car would deserve further consideration. In Figure 58, the main analysis results for all the test cars are summarized.

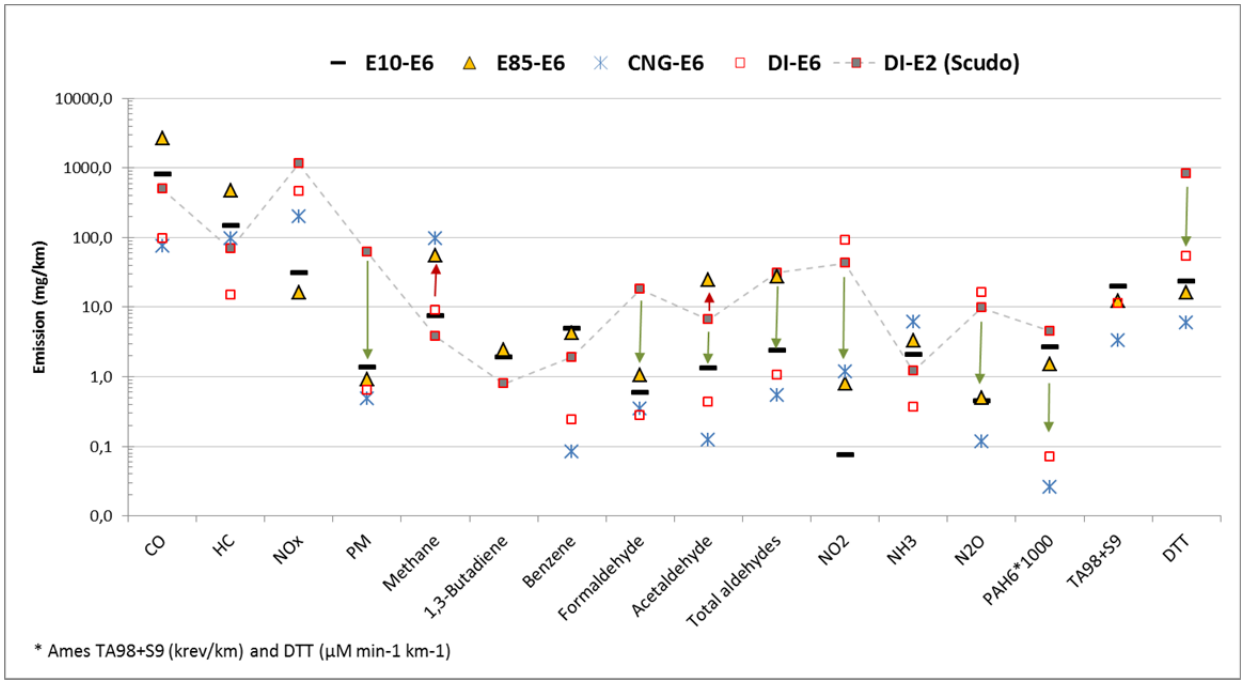



*Figure 58. Exhaust gas emissions for Euro 2 diesel car and four Euro 6 cars over the European test cycle at -7 °C.*

The aim of the measurement campaign was to improve, develop and validate (new) emission measurement methods for more comprehensive characterization and impact assessment of the exhaust gases from low-emitting cars and vehicles using alternative fuels. These aims were achieved and the measurement campaign was a success. Much new information was collected and new methods and tests for future needs were validated. In future projects, volume-based approach developed here will be used for PAH, microAmes, and oxidative potential (DTT) tests and Empore disk collection for semivolatile samples will be utilized for low emitting cars/vehicles using alternative fuels.

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