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Size-specific chemical analysis of engine-emitted nanoparticles with traps and fuel additives

Size specific chemical Analysis of Engine-emitted Nanoparticles with Traps and Fuel Additives

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Swiss emission regulation supports retrofit of particulate trap systems but in case of catalytic substances either used as coatings or as fuel additives a so-called Secondary Emission Test VSET is mandatory to prove that no additional toxic substances are created.

Fuel additives, added to the fuel in organometallic form, thus perfectly dispersed, become catalytically active when oxidized during combustion, accelerate soot combustion during expansion phase, leave the engine as ultrafine oxide clusters (5-10 nm) mixed with soot particles and are deposited together with soot in the traps. They catalyse soot oxidation and while carbon leaves the system as CO2-gas these oxide clusters remain (hopefully) in the trap thus gradually clogging the trap.

Beside of the tradeoff regeneration improvement/trap clogging it must be investigated whether this system-build-in catalytic activity has other negative consequences keeping in mind that the trap provides an ideal environment for the formation of new products since due to the extremely high specific surface of the trap-system (up to 200 m2/g) the residence time of a variety of engine emitted species, adsorbed by the trap or the soot deposited in the trap will be remarkably extended and be available for chemical reactions at relatively high temperatures.

One fuel additive, containing copper was identified during VSET to accelerate denovo systhesis of PCDD/F by more than 3 orders of magnitude and had to be excluded from application. Others, containing Cerium an Iron did not show these negative effects, could therefore officially be approved and are now widely used in the retrofit and OEM-market.

A new substance has been proposed by Clean Diesel Technology Inc. CDT, consisting of a combination of Cerium and Platinum, added to the fuel in rather low concentrations (7.5 / 0,5 ppm for Cerium/Platinum) which had to be tested.

First results proved a quite low soot light-off temperature of < 325 °C and, looking at regulated emissions, a reduction of PM and an impressively high conversion of HC and CO. Trapping efficiency using the BUCK knitted fiber deep bed filter was on the same level as without additive and size distributions of particles upstream and downstream of the trap did not reveal any sign of oxide particles in particular no dual mode distributions as found before with other additives.

Where are the additives ? This was one of the questions to by answered by the VSET and only this part is reported here. And furthermore: how much of the additive added to the fuel is emitted to the atmosphere, what is the size distribution of such emitted substances, there chemical composition and surface morphology ?

The VSET is based on the ISO 8178-cycle which is performed twice over a total time of 200 minutes. Gas and particulate matter is sampled during this time thus representing an average cycle emission. Also size specific sampling is performed using an 13-stage ELPI device downstream of the AVL part-flow dilution tunnel at average dilution of 6.45. After this 200 min. sampling period the 13 carbonyl-films of the ELPI were available for analysis while mass per stage was already evaluated during the test using the electrical information and software of ELPI.

Analytical methods used: XRD, SEM, EDX, ICP-MS

Results:

- overall PM-mass was very much influenced by sulfation due to the catalytic activity of the additive. Mass downstream of the trap was equal or even higher then upstream thus demonstrating again the uselessness of this criterion.
- NanoMet-Sensors showed clearly the reduction of carbon due to the additives
- Not much information from XRD because of the extremely small amount of additive
- SEM/EDX again did not supply much additive specific information
- ICP-MS however, being as sensitive as 0,001 ì g per stage supplied ample information on the size distribution of the additive mass, filtration efficiency and balance – showing that 99.85 % of the Pt remains trapped in the system.

It can be concluded from this study that not only size distribution metrology for submicron particles is readily available but also very sensitive size specific substance analysis is possible and can be used during certification procedures to be applied for catalytically active substances used in the combustion system.

For the Ce/Pt-additive investigated here is can be stated that this new fuel additive has not only interesting properties regarding regeneration temperature and ash formation but also that the additive-products remain deposited in the system for catalysis – less than 0,1 % of Pt is emitted, which is less than ¼ of the emission of a modern catalyst equipped petrol car. The investigation also revealed that no secondary toxic substances are created such as PCDD/F and PAH.

Swiss clean air authorities have therefore decided to include this analytical technology in the certification process for catalytically active trap systems.

Why Fuel Additives?

- Additives are metallorganic compounds perfectly dispersed in Fuel on molecular basis

- Metals (usually transmission metals) form oxides which are catalytically active to accellerate soot oxidation in the engine and traps

However:
- oxide particle clog the trap
- regeneration temperature > 350 °C
- secondary toxic compounds may be generated

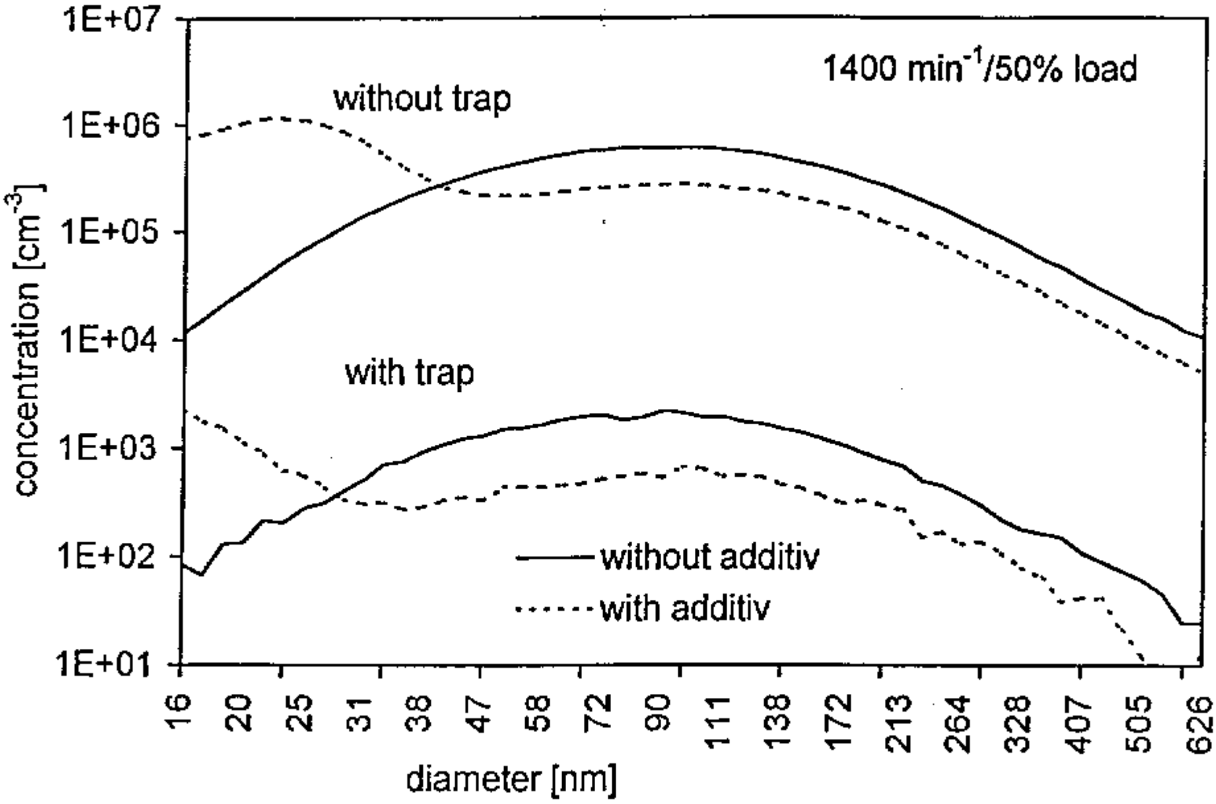
New approached: Ce + Pt

Mixture of transition and noble metals provides synergetics:
- Ash concentration lower (metal concentration 8 ppm compared to > 25 ppm)
- Regeneration starts < 300 °C
- CO and HC are perfectly oxidized

Open questions
- Sulfate formation ?
- NO2-Slip ?
- Secondary emissions

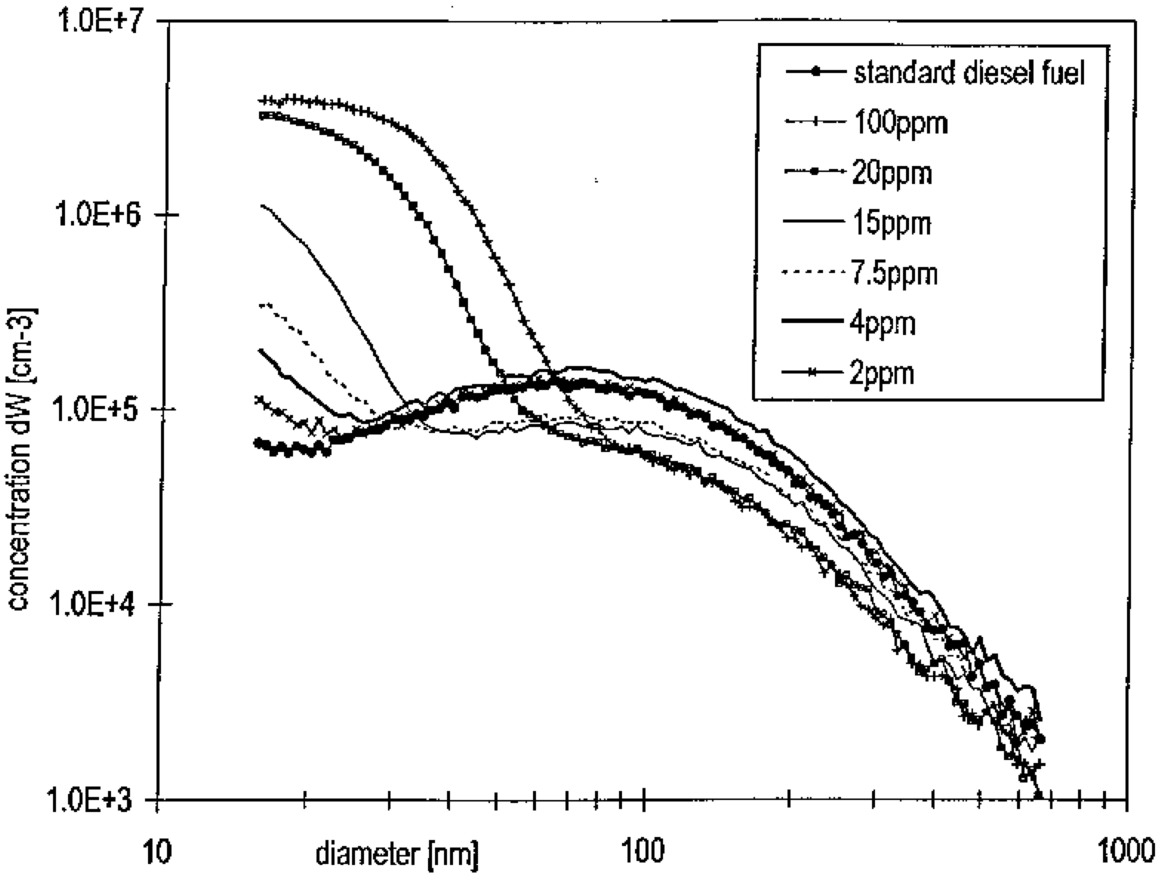
Where are the Additive Oxides left?

