Engine Emitted Toxic Metal Oxide Nanoparticles

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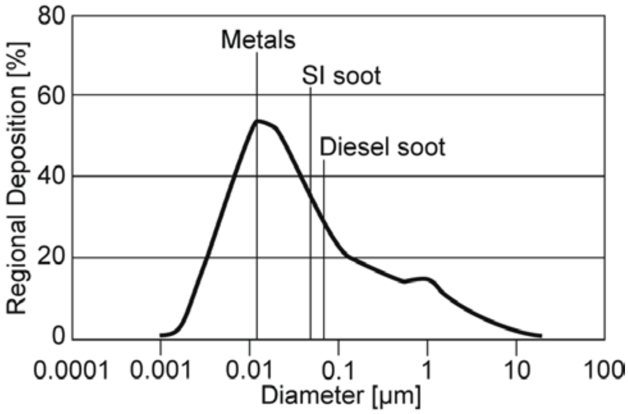
All conventional piston-driven combustion engines emit metal oxide particles of which only little is known. The main sources are abrasion between piston-ring and cylinder, abrasion of bearing, cams and valves, catalyst coatings, metal-organic lubrication oil additives, and fuel additives. While abrasion usually generates particles in the µm-range, high concentrations of nanosize metal oxide particles are also observed, probably resulting from nucleation processes during combustion.



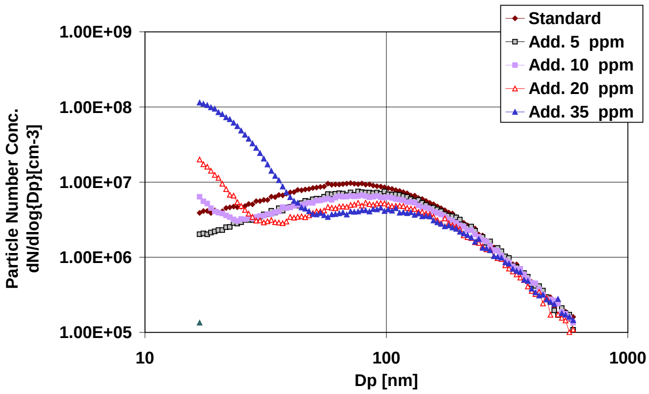
Size specific deposition of nose-inhaled particles in the human alveoli. Diesel soot particles (mean diameter 80 nm = 0.08 µm), SI soot particles (50 nm) and free metal oxide particles (15 nm) are all in the range of maximum alveoli deposition.

These small metal-oxide particles, discussed here, can penetrate the alveoli tissue and enter into the blood circulation. Subsequently, these nanoparticles might be rapidly transported into the entire organism. Similar to the soot particles, the metal-oxide particles can cross the blood brain barrier and can also cross the placenta and enter into the fetus. The nanoparticles also can enter the brain via the olfactory nerve ending in the nose. The biological impact of nanosize particles is being intensively researched; medical research is also focusing on cell toxicity due to metal and metal oxide particles. Responsible institutions recommend restricting body intruding insoluble metal emissions to an extreme minimum. Oxide particles of Iron, Copper and Zinc, which are typical for emissions from combustion engines, may be 10 – 100 times more toxic than soot particles.

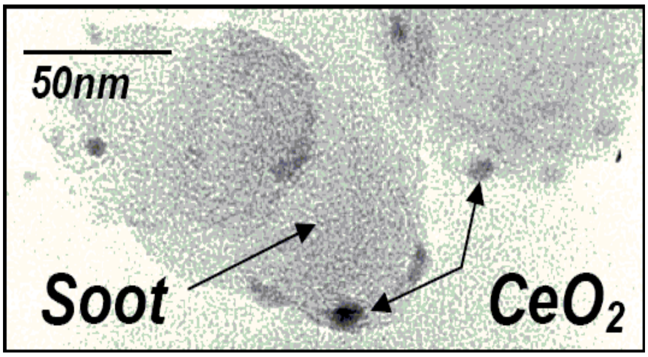
Hence, these particles must be scrutinized for concentration, size distribution and composition. Published data are summarized and data from investigations of various engines with respect to metal oxide particle emission are reported. These investigations were performed without and with VERT approved particle filters, where VERT is an international verification standard for emission reduction technologies, which, besides of filtration effectiveness, durability and limited pollutants also includes the analysis of secondary emissions, potentially formed by these technologies and of size specific metal emissions. In good agreement with literature, the overall metal mass in the exhaust of IC-engines without particle filter is in the range of 0.1–1 mg/km metal. This combines wear metals and metals from lubrication oil additives.

Size specific chemical analysis has shown that a large part of metal oxide particles are to be found in the size classes below 60 nm. However there are more metal oxide particles in the exhaust attached to soot particles of larger size, as chemical analysis also revealed. If there are less soot particles prevalent, like at idle conditions some of them do appear unattached in a separate fraction of much smaller size. SMPS particle size distribution at idle shows peaks of up to 10^8 particles per cc in the size range of 10-30 nm. It must be assumed that these are all metal oxide particles since PMP sampling was applied which means that these particles survived 300 °C and thus can not be volatiles.

The following figure shows on the left side an example of a cerium oxide based additive in Diesel fuel. SMPS measurements indicate a bimodal size distribution with a marked peak at very small sizes, when the fuel additive exceeded 10 mg metal per kg fuel. The particles were collected and analyzed for their Cerium content, which proved the assumption that this peak consisted of Cerium oxide particles. At additive concentrations of 5 ppm, a peak at small size ranges is not visible. The metal oxide particles are probably deposited on larger soot particles (picture right side), whereas with increasing concentrations the peak height increases dependent on the additive dose.



Particle size distribution with a FBC (cerium based additive) dosed in different concentrations.



Cerium oxide FBC hooked on soot particles

For Diesel engines, industry has demonstrated that particle filters are available which can very efficiently filter those nanoparticles.

There is however little known about metal oxide emissions of other engines like SI engines or CNG-engines but it must be anticipated that all IC piston engines do emit such particles – with a tendency of more particles with increasing engine RPM and with engine age or lubrication oil consumption. Elimination of such metal oxide particles therefore might become an urgent future requirement for all engine categories.

There are two practical and proven technologies available to rectify the problem:

- Firstly, deploy highly efficient particle filter systems on all combustion engines as this paper demonstrates in 2 cases with VERT-certified particle filter systems: one regenerated with the aid of a precious metal catalyst coating; the other with a base metal coating and fuel borne metal catalyst..
- Secondly, diminish the metal content of the lubrication oil, which has been investigated with small 2-stroke engines and described in earlier SAE-papers by the authors.

Since technologies are available and health concerns are mounting, further emission curtailment requires that the size dependent chemical composition of IC engine exhaust particles must be addressed by engineers, scientists, and governments. Toxic substances must be specifically identified. Hence, the metal content of the particles must be determined and legislatively limited to levels as attained by best available control technology.

