R e s e a r c h R e p o r t

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CHARACTERISATION OF ENGINE EXHAUST PARTICULATE FINGERPRINTS AND THEIR CONTRIBUTION TO AIR QUALITY - VTT's CONTRIBUTION

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ABSTRACT

Target of the European Commission project ”Characterisation of engine exhaust particulate fingerprints and their contribution to air quality” was to identify the contribution of different engine technologies on ambient particulates through chemical mass balance modelling (CMB). The modelling requires as source information the evaluation of the feasibility of possible fingerprints from the analysis data obtained from particulates from several engine/vehicle technologies and similar data from ambient air particulates. Several technologies were selected for this project. VTT Energy was responsible of sampling and analysis of the particulate matter from heavy-duty diesel engine and spark-ignition vehicle.

In the first phase of the project round-robin tests were carried out to find out, if the results from different laboratories are comparable with each other and to select analysis methods for actual samples. The analysis, which were selected for further work were SOF, PAH, fuel/lube, anions and metal analysis.

The heavy-duty tests included three different load conditions with and without oxidation catalyst. The particulates were collected in two different size groups. The total particulates and fine particulates smaller than 2.5 µm were collected separately. The tests with spark-ignition stoichiometric gasoline fuelled vehicle were carried out at two load conditions, with and without three-way-catalyst (TWC). In addition, European test cycle was used as a reference. Unleaded CEC reference gasoline was used in the tests with the spark-ignition vehicle with TWC. However, lead additive was added into gasoline for the tests without catalyst.

Significant amount of sulphates were present in the particulates only in the conditions, where the catalyst was warm enough to generate sulphates from sulphur of the fuel. Bromide and chloride were found from the particulates of spark-ignition vehicle in the tests with leaded fuel.

Profiles of the PAH compounds were rather different from the spark-ignition vehicle and diesel engine. Concentration of the heaviest PAH compounds in particulates from gasoline fuelled vehicle was high when compared with the particulates from diesel engine.

Comparison of the metal analysis results from gasoline vehicle and diesel engine suffered from low level of metals in diesel particulate samples and disturbing effect of bromide and chloride in the gasoline particulate samples. However, it was noted e.g. that calcium was found only from the particulates from diesel engine.

PREFACE

European Commission project ”Characterisation of engine exhaust particulate fingerprints and their contribution to air quality, PARFIN JOF3-CT97-0040” was carried out in 1998 and 1999. The participants of the project were:

IFP (France), co-ordinator, Brigitte Martin
Euron (Italy), Fulvio Giavazzi
Enitechnologie (Italy), Patrizia Buttini
JRC Ispra (Italy), Bo Larsen
VTT Energy (Finland), Päivi Aakko

Target of the project was to identify the contribution of different engine technologies on ambient particulates through chemical mass balance modelling (CMB). The modelling requires as source information the evaluation of the feasibility of possible fingerprints from the analysis data obtained from particulates from several engine/vehicle technologies and similar data from ambient air particulates. The technologies selected for this project were heavy-duty engine, light-duty diesel vehicle, stoichiometric and lean-burn gasoline vehicles. All engines/vehicles were studied with and without aftertreatment technologies.

The project is expected to generate new information of the particulates from different engine technologies, especially from gasoline fuelled vehicles, for which only limited data is available. The main expected benefit of the project is the methodology to identify the contribution of engine emissions to ambient air particulates in different regions. The contribution of traffic on ambient air particulates is a gap in knowledge at the moment, which was evidenced also in EPEFE program.

VTT Energy was responsible for studying the particulates from heavy-duty diesel engine and stoichiometric gasoline fuelled vehicle. Other participants studied different light-duty technologies and ambient air particulates from Paris and Milan. Enitechnologie is responsible of the CMB modelling work.

Analyses of particulate samples required a lot of effort, knowledge and co-operation. VTT would like to thank the following institutes for participating in analyses of the samples collected at VTT Energy.

Gent University, Prof. Willy Maenhaut and Jan Cafmeyer
Fortum Oil and Gas, Anne Ruonansuu and Tuija Virtanen
VTT Chemical Technology, Sirpa Himberg and Jan Wikström

In addition, Risto Hillamo and Timo Mäkelä from the Finnish Meteorological Institute are acknowledged for their help in the tests with virtual impactor.

This report is a documentation of the tests and the results that VTT Energy was responsible for. The summarized results of all partners are reported by co-ordinator of the project.

CONTENTS

ABBREVIATIONS

ECE R49	Exhaust emission test procedure for heavy-duty engines according to ECE Regulation No. 49, test method includes 13 load modes
Euro	European exhaust emission test for light-duty vehicles according to directive 70/220/EEC and it's amendments (driving cycle in amendment 91/441/EEC), start of the test carried out as in forthcoming directive
HD	heavy-duty
DI	direct injection
LD	light-duty
SI	spark-ignition
HD cat	HD engine equipped with oxidation catalyst designed for fuels up to 500 ppm sulphur content
SI cat	spark-ignition gasoline fuelled vehicle equipped with three-way catalyst
TWC	three-way catalyst
INAA	instrumental neutron activation analysis
PIXE	particle induced X-ray emission
HPLC	high performance liquid chromatography
GC	gas chromatography
MS	mass spectrometry
VI	virtual impactor
Teflo	Gellman Teflo R2PJ047 filter
PUF	polyurethane foam
HC	total hydrocarbons in exhaust gases
CO	carbon monoxide in exhaust gases
NO_x	oxides of nitrogen in exhaust gases
PM	particulate matter emission
PM2.5	particles smaller than 2.5 µm
PAH	polyaromatic hydrocarbons
SOF	soluble organic fraction of particulate matter
SO_4	sulphates
TEL	tetraethyl lead additive

abbreviations of individual PAH compounds (3-7 ring PAH compounds with bold-face)

NAF	naphthalene	**BaFLU**	**benzo(a)fluorene**
2mNAF	2-methylnaphthalene	**BbFLU**	**benzo(b)fluorene**
1mNAF	1-methylnaphthalene	BbN21	benzo(b)naphtho(2,1-d)thiophene
BiF	biphenyl	BbN12	benzo(b)naphtho(1,2-d)thiophene
3mBiF	3-methylbiphenyl	**BaANT**	***benz(a)antracene**
ANAF	acenaphthene	**KRY/TRI**	***chrysene/triphenylene**
diBzFUR	dibenzofurane	**BbFLUT**	***benzo(b)fluoranthene**
FLU	***fluorene**	**BkFLUT**	***benzo(k)fluoranthene**
diBzTIO	dibenzothiophene	**BePYR**	***benzo(e)pyrene**
FEN	***phenanthrene**	**BaPYR**	***benzo(a)pyrene**
ANT	***antracene**	**PERY**	**perylene**
2mANT	**2-methylantracene**	**IPYR**	***indeno(1,2,3-cd)-pyrene**
1mFEN	**1-methylphenanthrene**	**dBahA**	***dibenzo(a,h)anthracene**
2fNAF	**2-phenylnaphthalene**	**BghiPER**	***benzo(g,h,i)perylene**
FLUT	***fluoranthene**	**KOR**	**coronene**
PYR	***pyrene**		

abbreviations of individual metals included in this report

Na	Sodium	Cr	Chromium	Sr	Strontium	Ba	Barium
Mg	Magnesium	Mn	Manganese	Y	Yttrium	La	Lanthanum
Al	Aluminium	Fe	Iron	Zr	Zirconium	Ce	Cerium
Si	Silicon	Co	Cobalt	Nb	Niobium	Sm	Samarium
P	Phosphorus	Ni	Nickel	Mo	Molybdenum	Eu	Europium
S	Sulphur	Cu	Copper	Ag	Silver	Lu	Lutetium
Cl	Chlorine	Zn	Zinc	Cd	Cadmium	W	Tungsten
K	Potassium	Ga	Gallium	In	Indium	Au	Gold
Ca	Calcium	As	Arsenic	Sn	Tin	Pb	Lead
Sc	Scandium	Se	Selenium	Sb	Antimony	Th	Thorium
Ti	Titanium	Br	Bromine	I	Iodine		
V	Vanadium	Rb	Rubidium	Cs	Cesium		

1 OVERVIEW OF THE PROJECT

The tasks at VTT Energy were divided into three main parts

1) Analysis of the round-robin samples
2) Tests with light-duty spark-ignition (SI) gasoline fuelled passenger vehicle with and without catalyst
3) Tests with heavy-duty (HD) bus engine with and without catalyst

The round-robin phase of the project included two different goals: to find out, if the results from different laboratories are comparable with each other and to select analysis methods for actual samples. The samples collected at IFP were analysed as completely as possible (SOF, PAH, fuel/lube, elementary analysis, anions, metal analysis, simulated distillation). The analyses showing good correlation between laboratories were selected for actual samples.

The technical risk at VTT was linked with stoichiometric gasoline fuelled vehicle (SI) due to it's extremely low particulate emission level. It was not obvious that sufficient amount of particulates could be collected, especially as the tests were carried out with constant load conditions and warm engine. The tests were carried out at two load conditions, with and without three-way-catalyst (TWC). European test cycle was used as a reference. CEC reference fuel was used in the tests. However, lead additive was added into fuel for the tests without catalyst. The total particulates and fine particulates smaller than 2.5 µm were collected separately. Thus the total number of load/aftertreatment/size combinations was 8.

The heavy-duty tests included three different load conditions with and without oxidation catalyst. The particulates were collected in two different size groups in the similar way as in the light-duty tests. The total number of technical combinations studied with heavy-duty engine was 12.

2 VIRTUAL IMPACTOR

One-stage virtual impactor was purchased from the Finnish Meteorological Institute for collecting the particulates with diameter lower than 2.5 µm. The schematic figure of the virtual impactor is shown in Figure 1. Pre-tests with one-stage impactor were carried out with Volvo DH10A-285 engine to practise the handling of the equipment. An expert from the Finnish Meteorological Institute helped with installations and practises of use of the impactor.

One-stage virtual impactor divides the particulates in two stages: fine particulates below 2.5 µm are collected on one filter and coarse particulates on the other filter. However, in the calculations it has to be taken into account that fine particulates partly drift on coarse filter. Approximately 10 % of the particulate mass weighted from coarse filter are fine particulates. The flow-rate of virtual impactor is 17 l/min to obtain the correct cutting-point of particulates.

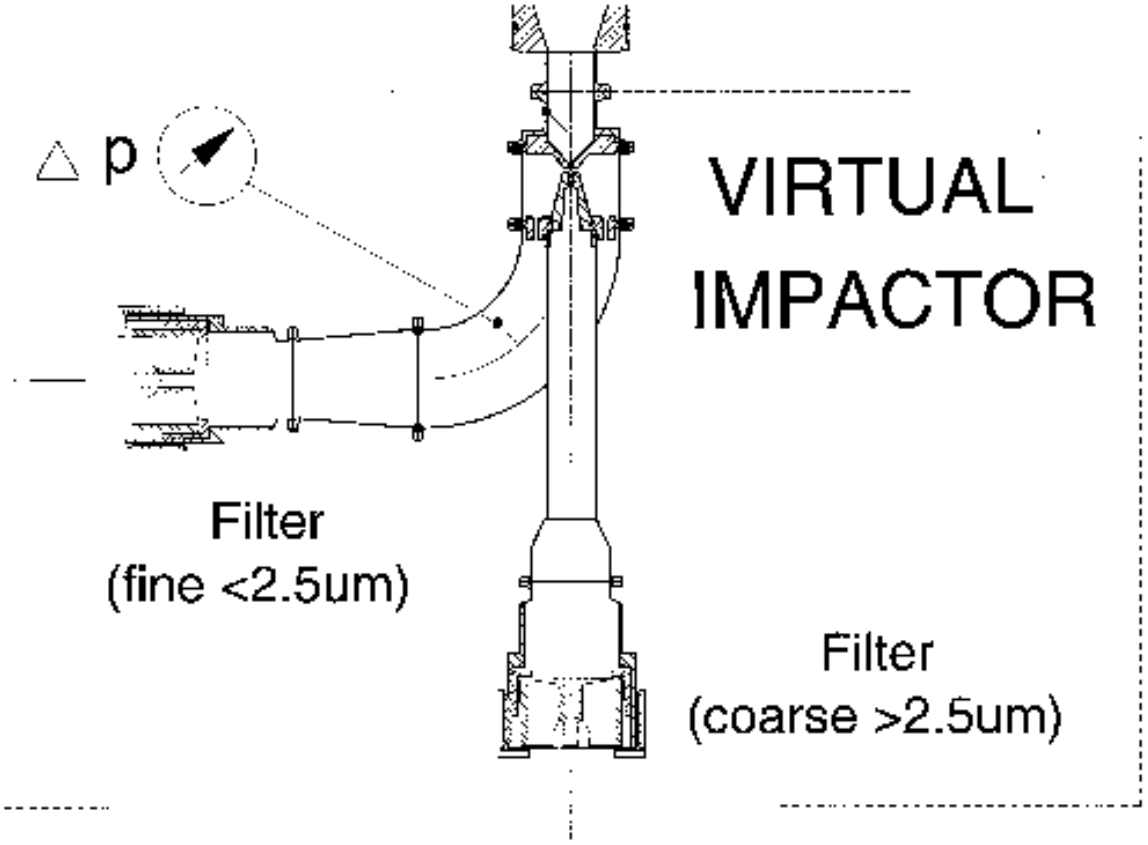


Figure 1. Schematic figure of virtual impactor.

3 ANALYTICAL METHODS

3.1 POLYAROMATIC HYDROCARBONS

Analysis of 29 PAH compounds from naphthalene to coronene with GC/MS SIM technique is accreditated routine analysis at VTT Chemical technology (T044, EN45001). The samples of this project were extracted with dichloromethane. Internal standards d_{10}-pyrene, β,β-binaphtyl and indeno(1,2,3-cd)fluoranthene were used for all samples. Analysis of the PAH compounds was carried out with GC/MS SIM tecnique.

Uncertainty of the PAH analysis from engine exhaust samples is estimated to be around ±30 % of the result.

3.2 ANIONS

Analysis of sulphates with capillary electrophoresis is a routine analysis for engine exhaust particulates at VTT Energy. However, no previous experience was available of analysing

other anions than sulphates and nitrates from exhaust particulates before these tests. Pre-tests of anion analysis were carried out with heavy-duty engine exhaust particulates to practise the methodology.

Handling of the samples was carried out according to IP method (water/iso-propanol extraction). Anion analyses were carried out from untouched particulate samples to avoid possible loss of sulphates. Usually, the anions can be determined from the same samples that have been extracted for PAH analysis. In this case, high levels of sulphates were expected in some samples and thus the separate filters were reserved for anion analysis. The following anions were analysed from particulate samples: sulphate, nitrate, phosphate, fluoride, oxalate, acetate, bromide and chloride.

Usually in the reports of exhaust particulate analysis the sulphates and combined water are shown in the final results. It has to be noted that combined water was not taken into account in this report. Thus "combined water" is included in the compositional part "others" and possibly in some case also in the soluble organic fraction (SOF) in the figures of the report. The amount of combined water depends on the humidity of weighting chamber. These samples were weighted at 50 % relative humidity and thus the amount of "combined water" is expected to be 1.32 x sulphates[1]. The factor for "combined water" is based on the assumption that sulphates are sulphuric acid. If all sulphates are not sulphuric acid, the factor is lower.

Uncertainty of the anion analysis is estimated to be around ±20 % of the result. However, deviation of parallel samples in these measurements proved to be even better than ±5% of the result, when the level of anions were high.

3.3 SOF AND FUEL/LUBE ANALYSIS

Soluble organic fraction (SOF) was determined by weighing the particulate samples before and after the extraction with dichloromethane (extraction for PAH analysis). Deviation of the SOF results was generally below 10 % of the result. However, many exceptions were found in the cases where the particulate mass on filter was low.

The fuel/lube analysis has been developed to screen, which part of the diesel particulate SOF originates from the lube oil and which part from the fuel[1]. Fuel/lube analysis from particulate sample was carried out with GC / solid injection method by Fortum Oil and Gas. The analysis is based on the standard chromatograms of lube oil and 10 % distillation residue of the fuel. An example of the chromatograms of the particulate sample (diesel) and standards (lube oil and 10 % distillation residue of diesel fuel) are shown in Figure 2. For diesel particulates, the 10 % distillation residue of fuel is used to calculate the amount of the lower boiling components of the particulate SOF sample (fuel originating part) and the lube standard to calibrate the amount of heavier compounds (lube originating part). When analysing the gasoline particulates the fuel standard can not be obtained similarly as for the diesel fuel due to the lower final boiling point of gasoline (about 200 °C). For gasoline particulates it is assumed that compounds other than those found in the boiling area of the lube standard originate from the fuel. However, significant uncertainties are included in the analysis of fuel/lube from gasoline particulates.

[1] Chemical methods for the measurement of nonregulated diesel emissions. 1990. SAE J1936.

Deviation of the fuel/lube results from parallel diesel samples was generally below 10 %. Deviation of the results from gasoline samples was typically much higher, even more than 50 % of the result. In addition, in the case of gasoline sample there is uncertainty of the correct level of the result.