- Some coat the engine surfaces (catalytic activity) mainly in the initial phase
- Some end up in the lube oil (effects unknown)
- Some leave the engine attached to soot particles
- Some leave the engine as small oxide clusters



VERT-data with transition metal additives
Concentration: 100 ppm Ce

Additive Emission Characteristics strongly depend on Concentration



Swiss Trap-System Certification Test

Consists of 3 Parts

Part 1: Filtration Test
+ Secondary Emission Test

Part 2: Field Test 2000 hrs

Part 3: Repetition of Filtration Test

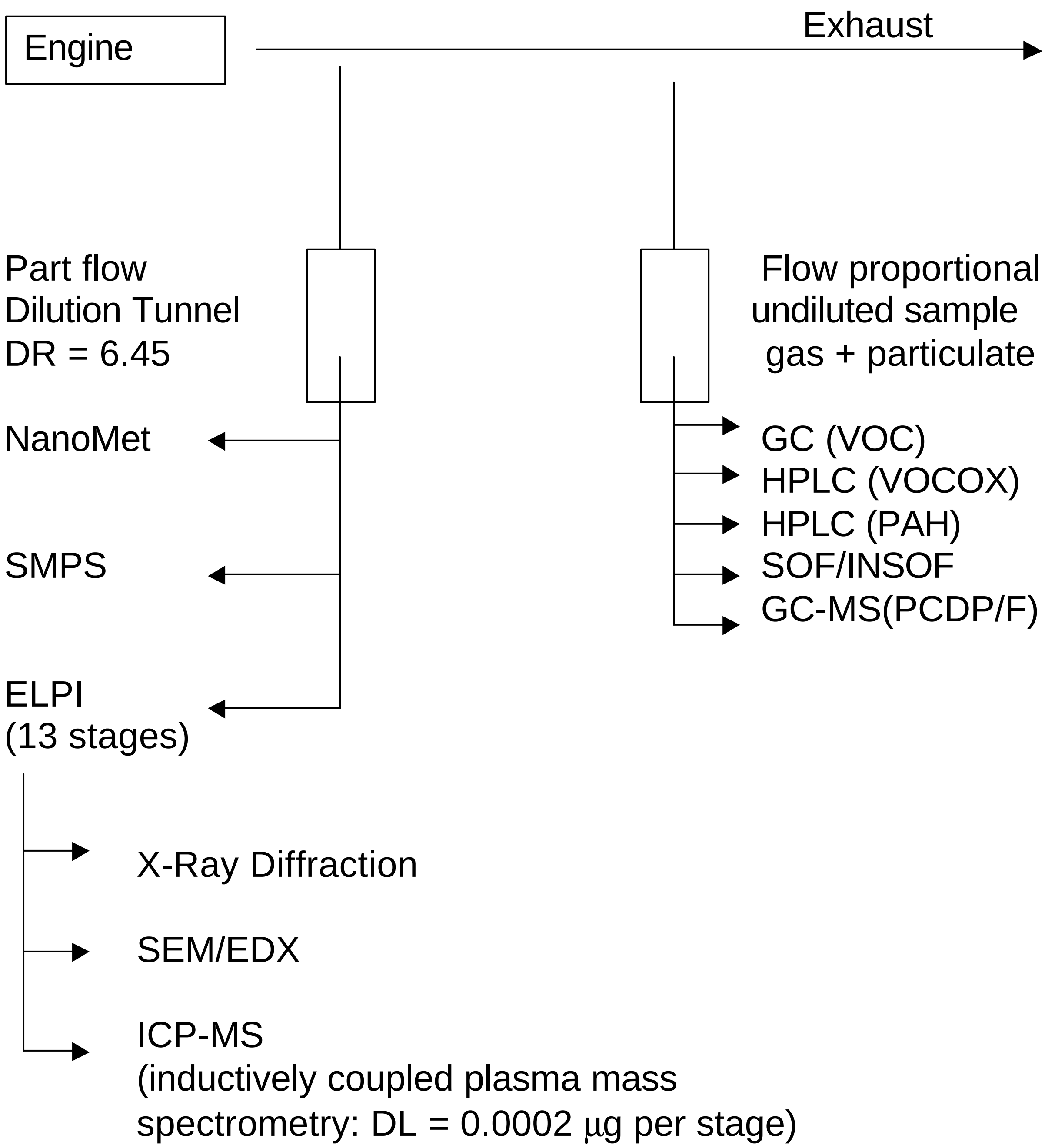
Part 1: Filtration Test: VFT

- Cycle: ISO 8178 C1, 4 stationary points
  + free acceleration
- Trapping efficiency: Mass / BS / EC / OC / Number / Surface
- Emissions during regeneration

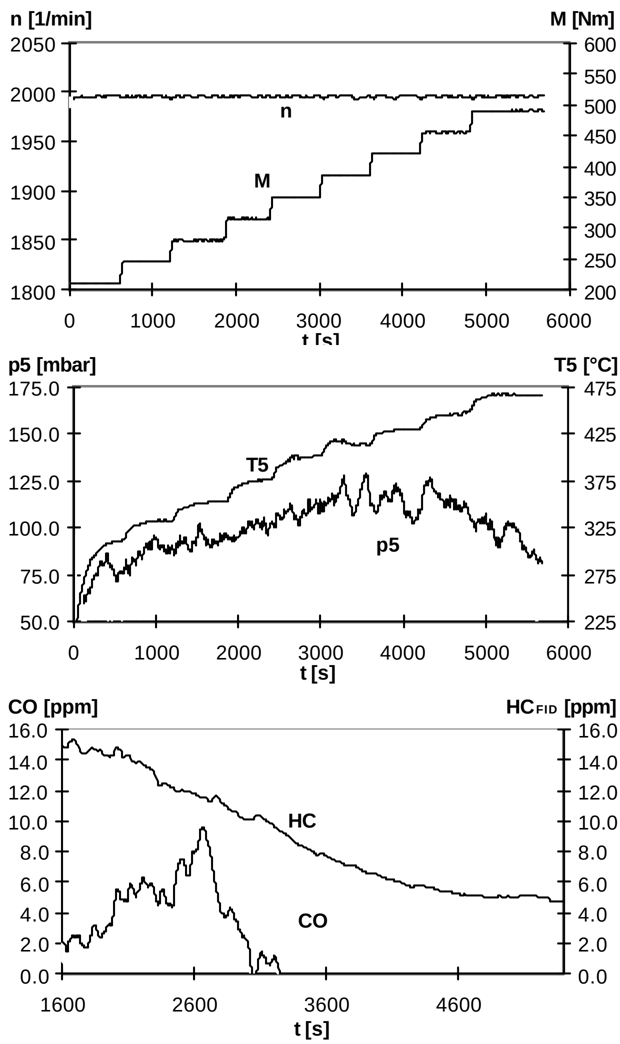
Part 1 – Secondary Emission Test: VSET

- Cycle: ISO 8178 C1: 8 points including transients: 200 min.
- Chemical Sampling and Analysis (EMPA 17 28 47)
  PCDD/F, PAH, Nitro-PAH, SOF/INSOF
- Particulate Sampling: ELPI, SMPS, NanoMet
  → how many particles are emitted?
  → in which size range?
  → what is their chemical composition?
  → what is their surface morphology?
  → what is their crystalline structure?