Engine Emitted Metal Oxide Particles

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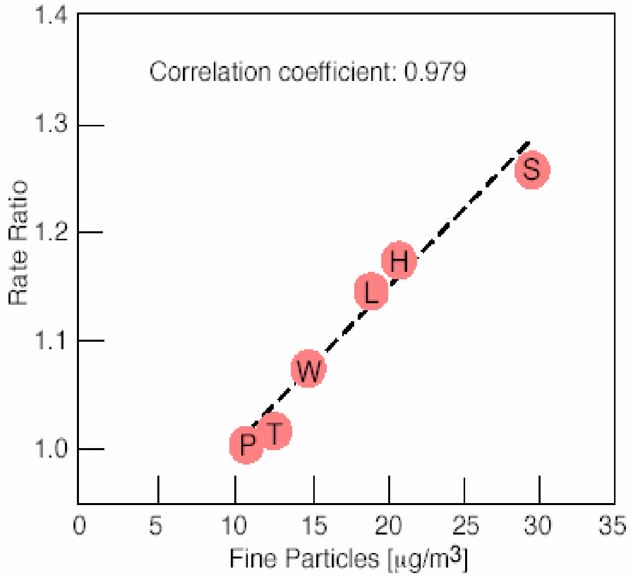
14.ETH-Conference on Combustion Generated Nanoparticles – August 2010

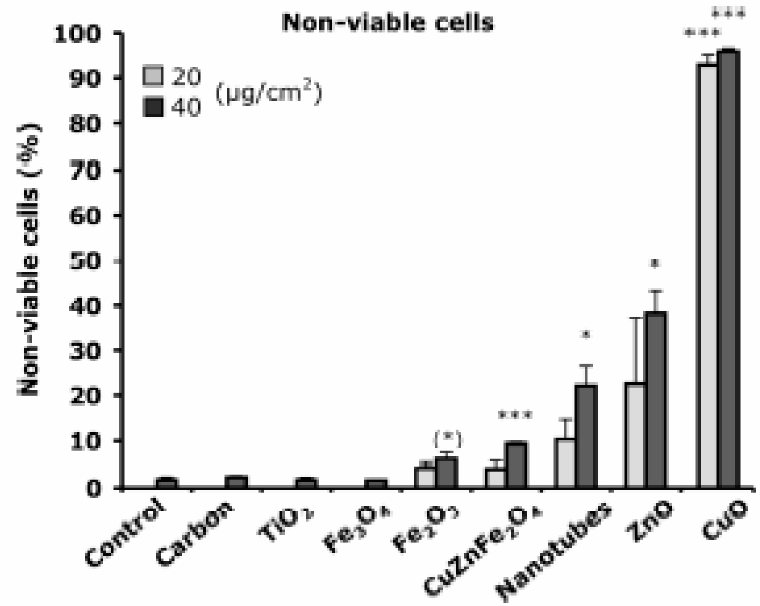
What makes Particles toxic ?



Substances in soot particles have very different toxicity

% cells not surviving

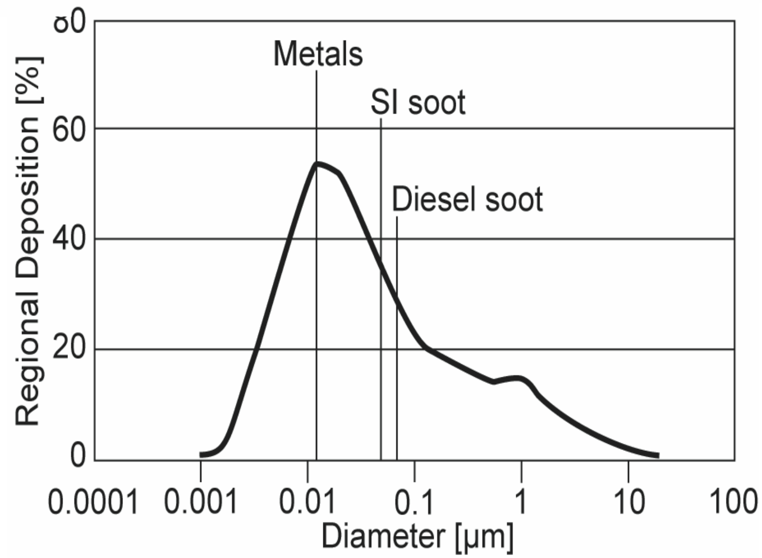
Karlsson, Chem, Res.Tox 1998



Exposition to mass (or equivalent number) increases mortality proportional

6 cities study

Dockery 1993



Size is decisive for system penetration

Oberdörster ETH-NPC 2005

Metals in the Engine Exhaust

Engine Wear:	Fe, Ni, Cr, Al, Si
Bearing Wear:	Cu, Sn
Lube Oil:	Zn, Ca, P
Cat.Coatings:	Pt, Pd, V, Cu, Ce
FBC:	Fe, Ce, Pt, Cu

VERT-DPF-certification protocol

looks at metal emissions size-specific –
part of the secondary emissions test VSET

2 Tests selected from VERT-verifications

- with ICP-MS size specific Metal-Oxide Analysis

- ISO 8178- 8 operation points - steady state

CASE A

Engine LIEBHERR 924; PM: 65 mg/kWh

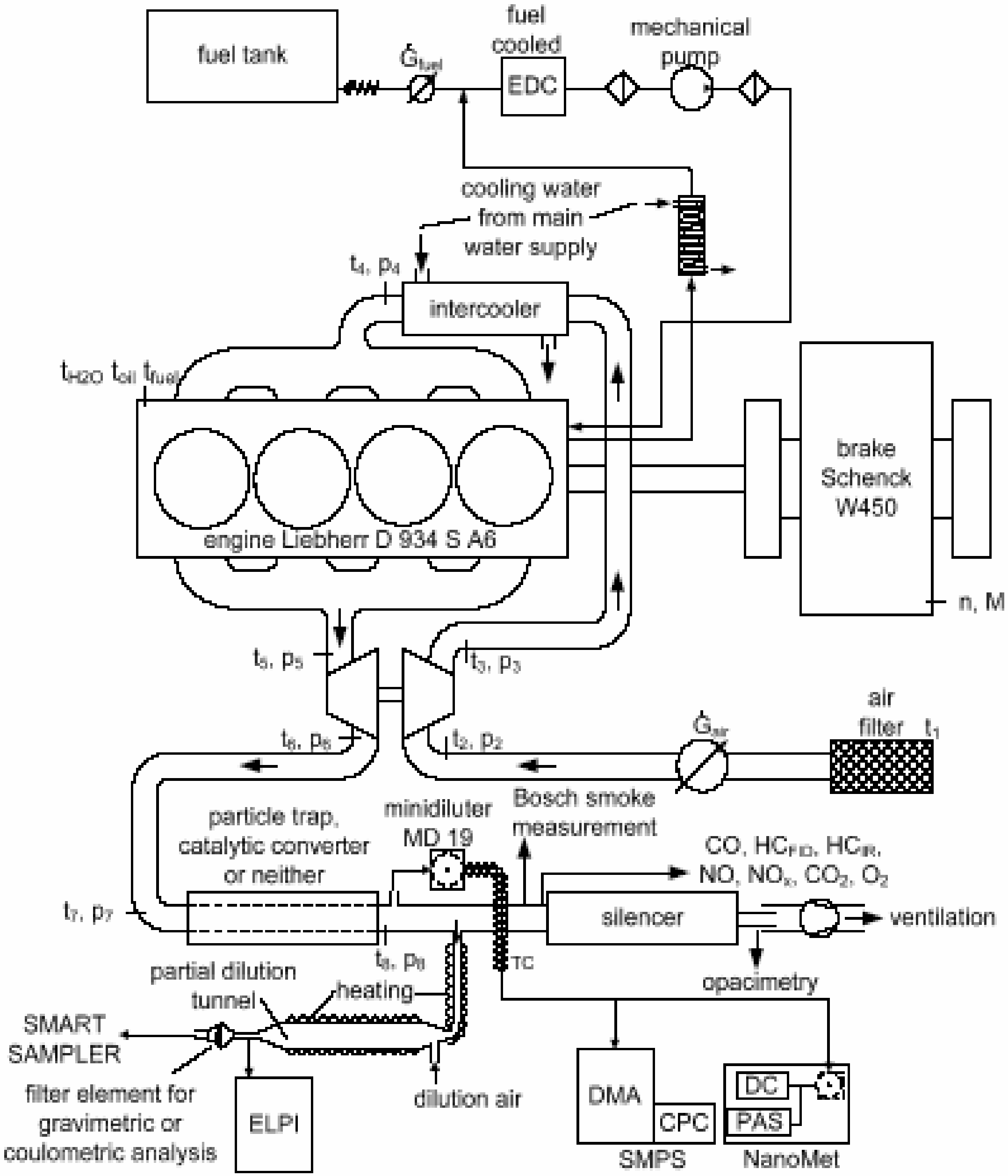
DPF SiC 15 µm pore size; Coating Pt + Rh