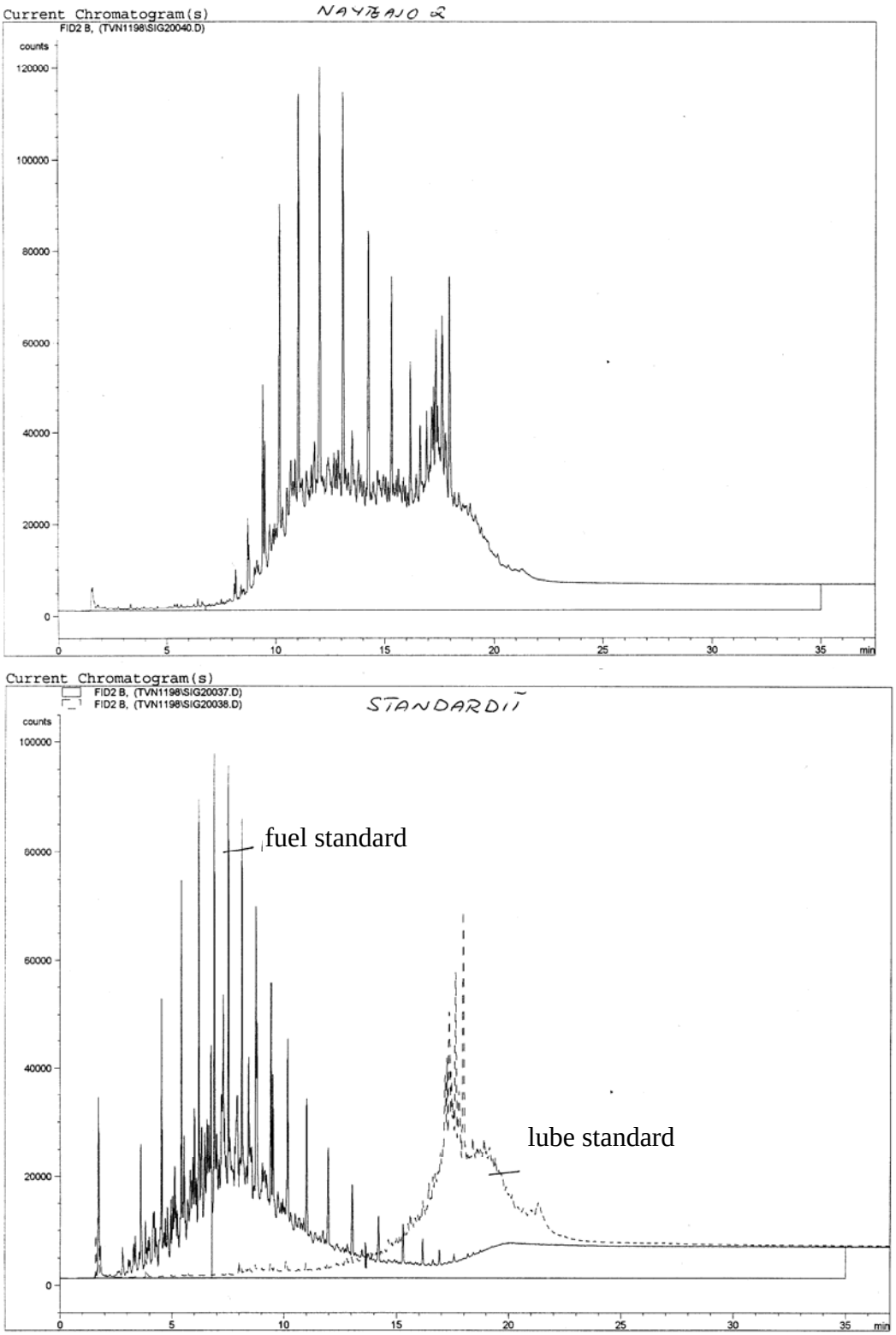


Figure 2. Chromatograms of sample (A5) and standards of fuel/lube analysis (VTT).

3.4 METALS

The metal analysis of the samples were carried out by Gent University (Belgium) with INAA and PIXE methods. PIXE method requires polycarbonate filter papers for collecting the particulate samples. Back-pressure of polycarbonate filter is high and thus low flow rate of diluted exhaust gas through filter (around 15 l/min) is required. The lowest flow rate that is used normally in the standardised sampling systems of VTT is around 28 l/min for the light-duty tests and around 100 l/min for the heavy-duty tests. It would have been difficult to build-up a new test installation, especially because additional instrumentation was already needed for the virtual impactor. Thus the other filter material was considered for the collection of metal samples at VTT.

According to information from Gent University one type of teflon filters, Gellman Teflo R2PJ047 (hereinafter "Teflo"), can be used for metal analysis. Teflo filters tolerate higher flow rates than polycarbonate filters. However, metals from Teflo filters can be analysed only by INAA method (not PIXE). Gent University has found good correlation between the results obtained with polycarbonte/INAA+PIXE and Teflo/INAA methods. In this project, polycarbonate filters were used in one test condition in parallel with Teflo filters (heavy-duty with catalyst, mode 5). The comparison of the selected metal results exceeding the detection limit are shown in Table 1. The levels of the most metals in the samples were very low, which made the analysis difficult, but very good comparability was found for e.g. K, Ca, V, Mn, Fe, Cu, Zn and In.

Table 1. Comparison of the results from the polycarbonate (analysed by INAA and PIXE) and Teflo filters (analysed by INAA). Samples collected from HD engine with catalyst in mode 5.

MODE 5, comparison of polycarbonate/PIXE and Teflo/PIXE+INAA

	Na µg/m^3	Al µg/m^3	Cl µg/m^3	K µg/m^3	Ca µg/m^3	V µg/m^3	Cr µg/m^3	Mn µg/m^3	Fe µg/m^3	Cu µg/m^3	Zn µg/m^3	In µg/m^3	Sb µg/m^3
99105P1 INAA	0.27	0.08	0.24	2.28	17.02	0.97	0.13	0.14	1.45	0.35	3.85	0.003	0.002
99106P1 INAA	0.32	0.09	0.25	2.11	15.50	0.98	0.04	0.13	0.94		3.54	0.003	0.002
99109P1 PIXE+INAA		0.11	1.66	2.69	15.53	0.93	0.14	0.13	0.74	0.25	3.93	0.003	
99110P1 PIXE+INAA	1.14	0.23	1.25	3.28	16.14	1.03	0.21	0.15	0.83	0.30	3.79	0.004	0.009
average, INAA	0.30	0.09	0.25	2.2	16.3	0.98	0.09	0.13	1.19	0.35	3.7	0.003	0.002
average, PIXE+INAA	1.14	0.17	1.45	3.0	15.8	0.98	0.18	0.14	0.79	0.27	3.9	0.004	0.009

The metal analysis was carried out from two separately collected particulate samples from each engine/aftertreatment/load combination. Thus it was possible to evaluate total deviation of the results from exhaust particulate samples including the deviation of sampling. Summary of analytical deviation and total deviation calculated from the results of this project is shown in Table 2.

Level of the metals in heavy-duty particulate samples was low. High level of bromine and chlorine disturbed the analysis of samples from light-duty tests. However, deviation of certain metals, e.g. Zn, was really low. Deviation of the most metals that exceeded the detection limit was generally lower than 25 % of the result.

Table 2. Averages of the analytical and total deviations of the metal results of this project.

		Na	Mg	Al	P	S	Cl	K	Ca	Sc	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
HD	anal.dev%	12.9	32.1	23.0	13.0	0.5	20.6	5.2	8.5		4.1	11.6	6.5	16.1	46.6	31.4	17.6	2.5
HD	total dev%	18.5		28.4	3.7	26.1	4.0	8.6	6.2		7.4	43.4	8.4	17.5			10.3	10.2
LD	anal.dev%	36.2		27.9			3.5	19.4		21.0	30.3	8.4	37.9	15.3	50.3			2.0
LD	total dev%			1.8			17.7					22.1	20.4	14.3				1.5
	min	*13*		*2*	*4*	*0*	*3*	*5*	*6*		*4*	*8*	*6*	*14*	*47*		*10*	*2*
	max	*36*		*28*	*13*	*26*	*21*	*19*	*8*		*30*	*43*	*38*	*18*	*50*		*18*	*10*
	average	***23***	***32***	***20***	***8***	***13***	***11***	***11***	***7***	***21***	***14***	***21***	***18***	***16***	***48***	***31***	***14***	***4***

		As	Se	Br	Mo	Ag	Sn	In	Sb	I	Ce	Cs	La	Sm	Eu	W	Au
HD	anal.dev%	21.6	17.7	31.6	22.7			4.0	13.0	25.8		35.3	26.7	14.6	21.4	33.1	22.7
HD	total dev%	22.0	15.4	4.4	23.0	19.7		10.7	13.1				24.0	16.2	17.8		32.6
LD	anal.dev%			4.6	6.8	27.0	29.3		20.4		32.9				27.6	22.7	
LD	total dev%			7.3					28.4		17.1						
	min	*22*	*15*	*4*	*7*	*20*		*4*	*13*		*17*		*24*	*15*	*18*	*23*	*23*
	max	*22*	*18*	*32*	*23*	*27*		*11*	*28*		*33*		*27*	*16*	*28*	*33*	*33*
	average	***22***	***17***	***12***	***18***	***23***	***29***	***7***	***19***	***26***	***25***	***35***	***25***	***15***	***22***	***28***	***28***

3.5 SIMULATED DISTILLATION

Particulate samples were extracted with dichloromethane and analysed with GC. Temperature calibration of GC was performed with a standard that contain paraffins from C5 to C40. No information of the deviation of the method is available.

3.6 CALCULATION OF THE RESULTS

The results shown in the Appendices are calculated in three units: mass/m^3 of raw exhaust gas, mass/mg of particulates and standard unit of the exhaust emission procedures (mass/kWh for heavy-duty engine and mass/km for spark-ignition vehicle).

Results as mass/m3 of raw exhaust gas and mass/mg were calculated using the real values of each sample (e.g. true sample mass, exhaust volume). The results as mass/kWh or mass/km were calculated using the average results shown in the Appendices for each test condition.

4 ROUND-ROBIN TESTS

4.1 ROUND-ROBIN SAMPLES

IFP collected particulate samples with light-duty diesel vehicle for round-robin tests. VTT Energy received the particulate samples, which are shown in Table 3. Mass of each particulate sample was around 2 mg. Anions, PAH analysis and simulated distillation were carried out at VTT. Other samples were delivered to the other laboratories for metal and fuel/lube analysis.

Table 3. Round-robin samples collected by IFP.

Sample	Filter type	analysis
A3 (+A13 blank)	Pallflex Teflon coated glass fibre (T60A20)	PAH analysis
A4 (+blank)	Pallflex Teflon coated glass fibre (T60A20)	anions
A5	Pallflex Teflon coated glass fibre (T60A20)	fuel/lube
B4 (+B10 blank)	Polycarbonate membrane, Millipore 0.6 µm	metal analysis
C5 (+C10 blank)	PTFE membrane, Millipore 0.2 µm (RGLP04700)	metal analysis
D2 (+D13 blank)	Glass fibre, Millipore (AP40)	simulated distillation
D6	Glass fibre, Millipore (AP40)	elementary analysis
F2	NIST 1650 material 41.8 mg	PAH, anions and metals
G2	XAD-2 extract	PAH analysis

4.2 PAH-ANALYSIS

Round-robin samples A3 (sample filter) and A13 (blank filter) were extracted with dichloromethane. NIST reference particulate matter (SRM 1650) was weighted as two samples and extracted with dichloromethane, as well. Semivolatile sample, XAD-2, was received from IFP as dichloromethane extract.

VTT's results of the PAH analysis of blank filter (A13), particulate sample (A3, blank reduced), semivolatile sample (XAD-2) and NIST reference material are shown in Table 4. No problems were observed with the PAH analysis of particulate material and semivolatile samples. The results of NIST material were in good accordance with certified values. This report does not include the results of the other laboratories, but it can be mentioned that especially the results from IFP and VTT were very close to each other. E.g. IFP's value for pyrene in particulate sample was 146 µg/g and for benz(a)antracene 4.9 µg/g. Higher discrepancies were observed for lighter PAH compounds. Thus it was decided that PAH analysis is selected for further work, but only the PAH compounds heavier than phenathrene will be taken into account in the modelling work.

4.3 ANION ANALYSIS

The anion results of round-robin sample A4 (blank reduced) and two samples of NIST reference material are shown in Table 5. Other anions than sulphates or nitrates did not exceed clearly the detection limit. The sulphates and nitrates showed good correlation between the laboratories and the analysis was selected for further work.

Table 4. Results of the PAH analysis of the round-robin samples.

Compound	BLANK FILTER A13 ng/sample	LOADED FILTER A3 - A13 µg/g	SEMIVOLATILE XAD-2 ng/ml of liquid	NIST Average µg/g
naphthalene	247,1	0,00	2549,1	5,9
2-methyl-naphthalene	54,3	0,00	1899,2	4,3
1-methylnaphthalene	22,3	0,00	1386,7	2,3
biphenyl	22,6	0,00	744,5	3,4
3-methylbiphenyl	13,2	2,82	522,9	1,7
acenaphthene	18,8	1,82	68,6	0,0
dibenzofurane	26,3	1,09	169,3	5,0
fluorene	17,3	1,21	140,2	1,6
dibenzothiophene	4,9	5,11	8,0	10,5
phenanthrene	60,4	176,83	94,6	64,5
anthracene	6,8	9,62	12,8	7,8
2-methyl-anthracene	6,6	151,19	14,8	56,0
1-methyl-phenanthrene	8,7	144,93	8,7	32,0
2-phenyl-naphthalene	3,9	33,15	0,0	7,8
fluoranthene	19,9	121,44	3,3	50,0
pyrene	20,3	125,27	3,8	48,5
benzo(a)fluorene	0,0	6,97	0,0	3,3
benzo(b)fluorene	0,0	2,54	0,0	0,0
benzo(b)naphtho(2,1-d)thiophene	0,0	5,00	0,0	7,0
benzo(b)naphtho(1,2-d)tiophene	0,0	2,35	0,0	1,6
benz(a)antracene	0,0	6,80	0,0	7,3
chrysene/triphenylene	5,4	23,23	0,0	16,5
benzo(b)fluoranthene	0,0	3,20	0,0	7,6
benzo(k)fluoranthene	0,0	0,00	0,0	2,8
benzo(e)pyrene	0,0	3,24	0,0	6,4
benzo(a)pyrene	0,0	0,00	0,0	1,2
perylene	0,0	0,00	0,0	0,00
indeno(1,2,3-cd)pyrene	0,0	0,00	0,0	4,3
dibenzo(a,h)anthracene	0,0	0,00	0,0	0,0
benzo(g,h,i)perylene	0,0	0,00	0,0	4,8
coronene	0,0	0,00	0,0	0,0
TOTAL	*559,1*	*796,69*	*7626,4*	*363,5*
SUM OF PAH14	*130,2*	*470,86*	*254,8*	*223,1*

Table 5. Results of the anion analysis of round-robin samples.

Sample	*Particulates mg*	Sulphate mg/g	Phosphate mg/g	Nitrate mg/g	Fluoride mg/g	Acetate mg/g	Oxalate mg/g	Formiate mg/g
A4-BLANK	*2,098*	2,5	0,1	1,5	-0,3	bd	bd	bd
NIST 1650, A	*2,966*	36,8	1,2	bd	0,1	1,2	0,8	0,8
NIST 1650, B	*1,670*	36,1	2,0	bd	0,4	bd	0,7	bd

bd = below detection limit

4.4 SOF, FUEL/LUBE ANALYSIS

Result of fuel originating part was 194 µg and fuel originating part 331 µg of the particulate sample A5 (2.136 mg). Soluble organic fraction (SOF) was not determined at VTT by weighting method, because the filter papers were not weighted before extraction

procedure. If it is assumed that SOF contains only fuel and lube originating hydrocarbons, the SOF result at VTT would be 25 %, which is 5 % lower result than those obtained by other laboratories. Fuel/lube analysis showed that soluble organic fraction of particulates was divided as follows: 37 % of particulate SOF was originating from fuel and 63 % from lube oil, which is very close to the result obtained by Euron. Due to satisfactory round-robin results fuel/lube analysis was selected for further work.

4.5 METAL ANALYSIS

The metal analysis of the round-robin samples B4 and C5 were analysed at Gent University with INAA (C5) and PIXE methods (B4). Reference diesel material, NIST, was analysed with INAA. The results of the metal analysis of B4 sample and NIST material are shown in Table 6. The results from PTFE sample C5 were not reasonable possibly due to contamination or unsuitability of filter material for analysis.

The results from sample B4 showed some variation when compared to the results from other laboratories, but the results from NIST sample analysed by Gent University were in good agreement with the results analysed in France. Actually the results from NIST material were practically the same in these two laboratories. The metal analysis was selected for further work.

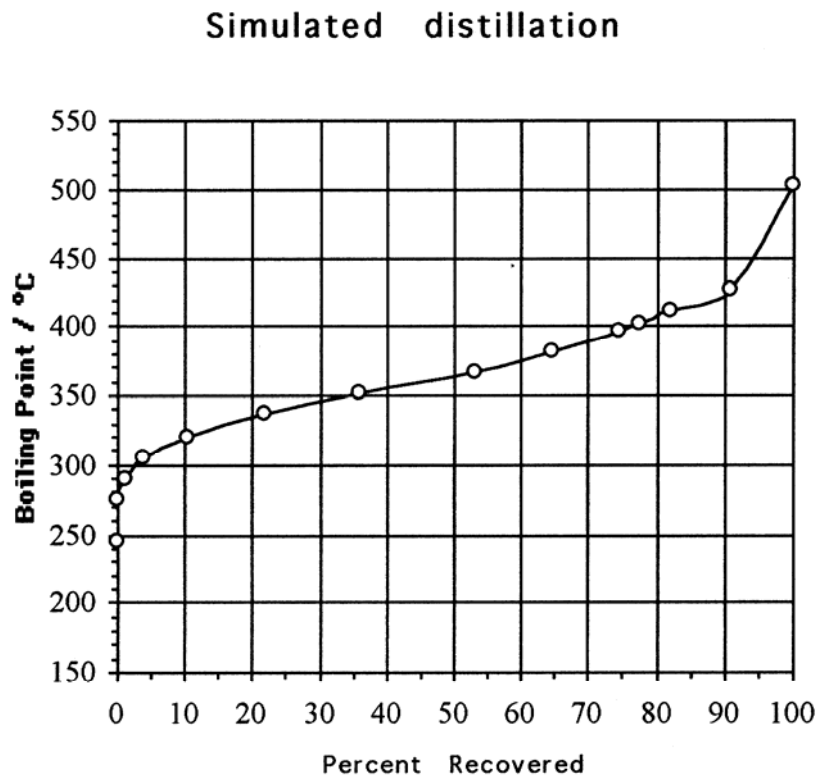
Table 6. Results of metal analysis of round-robin samples (VTT - Gent University).

