Research of sampling for Particle Analysis of 2-Stroke Scooters

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ABSTRACT

In the present work detailed investigations of sampling of particle emissions of 2-stroke scooters with direct injection and with carburetor were performed.

The nanoparticulate emissions were measured by means of SMPS and NanoMet⁾. Also the particle mass emission (PM) was collected and analysed with different methods.*

The variations of sampling concerned: the thermoconditioning, thermodesorption, dilution factor, residence time, dilution- and sampling position.

It can be stated, that the conditioning of the sampled probe and the positions of dilution- and of sampling point and the composition of aerosol have a considerable influence on the particle emissions, which are mainly oil condensates.

The engine technology influences the (nano)particle emissions and the composition of aerosol by: mixture preparation, mixture tuning, oil consumption, postoxidation, quality, condition and temperature of the catalyst, quality of oil and fuel.

The presented work is a part of the Swiss activity mandated by the Swiss Agency of Environment Forests and Landscape (SAEFL, BUWAL)⁾ and by the Swiss Associations of Oils and Lubricants (EV and VSS) in the scope of an international project network „Particle Emissions of 2-S Scooters".*

Key words: 2-S emissions, (nano)particles, sampling, 2-S aerosol, aerosol composition

1. INTRODUCTION AND OBJECTIVES

In the several investigation programs of AFHB [1, 2, 3, 4]**⁾ the problem of particle mass and particle counts emissions of 2-S engines was particularly addressed. The work about influences of different lubricating oils, different fuels and different conditions of oxidation catalyst 2003, [5], showed in reality considerable potentials, but also necessities of further more extended, interdisciplinary research.

This situation led to the need of participation of several analytical laboratories and industrial partners and due to general interest and support a project network was created. In this network the Swiss Research Partners: TTM, AFHB, EMPA, ME, SUVA collaborate with several industrial partners and foreign research institutes, like JRC Ispra, VTT Finland, Toxicity Network France and ARAI India. This network is open to the interested parties to join it and it exchanges informations about the 2-S 2-wheelers research with the Annex XXXIII of IEA Implementing Agreement AMF, [6].

This paper represents a part of results concerning particularities of sampling and analytics of nanoparticles and particle mass.

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*⁾ Abbreviations see at the end of paper
**⁾ References see at the end of paper

The specific questions where:

- influences of thermoconditioning and thermodesorption,
- influences of engine technology TSDI-Carburetor,
- check of sampling point and sampling procedure for nanoparticles.

2. INVESTIGATED SCOOTERS

The investigated scooters were:
Peugeot Looxor TSDI and Peugeot Looxor Carburetor (see Table 1)

	Peugeot	Peugeot
vehicle identification	Looxor TSDI	Looxor
model year	2002	2004
transmission no. of gears	variomat	variomat
km at beginning	1400	0
engine: type displacement cm^3 number of cylinders	 2 stroke 49.1 1	 2 stroke 49.1 1
cooling	Air forced	Air forced
rated power kW rated speed rpm idling speed rpm	3.6 7800 1700	3.72 8100 1800
max vehicle speed km/h	45	45
weight empty kg	94	94
mixture preparation	direct injection with automatic oil pump	carburetor with automatic oil pump
catalyst	yes	yes + SAS (secondary air system)
catalyst data	Pt/Rh 5/1 50 g/ft^3 200 cpsi metal support ∅ 60,5 / L 40	Pt/Pd/Rh 1/28/1 50 g/ft^3 100 cpsi metal support ∅ 60,5 / L 40

Table 1: Data of the scooter Peugeot Looxor TSDI and Carburetor

Fig. 1 shows these scooters in the measuring laboratory.

The Peugeot TSDI-System uses crankshaft driven air compressor.Gasoline is injected in the pressurised air of the feed rail where the premixing of air and fuel takes place. The air injector controls the admission of the rich mixture in the combustion chamber. The lubrication oil is dosed in the intake air of the engine by means of the oil pump.

For the vehicles with carburetor simple, conventional carburetors with a cable-controlled throttle body and needle are used. The lubrication oil is also dosed in the intake air of the engine.

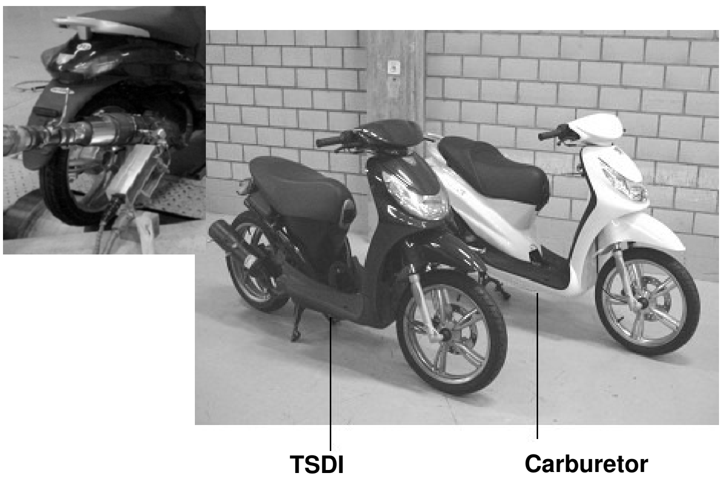


Fig. 1: Investigated scooters: left TSDI, right Carburetor

3. MEASURING APPARATUS

3.1. Chassis dynamometer

- roller dynamometer: Schenk 500 G5 60
- driver conductor system: Zöllner FLG, 2 Typ. RP 0927-3d, Progr., Version 1.4
- CVS dilution system: Horiba CVS 9500T with Roots blower
- air conditioning in the hall (intake-and dilution air) automatic, temperature: 20 - 30 ^oC
  humidity: 5.5 – 12.2. g/kg

3.2. Test equipment for regulated exhaust gas emissions

This equipment fulfils the requirements of the Swiss and European exhaust gas legislation – 70/220/EWG 98/69/EG.