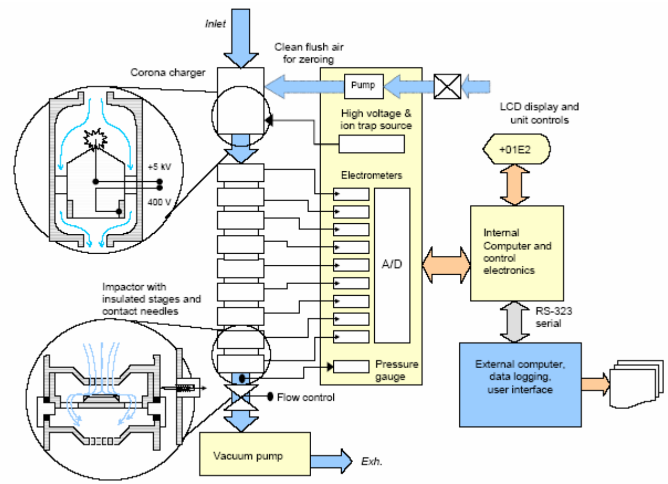
Case B

Engine LIEBHERR 914; PM: 125 mg/kWh

DPF SiC 25 µm; Coating Base Metal; FBC: Fe+Sr

Test Setup



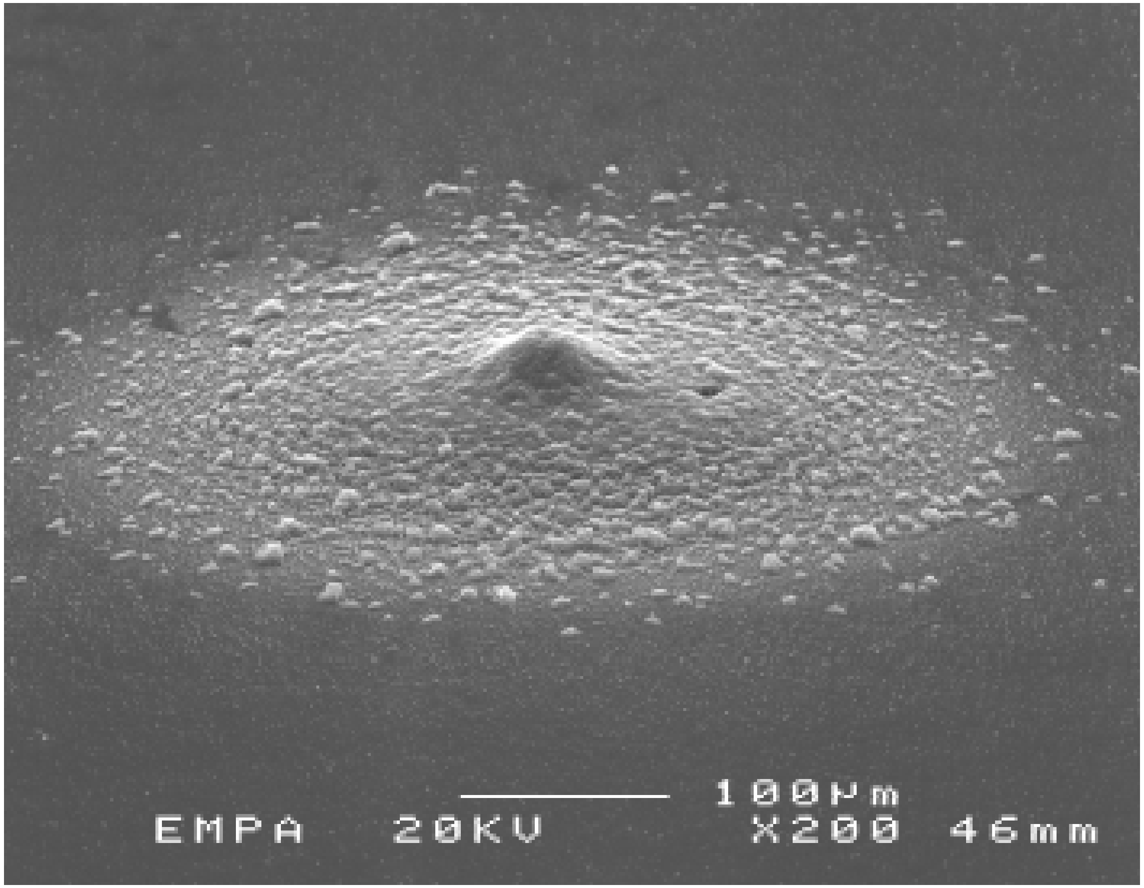


ELPI – Impactor