			Na	Mg	Al	Si	P	S	Cl	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Se	Br
B4-blank	PIXE+INAA	µg/g	84.7	<795	55.8	<78	<47	405.6	350.0	<16	58.6	0.01	<5	<0,5	<5	0.7	<18	<0,1	<1,5	15.2	24.0	<0,6	<0,3	<1,1	<3,7
NIST-DP	INAA	µg/g	67.4	119.5	60.6				119.1	22.5	2705.5	0	9.9	3.4	80.0	18.9	862.1	2.5	75.6	68.0	1115.5	<0,07	1.9	5.0	5.5

			Rb	Sr	Y	Zr	Nb	Mo	Ag	Cd	In	Sn	Sb	I	Cs	Ba	La	Ce	Sm	Eu	Lu	W	Au	Pb	Th
B4-blank	PIXE+INAA	µg/g	<2,9	<3,0	<3,8	<3,6	<5,7	<6,1	<1,0	<8,8	<0,04	<64	<0,2	<1,6	<0,3	42.1	<0,2	<2,0	<0,04	<0,05	<0,09	<0,4	<0,005	<2,8	<0,3
NIST-DP	INAA	µg/g	<1,6	12.2				8.0	0.4	7.3	0.01	13.7	0.14	30.5	<0,08	<10,8	0.03	<0,83	0	0.01	<0,008	0.5	0.001		<0,04

4.6 SIMULATED DISTILLATION

Particulate sample D2 was extracted with dichloromethane and analysed with GC. Distillation curve of sample D2 is shown in Figure 3. Gas chromatogram of sample D2 (blank sample D13 reduced) is shown in the Figure, as well. Distillation range of particulate SOF was from 250 °C to 500 °C. Other laboratories did not carry out the similar analysis as simulated distillation. However, VTT Energy decided to keep this analysis in the further work to obtain more data on different technologies, even though it is not reasonable to include these results in CMB modelling work.



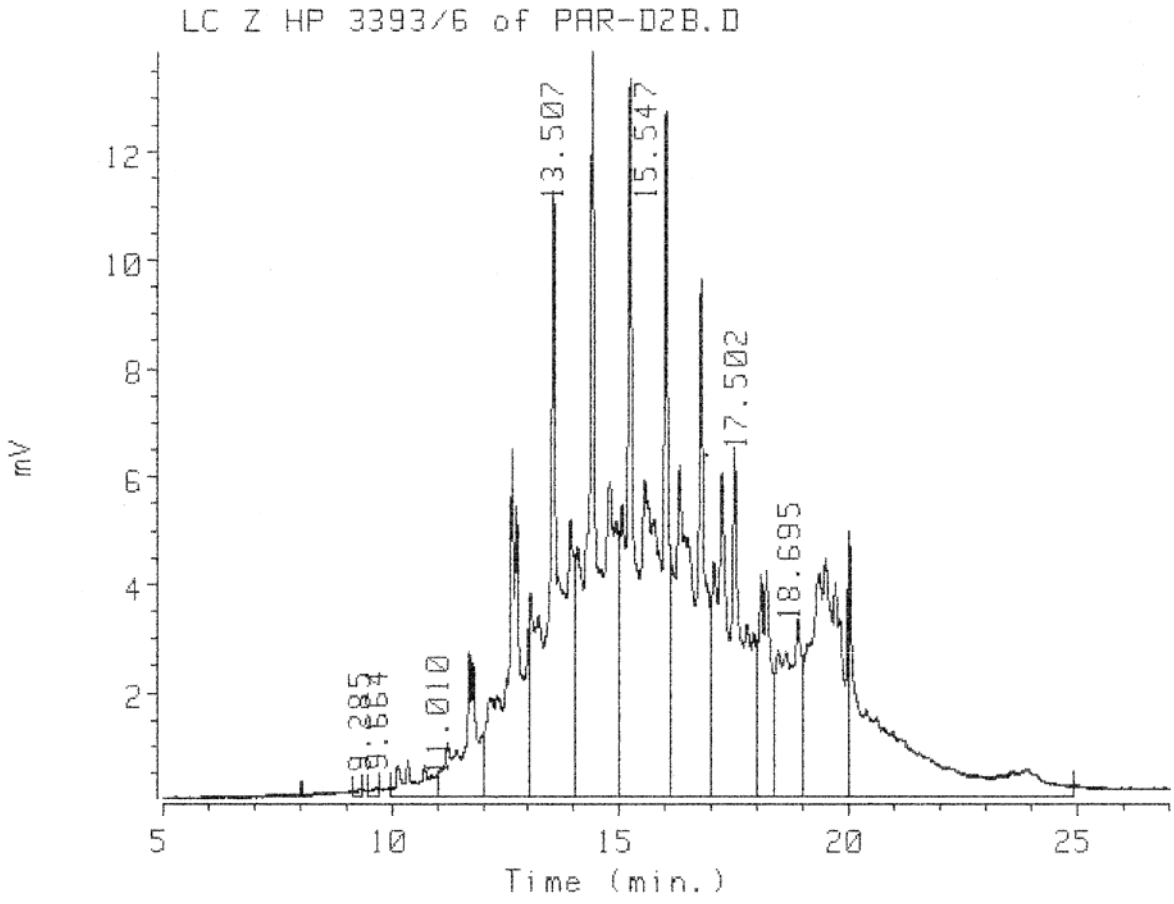


Figure 3. Simulated distillation of round-robin sample.

4.7 ELEMENTARY ANALYSIS

Pre-tests of elementary analysis of diesel particulates were carried out with particulates collected with a heavy-duty tractor engine. Particulates were analysed with CHN instrument, which is developed for micro samples (1 - 20 mg of sample required). The first experiments were promising: the particulate matter was taken from the filter (about 5 mg particulates/sample) and analysed with CHN instrument. The following results were obtained from pre-tests: 94.8 – 95.3 % carbon, 0.2 – 0.39 % hydrogen and 0.14 – 0.21 % nitrogen.

Elementary analysis of the round-robin sample D6 could not be carried out reliably. The amount of particulate matter on the filter paper was not high enough (around 2 mg). In addition, the particulate matter was stuck on the filter paper so tightly, that it was impossible to take a sample for the analysis. As a result, it can be concluded that CHN instrument can be used for elementary analysis of diesel particulates, if particulate matter load on filter is high enough (over 5 mg). The analysis method was not selected for further work.

5 TEST FUELS

Diesel fuel CEC RF-73-A-93 and gasoline CEC RF-08-A-85 representing current European qualities were purchased for the tests from Carless (A Repsol Company).

Manufacturer of CEC reference fuels provided analyses certificates with the fuels. Some additional analyses were carried out at VTT Energy to compare the results and to obtain complementary information. The analysis results of the test fuels are shown in Appendix 1.

Sulphur level of diesel fuel was around 400 ppm, which is typical level of European diesel fuel at the moment.

Lead additive (TEL) was added at VTT to a part of gasoline for the tests without the catalyst. The target lead level was 0.13 gPb/l and the analysed value was 0.16 gPb/l.

6 TESTS WITH HEAVY-DUTY ENGINE

6.1 TEST SET-UP

The diesel engine particulates were collected with an Euro 2 emission level bus engine, Volvo DH10A-285. Characteristics of the engine are as follows:

Table 7. Characteristics of the heavy-duty engine.

	VOLVO DH10A-285
Displacement	9.6
Number of cylinders	6, in-line
Maximum power	210 kW @ 2000 1/min
Maximum torque	1200 Nm @ 1450 1/min
Injection system	direct-injection, Bosch, in-line pump with EDC
Other	turbo, water/air cooling
Bore x stroke	120.65 mm x 140 mm

Heavy-duty engine was tested at three load conditions representing modes 3, 5 and 8 of ECE R49 test procedure as follows:

- mode 3: 42 kW at 1450 rpm (intermediate speed, 25 % load)
- mode 5: 125 kW at 1450 rpm (intermediate speed, 75 % load)
- mode 8: 205 kW at 2000 rpm (rated speed, 100 % load)

The tests were conducted with and without oxidation catalyst. The oxidation catalyst suitable for diesel fuels up to 500 ppm sulphur level was used in the tests.

The particulates were collected using AVL Mini Dilution Tunnel 474. Filter material used for collection of the total particulates for compositional and PAH analysis was conventional Pallflex filter. Semivolatiles were collected with polyurethane foam (PUF) material located after particulate filter.

Virtual impactor (VI) was installed in parallel with standard sampling system so that dilution ratio of the raw exhaust gas was the same as for the other samples. The flow rate of virtual impactor was around 17 l/min to obtain correct cutting point for fine particulates below 2.5 µm. The flow rate of virtual impactor was significantly lower than the flow rate through standard filters (about 100 l/min). Millipore filter material, which is suitable for weighting very low particulate masses was used with virtual impactor.

The samples for metal analysis were collected with Gelman Teflo filters. Two additional samples were collected with polycarbonate filters using as low flow rate as possible. The comparison of the metal results from the samples collected with Teflo and polycarbonate filters are discussed in chapter 3.4.

The collection of particulates was repeated several times in each test condition to obtain sufficient amount of particulates and semivolatile samples for different analyses. The summary of the test program is shown in Table 8. More complete list of the tests and test conditions is shown in Appendix 2.

In addition to analyses described in this report, filter papers and semivolatile extract from each test combination was sent to JRC Ispra for PAH and nitro-PAH analysis.

Table 8. Collection of the particulate samples with HD engine.

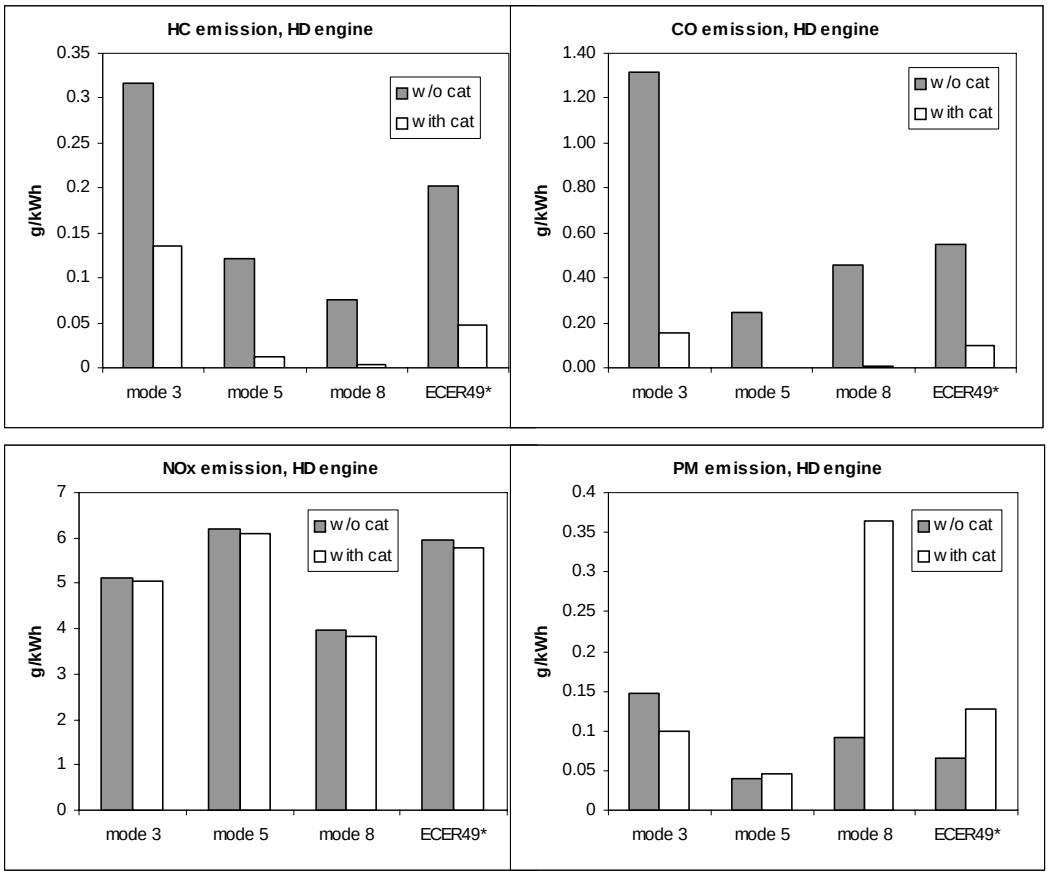
Load mode	after-treat-ment	no. of tests	filter type – total PM	filter type – PM 2.5	semivolatile sam-pling (height x diameter, mm)
Samples for compositional analysis (PAH, anions etc.)					
3, 5, 8	no	21	Pallflex TX40H120WW70	Millipore FSLW04700	PUF 50 x 50 (9 PUF sampl.)
3, 5, 8	ox.cat	21	Pallflex TX40H120WW70	Millipore FSLW04700	PUF 50 x 50 (9 PUF sampl.)
Samples for metal analysis					
3, 5, 8	no	7	Gelman Teflo R2PJ047	Gelman Teflo R2PJ047	no
3, 5, 8	ox.cat	6	Gelman Teflo R2PJ047	Gelman Teflo R2PJ047	no
5	ox.cat	2	Polycarbonate, Millipore 0.6 µm (DTTP04700)	no	no

6.2 TEST RESULTS

6.2.1 Overview of the regulated emissions

The numerical results of the regulated emissions and fine particulates of heavy-duty engine are shown in Appendix 3.

The results of regulated emissions as g/kWh are screened in Figure 4 in individual modes and as a typical result over ECE R49 test. The level of gaseous regulated emissions as g/kWh was in good accordance in individual modes with the previous results obtained at VTT with this specific engine. Particulate emissions have not been measured previously in individual modes with this engine at VTT.



*) fuel quality was slightly different for the results over ECE R49 test.

Figure 4. Regulated gaseous emissions as g/kWh, HD engine.

6.2.2 Composition of particulates

The results of the compositional analysis are presented in Appendix 4. The final results calculated as mass/m^3 of raw exhaust gas can not be directly compared to the results from the stoichiometric vehicle, because the excess air of the combustion process of diesel engine was not taken into account.

The results of the total and fine particulates are shown in Figure 5. The total particulate results shown in the Figure 5 were calculated from the results obtained with standard collection system (MDT). The results of fine particulates represent the values obtained using the share of fine particulates measured with virtual impactor. The total particulate results calculated from the measurements with virtual impactor were within ±10 % the same as calculated from the measurements with MDT. The only exception was mode 8 in the tests with catalyst, in which virtual impactor gave 25-35% lower results than MDT.

In the tests without the catalyst the particulate emissions were at the lowest level at mode 5 (intermediate speed, 75 % load). The highest particulate results were obtained at mode 8 (rated speed, 100 % load). In the tests with oxidation catalyst

the particulate emissions were several times higher at mode 8 than at modes 3 and 5 due to formation of sulphates with the oxidation catalyst at mode 8, which was not seen at lower load conditions. The share of fine particulates smaller than 2.5 µm was about 90% of the total particulates.

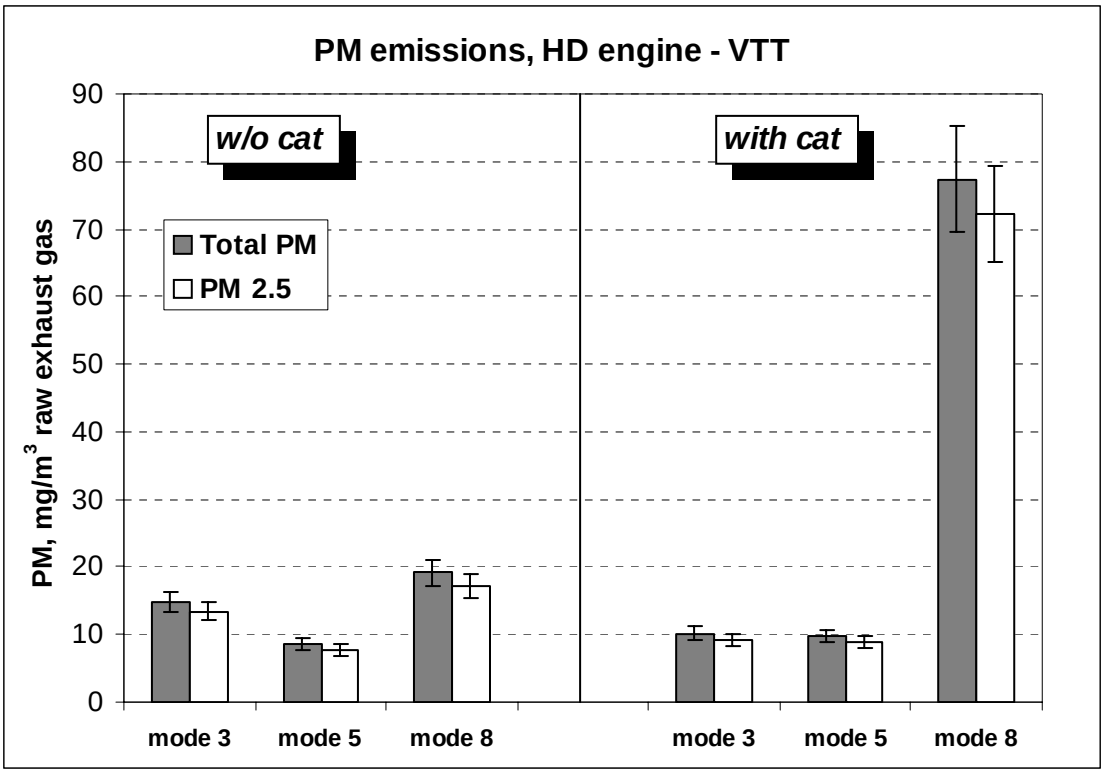


Figure 5. Total and fine particulates at different load conditions with heavy-duty engine.