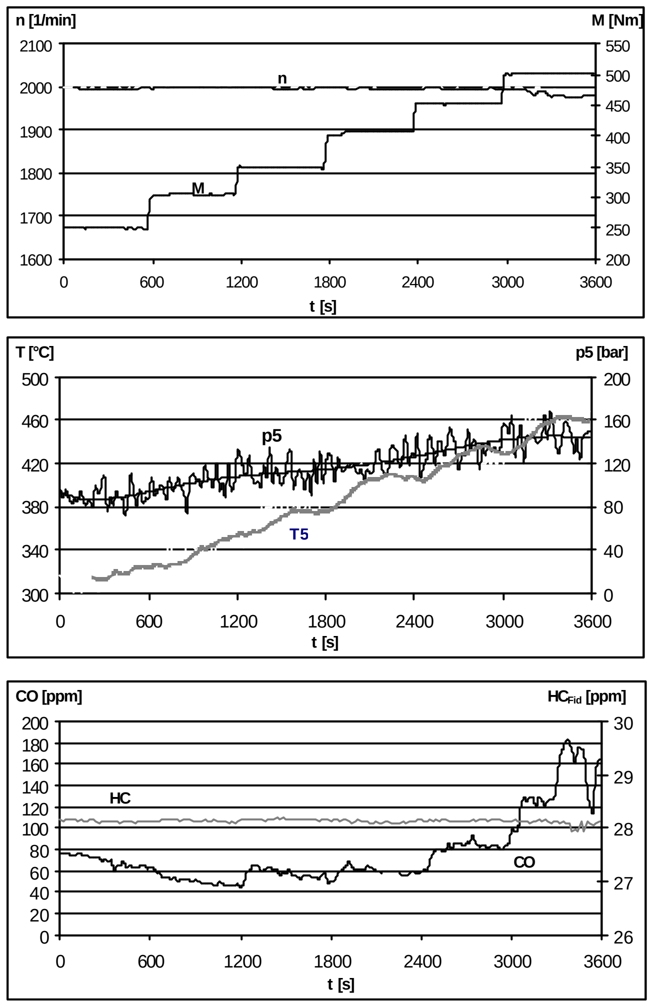
Test – Setup for VSET
Secondary emission test



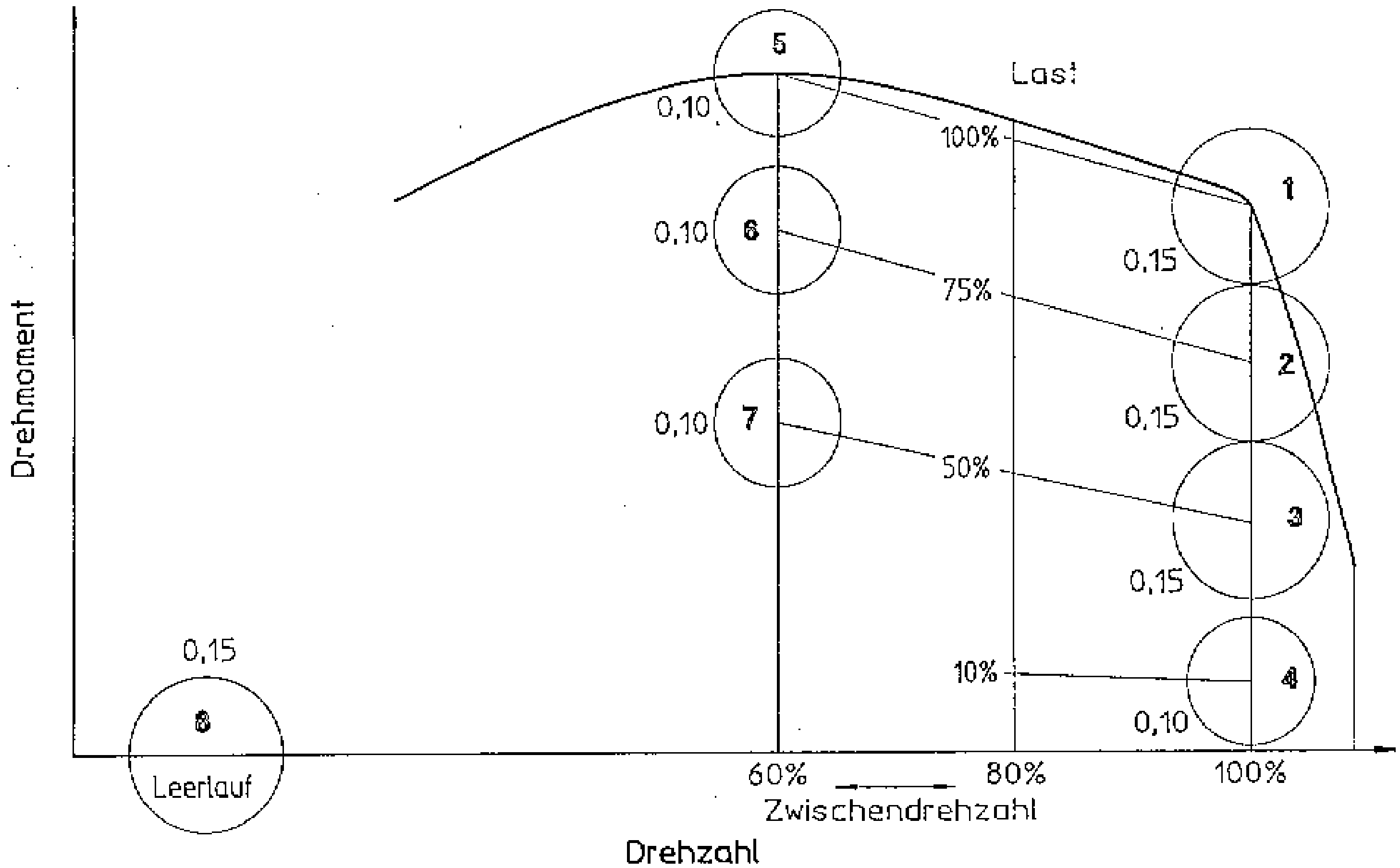
Regeneration with two different additives



15 ppm Ce + 1 ppm Pt



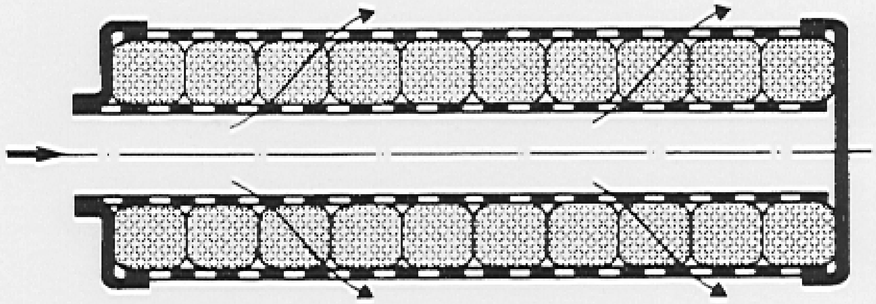
18 ppm Fe



ISO 8178 C1-Test

Hauptelement des BUCK'schen Strickfilters ist die Filterkerze, die in einem automatischen Fertigungsprozeß durch Rundstricken und Plissieren entsteht.

Standard-Dimensionen:



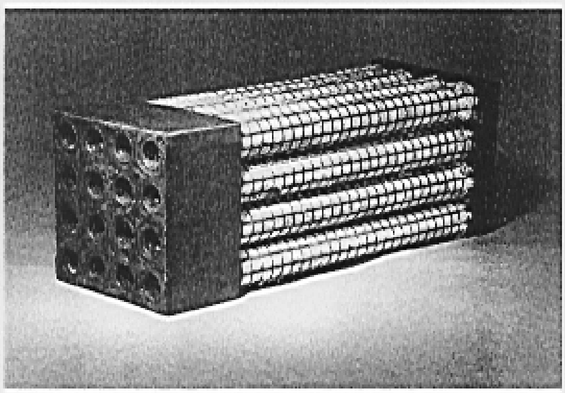
- Länge 500 mm
- Außendurchmesser 50 mm
- Gesamtgewicht 760 g
- Gestrickgewicht ca. 500 g
- Porosität 55–80%
- Durchsatz ca. 20 l/s bei
- Druckverlust 50 mbar

Sonderdimensionen auf Anfrage.

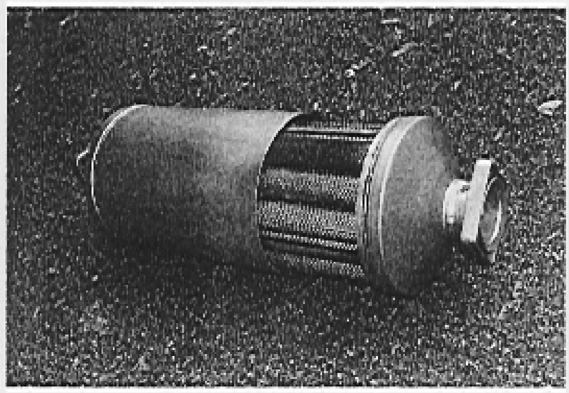
Die Filterkerzen werden verschweißt in Edelstahlqualität geliefert, für den Einbau bereits vorbereitet mit einem Dehnungselement mit schwingungsdämpfenden Eigenschaften. Für die Anordnung im freien Auspuff des Dieselmotors (nach Turbolader) kommen Hochtemperatur-Glasgarne zum Einsatz – Dauertemperatur bis 800 °C.
Für höhere Einsatztemperaturen können Quarz- oder Keramikfasern gewählt werden. Die Kerzen können zum Aufbau beliebig großer Filter in freier konstruktiver Gestaltung zusammengesetzt werden.