13 size classes

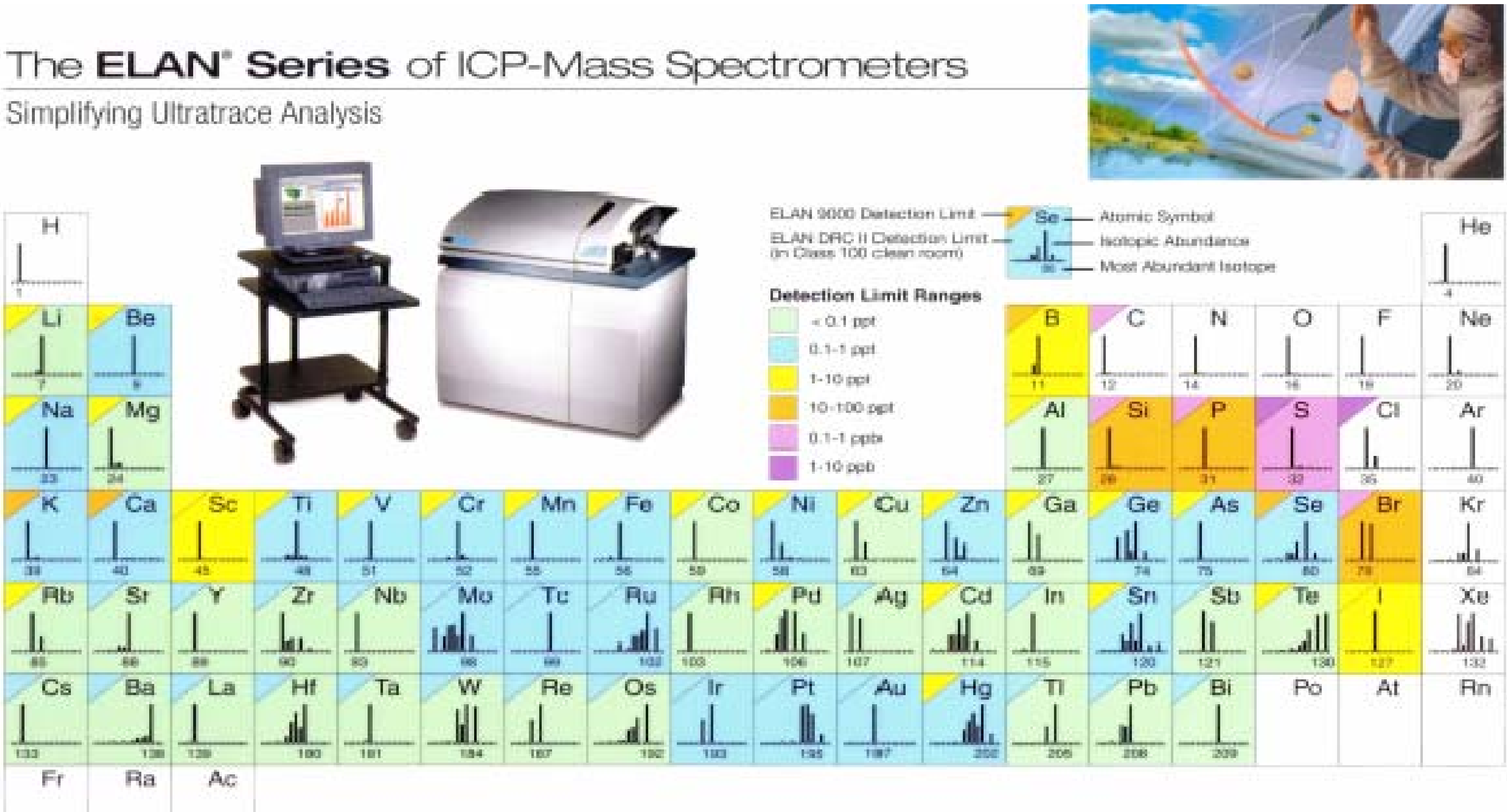
30 nm – 10 µm

ELPI-sample

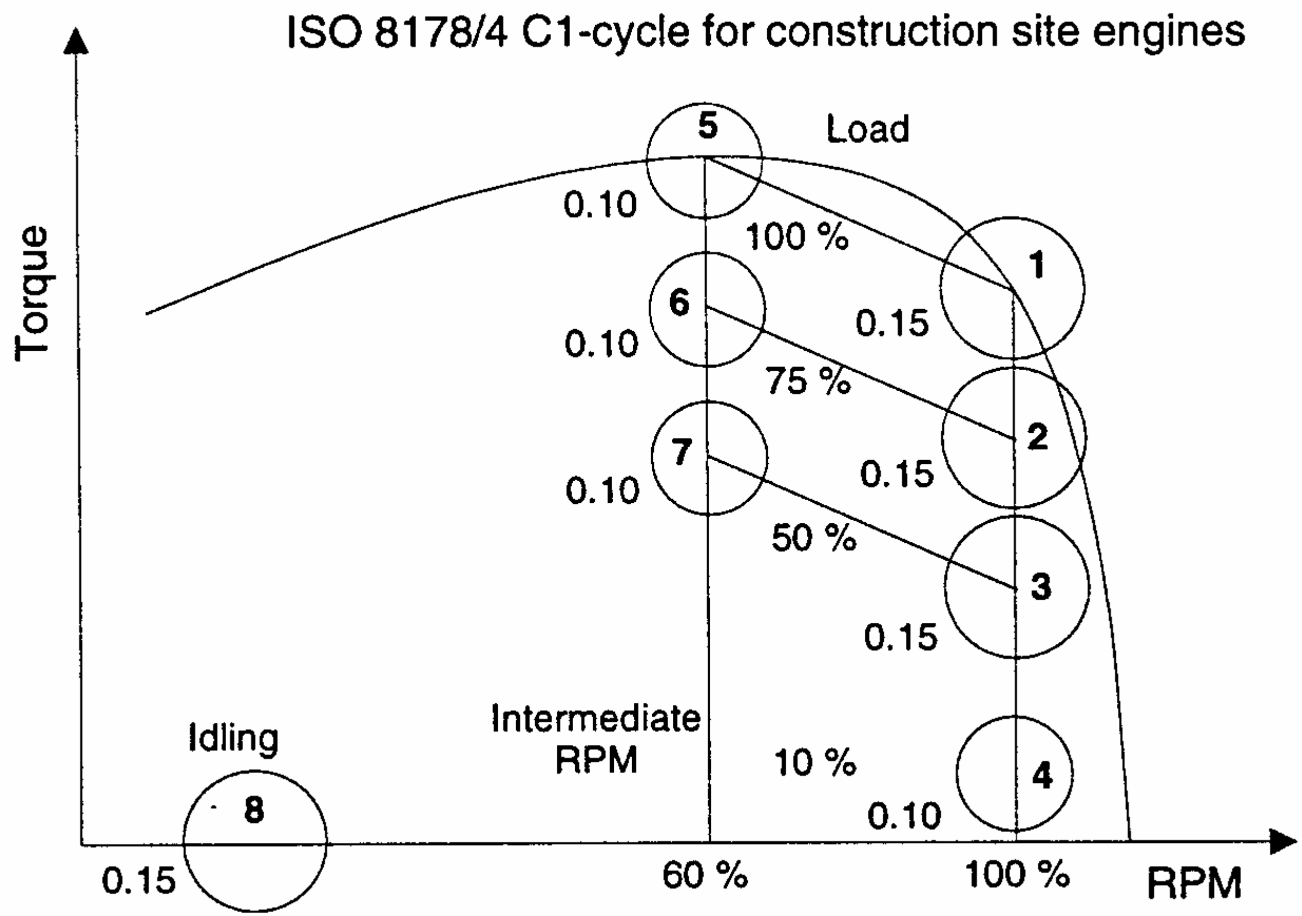


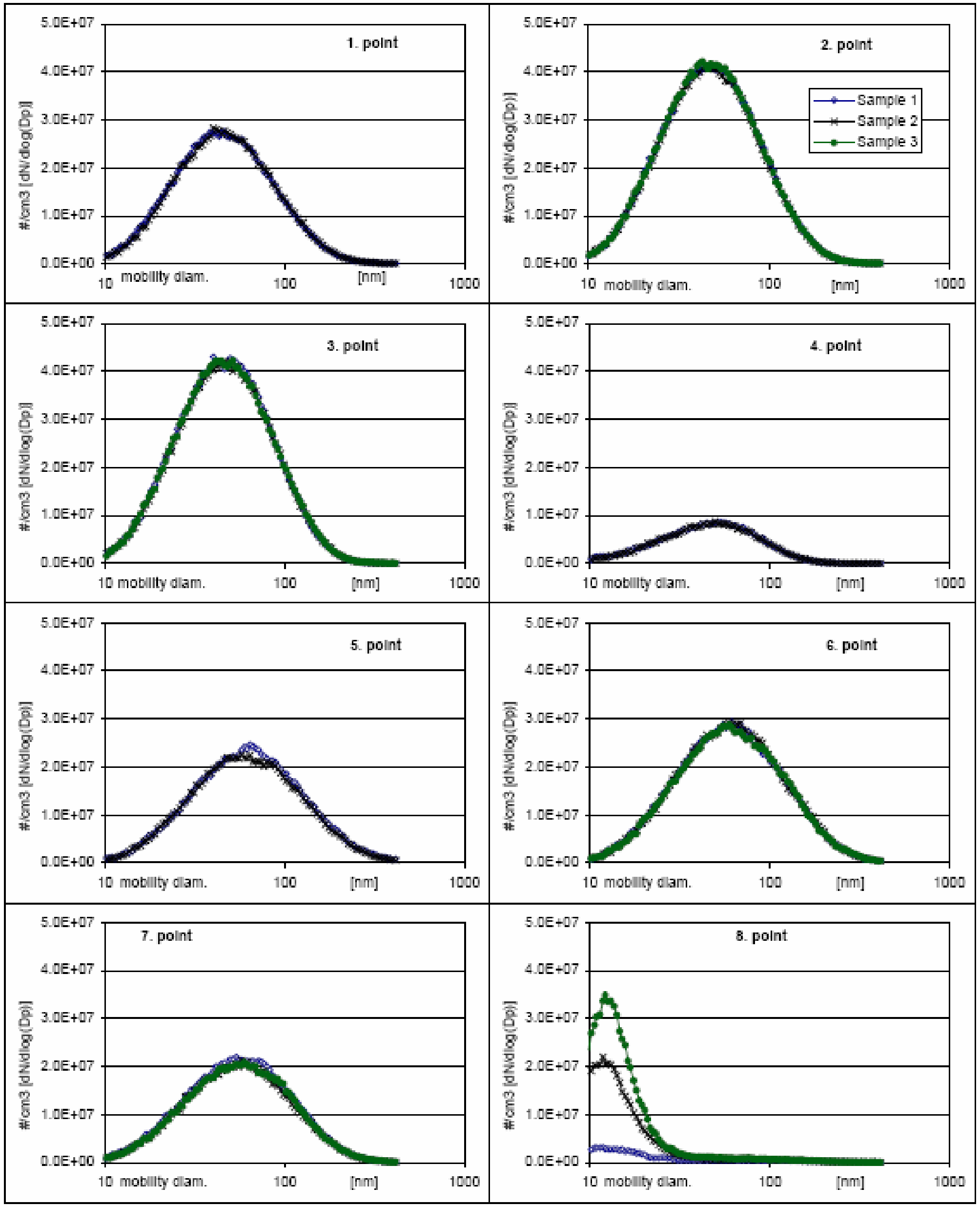
Plasma Mass Spectrometry ICP-MS