Particulate emission composition divided as SOF, sulphates and others is shown in Figure 6.

Share of SOF was 10-25 % in the tests without catalyst. In modes 3 and 5 share of SOF was about 10 %. The most peculiar result in compositional analysis of heavy-duty particulates was the extremely high share of SOF in mode 8 in the tests with catalyst. “Others”, that represent usually mostly the carbon part of particulates, show logical result at mode 8 (catalyst is not expected to increase carbon). The sulphate analysis has given acceptable results in this and the previous round-robins and thus it has to be regarded reliable. However, sulphate result does not include “combined water”, which is normally added to original sulphate result. As the amount of “combined water” is 1.32 x sulphates, it plays a significant role in the tests with oxidation catalyst when a lot of sulphates are formed. Most probably part of the water has come along in extraction process so that the real value of SOF is significantly lower than shown in Figure 6 and the rest of SOF is probably water.

Formation of sulphates was low in the tests without catalyst and at modes 3 and 5

in the tests with catalyst. In opposite to that, catalyst formed a high amount of sulphates in mode 8 as was mentioned earlier.

Extremely low amount of nitrates was detected in the particulates. Other anions than sulphates and nitrates were below detection limit. The detection limit of the INAA method for metal analysis is much better than the detection limit of capillary electrophoresis for anion analysis. According to the INAA results the level of chlorine was around 0.5 – 2 $\mu g/m^3$ and bromine around 0.4 – 0.7 $\mu g/m^3$ raw exhaust gas.

Fuel/lube results showed that oxidation catalyst may reduce effectively hydrocarbon part of particulates. Share of fuel originating hydrocarbons seemed to be more determining than lube originating hydrocarbons in the samples. The fuel/lube emission per exhaust volume was significantly higher in the lowest load condition (mode 3) than in the other loads tested.

Compositional analysis of fine particulates collected with virtual impactor was difficult due to low particulate mass on each filter. SOF analysis results were not reliable enough to be discussed. Fuel/lube analysis could not be carried out due to low temperature resistance of the filter material. The only compositional analysis that could be done was the anion analysis shown in Figure 7. Fine particulates seemed to contain slightly less sulphates than the total particulates. E.g. the share of sulphates in total particulates was 34% and in the fine particulates 27% in mode 8 of the tests with catalyst. There seemed to be no trend concerning nitrates due to very low level.

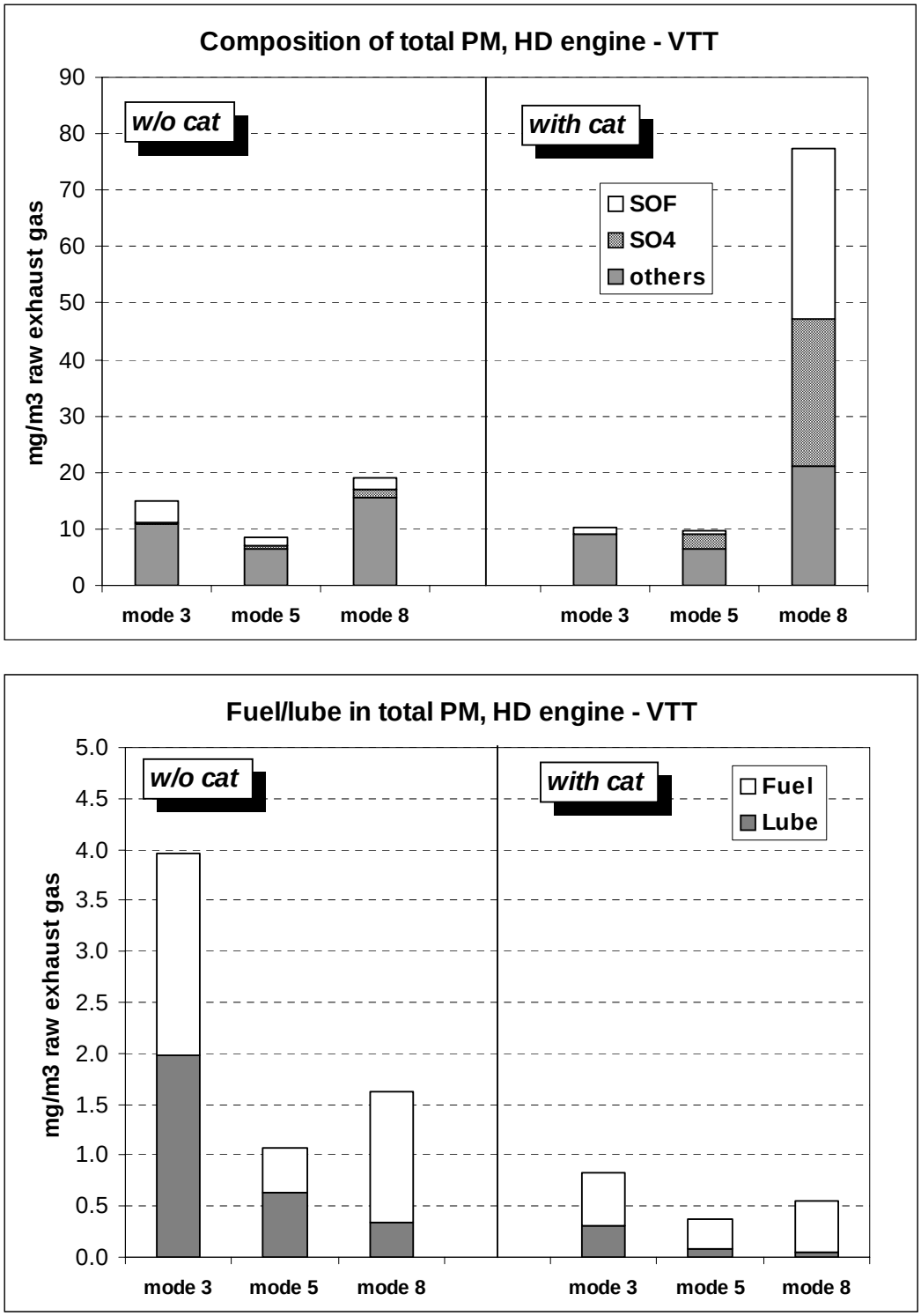


Figure 6. Composition of particulates and fuel/lube-results at different load conditions with heavy-duty engine. "Combined water" is not shown in the figures. In mode 8 with the catalyst, "combined water" (34 mg/m^3) is presumed to be included partly in SOF and partly in "others".

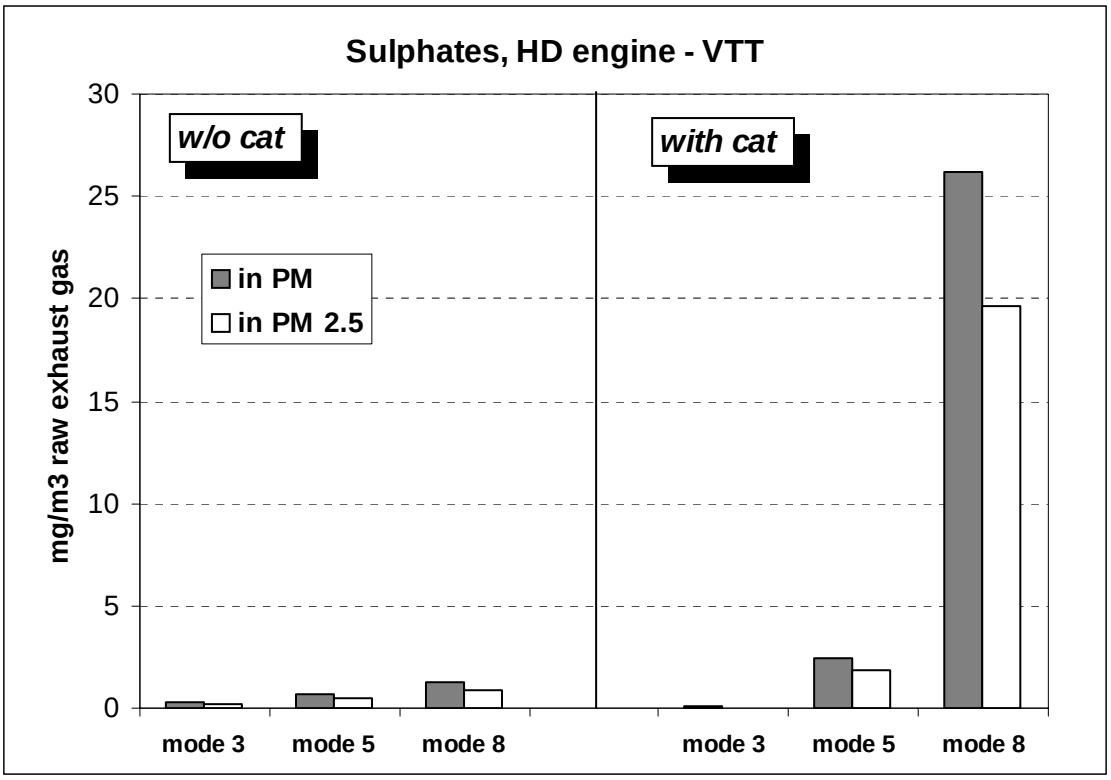


Figure 7. Sulphates in total and fine particulates at different load conditions, heavy-duty engine.

6.2.3 PAH results

The numerical results of PAH analysis of heavy-duty engine tests are shown in Appendices 5-9.

About 30 PAH compounds were analysed from particulates and semivolatile samples. The sum of PAH compounds containing 3-7 rings (20 compounds, marked with bold-face in the Appendices) in the total particulates and semivolatile phase are shown in Figure 8.

The major part of the PAH compounds was observed in the semivolatile phase of heavy-duty engine. Oxidation catalyst reduced PAH emissions effectively, especially from the semivolatile phase. The PAH emissions seemed to be at the highest level at the lowest load condition (mode 3). Particulates contained the lowest level of PAH emissions at medium load (mode 5), but semivolatile PAH's were at the lowest level at high load condition (mode 8).

Concentration of PAH-compounds in fine particulates was higher than in the total particulates at all load conditions with and without catalyst. One reason for this could be the lower flow rate of diluted exhaust gas with virtual impactor (~17 l/min) when compared to sampling of total particulates (~100 l/min). It can be assumed that a part of the PAH compounds found from the semivolatile phase

with the sampling system for total particulates could stay in the particulate phase with the sampling system for fine particulates.

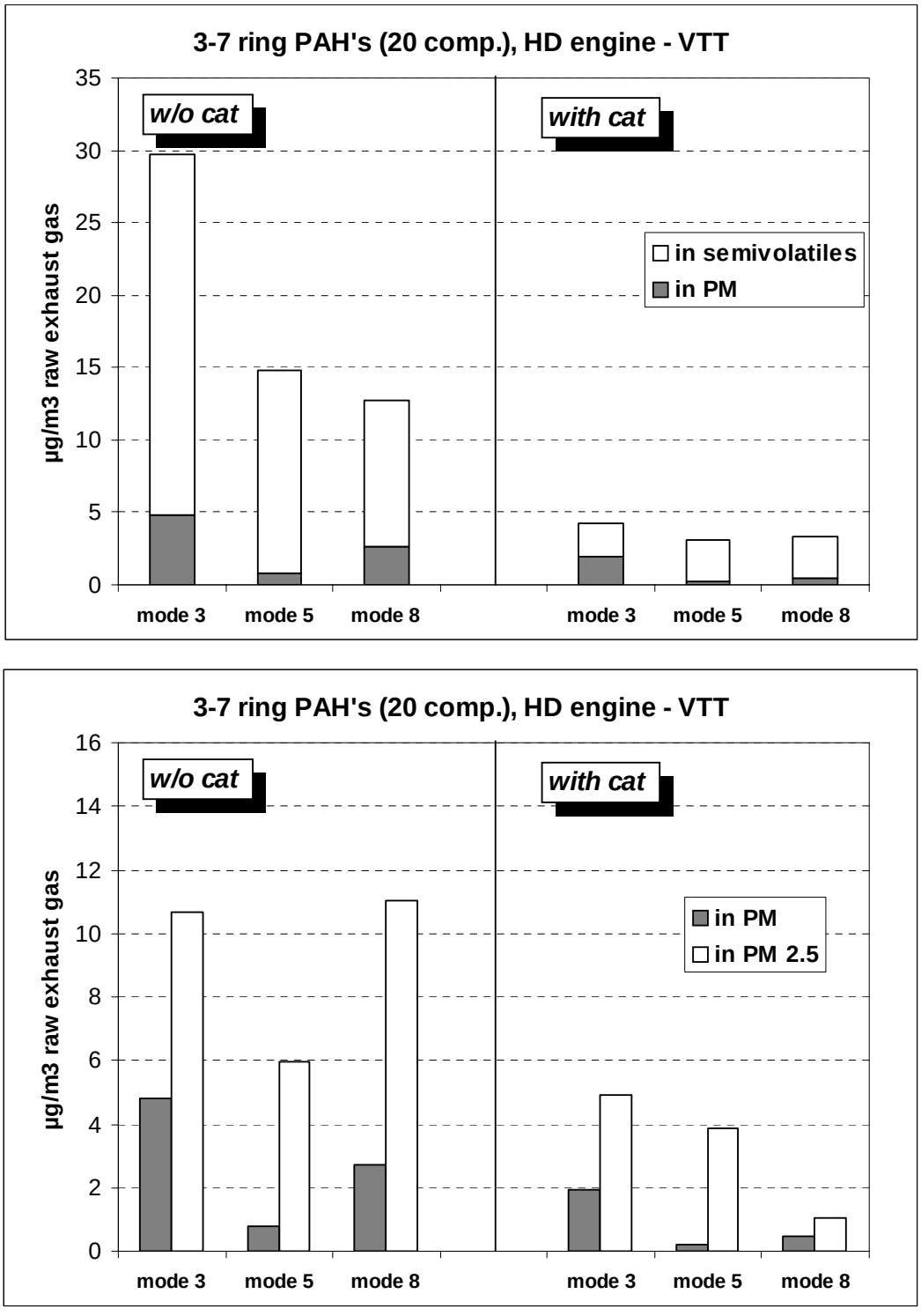


Figure 8. PAH compounds including 3-7 rings in total particulates, semivolatile phase and fine particulates at different load conditions, heavy-duty engine.

Individual PAH compounds from SOF of total and fine particulates are shown in Figure 9 as µg/mg. Generally, the profile of PAH compounds in total particulates seems to be rather similar regardless of load conditions or aftertreatment technology. However, mode 3 gave slightly different profile both with and without oxidation catalyst. E.g. the concentration of pyrene was higher at mode 3 than at the other modes.

The effect of load on PAH was not very significant for fine particulates. Pyrene was the major PAH compound found from the total and fine particulates at low load conditions (mode 3). PAH profile of the fine particulates was not very different from the PAH profile of the total particulates in the tests without catalyst. The PAH profile in the tests with the oxidation catalyst included some differences when compared to the other PAH profiles, which is most probably due to the very low level of PAH compounds – near to the detection limit.

Individual PAH compounds analysed from the semivolatile phase calculated as µg/mg of particulates is shown in Figure 10. Semivolatile phase contained several magnitudes higher level of light PAH compounds than the particulate phase. However, the heavier PAH compounds than pyrene did not exceed the detection limit in the semivolatile phase samples.