Beispiele:

Modulaufbau für Stationärmotoren
Zwischendichtung mit Gestrick

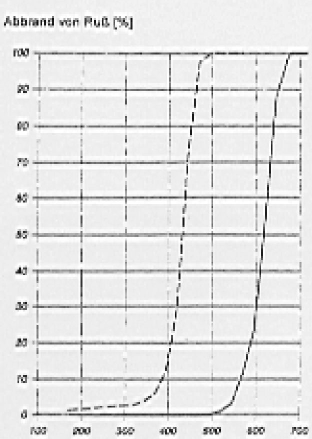


Fahrzeugfilter in den Dimensionen des Schalldämpfers
(den er ersetzt)

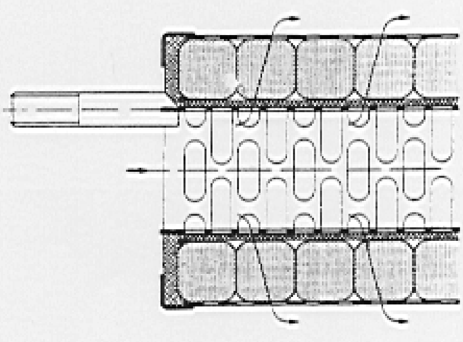


Regenrationsausstattung

Die Filterkerzen wurden mit Dieselbrennern, Elektroheizungen und Additivsystemen erfolgreich geprüft. Die gleichmäßige Verteilung des Rußes, guter Wärmeaustausch, geringe Übertemperaturen und die Thermoschock-unempfindlichkeit erleichtern die Regeneration erheblich.
Aus Eigenentwicklungen stehen zwei integrierte Regenerationssysteme zur Verfügung:

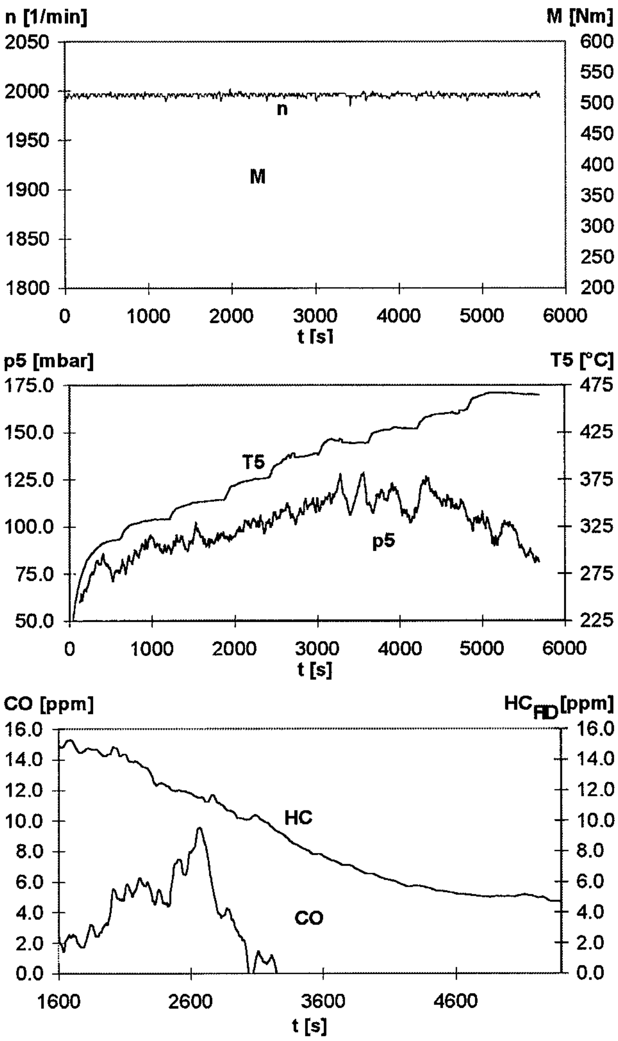


Katalytische Beschichtung reduziert die Abbrandtemperatur um nahezu 200 °C. Linke Kurve beschichtet, rechts unbeschichtet.
TAG-Analyse mit trockenem, künstlichem Ruß