- gaseous components:
  exhaust gas measuring system Horiba MEXA-9400H
  CO, CO_2 – infrared analysers (IR)
  HC_{IR}... only for idling
  HC_{FID}... flame ionization detector for total hydrocarbons
  NO/NO_X... chemoluminescence analyser (CLA)
  O_2... Magnos
  The dilution ratio DF in the CVS-dilution tunnel is variable and can be controlled by means of the CO_2-analysis.
- measurement of the particulate mass (PM):
  sampling from the full-flow dilution tunnel
  filter temperature ≤ 52 ^oC
  conditioning of filter: 8 - 24 h (20^{o}C, rel. humidity 50%)
  scale: Mettler, accuracy ± 1 μg

3.3. Particle size analysis

In addition to the gravimetric measurement of particulate mass, the particle size and counts distributions were analysed with following apparatus:

- SMPS – Scanning Mobility Particle Sizer, TSI (DMA TSI 3071, CPC TSI 3025 A)
- NanoMet – System consisting of:
  - PAS – Photoelectric Aerosol Sensor (Eco Chem PAS 2000)
  - DC – Diffusion Charging Sensor (Matter Eng. LQ1-DC)
  - MD19 tunable minidiluter (Matter Eng. MD19-2E, see Fig. 1).
  - Thermoconditioner (TC) (i.e. MD19 + postdilution sample heating until 300°C)
  - Thermodesorber (TD)

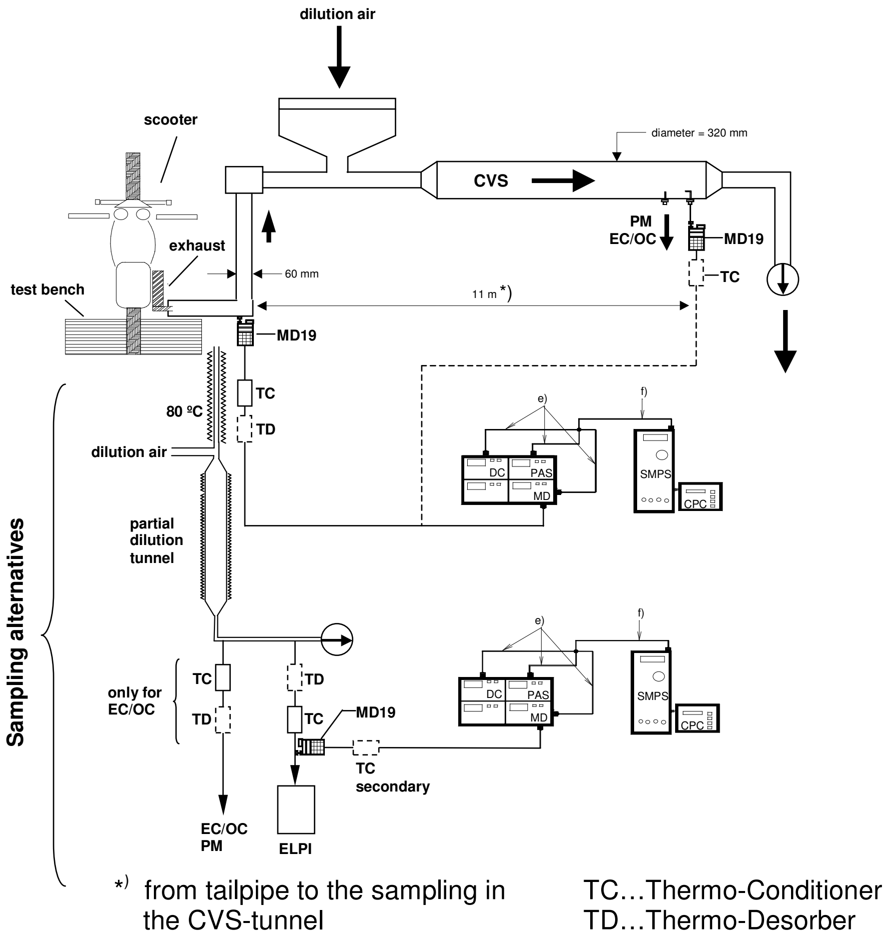
A detailed description of those systems can be found in the manufacturers informations. The sampling and measuring set-up during the tests shows Fig. 2.

3.4. Measuring procedures

In the research of sampling for NP-analysis several variants of sampling were used, which are alternatively represented in Fig. 2.

At tailpipe (TP) were applied:

- minidiluter alone (MD)
- minidiluter + thermoconditioner (TC)
- minidiluter + thermodesorber (TD) – all of them for SMPS and NanoMet
- partial flow dilution tunnel (PDT) – for PM, EC/OC, SOF/INSOF, PAH.



<u>Fig. 2</u>: Sampling and measuring set-up for nanoparticulates analysis of the scooters with different variants of sampling methods.