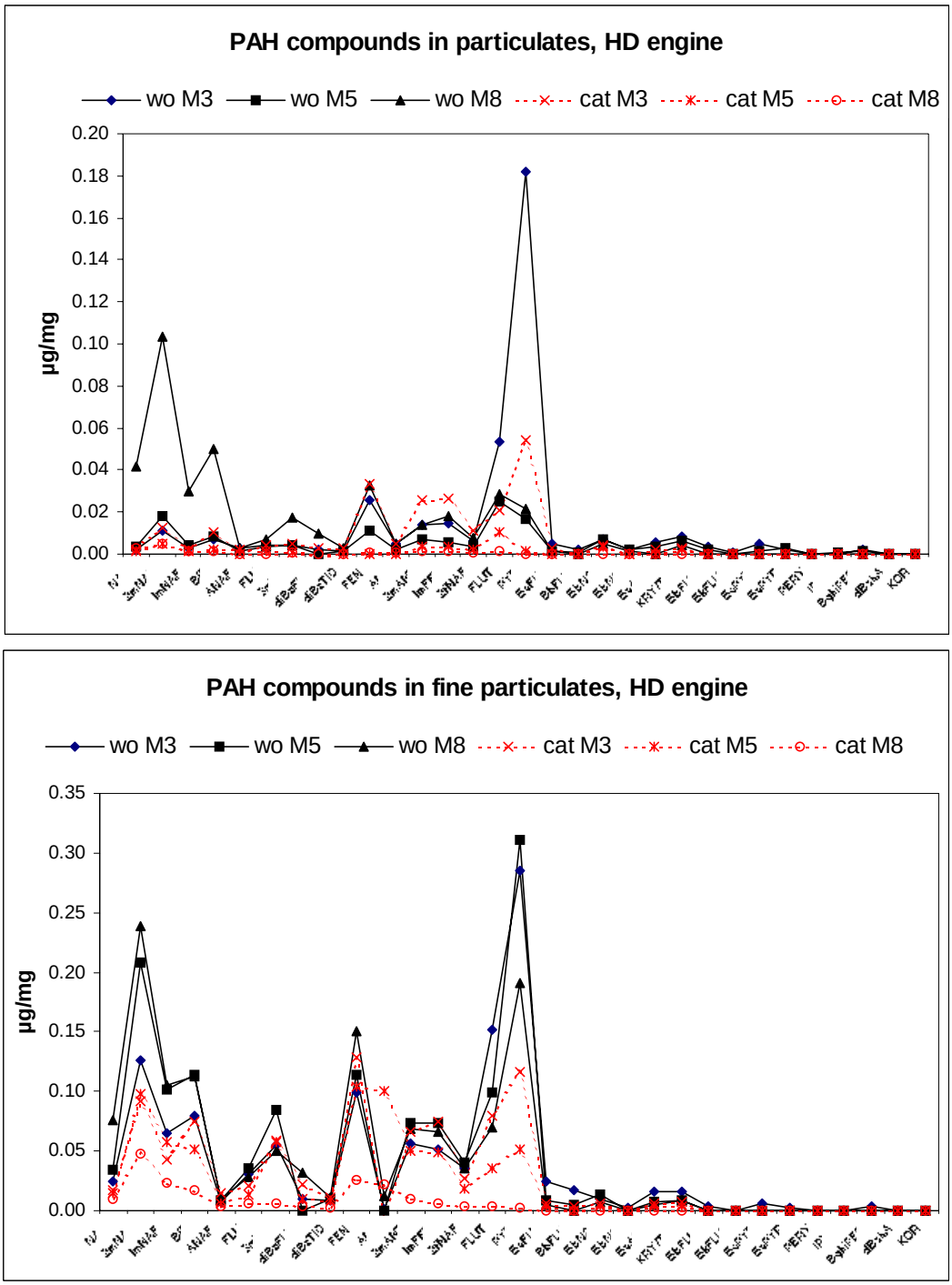


Figure 9. Individual PAH compounds including 3-7 rings in total and fine particulate samples, heavy-duty engine.

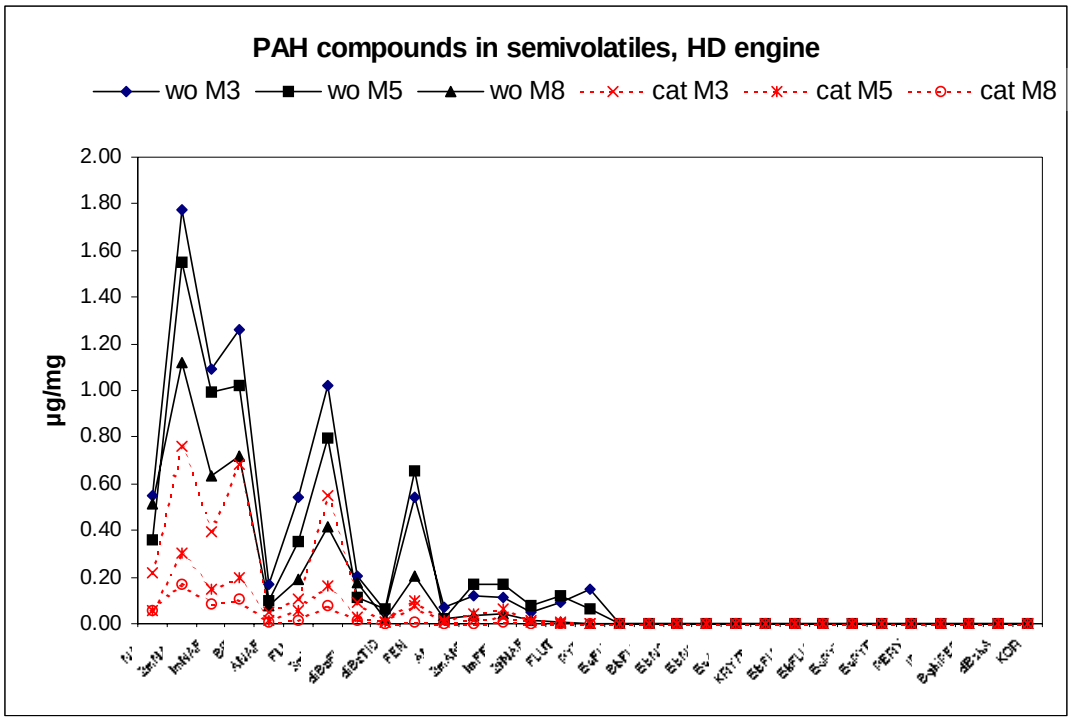


Figure 10. Individual PAH compounds including 3-7 rings in semivolatile phase, heavy-duty engine.

6.2.4 Metal results

The results of the metal analysis as ng/sample are shown in Appendices 12 and 13. Other numerical results are shown in Appendices 10-11. The samples of total and fine particulates were analysed by INAA method from Teflo filters (39 different metals). Additional analysis in one load condition was carried out with PIXE+INAA method from polycarbonate filters to confirm that the methods give the same level of results, which is discussed in chapter 3.4. Si, P, S, Y, Zr, Nb and Pb were analysed only with PIXE+INAA method. The Br and Cl results are included in chapter 6.2.2, because the anion analysis included those elements as well.

Detection limits varied depending on the metal analysed, which is seen in Appendix 12. About 20 metal compounds of those analysed exceeded the detection limit. The highest results were observed for Ca, K, Fe, Zn, Na and Al (Figure 11). The level of the other metals was low when compared to overmentioned metals. Some variation was observed between different load/aftertreatment combinations. The lowest level of metals was observed from samples obtained at mode 8 in the tests with the oxidation catalyst. In addition, a few metals were detected only in one or two load conditions (Co, Ag, W).

No significant differences between the metal concentrations in total and fine particulates were observed (Figure 12).

The results indicate that an average of all studied load/aftertreatment combinations can be used for further analysis.

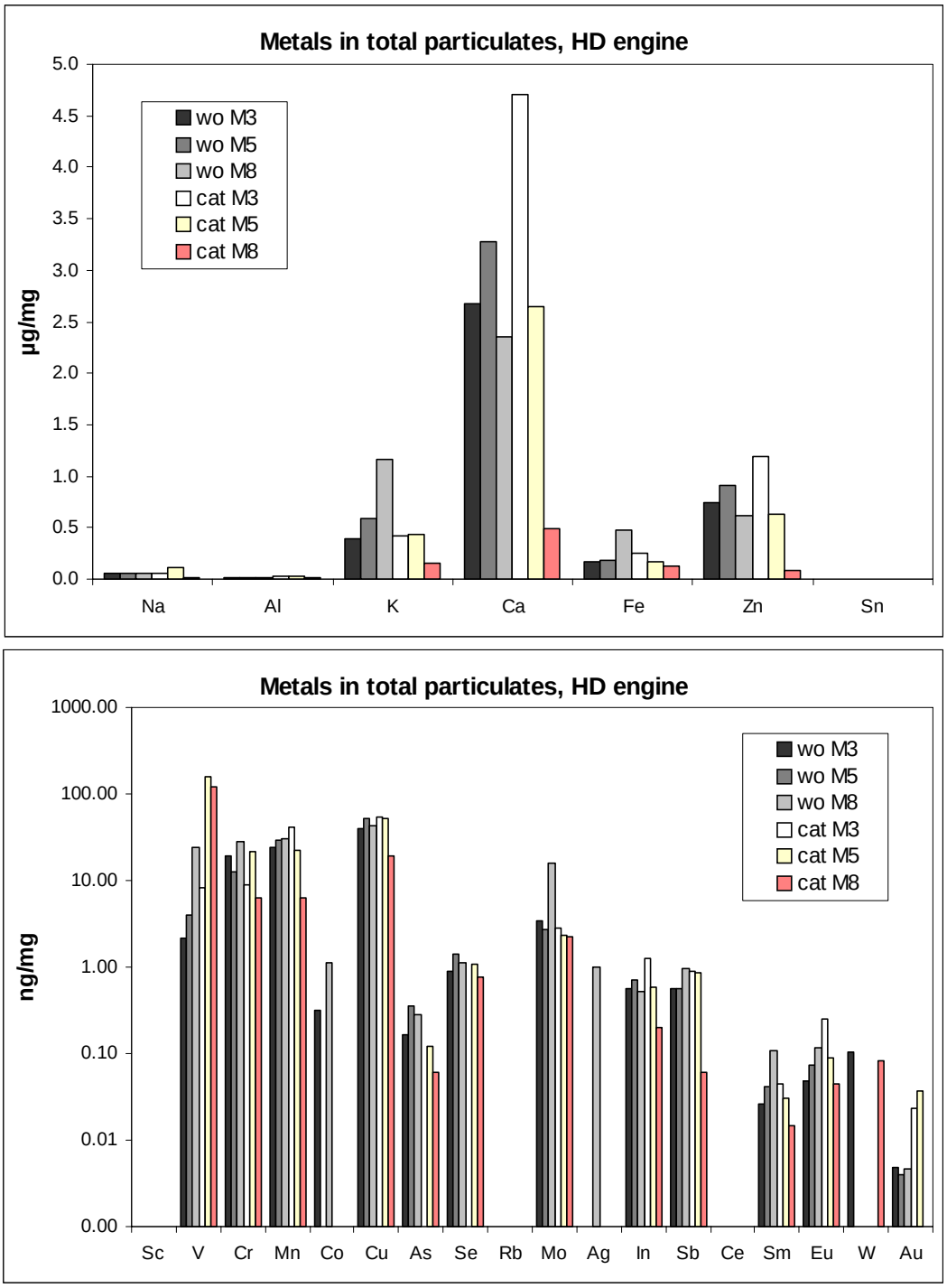


Figure 11. Selected results of metal analysis from total particulates at different load/aftertreatment combinations, HD engine. Note: scale in the second figure is logarithmic and unit is ng/mg.

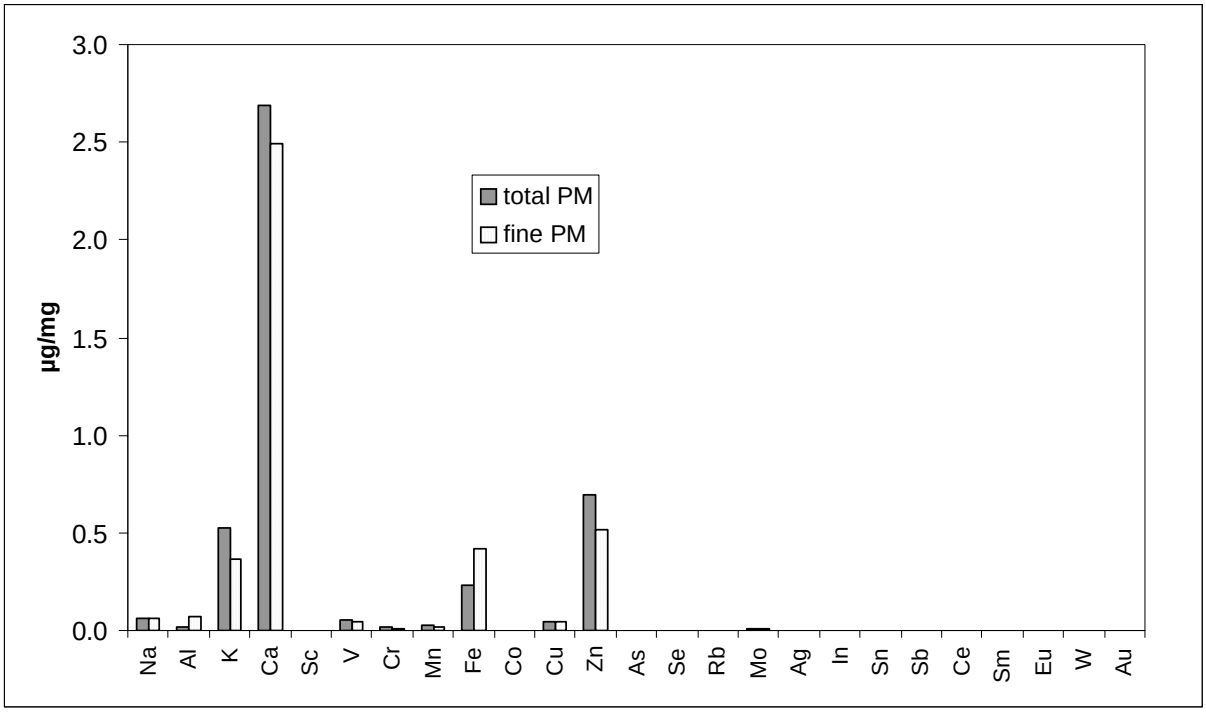


Figure 12. Average results of metal analysis from total and fine particulates at different load and aftertreatment combinations, HD engine.

7 TESTS WITH SPARK-IGNITION VEHICLE

7.1 TEST SET-UP

The particulates from gasoline fuelled stoichiometric vehicle were collected with rented Ford Mondeo 1.6 l passenger car equipped with three-way catalyst (66 kW at 5250 min^{-1};140 Nm at 3500 min^{-1}; model year 1998). Mondeo was stoichiometric gasoline fuelled vehicle with multi-point fuel injection system. Odometer reading of the vehicle was 29 000 km before the tests.

The particulate emissions from the gasoline fuelled stoichiometric vehicles equipped with TWC are very low when compared to diesel vehicles. VTT Energy has developed a high-capacity particulate collection system specially for gasoline fuelled vehicles. However, until now the tests have been carried out with transient test cycles including the cold-start of the vehicles. The situation is much more difficult in the steady-state tests when the vehicle is fully warmed-up. Several speed and load conditions were tested to select the final steady-state load conditions. It was observed that low speeds, e.g. 50 km/h, were not acceptable due to extremely low particulate masses on filters, even though higher chassis dynamometer load settings or lower gear than recommended were used. 80 km/h and 120 km/h resulted in sufficient mass of particulates for special analysis. The load conditions selected were as follows:

- 80 km/h, 6.8 kW, 3000 rpm, 4^{th} gear
- 120 km/h, 23 kW, 3450 rpm, 5^{th} gear

The particulates were collected with and without catalyst. Leaded gasoline was used in the tests without the catalyst (TEL -> 0.13 gPb/l). The filter materials for different analyses followed the similar patterns as described for heavy-duty tests.

Two different sampling systems were used for the collection of particulate samples. The samples for compositional analyses were collected with high-capacity sampling system using flow rates from 1000 to 1800 l/min through two parallel filter papers (diameter 142 mm). The samples for metal analyses were collected with standard sampling system with flow rate of 28.5 l/min with ∅ 47 mm filter papers. Virtual impactor was used in parallel with both collection systems. The flow rate of virtual impactor was 17 l/min.

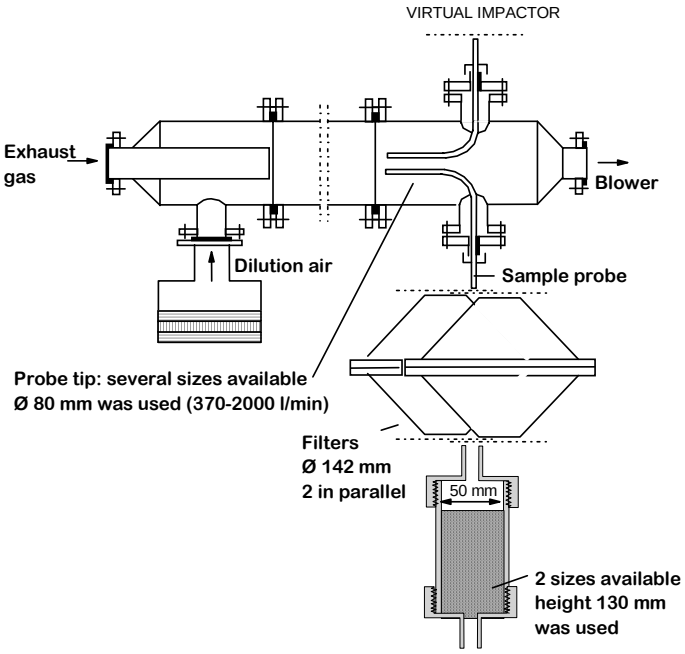


Figure 13. Schematic figure of the high-capacity sampling system for total particulates and virtual impactor system for fine particulates, spark-ignition vehicle. Total particulates for metal analysis were collected with standard sampling system (∅47 mm filters).

In addition to the steady-state tests, two tests were carried out according to the European test cycle (described in amendment 91/441/EEC of directive 70/220/EEC) to screen the general emission level of the vehicle. Start of the European test cycle was carried out with 11-seconds idle period in the beginning of the test according to the oncoming directive. The summary of the tests with SI vehicle is shown in Table 9. More exact description of the test conditions is shown in Appendix 14.

Table 9. Collection of the particulate samples with SI vehicle.