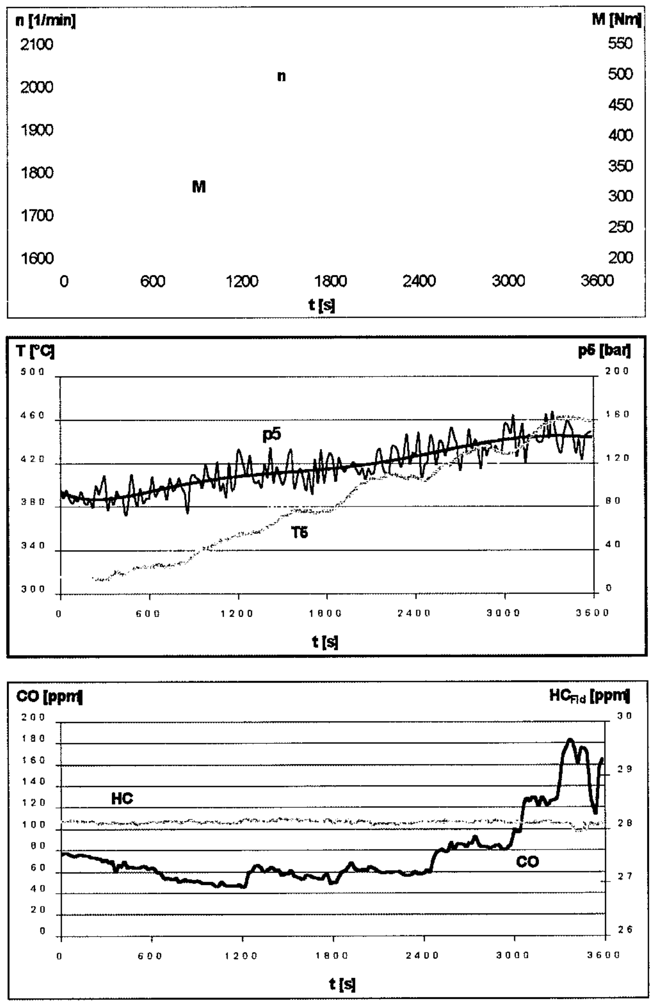


Elektrische Innenbeheizung mit spez. Wärmeüberträgerelement

Regeneration with two different additives



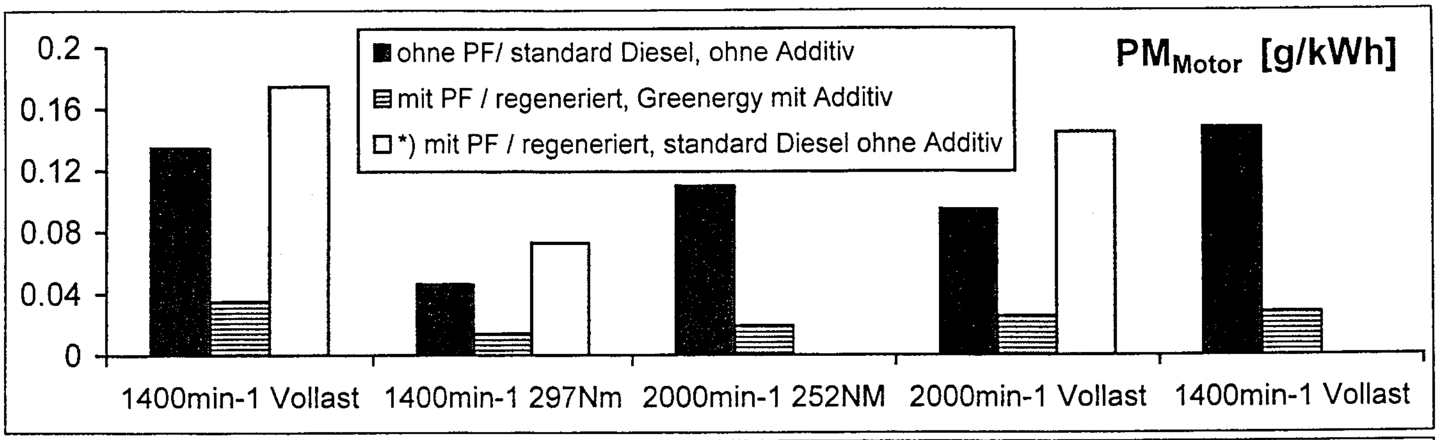
15 ppm Ce + 1 ppm Pt

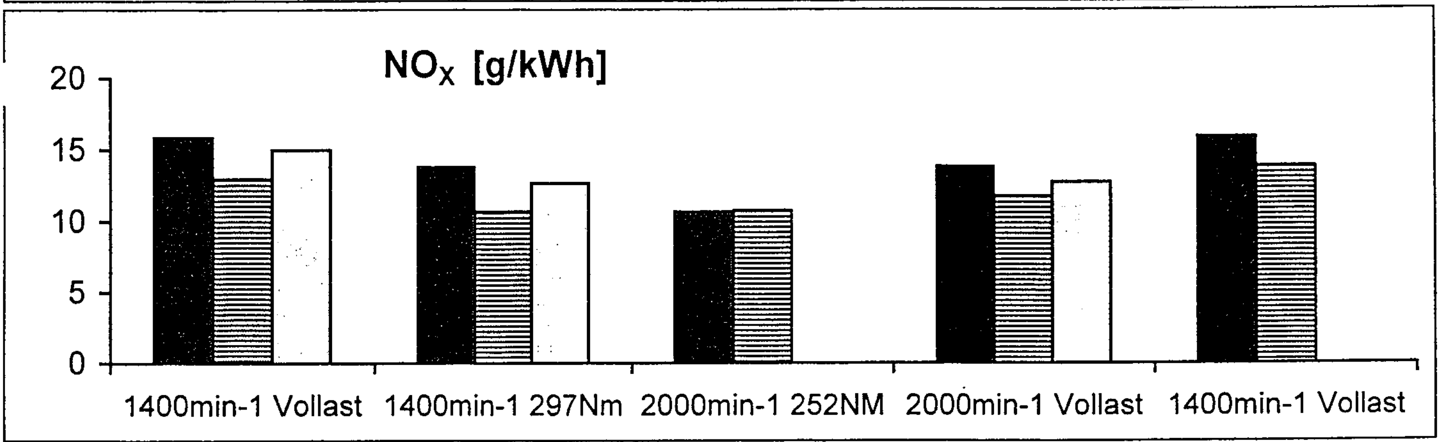


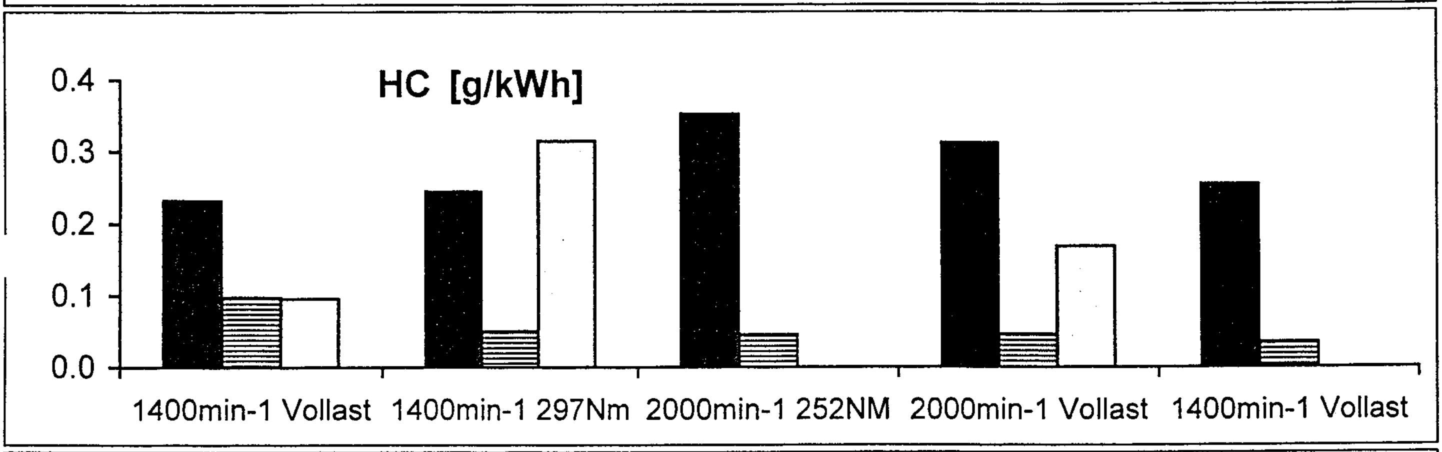
18 ppm Fe

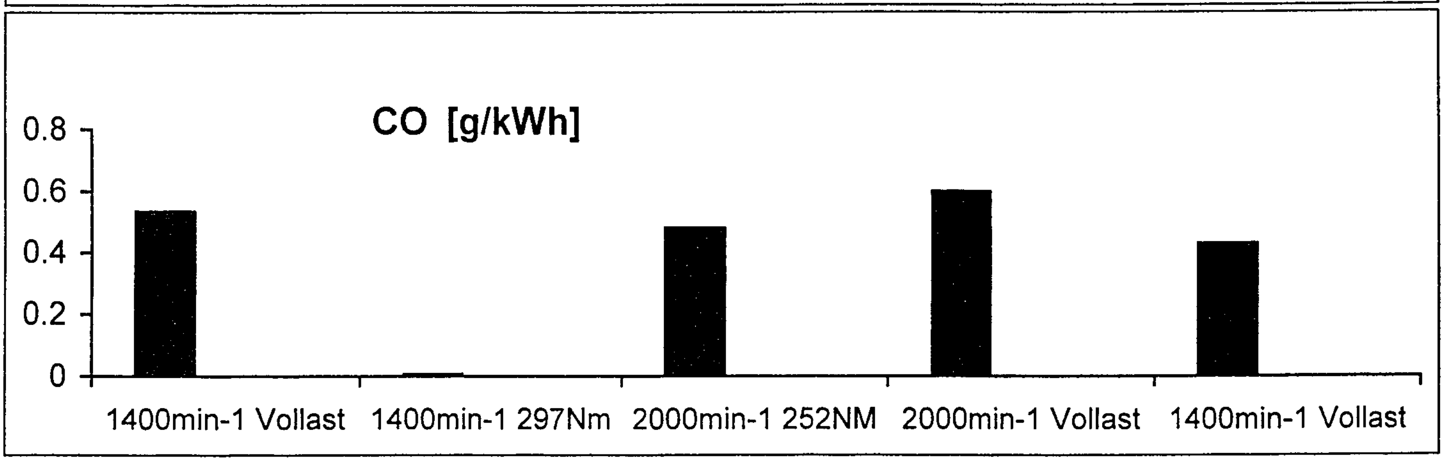
Vergleich der Emissionswerte

mit / ohne Ammann Partikelfilter ARF 10 Typ-B
mit / ohne Additiv







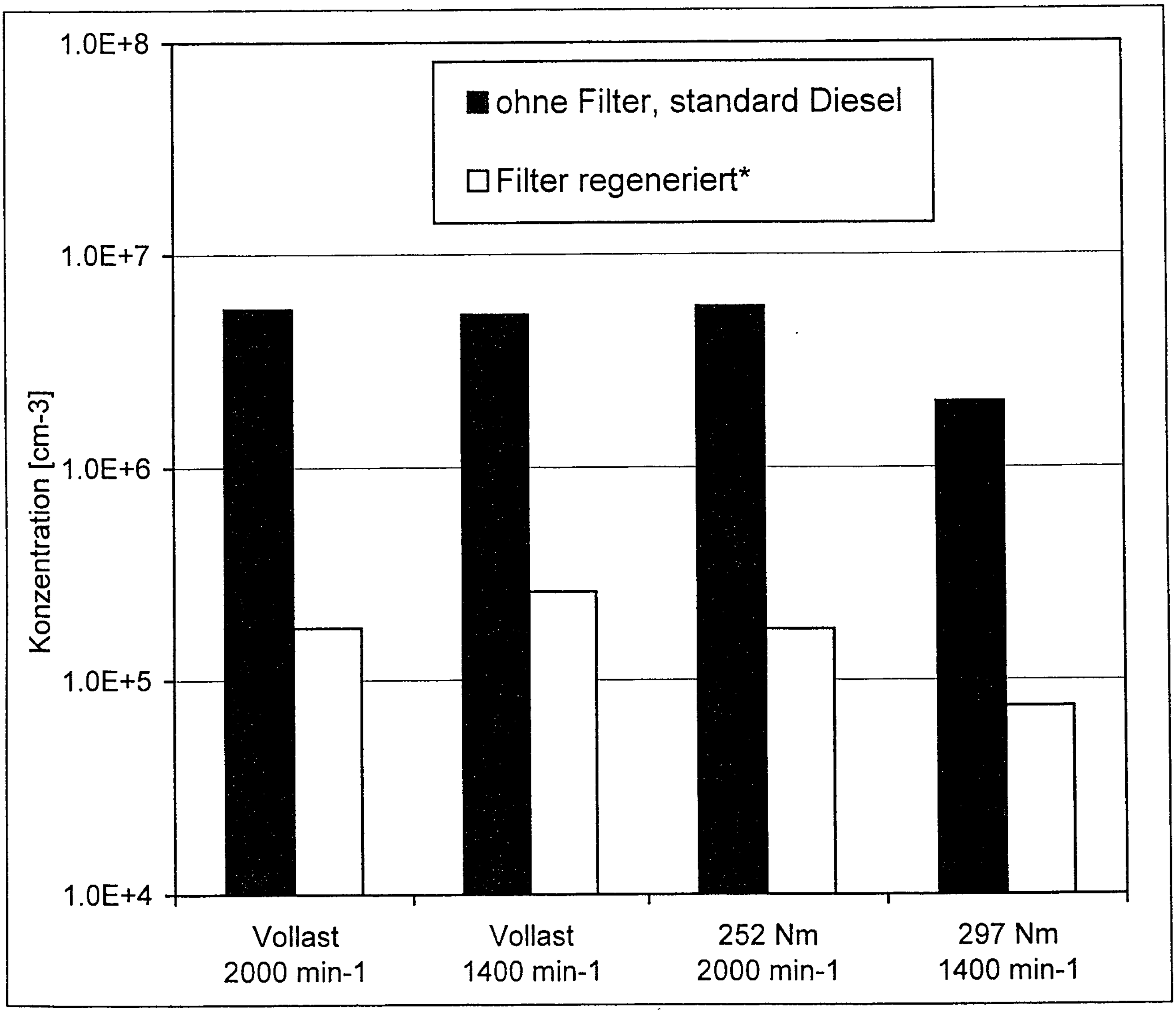