Fast Multi-Element Technique: 75 Elements in 2 min.
High Sensitivity ppt Levels (ng)



ISO 8178/4 C1 – VERT DPF certification cycle



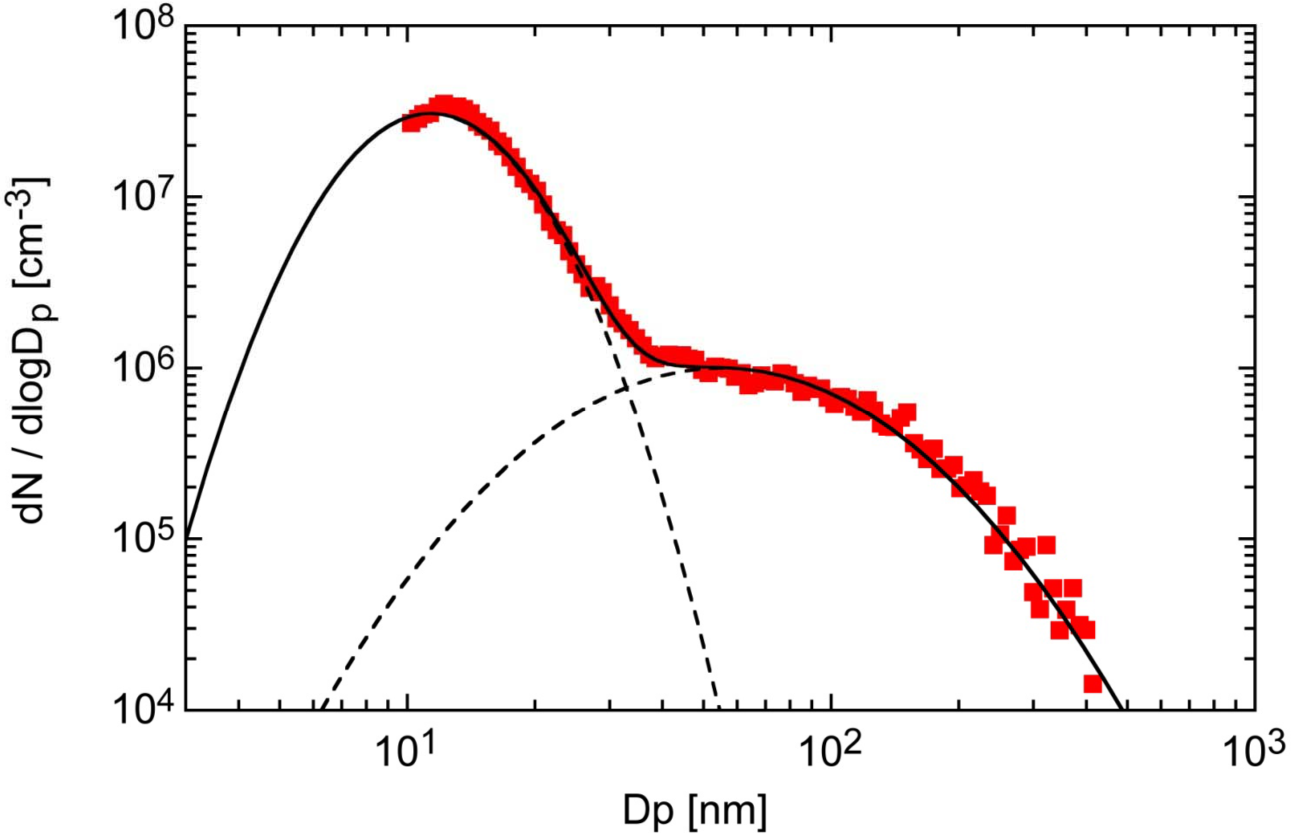


Case A:

Baseline LH 924
Size distributions
without DPF
8 operation points

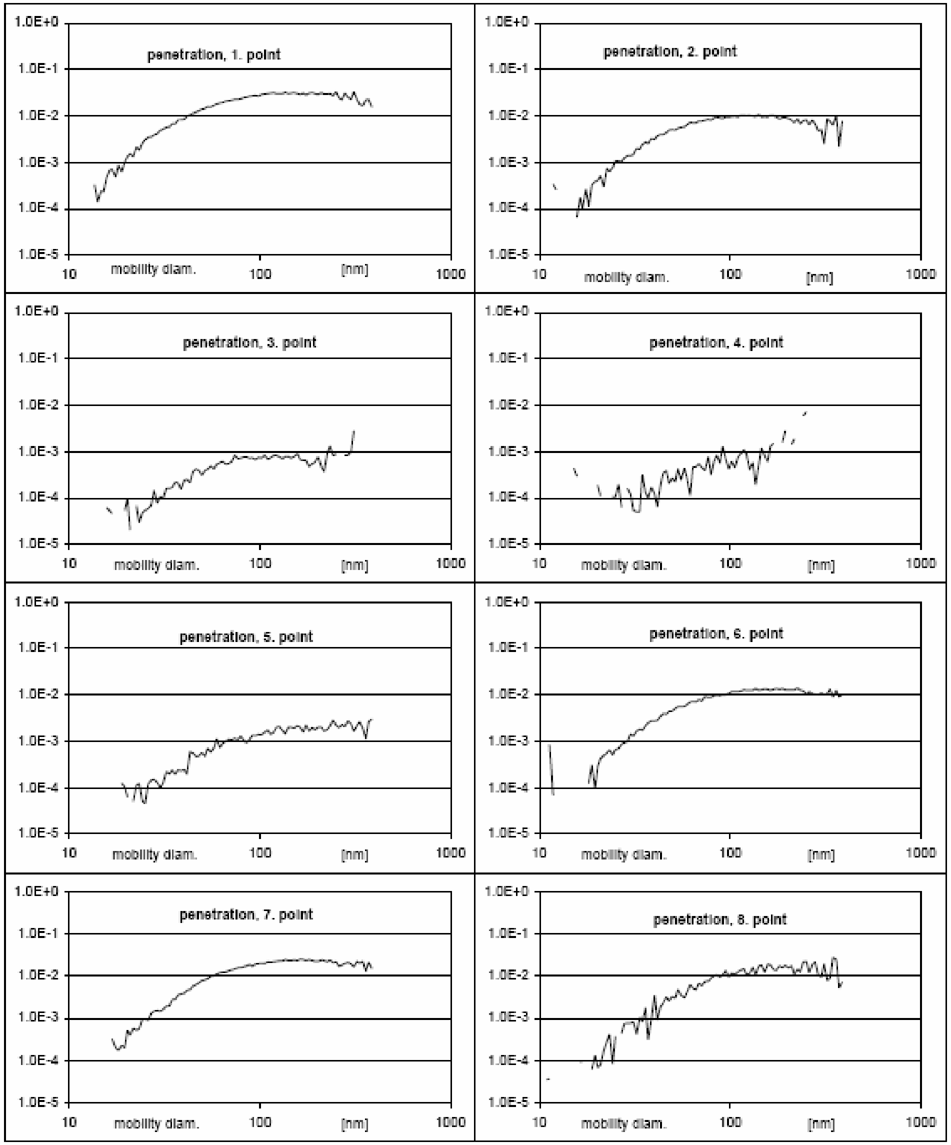
OP 8 = idle
Sampling: 300°C,
DR=100

Double-LogNormal Fit of a Bimodal Particle Distribution for OP8 (idling) of case A w/o DPF



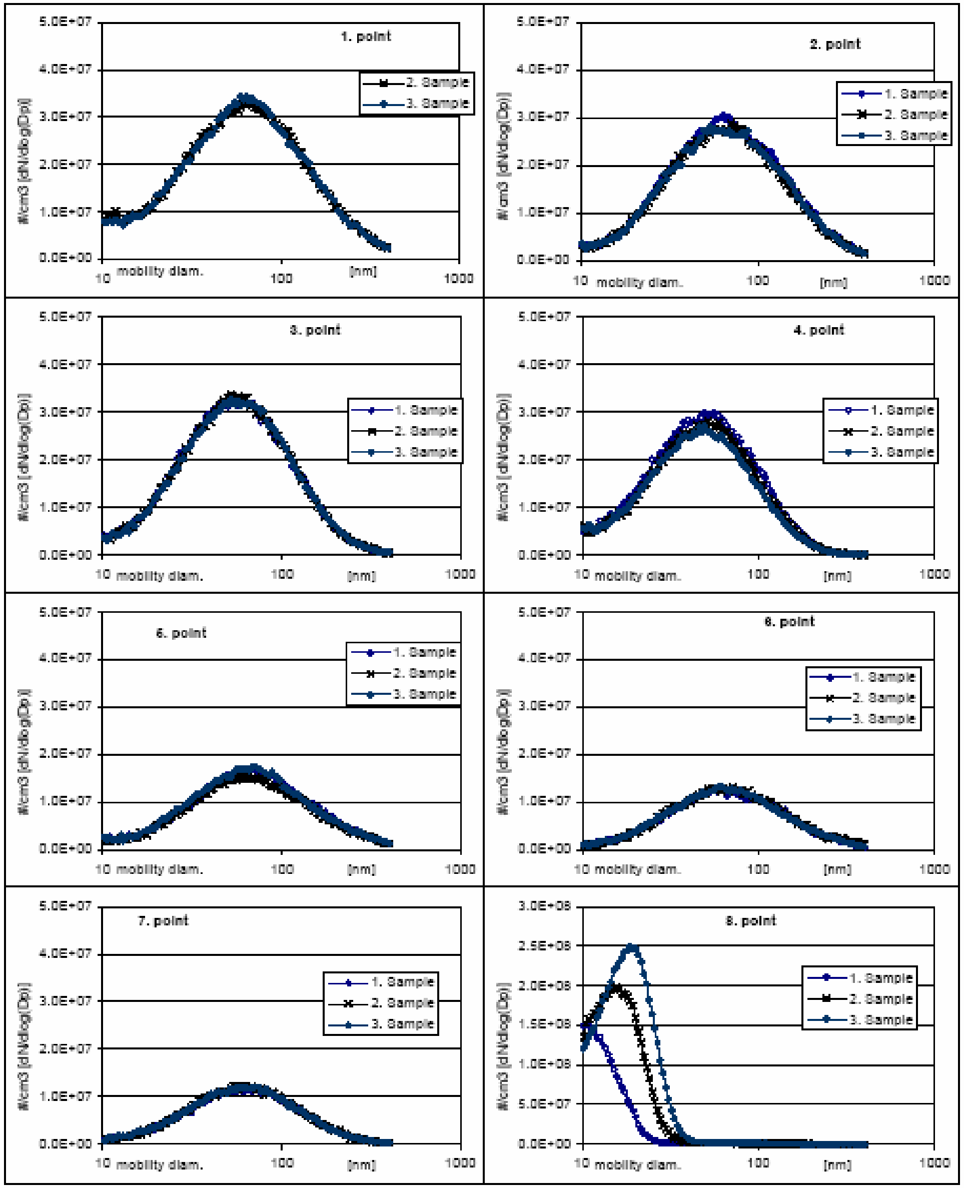
Double-LNDF Fit of a Bimodal Particle Distribution OP8 (idle) compared to 50%load of case A w/o DPF

	OP 8 = Idle	OP 5 = 50% load
N tot [1/cc]	1.46E+07	1.80E+07
N ash [1/cc]	1.37E+07	-
N soot [1/cc]	8.56E+05	1.80E+07
D ash [nm]	11.8	-
D soot [nm]	48.3	61.1