Vehicle speed	Collect. time per test, min	no. of tests	**Total PM,** filter type and flow of di. exh. gas through filter, l/min	**Virtual impactor** filter type, flow	**Semivolatiles** (height x diameter, mm)
Samples for compositional analysis (PAH, anions etc.)					
80 km/h w/o cat	30	6	Pallflex T60A20-142 flow 1800 l/min	Millipore FSLW04700 flow 17 l/min	PUF 50 x 130 (3 PUF samples)
120 km/h w/o cat	15	6	Pallflex T60A20-142 flow 1100 l\min	Millipore FSLW04700 flow 17 l/min	PUF 50 x 130 (3 PUF samples)
80 km/h with TWC	60	6	Pallflex T60A20-142 flow 1800 l\min	Millipore FSLW04700 flow 17 l/min	PUF 50 x 130 (3 PUF samples)
120 km/h with TWC	15	6	Pallflex T60A20-142 flow 1000 l/min	Millipore FSLW04700 flow 17 l/min	PUF 50 x 130 (3 PUF samples)
Samples for metal analysis					
80 km/h w/o cat	60	2	Gelman R2PJ047, 28.5 l/min	Gelman R2PJ047 flow 17 l/min	no
120 km/h w/o cat	10	2	Gelman R2PJ047, 28.5 l/min	Gelman R2PJ047 flow 17 l/min	no
80 km/h with TWC	60	2	Gelman R2PJ047, 28.5 l/min	Gelman R2PJ047 flow 17 l/min	no
120 km/h with TWC	10	2	Gelman R2PJ047, 28.5 l/min	Gelman R2PJ047 flow 17 l/min	no
Additional samples					
European test cycle with and w/o TWC	standard	2	Pallflex T60A20-142 flow 1440 l/min	Millipore FSLW04700 flow 17 l/min	PUF 50 x 130

7.2 TEST RESULTS

7.2.1 Regulated emissions

The results of the regulated emissions for SI vehicle with European test cycle (11-seconds idling period) were as follows:

	with TWC	without TWC
CO, g/km	1.7	9.8
HC, g/km	0.16	1.3
NO_x, g/km	0.07	2.1
PM, mg/km	0.5	3.4

The emissions of the vehicle were at normal level of the mid-size gasoline fuelled stoichiometric passenger car. Numerical results of the regulated emissions and fine particulates are shown in Appendix 15.

The sampling of total particulates, fine particulates and particulates for metal analysis were carried out with extremely different conditions e.g. flow rate through filters 1800 l/min vs 17 l/min (face velocity 4 times higher in high-capacity sampling than in virtual impactor sampling). Thus it was interesting to observe that the total particulate results calculated as mg/km from different tests were at the same level, except for the sampling for metal analysis at 120 km/h speed (Figure 14). First it was thought that the increase in particulate mass at 120 km/h speed was due to condensed water. Later on, as the results from metal analysis were available, it was noticed that those samples contained a lot of bromide. Sampling for metal analysis was carried out after the sampling with

high-capacity system for the other analysis to avoid duplicate changes of instrumentation. Thus the tests with leaded fuel were carried out before the sampling for metal analysis. Most probably bromine of TEL additive accumulated in the sampling system during the tests without catalyst and suddenly came out during the high-speed testing condition. Thus the bromine results from metal analyses of the tests with catalyst at 120 km/h speed were discarded.

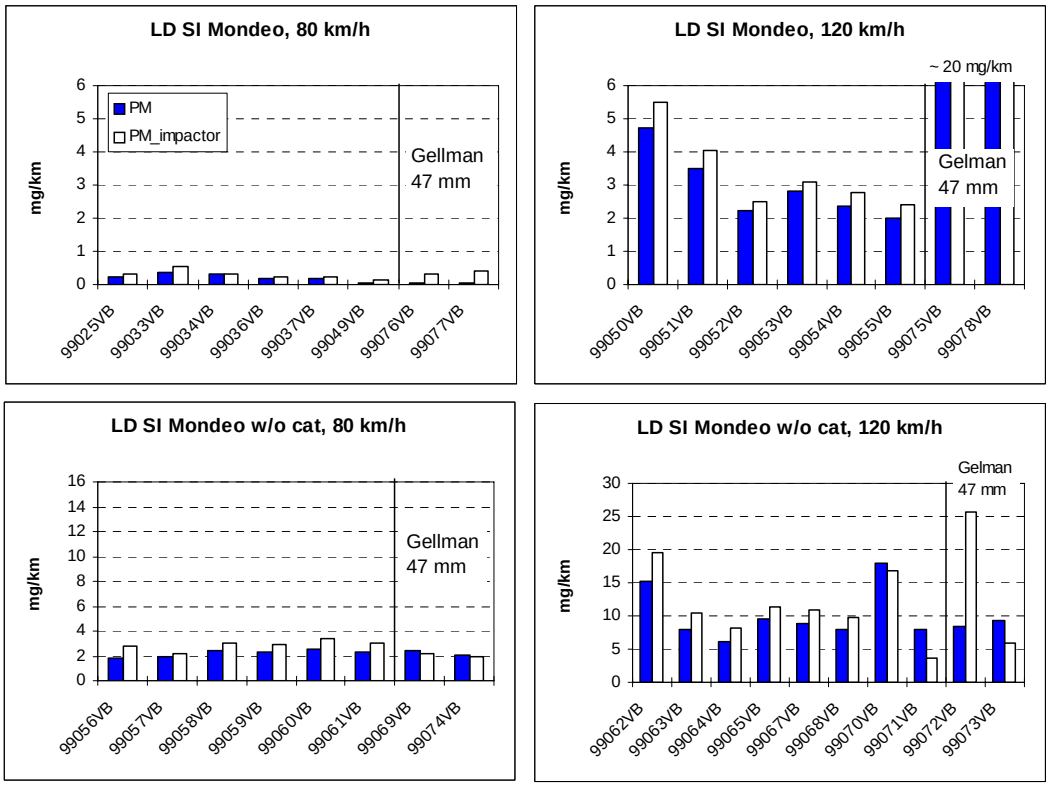


Figure 14. Results of the total particulates as mg/km obtained by various collection systems.

7.2.2 Composition of particulates

The numerical results of the steady-state tests (calculated as mass/m^3 raw exhaust gas) are shown in Appendix 16.

The particulate emission level at 120 km/h speed was significantly higher than at 80 km/h speed or over European test cycle (Figure 15). Fine particulates represented about 80-90 % of total particulates. Load conditions did not seem to effect significantly on the share of fine particulates.

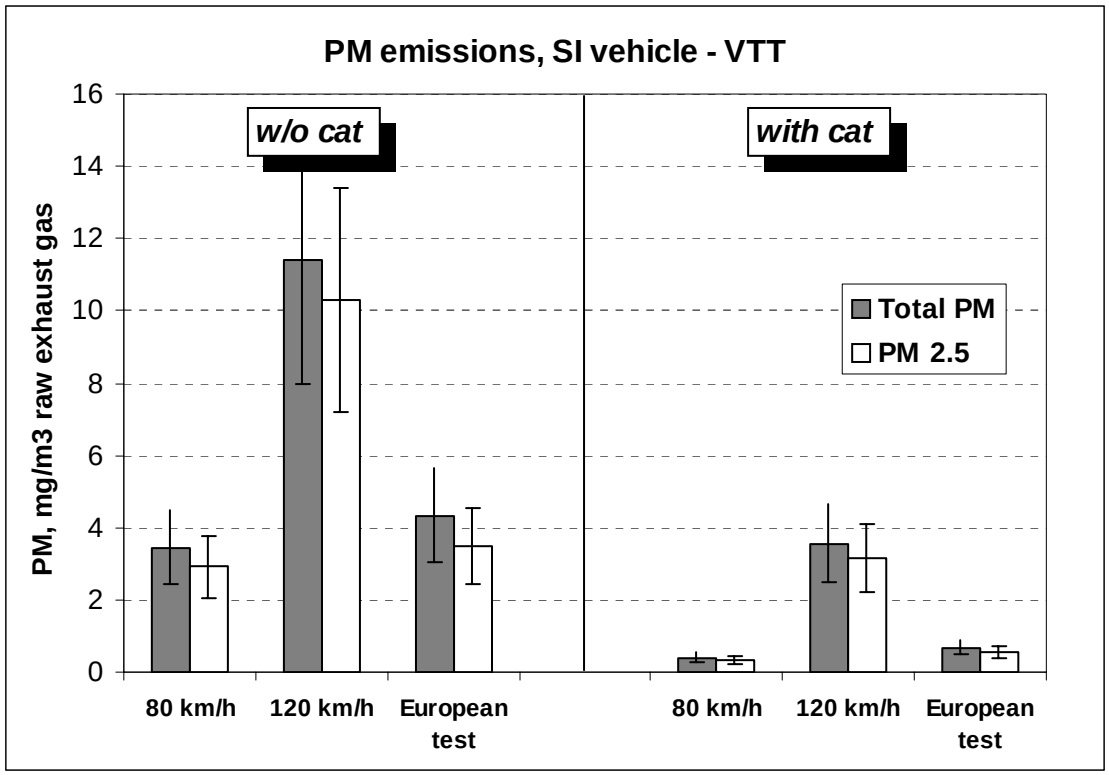
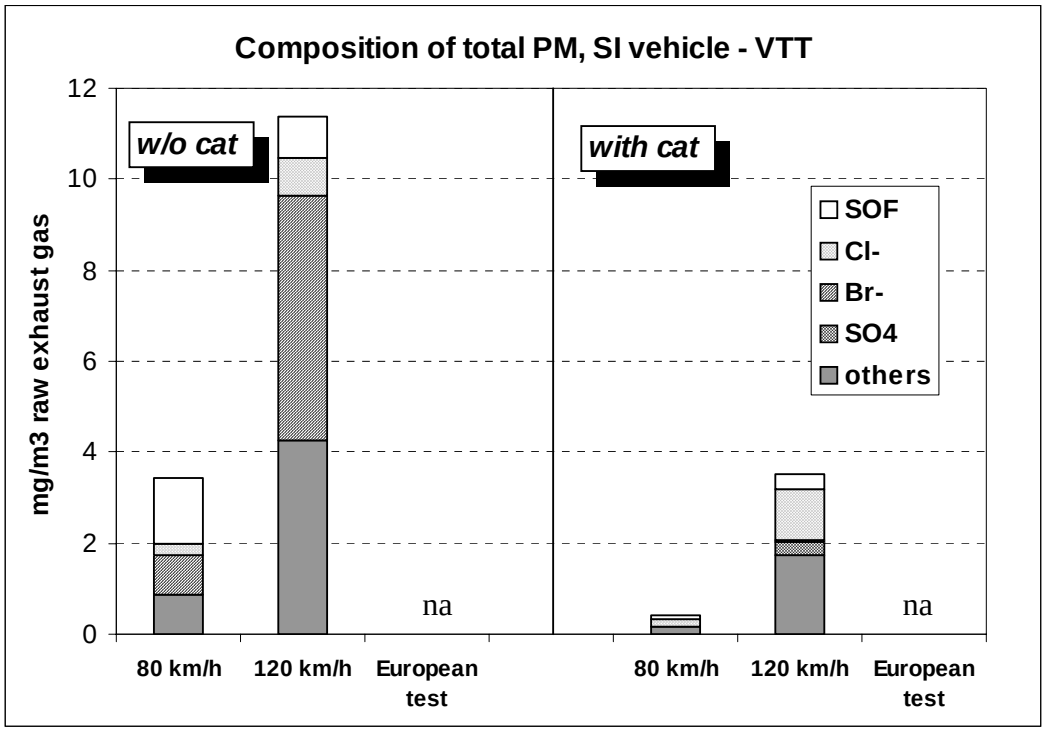


Figure 15. Total and fine particulates at different load conditions with spark-ignition vehicle.

Particulates contained almost 40% SOF at 80 km/h speed in the tests without the catalyst (Figure 16). In the other conditions the share of SOF was 10 – 15%. Three-way catalyst reduced efficiently SOF of particulates. Lube originating SOF was more determining than fuel originating SOF in particulates.

It seemed that the major part of the particulates from gasoline fuelled stoichiometric engine were anions (Figure 16). In the tests without catalyst leaded fuel was used and thus the bromide content of particulates was high (scavengers of TEL additive). At both load conditions, with or without the catalyst, the particulates contained chlorides. Sulphates occurred significantly only in the test with the catalyst at 120 km/h speed. This was most probably due to capability of catalyst to produce sulphates from fuel sulphur. The level of fluorides and nitrates in the particulates were insignificant when compared to the other anions.



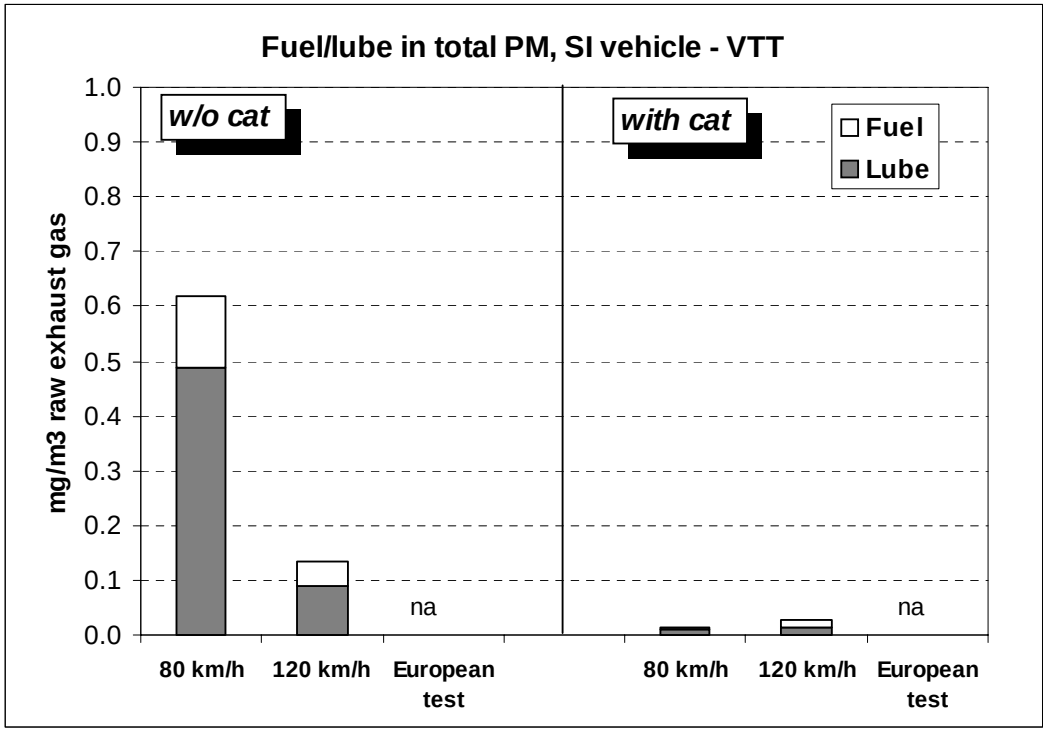


Figure 16. Composition of total particulates and fuel/lube –results with spark-ignition vehicle.

7.2.3 PAH results

The numerical results of the PAH analysis are shown in Appendices 17 - 21.

Catalyst reduced effectively the PAH level both in particulates and semivolatile phase. The major part of the PAH compounds from the SI vehicle were present in the semivolatile phase (Figure 17). In the tests without the catalyst at 80 km/h speed, the PAH emission level was higher in the particulates, but lower in the semivolatile phase, than at 120 km/h speed or over European test cycle.

Particulates lower than 2.5 µm seemed to contain higher level of PAH compounds than the total particulates. However, it has to be noted that the sampling conditions for total and fine particulates were different. It can be assumed that a part of those PAH compounds that were observed in semivolatile phase for total particulates stayed in the particulate phase for fine particulates. The reason for this could be low flow rate of diluted exhaust gas in the sampling of fine particulates compared to high flow rate in the sampling of total particulates.

In the tests without the catalyst the total particulates contained significant amounts of heavy PAH-compounds, which was not the case with fine particulates (Figure 18). Heavy PAH compounds were observed in the fine particulates only at 80 km/h speed in the tests without catalyst. On the other hand, the mass of fine particulate sample for PAH analysis was really low – perhaps too low for reliable analysis.

Profiles of gasoline particulates at different load conditions were not as consistent as was seen in the heavy-duty tests. One surprising result was that the highest levels of the heaviest PAH compounds were observed in the test with catalyst according to European test cycle. For the further analysis of these results it might be reasonable to separate PAH profiles from the tests with the catalyst and without the catalyst.

Semivolatile phase did not contain significantly heavier compounds than pyrene (Figure 19).