After CVS-dilution tunnel the sampling was:
- minidiluter (MD) alone
- minidiluter + thermoconditioner (TC) – both for SMPS and NanoMet
- directly: PM, SOF/INSOF, PAH.

During these investigations the dilution factor, the temperatures of gas sample heating in the TC and TD and the sample flow (residence time) were varied.

The measurements were performed on the Peugeot scooters (TSDI and Carburetor), with the oil Panolin TS (6250 ppm S, see Table 2) and at warm operating conditions of the engine and catalyst (maximum speed 45 km/h).

Several measuring filters (Pallflex and Quartz) were charged with particle mass and were sent for analysis to:
· SUVA Analytical Laboratory, Lucerne, for coulometry (EC/OC)
· JRC Analytical Laboratory, Ispra, for SOF/INSOF and PAH
· EMPA Analytical Laboratory, Dübendorf, for Soxhlet extractions SOF/INSOF.

The driving resistances of the test bench were set according to the Swiss exhaust gas legislation for motorcycles.

3.5. Used lube oil and fuel

The data of used semi-synthetic lube oil are represented in Table 2.

The fuel used during the measurements was a standard market gasoline with zero sulfur content

Property	Unit	Panolin TS
Viscosity kin 40°C	mm^2/s	90
Viscosity kin 100°C	mm^2/s	11.2
Density 15°C	kg/m^3	882
Pourpoint	°C	- 27
Flamepoint	°C	> 150
Total Base Number TBN	mg KOH/g	3
Sulfur	mg/kg	6250
Fe	ppm	0
Mo	ppm	1
Mg	mg/kg	2
Zn	mg/kg	105
Ca	mg/kg	617
P	mg/kg	90

Table 2: Data of the used lube oils

4. RESULTS

4.1. TSDI

This part of research was performed at stationary warm operating condition of engine and catalyst and at maximum speed 45 km/h.

Fig. 3 shows the thermograms with **Peugeot TSDI**, sampling at **tailpipe** with minidiluter (MD) and thermoconditioner (TC, ThC).

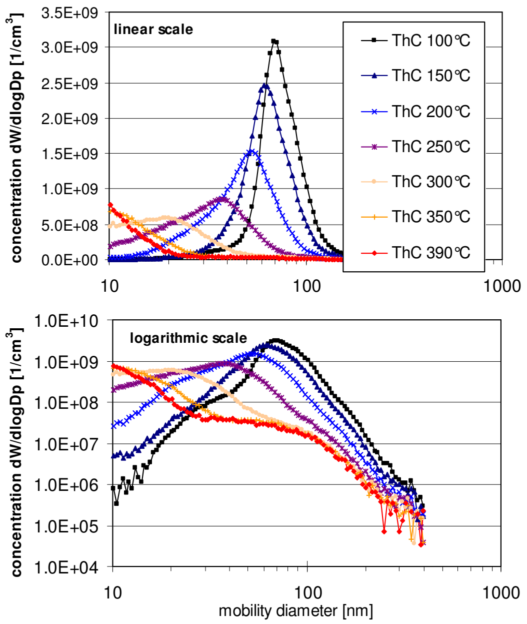


Fig. 3: SMPS size spectra with thermo-conditioning of sample

Peugeot Looxor **TSDI**, full load, with NanoMet diluter at **tail pipe**

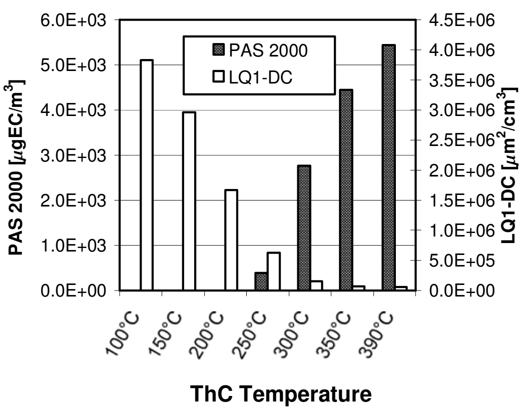


Fig. 4: NanoMet signals with thermo-conditioning of sample

Increased sample temperature in the TC provokes evaporation from the surface of particles and moves the SMPS PSD-spectrum to the lower peak-concentrations and smaller median diameters i.e. from the accumulation to the nuclei mode.

In the logarithmic scale a bimodality of the spectra with higher TC-temperatures is visible. This suggests that the particles in accumulation mode (60-90 nm), which remain at highest temperature are either very heavy compounds, or solids. These solids may have been formed already during combustion in the engine, similar to processes known from 4-stroke gasoline DI engines; another hypothesis would be their formation in the TC by thermal dehydration (pyrolysis) of heavy compounds which would imply a conditioning artefact, but due to the temperature level this artefact is probable only to a very little extend.

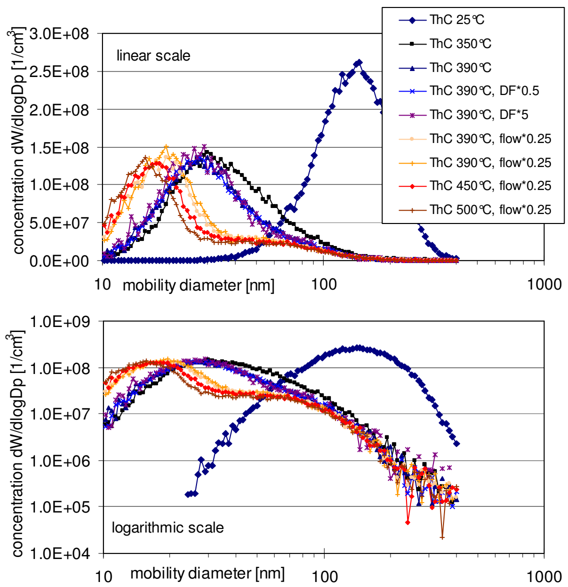
The NanoMet signals, Fig. 4, confirm the tendency of increased solid particle ratio showing a decreasing amount of condensates (DC) and increasing amount of carbonaceous surface (PAS) with the higher sample temperature.