*) nur Betriebspunkt 1400min-1 Vollast, 1400 min-1 297 Nm, 2000 min-1 Vollast

Integrierte Partikelzahlen im Grössenbereich 30 bis 200 nm

Ammann Partikelfilter ARF 10 Typ-B (Pt/Cer), mit Aktivkohlefalle

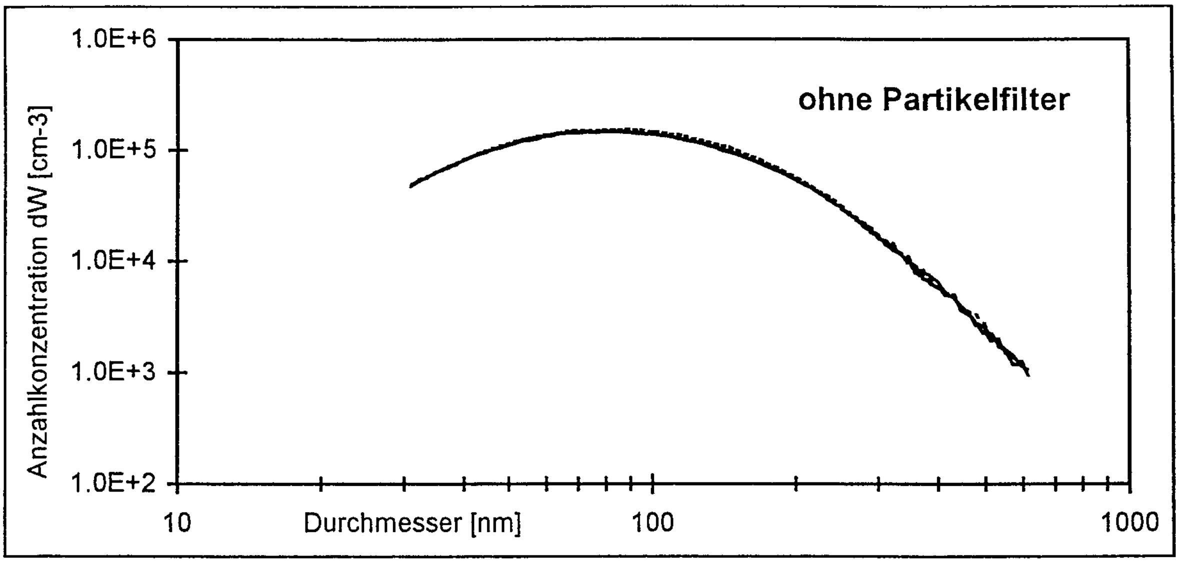
$1/cm^3$	2000 min-1 Vollast	1400 min-1 Vollast	2000 min-1 252 Nm	1400 min-1 297 Nm
ohne Filter	**5.53E+06**	**5.21E+06**	**5.68E+06**	**2.03E+06**
Filter regeneriert*	**1.76E+05**	**2.60E+05**	**1.74E+05**	**7.53E+04**