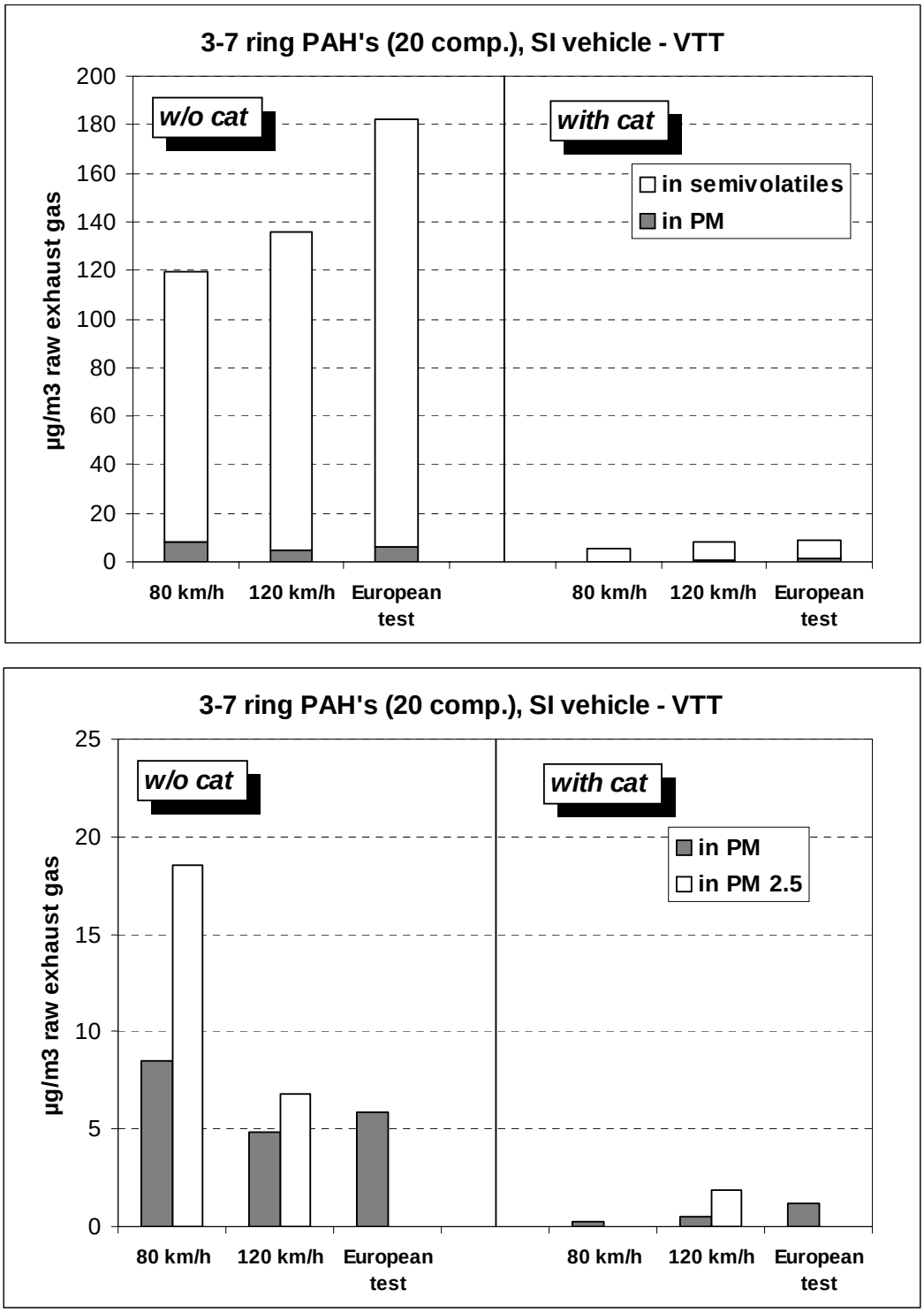


Figure 17. PAH compounds including 3-7 rings in total particulates, semivolatile phase and fine particulates at different load conditions, spark-ignition vehicle. The sampling conditions of total and fine particulates were different from each other.

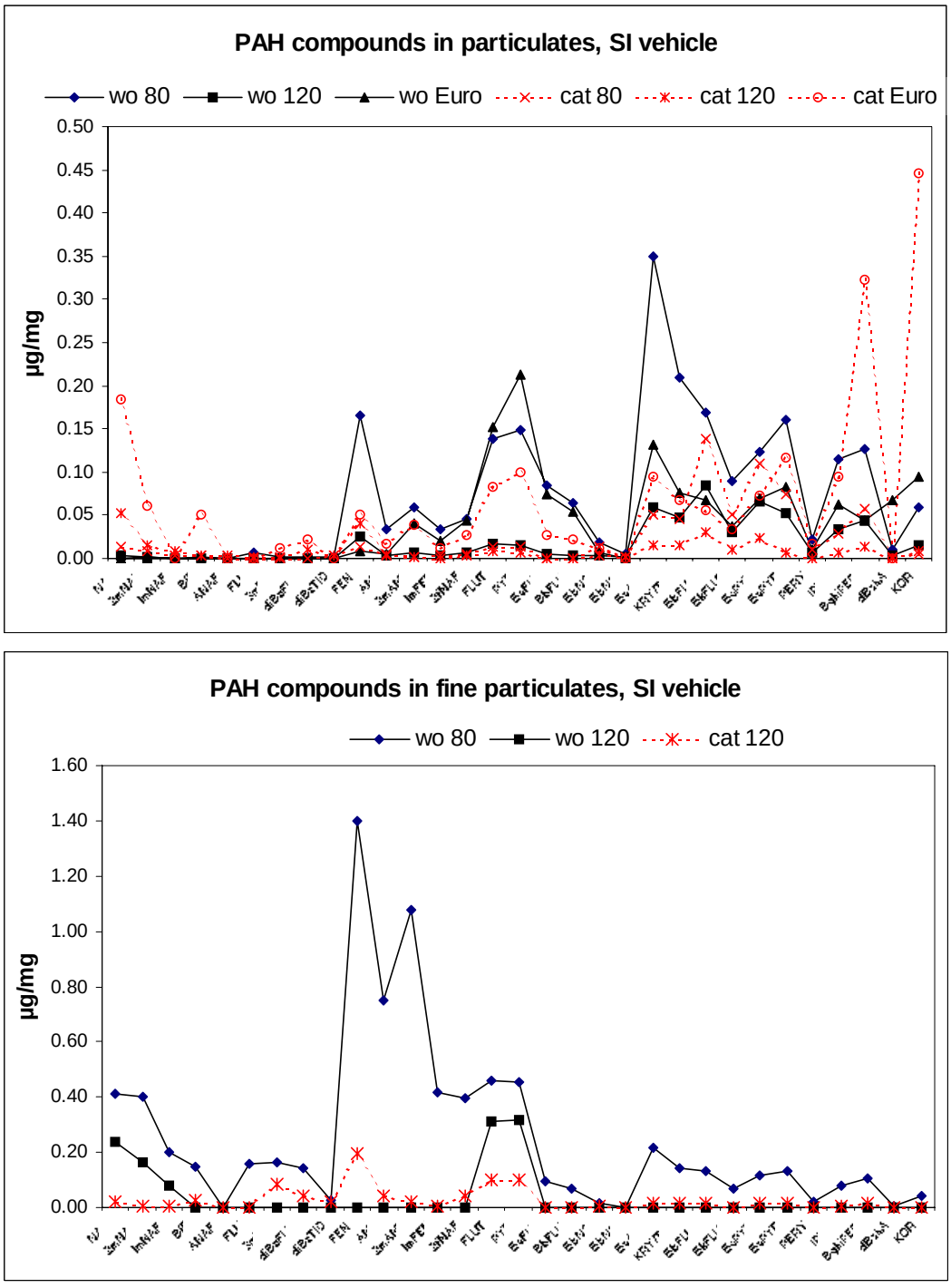


Figure 18. Individual PAH compounds in total and fine particulates, spark-ignition vehicle.

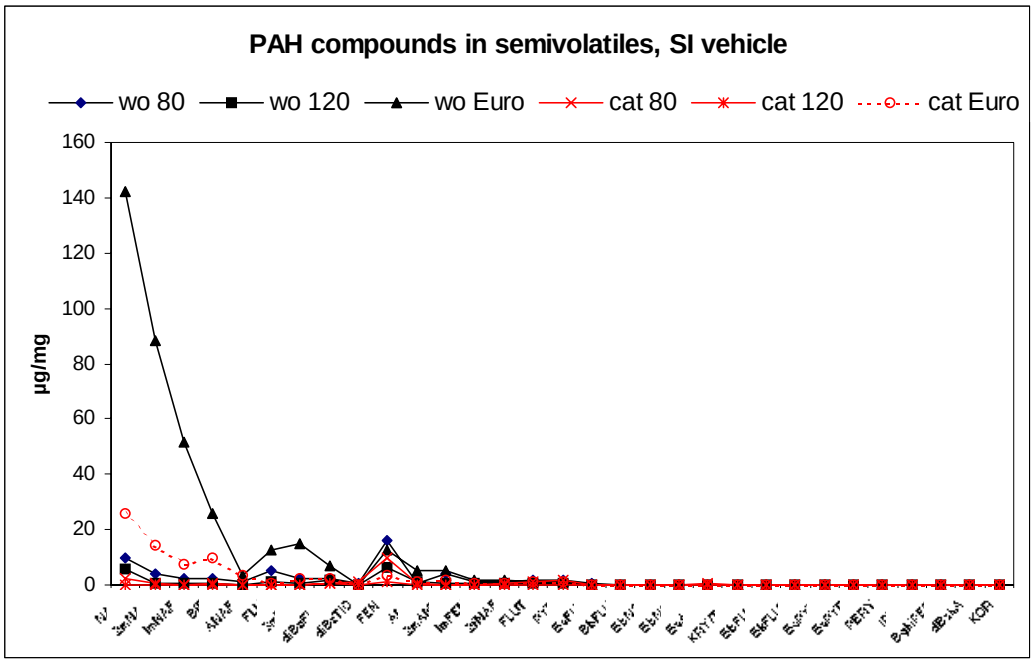


Figure 19. Individual PAH compounds in semivolatile phase, SI vehicle.

7.2.4 Metal results

Numerical results of metal analysis are shown in Appendices 22 – 24. High concentrations of bromine and chlorine in the particulate samples disturbed strongly the metal analysis of particulate samples from spark-ignition vehicle. This can be seen in Appendix 24 where the results are shown as ng/sample. Few metals exceeded the detection limit in the fine particulates (Figure 20). Level of the metals in fine particulates was significantly lower than in the total particulates.

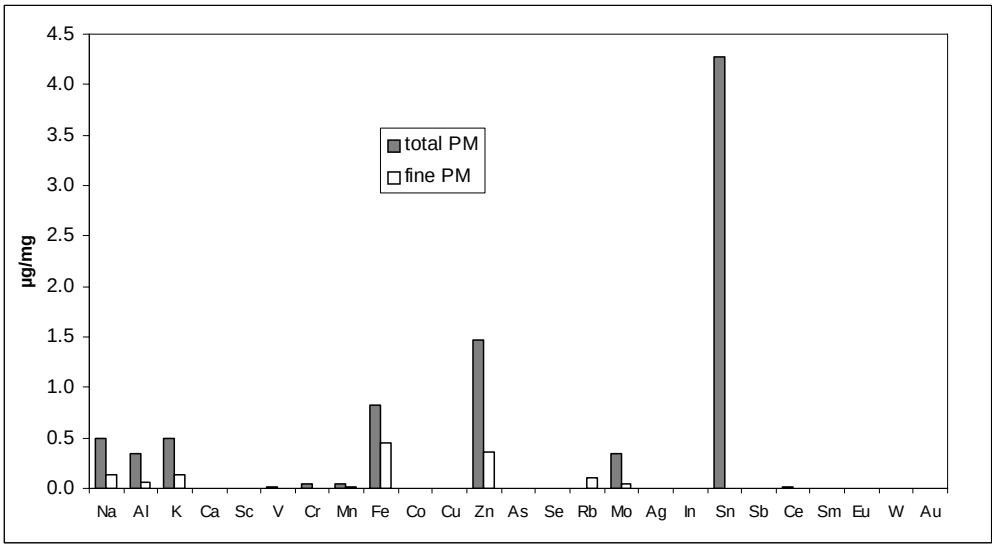


Figure 20. Average results of metal analysis from total and fine particulates at different load and aftertreatment combinations, SI vehicle.

The selected metals are shown in Figure 21 in the same way as for heavy-duty engine in chapter 6.2.4. The metals in gasoline particulates did not give as consistent results at different load/aftertreatment conditions as was seen for heavy-duty engine. For instance, several metals were observed only in one or two load conditions. Actually, only Zn exceeded the detection limit with all load/aftertreatment combinations studied.

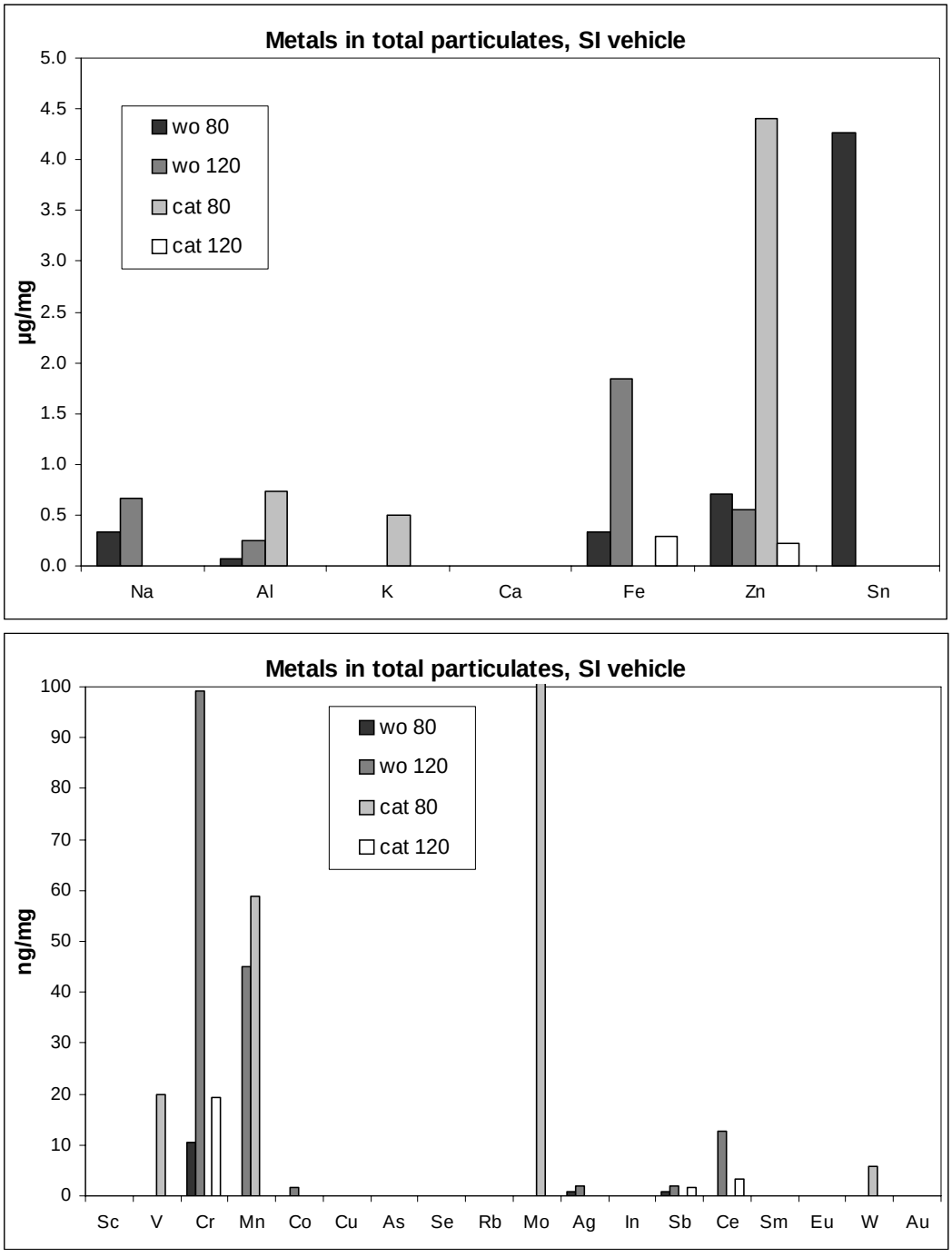


Figure 21. Selected results of metal analysis from total particulates at different load/aftertreatment combinations, SI vehicle. Note: unit in the second figure is ng/mg.

8 SIMULATED DISTILLATION

The results of the simulated distillation is shown in Figure 22. The distillation curves of the particulate SOF varied rather significantly, but no relation with engine/aftertreatment technology or load could be observed. The boiling point range for all samples analysed was from 220 to 580 °C. This was slightly different range than observed for round-robin sample of light-duty diesel vehicle (chapter 4.6).