PAS (photoelectric aerosol sensor) is sensitive to the surface of particulates and to the chemical properties of the surface. It indicates the solid particles.

DC (diffusion charging sensor) measures the total particle surface independent of the chemical properties. It indicates the solids and the condensates.

In Fig. 5 different variants of sampling from **CVS**, with MD + TC are represented for **Peugeot TSDI**. Additionally to the variations of temperature the variations of dilution factor (DF) and of the sample flow were performed. DF 0.5 or DF5 means a half, or fivefold value of dilution factor. Flow 0.25 means a quarter of the original flow-value i.e. roughly 4 times longer residence time.
During the variation of DF there are no differences of the PSD-spectra, which means that there are no effects of recondensation in, or after TC by reduced DF and no influences on spontaneous condensation at higher DF.

Peugeot Looxor **TSDI**, full load, with NanoMet diluter at **CVS tunnel**



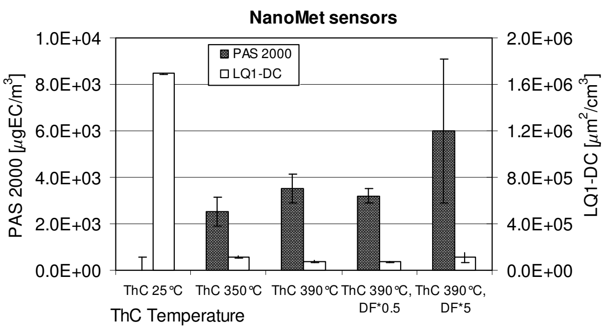


Fig. 5: SMPS size spectra with thermo-conditioning of sample

Fig. 6: NanoMet signals with thermo-conditioning of sample

Further increasing of sample residence time in the TC shows clearly a further evaporation of the heavy components, which is still intensified by a supplementary increase of the temperature until 500°C. The last spectra show a clear bimodality in the logarithmic scale and also in the linear scale, with maximum values of count concentrations in the accumulation mode of 2 - 3 x 10^7 [$1/cm^3$]. In these conditions the question appears: how much of the droplets of heavy compounds are thermally pyrolysed instead of being evaporated?
The information of PAS and DC, Fig. 6, confirms the increase of solids at higher sampling temperature.

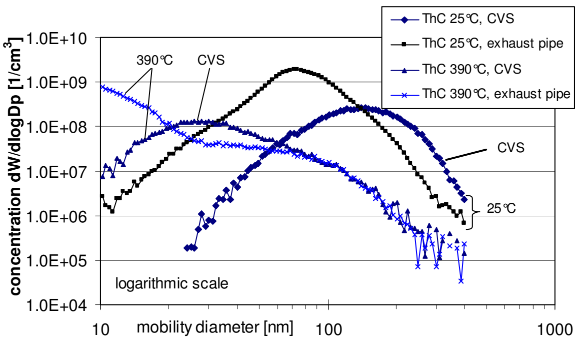


Fig. 7: Comparison of sampling : tailpipe – CVS with different sampling temperatures

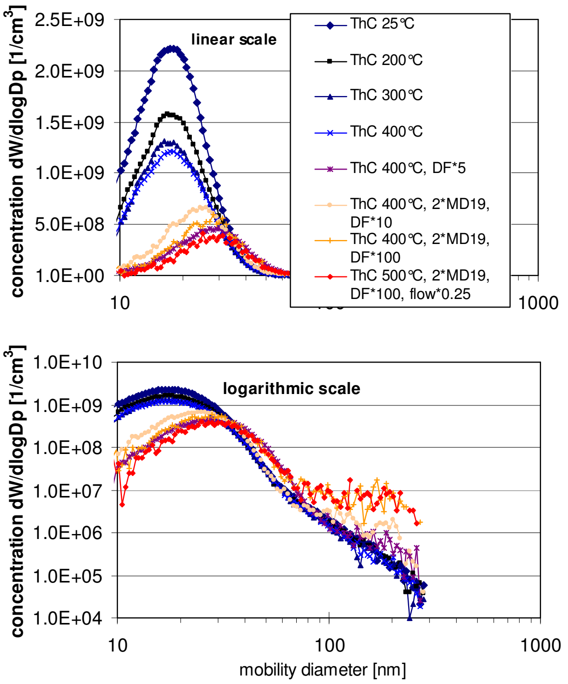
A comparison between the sampling: tailpipe – CVS with different sampling temperatures is depicted in Fig. 7. At 25°C (no thermal conditioning of the sample) there is a coagulation of particles between tail pipe – and CVS sampling points (distance approx. 11m), which is indicated by the CVS-spectrum moved to the lower count values and the bigger particles sizes. Also at 390°C the CVS-spectrum has little ultrafine particles (no nuclei mode) due to agglomeration effects. This coagulation between tailpipe and CVS takes place at approximately constant summary mass.