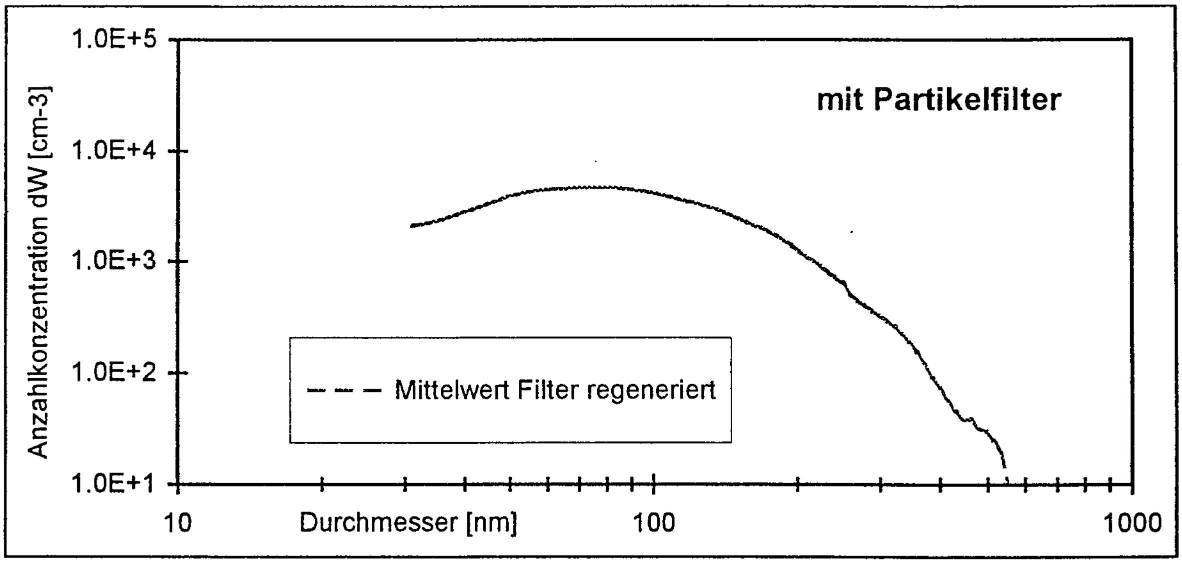


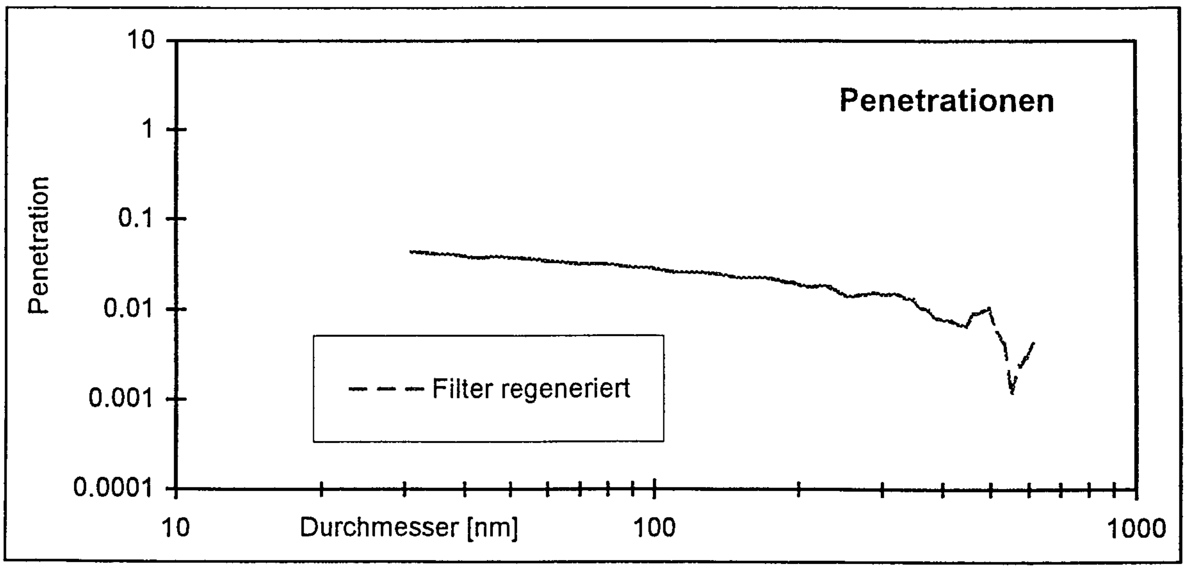
*) regeneriert mit Pt / Cer

Grössenverteilungen mit/ohne Ammann Partikelfilter

Liebherr D914 T, 2000 min^{-1}/ 252 Nm, Pt/Cer

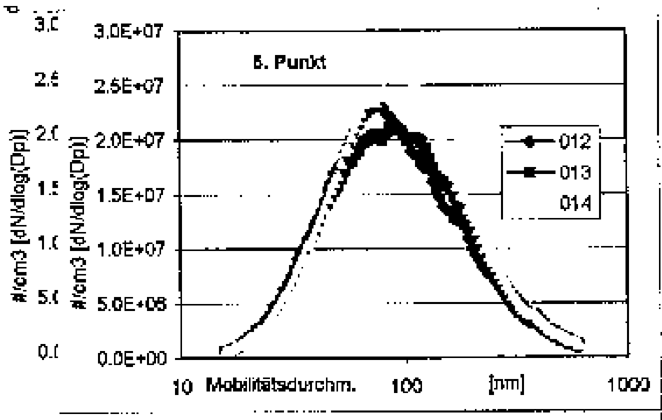


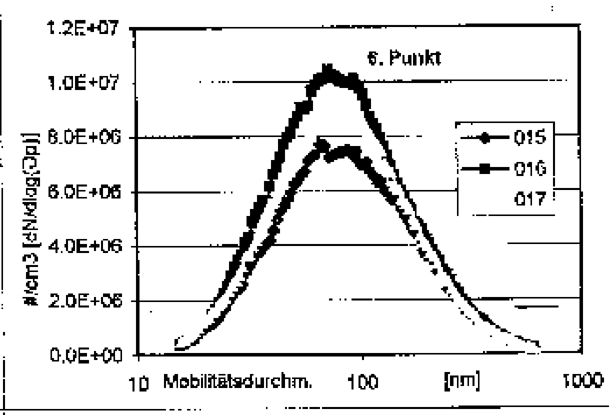




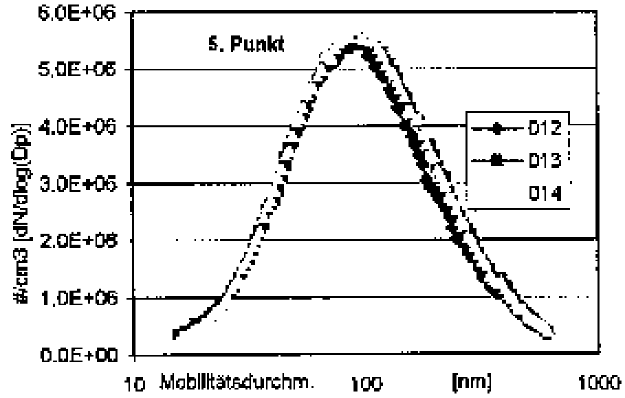
SMPS / Standard Diesel 400 ppm S

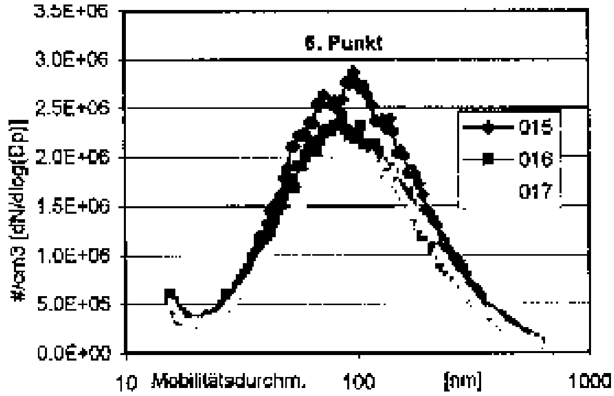
no Filter / no Additiv



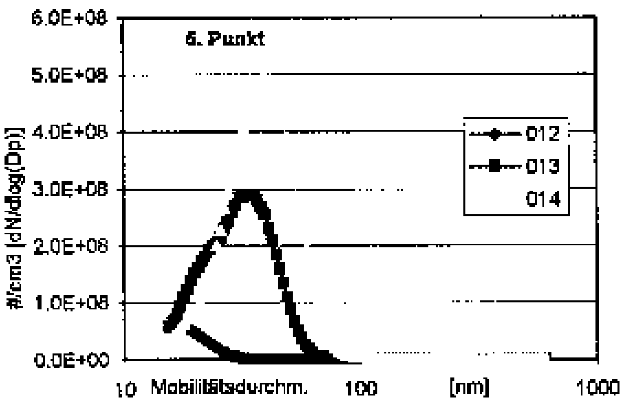


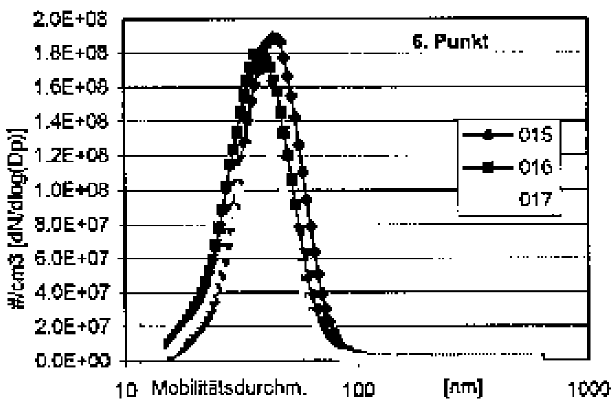
no Filter / with Additive



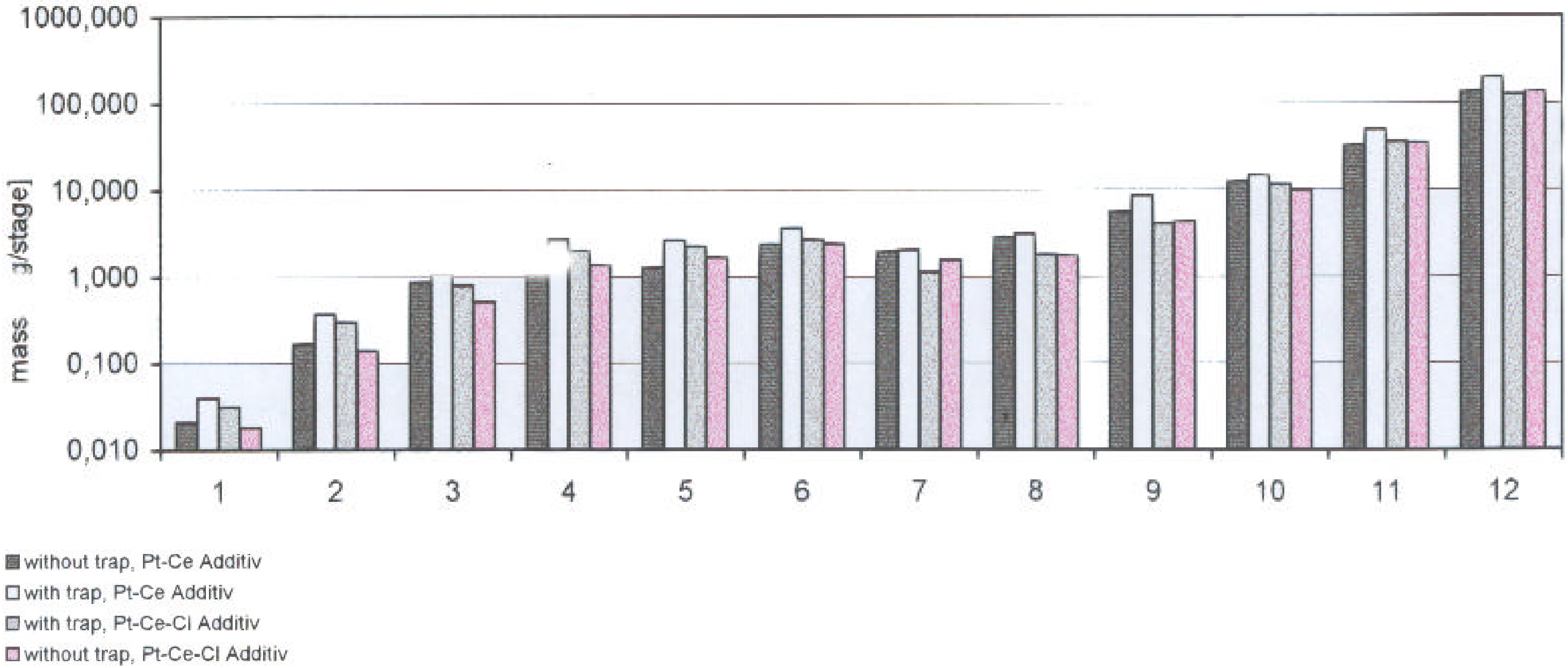


Downstream Filter / with Additive





ELPI / Total weight per stage
(Electric on-line data)



Size Specific Chemical Analysis for Pt

By ICP – MS / DL = 0.0002 µg/stage

ELPI Stage	Diameter D50 [nm]	upstream Trap [µg]		downstream Trap [µg]	Trapping eff. [%]
1	30	0.002		-	
2	63	0.006		-	
3	109	0.007		-	
4	173	0.005		0.001	
5	267	0.015		0.001	
6	407	0.022		0.002	
7	655	0.022		0.001	
8	1021	0.013		0.0005	
9	1655	0.007		0.0005	
10	2520	0.004		0.0002 DL	
11	4085	0.003		0.0002 DL	
12	6560	0.002		0.0002 DL	
13	9999	0.002		0.0002 DL	
	Sum:	0.117 µg		0.0068 µg	93%

<u>Balance per test</u>

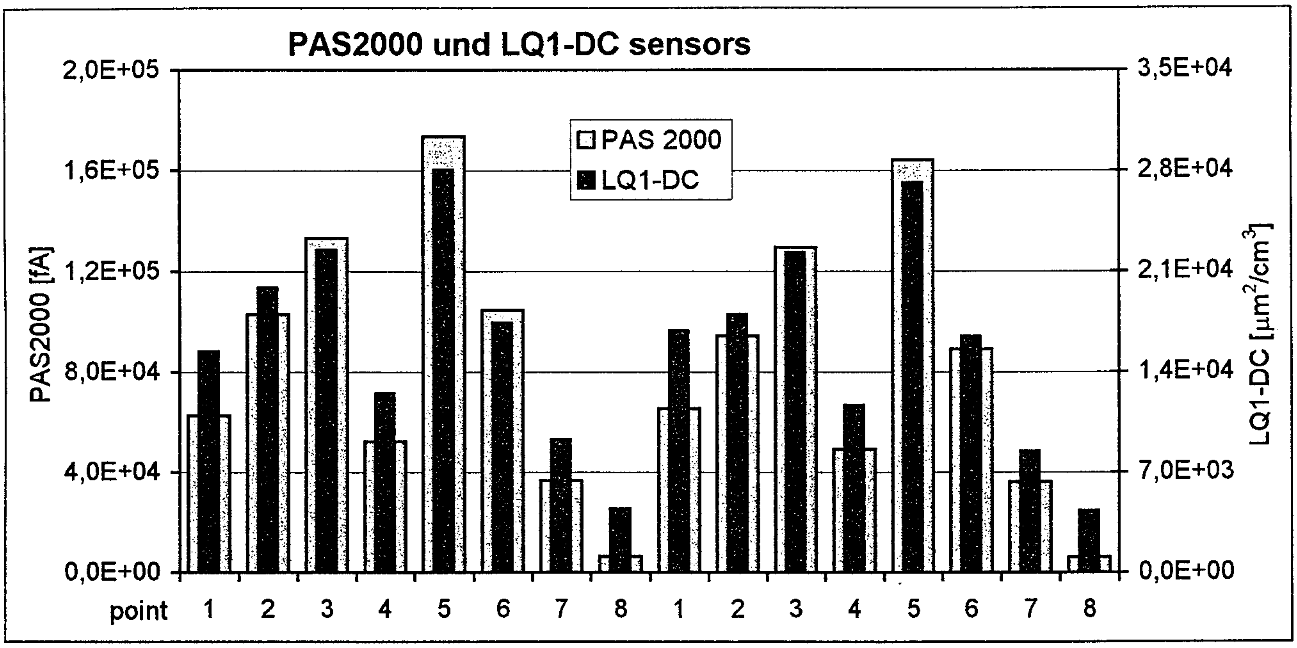
Total Pt-Input ***21,6 mg*** *(0,5 mg/kg fuel)*
Total Pt-Content in Exhaust ***0.447 mg***
Total Pt-Content in Exhaust downstream Trap ***0.032 mg***