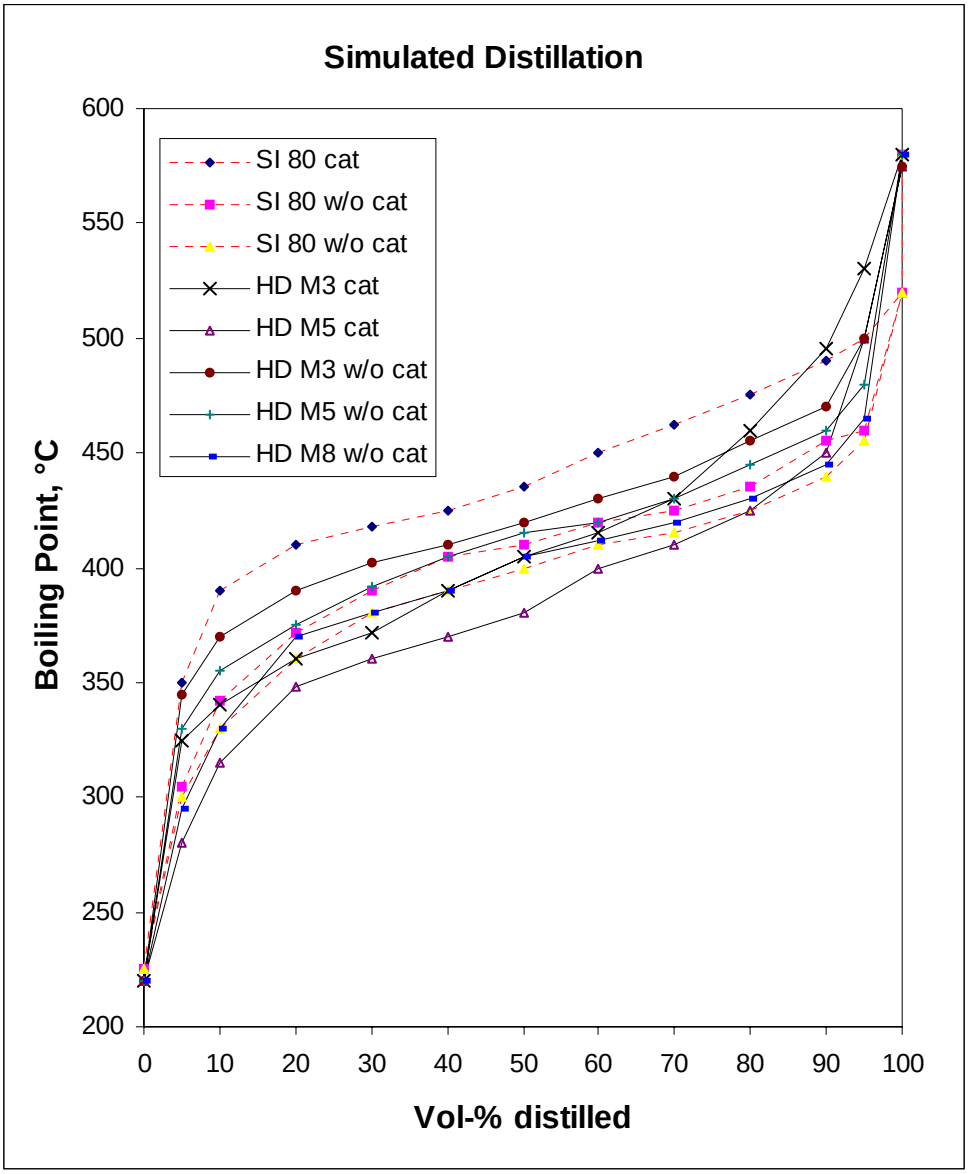


Figure 22. Results of the simulated distillation of particulate samples from HD engine and SI vehicle.

9 SUMMARY

European Commission project ”Characterisation of engine exhaust particulate fingerprints and their contribution to air quality, PARFIN JOF3-CT97-0040” was carried out in 1998 and 1999. The participants of the project were: IFP (France), co-ordinator, Euron (Italy), Enitechnologie (Italy), JRC Ispra (Italy) and VTT Energy (Finland).

Target of the project was to identify the contribution of different engine technologies on ambient particulates through chemical mass balance modelling (CMB). The modelling requires as source information the evaluation of the feasibility of possible fingerprints from the analysis data obtained from particulates from several engine/vehicle technologies and similar data from ambient air particulates. The technologies selected for this project were heavy-duty engine, light-duty diesel vehicle, stoichiometric and lean-burn gasoline vehicles. All engines/vehicles were studied with and without aftertreatment technologies. VTT Energy was responsible of sampling and analysis of the particulate matter from heavy-duty diesel engine and spark-ignition vehicle.

The tasks at VTT Energy were divided into three main parts

1. Analysis of the round-robin samples
2. Tests with light-duty gasoline fuelled passenger vehicle with and without catalyst (SI)
3. Tests with heavy-duty bus engine with and without catalyst (HD)

The round-robin phase of the project included two different goals: to find out, if the results from different laboratories are comparable with each other and to select analysis methods for actual samples. The samples collected at IFP were analysed as completely as possible. SOF, PAH, fuel/lube, anions and metal analysis were selected for actual samples. In addition, JRC Ispra carried out nitro-PAH analysis and VTT Energy analysis of simulated distillation.

The tests with spark-ignition stoichiometric gasoline fuelled vehicle were carried out at two load conditions, with and without three-way-catalyst (TWC). European test cycle was used as a reference. CEC reference fuel was used in the tests. However, lead additive was added into fuel for the tests without catalyst. The total particulates and fine particulates smaller than 2.5 µm were collected separately.

The heavy-duty tests included three different load conditions with and without oxidation catalyst. The particulates were collected in two different size groups in the similar way as in the light-duty tests.

Several differences between the particulates from heavy-duty diesel engine and stoichiometric gasoline fuelled vehicle were observed. The average figures of the selected results are shown in Figures 23 – 25.

Significant amount of sulphates were present in the particulates only in the conditions, where the catalyst was warm enough to generate sulphates from sulphur of the fuel.

Bromine and chlorine were found from the particulates of spark-ignition fuelled vehicle in the tests without catalyst, if leaded fuel was used. Similarly, it can be assumed that the elements of other fuel additives can be present in the particulates as well. E.g. if potassium and sodium based additives are used as valve seat protection additives in gasoline to replace lead additives, those elements probably are present in the exhaust particulates of gasoline fuelled vehicles, as well.

Profiles of the PAH compounds were slightly different when particulates from the spark-ignition vehicle and diesel engine were compared with each other. Concentration of the heaviest PAH compounds in particulates from gasoline fuelled vehicle was high when compared with the particulates from diesel engine.

Comparison of the metal analysis results from gasoline vehicle and diesel engine suffered from low level of metals in diesel particulate samples and disturbing effect of bromine and chlorine in the gasoline particulate samples. However, it was noted e.g. that calcium was found only from the particulates from diesel engine. Zinc was present in all samples as expected, because zinc dithiophosphate is the most common additive in lubricant oils. Tin exceeded the detection level only with gasoline fuelled vehicle, but only in one load condition. Thus it can not be regarded as significant possible fingerprint. Some metals, which were present in the samples as very low levels might be possible fingerprints, but those conclusions require data from the other laboratories and ambient air samples.

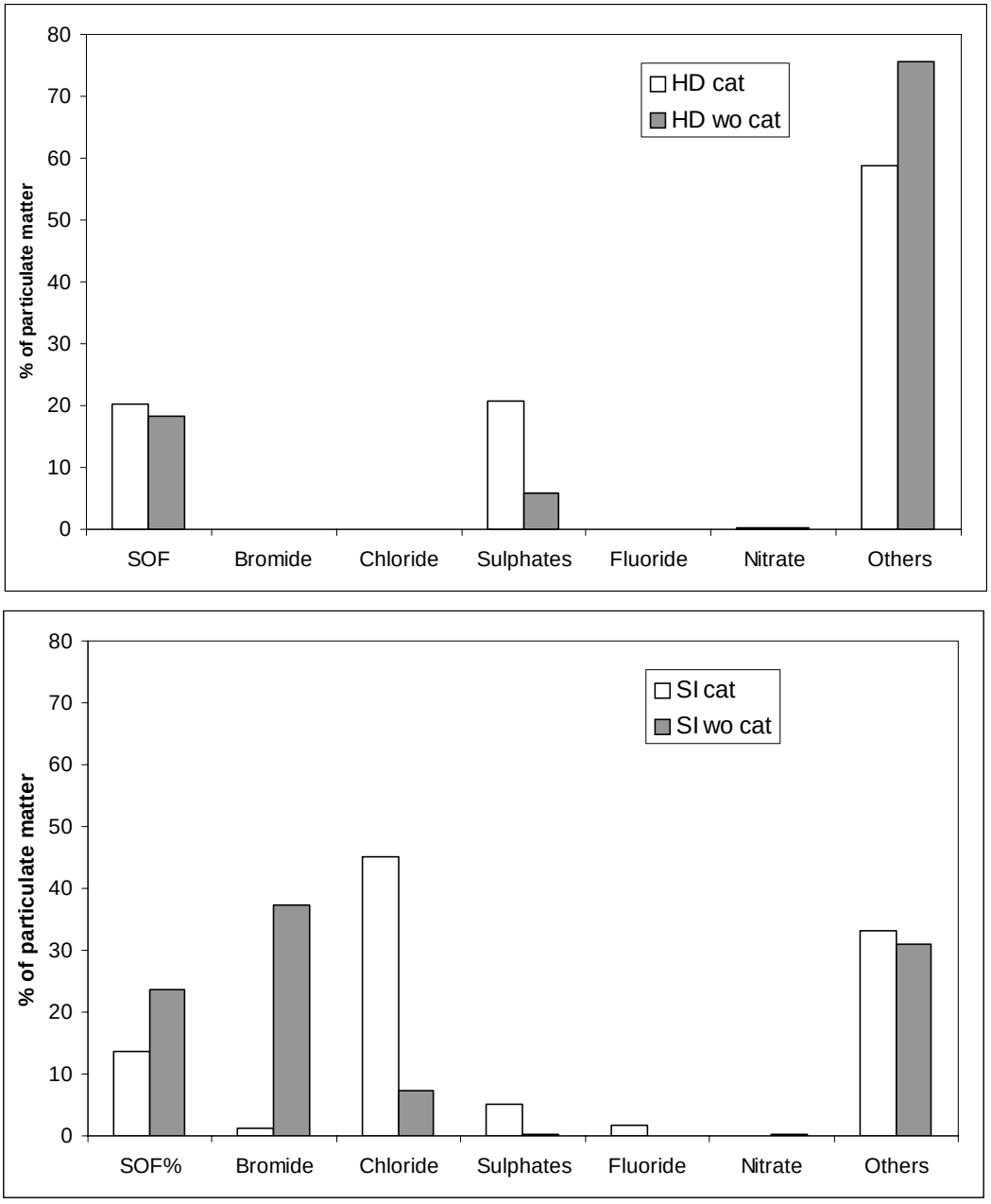


Figure 23. Average results of SOF and anion analyses from heavy-duty engine with and without oxidation catalyst and spark-ignition vehicle with and without TWC catalyst.

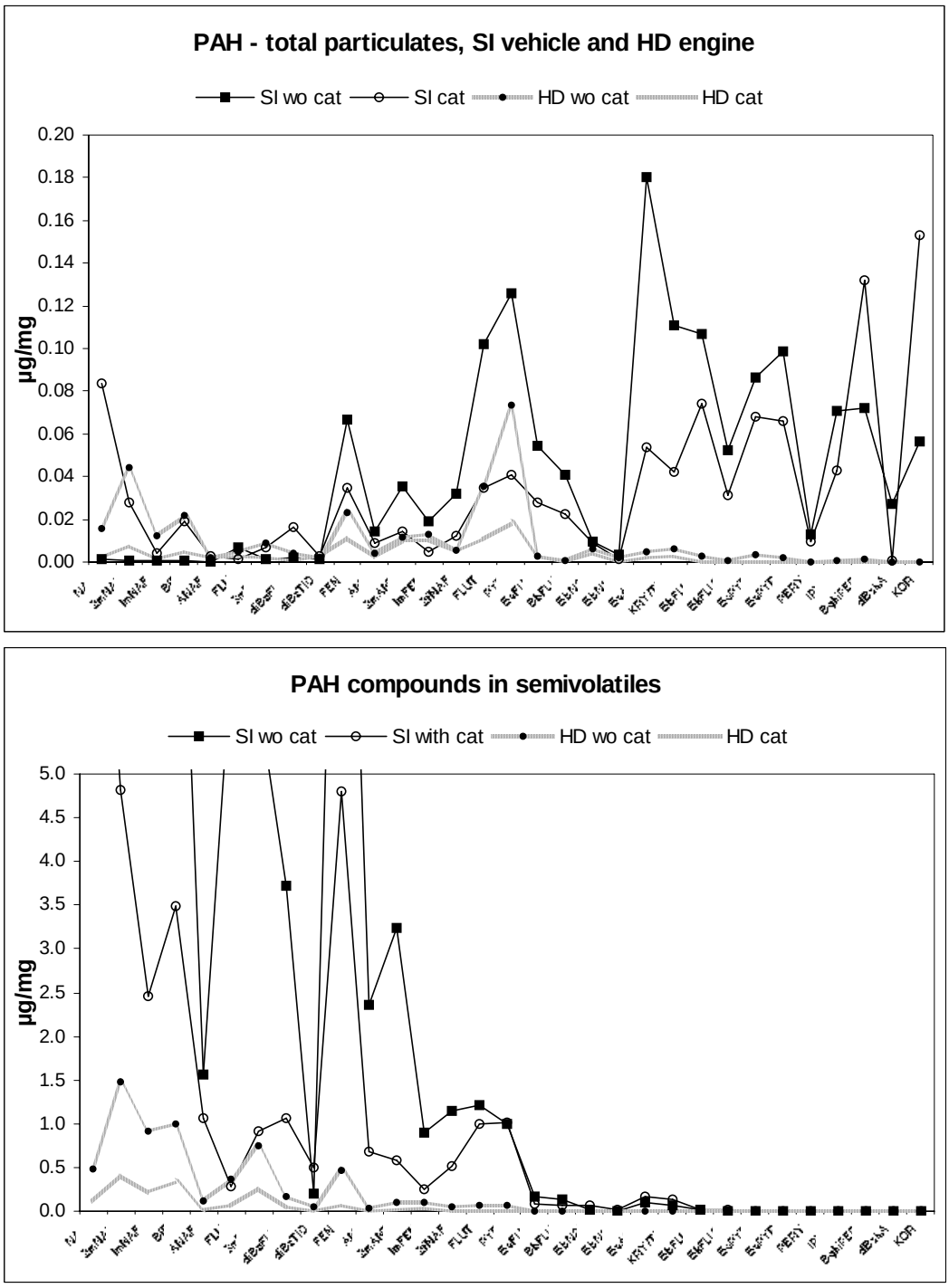


Figure 24. Average PAH profiles of total particulate and semivolatile samples from heavy-duty engine with and without oxidation catalyst and spark-ignition vehicle with and without TWC catalyst.

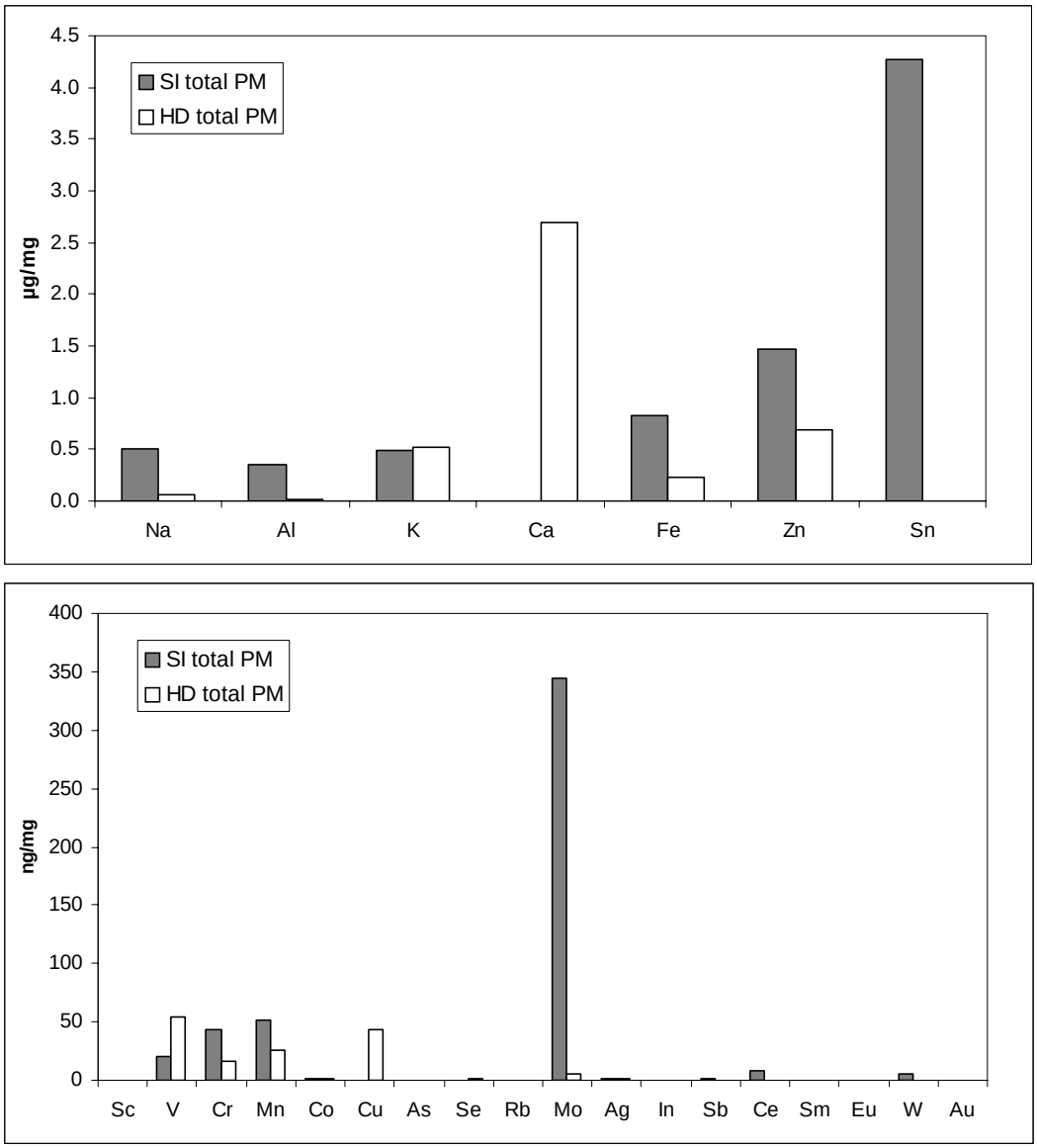


Figure 25. Average results of metal analysis of total particulates from heavy-duty engine with and without oxidation catalyst and spark-ignition vehicle with and without TWC catalyst.