The distance of 11 m consists of approx. 7 m no diluted exhaust gas line until the dilution point and after that approx. 4 m diluted gas until the CVS-sampling point. The described effects are supposed to happen mainly in the 7 m line before dilution.

4.2. Carburetor

The research of sampling at **tailpipe** with MD + TC for the **Peugeot Carburetor** is depicted in Fig. 8. With increasing of the TC-temperature the very high count concentrations in nuclei mode decrease and with application of stronger dilution (5x, 10 x, or 100x by mean of a second MD inline with the first one) it is possible to cut a part of this nuclei mode. This behavior of the aerosol from “Carb.” is quite different form the one of TSDI (Fig. 3). The Carburetor-version has a much higher exhaust gas temperature, which enables the creation of sulfates. The exhaust gas temperature of the TSDI is below the range of intensified sulfate production (oxidation SO_2 to SO_3).

Due to the higher exhaust gas temperature and the applied SAS (secondary air system) in the Carb.-version the oxidation of HC in the oxidation catalyst is more intense and the composition of aerosol is different than for TSDI.
The NanoMet data, Fig. 9, confirm this fact showing almost unchanged DC and no PAS with increasing temperature (compare Fig. 4 and Fig. 9). However, the present data leave open the question whether the solid particles observed in TSDI exhaust were formed early-on in the engine due to heterogeneous combustion conditions, during the oxidation in the exhaust system, or later by pyrolysis during sample conditioning in the TC.



Peugeot Looxor with **Carburetor,**
full load, with NanoMet at **tail pipe**

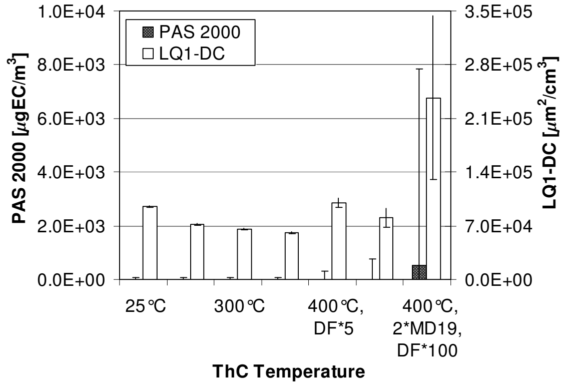
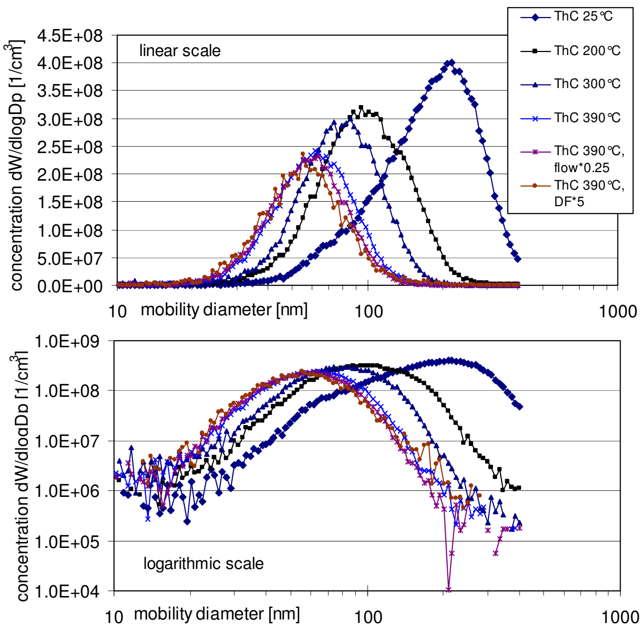


Fig. 8: SMPS size spectra with thermo-conditioning of sample

Fig. 9: NanoMet Signals with thermo-conditioning of sample

Fig. 10 represents the sampling at **CVS tunnel** with MD + TC for **Peugeot Carburetor**. The tendencies of SMPS spectra with increasing temperature are similar, as for TSDI (at CVS), but the NanoMet, Fig. 11, shows much higher DC-, and much lower PAS-values, indicating differences of the composition of aerosol (compare Fig. 11 and Fig. 6).



Peugeot Looxor with **Carburetor,**
full load, with NanoMet at **CVS tunnel**

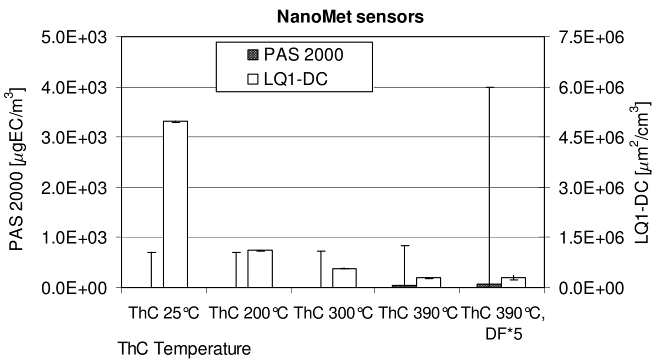


Fig. 10: SMPS size spectra with thermo-conditioning of sample

Fig. 11: NanoMet Signals with thermo-conditioning of sample

Fig. 12 compares the sampling: tailpipe-CVS with different temperatures in TC for the Carburetor-variant. With no-conditioning (25°C) there is a tremendous change of the aerosol measured between those two sampling points: in CVS there are much bigger particles, with lower count concentrations and with much bigger mass. The results from the SMPS mass calculation and from the coulometric analysis (not represented) confirm the increase of mass with a simultaneous decrease of the EC-portion in PM (due to the condensates).