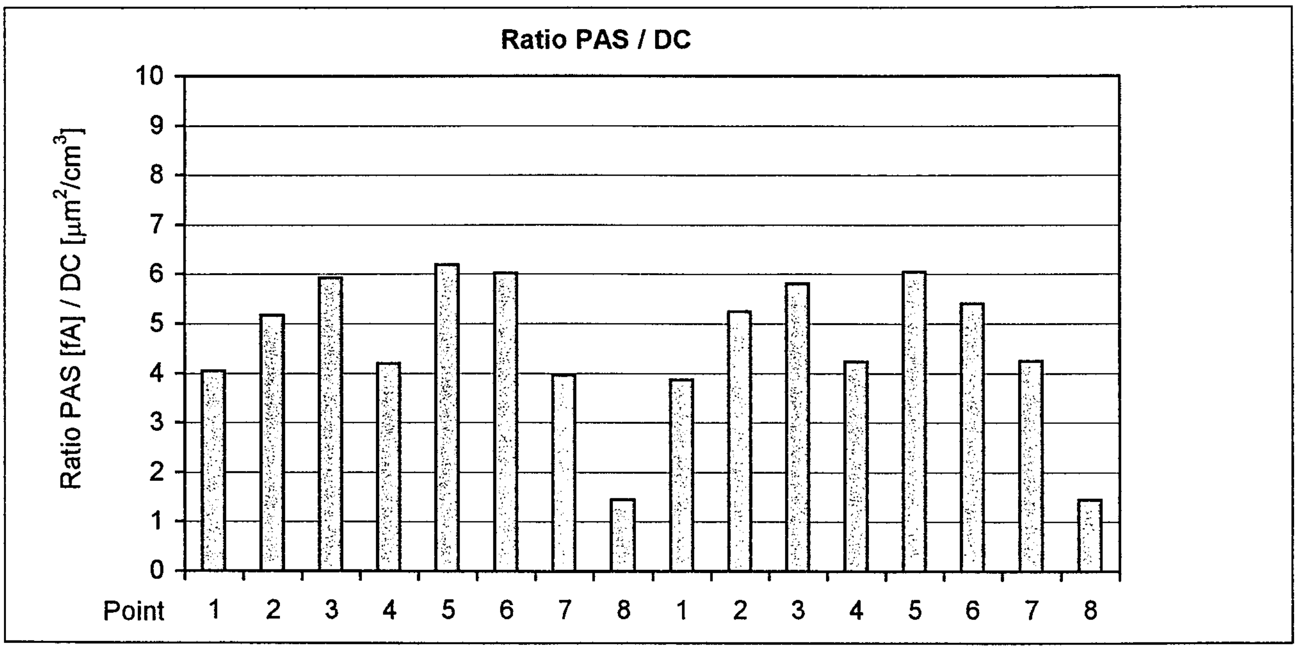
Deposited in engine ***97.9 %***
Deposited in trap ***93%***
Deposited in trap + engine ***99.85%***

NanoMet measurement, secondary emission test
mean values for each operating point

date: 31.03.00

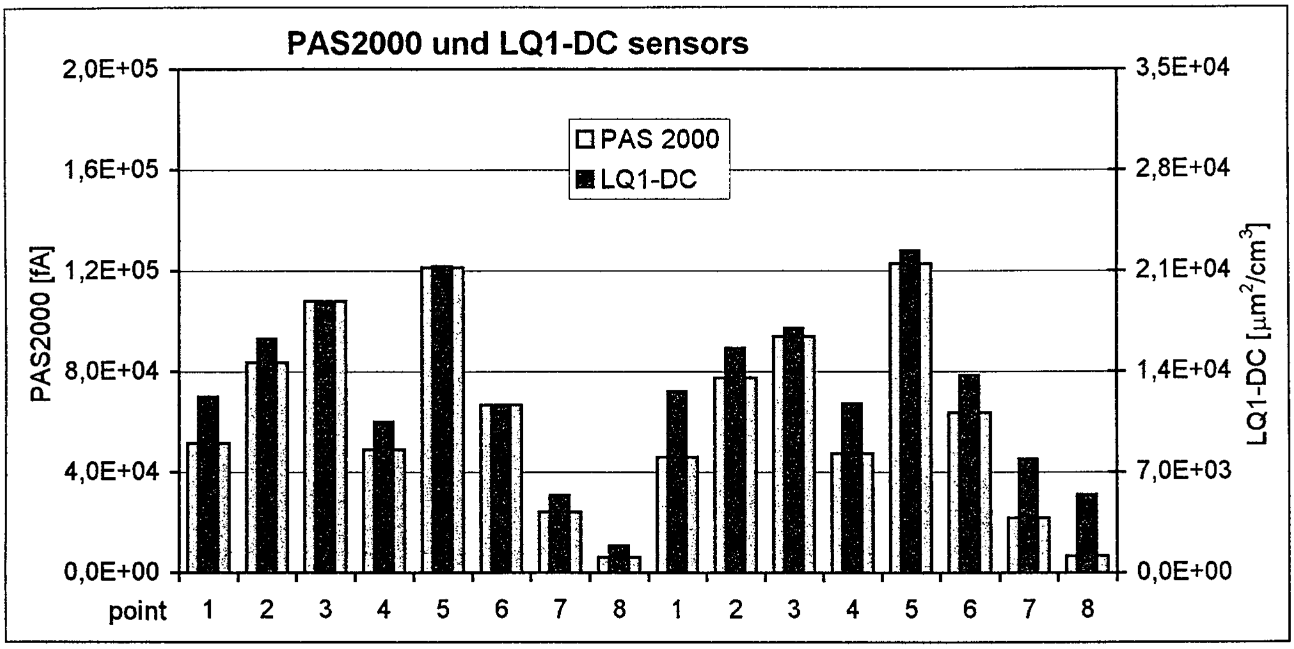
additiv: -
fuel: standard diesel fuel
particle trap: -

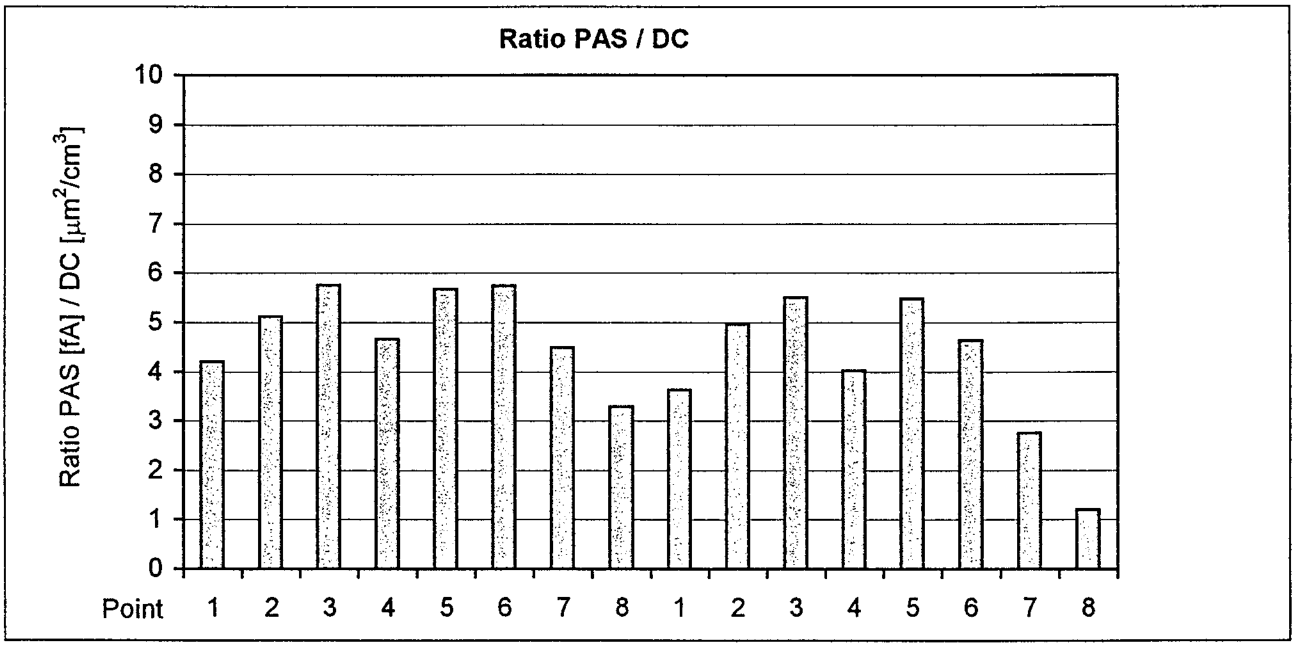




NanoMet measurement, secondary emission test
mean values for each operating point

date:	**06.04.00**	**additiv:**	**Pt - Ce**
		fuel:	**standard diesel fuel**
		particle trap:	**-**





Size Specific Chemical Analysis for Ce

By ICP – MS / DL = 0.001 µg/stage

ELPI Stage	Diameter D50 [nm]	upstream Trap [µg]	downstream Trap [µg]	Trapping eff. [%]
1	30	0.28	-	
2	63	0.47	-	
3	109	0.51	0.02	
4	173	0.39	0.09	
5	267	0.78	0.11	
6	407	1.02	0.13	
7	655	0.94	0.02	
8	1021	0.58	0.007	
9	1655	0.42	0.003	
10	2520	0.33	0.002	
11	4085	0.29	0.001	
12	6560	0.23	0.002	
13	9999	0.18	0.001	
	Sum:	6.42 µg	0.38 µg	94%

Balance per Test

Total Ce-Input ***324 mg***

Total Ce-Content in Exhaust **25,29** ***mg***

Total Ce-Content in Exhaust downstream Trap **1.52** ***mg***

Deposited in engine ***92.2%***

Deposited in trap ***94%***

Deposited in trap + engine ***99.5%***

Conclusions

- Size-specific (metal) analysis of
  engine emitted soot particles is possible
- Ce/Pt additive at 7.5/0.5 ppm concentration
  does not produce a separate oxide cluster peak of ultrafines
- Ce/Pt oxide particles appear in the size spectrum
  proportional to each other
  and proportional to soot
- Ce/Pt oxide particles are very effectively deposited
  in the engine > 92 / 98 % (initial phase)
  and trapped in the filter > 94% (equal to solid soot part.)
- Only < 0,5 /0.1% of the total metal input is emitted

  → Pt: 0.17 µg/kWh
  (close to detection limit)

  → Ce: 8.1 µg/kWh
- SEM/EDX - Analysis and
  X-Ray - Diffraction
  was not possible because of the small amount of metal
- The Ce/Pt-additive fulfills the criteria of the VERT-secondary
  emissions and filtration test and has very promising
  properties when used for trap regeneration