With conditioning of the aerosol at tailpipe (400°C) the nuclei mode lowers the count concentration, but doesn't change the particle sizes. As suggested before these are most probably spontaneous condensates of sulfates.

With conditioning the aerosol at CVS (390°C) the mode moves to lower sizes, which suggest also the presence of hydrocarbons condensed on the particles at 25°C.

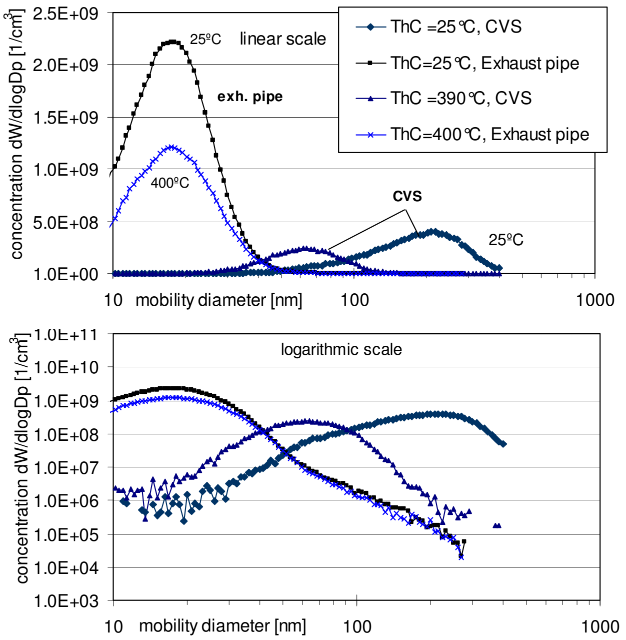


Fig. 12 Comparison CVS – tailpipe sampling, with /without thermoconditioning, Peugeot Carburetor

4.3. Cross-comparisons

The comparison of the SMPS PSD-spectra for both scooters at both temperatures and both sampling points in Figures 13 and 14 underlines the differences of aerosol composition for the different engine technology. Due to the much higher exhaust gas temperature of the Carburetor-variant the sulfates play a much more important role in the aerosol. There are different conditions of combustion (mixture tuning, mixture preparation) and different conditions of postoxidation (temperature, SAS for carburetor, different catalysts), which produce different HC-spectra in exhaust, in spite of using the same fuel and oil.

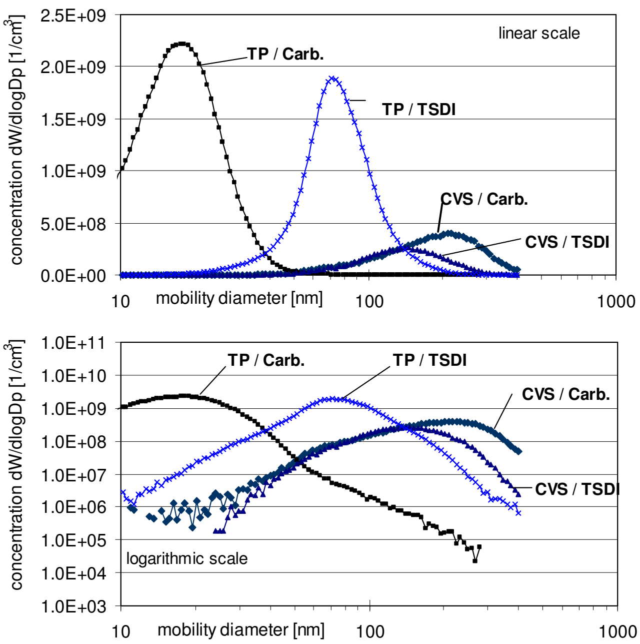


Fig. 13 Comparison between : Peugeot TSDI – Peugeot Carb. at two sampling points: tailpipe (TP) - CVS w/o thermoconditioning (25°C)

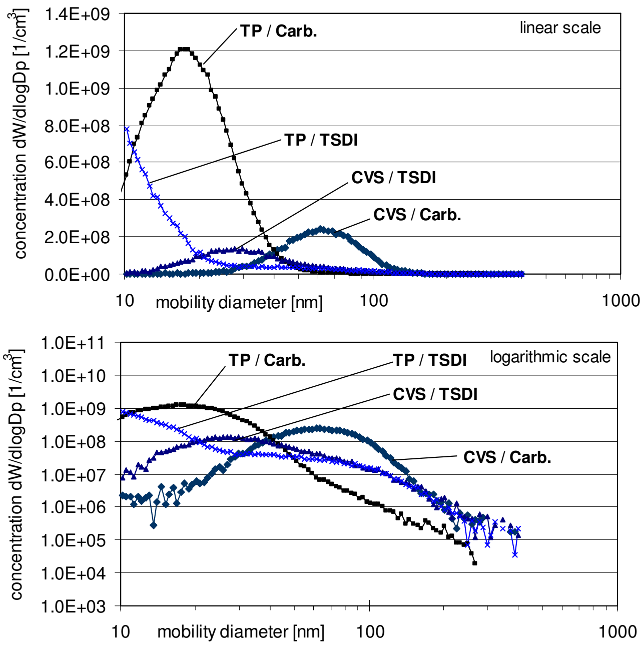


Fig. 14 Comparison between : Peugeot TSDI – Peugeot Carb. at two sampling points: tailpipe (TP) - CVS with thermoconditioning (390°C)

Fig. 15 shows the results of sampling at partial flow dilution tunnel, with different conditioning, with two thermoconditioners and with varied sample flow.
The change of PSD spectra with the increased conditioning is similar to the previous results for TSDI.

Without conditioning of the gas sample the maximum of the monomodal PSD is at particle size 60-70 nm (accumulation mode). Using the primary thermoconditioner the count concentration in accumulation mode decreases strongly and the spontaneous condensates appear in the size range below 50nm (nuclei mode) – a bimodal PSD results.
Further addition of the secondary thermoconditioner eliminates a big part of these spontaneous condensates in nuclei mode, but a further increasing of the residence time of the gas in the conditioner (lower flow rate) doesn't show any additional effects.

With thermodesorber the effects of recondensation are observed in nuclei mode, Fig. 16.

Generally it can be stated, that the sampling procedure: conditioning of the sample gas probe, dilution and sampling position have influence on the measured aerosol characteristics (PM, PSD, PAS, DC).

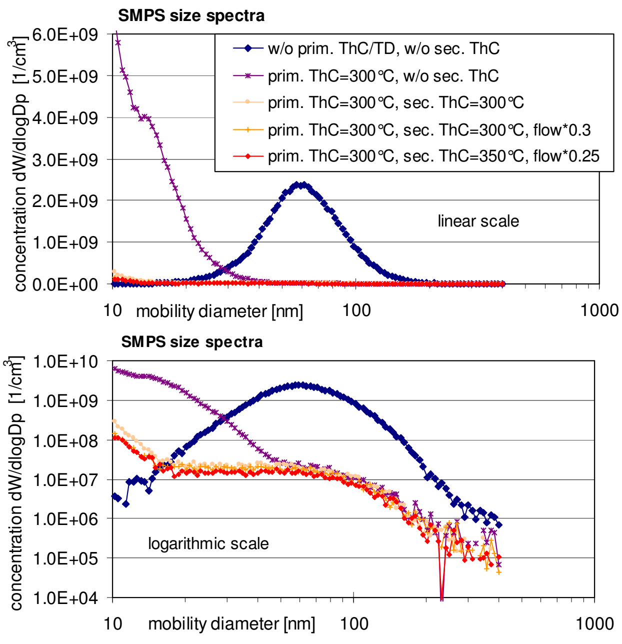


Fig. 15 Peugeot Looxor TSDI, full load with Nanomet diluter at partial dilution tunnel (PDT) - thermoconditioner

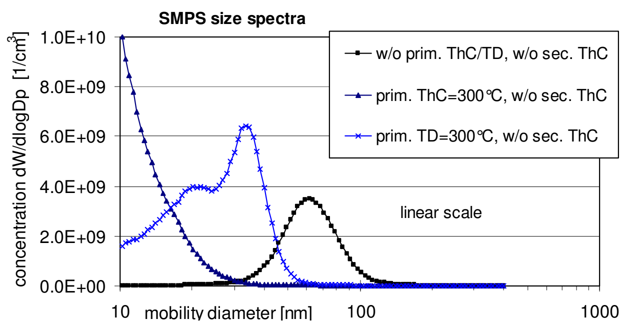


Fig. 16 Peugeot Looxor TSDI, full load with Nanomet diluter at partial dilution tunnel (PDT) - thermodesorber

4.4. Analysis of PM-residuum

Fig.17 summarizes the gravimetric and coulometric results obtained during this research phase.

The relationships of organic carbon OC between tailpipe and CVS confirm for both scooters the condensation effects in the line to CVS.
The sampling at tailpipe with TSDI causes lower PM-values. This is opposite with Carburetor. The apparent discrepancy results for Carburetor from the sulfates, which cause that having the total carbon at tailpipe 2.6 mg/km the particle mass increases to 20 mg/km (filter nbr. 24).

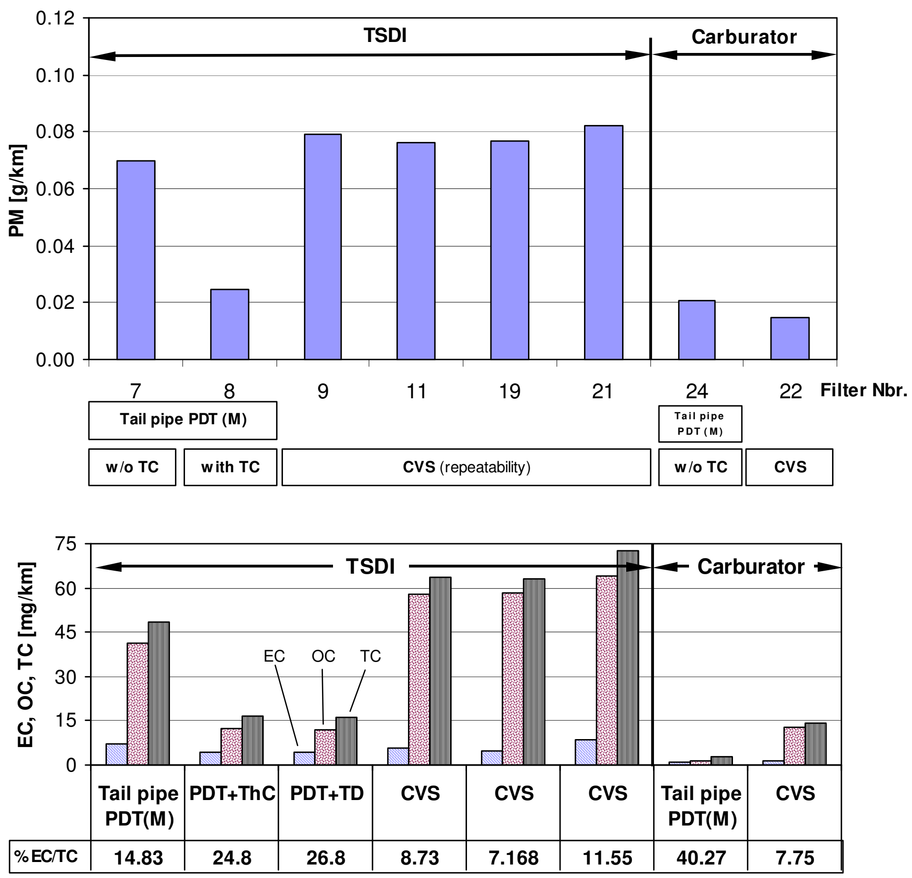


Fig. 17 Gravimetric and coulometric results during research of sampling

Due to the high exhaust temperature of the Carburetor scooter the sulfates are more present in the aerosol. Thanks to the SAS and the high temperature the oxidation of HC is much stronger, the particle mass PM for Carburetor is much lower.

4 measurements of PM and 3 coulometric measurements after CVS confirm a good repetability.
The coulometric results show principally to high amount of elemental carbon EC, which is a measuring artefact: during the thermal extraction of SOF a part of the heaviest compounds pirolises and is a source of EC, which doesn't originate in this form from the engine. This particularity will be addressed in further investigations.

5. CONCLUSIONS

In a previous work with chain saws, [8], a set of 2-S PM-filters was analyzed at the EMPA Laboratory for Organic Chemistry by means of the solvent method for SOF/INSOF. It resulted, that the particle mass consisted exclusively of lube oil for the oil treatment 2% and for 4% oil content there were INSOF portions up to 3% at full load.

With this background it can be assumed, that there is a similar situation for the modern investigated scooter engines with electronic oil dosing and the answers to the questions given at the beginning of the work can be as follows:

- a majority of emitted mass is SOF, nevertheless the composition of emitted aerosol depends on engine technology (DI-Carb.), exhaust gas aftertreatment (texh, SAS) and the used oil and fuel. The differences of the aerosol are visible by thermoconditioning of the sample,
- for Carburetor-variant with high exhaust gas temperature the sulfates create spontaneous condensates and take a share of PM,
- with direct injection (TSDI) the heterogeneous combustion of gasoline contributes to the formation of solids,
- the sampling devices: thermoconditioner and thermodesorber influence clearly the aerosol in the sense of elimination of condensates by increasing the sampling temperature – these influences depend on the composition of aerosol,
- the sampling place: tailpipe, or CVS influences strongly the particle size distributions (PSD) due to condensation – and coagulation effects,
- the engine technology: TSDI-Carburetor influences also the PSD and PM due to mixture tuning, mixture preparation, combustion, postoxidation in the exhaust (secondary air system), exhaust gas temperature and production of sulfates,
- solid particles observed in the exhaust of the TSDI engine after TC treatment at high temperatures have probably been formed during combustion due to heterogeneous distribution of fuel in the combustion chamber; this phenomenon is known from 4-stroke DI gasoline engines. However, they may just as well be artefacts formed by pyrolysis during high-temperature TC treatment in the sampling system. This issue requires further investigations.

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[6] IEA, International Energy Agency – Implementing Agreement AMF, Advanced Motor Fuels – Annex XXXIII, see : www.iea-amf.vtt.fi.

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8. ABBREVIATIONS

AFHB	Abgasprüfstelle der Fachhochschule, Biel CH (Lab. For Exhaust Gas Control, Univ. of Appl. Sciences, Biel-Bienne, Switzerland)
AMF	Implementing Agreement on Advanced Motor Fuels
ARAI	Automotive Research Association of India
BUWAL	Bundesamt für Umwelt, Wald und Landschaft (Swiss EPA, SAEFL)
Carb. (C)	Carburetor
CPC	condensation particle counter
CVS	constant volume sampling
DC	diffusion charging sensor
DMA	differential mobility analyzer
EMPA	Swiss Federal Laboratories for Materials Testing and Research
EPA	Environmental Protection Agency
ETHZ	Eidgenössische Technische Hochschule Zürich
EV	Erdöl-Vereinigung, Swiss Association of Oil Manufacturers
IEA	International Energy Agency
JRC	Joint Research Center, EU Laboratories, Ispra, Italy
MD	minidiluter
ME	Matter Engineering AG, CH
NanoMet	minidiluter + PAS + DC (+ ThC), (+TD)
NP	nanoparticulates
PAS	photoelectric aerosol sensor
PM	particulate matter, particulate mass
PSD	particles size distribution
SAEFL	Swiss Agency for Environment, Forests and Landscape (Swiss EPA, BUWAL)
SAS	secondary air system
SMPS	scanning mobility particles sizer
SOF	soluble organic fractions
SUVA	Schweizerische Unfallversicherungsanstalt
TD	thermodesorber
ThC (TC)	thermoconditioner
TSDI (T)	Two Stroke Direct Injection
TTM	Technik Termische Maschinen, CH
VOC	volatile organic compounds
VVT...	Transport Research Center, Finland