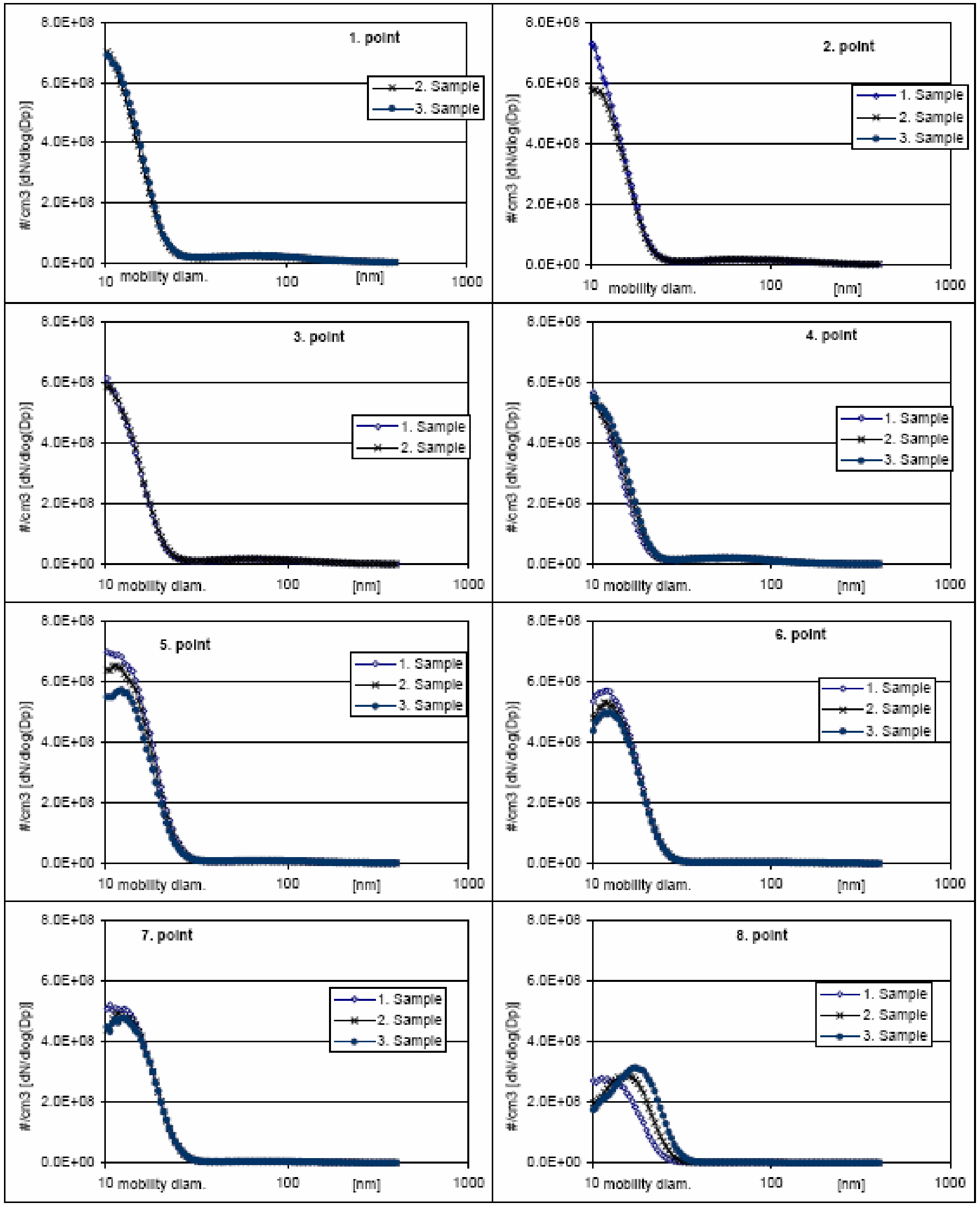
Case A:

Penetration at
the 8 operating points
of the coated filter



Case B:

Baseline LH 914 without DPF and without FBC

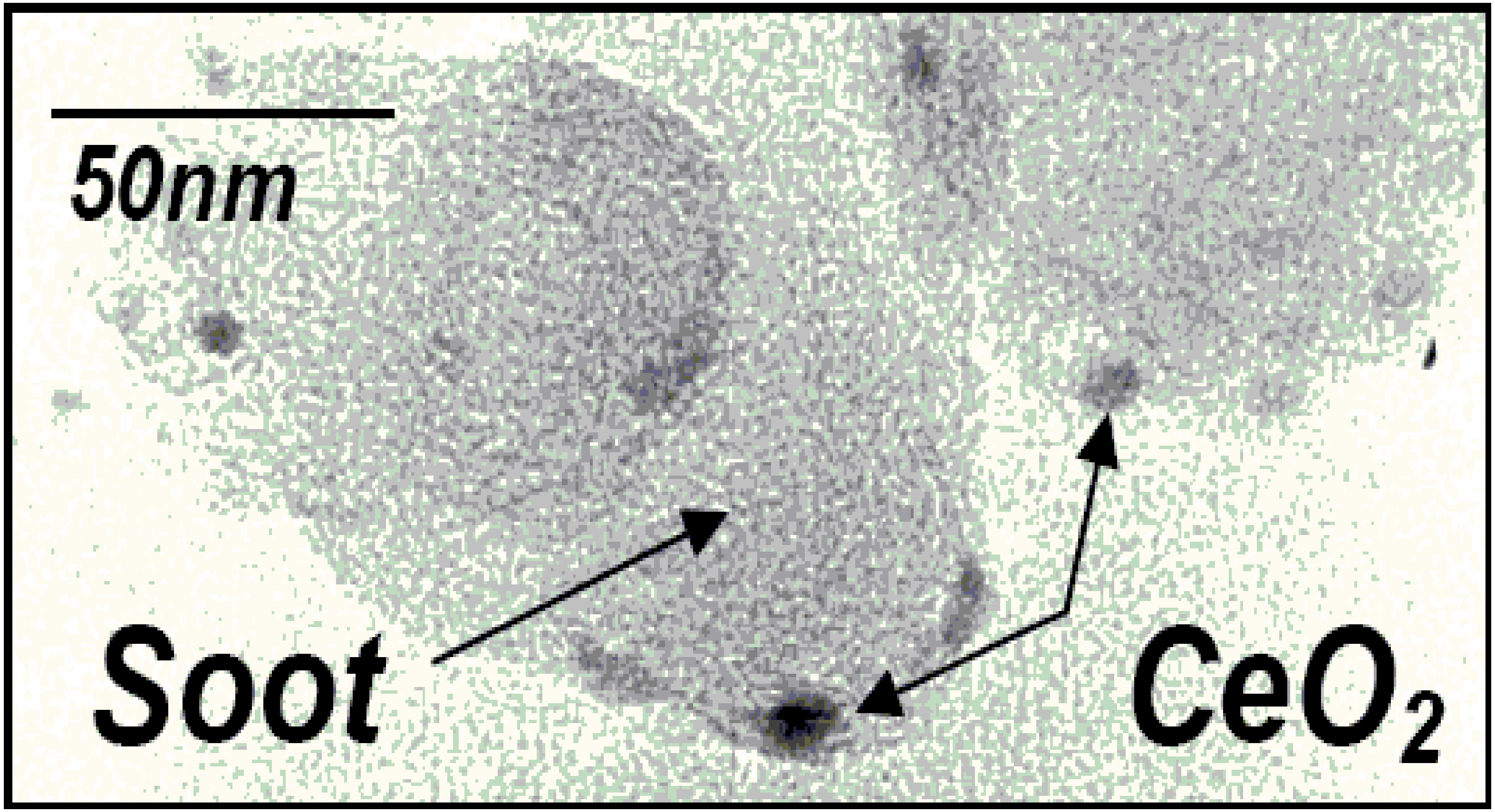


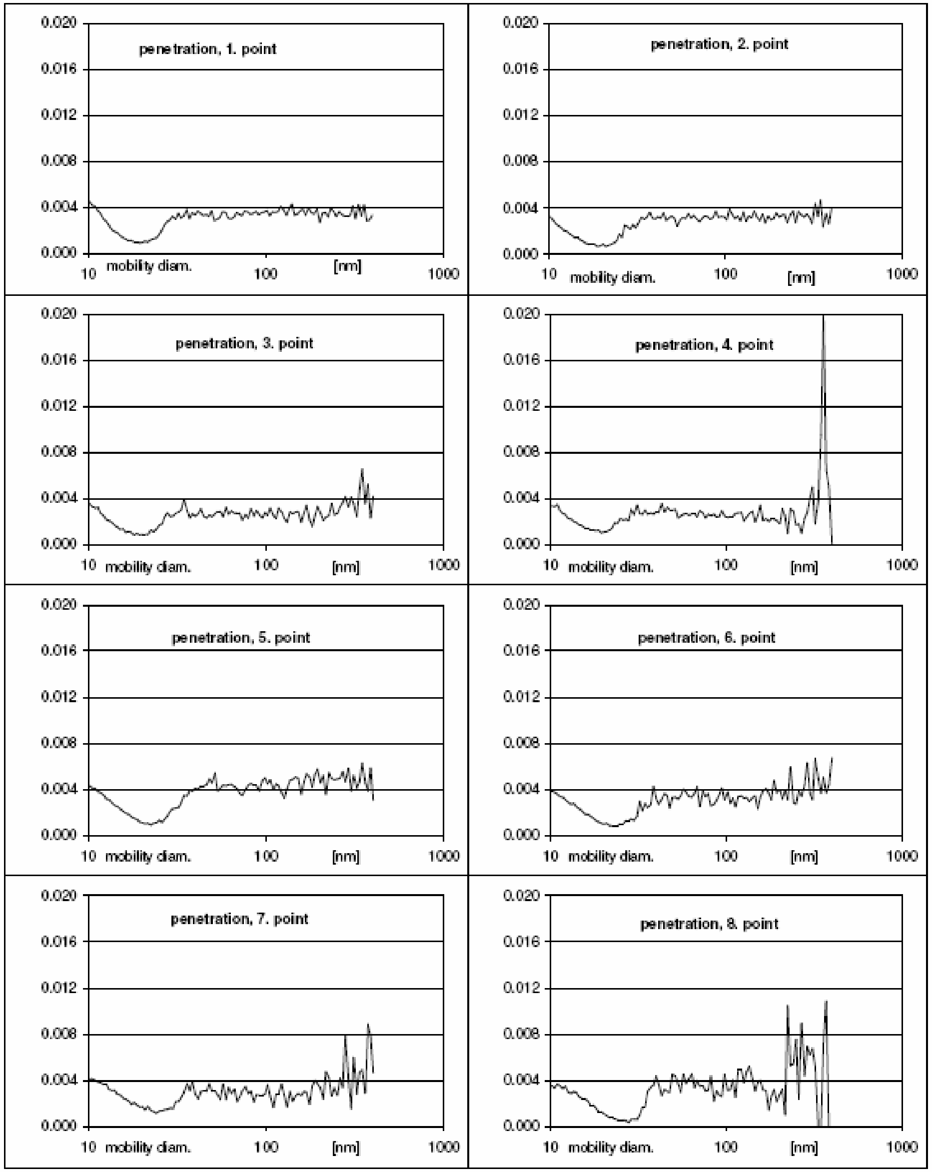
Case B:

without DPF
and with FBC
at 40 ppm Fe + Sr

Cerium oxide FBC on soot particles

source:Rhodia





Case B:

with DPF and FBC

PN-Penetration

Comparison

PN downstream filter

to PN upstream filter.

A – LH 924 – without DPF – ISO 8178

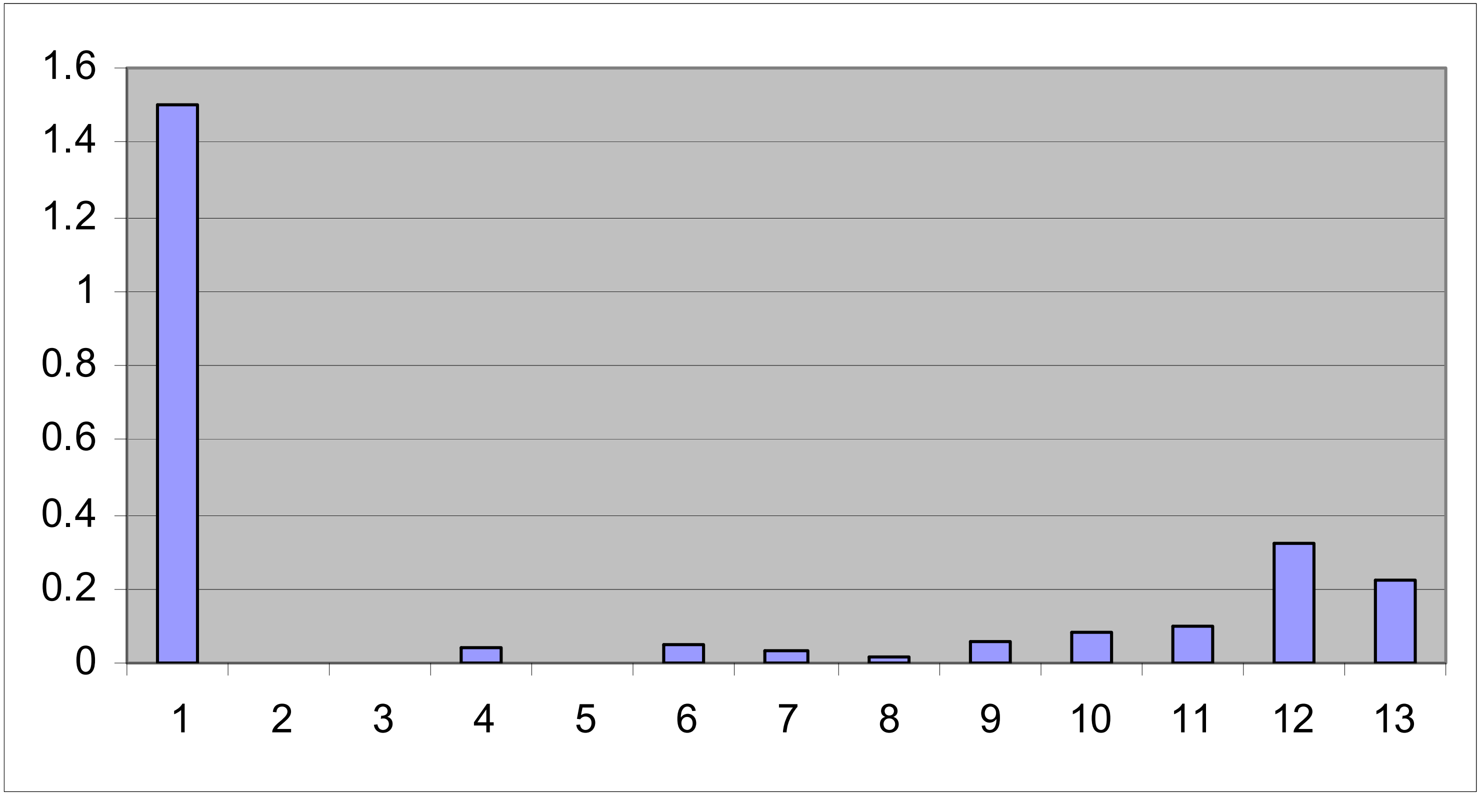
ELPI Stages	Size class D50%	Fe	Ni	Zn	Ca	Rh	Pt
	[µm]	[µg/stage]	[µg/stage]	[µg/stage]	[µg/stage]	[µg/stage]	[µg/stage]
Backup stage	< 0.03	1.4	0.0119	2.04	7.3	<DL	0.00004
1	0.03	0.14	0.014	0.36	8.7	0.00002	0.00012
2	0.06	0.08	0.012	0.57	8.6	0.00001	0.00005
3	0.11	0.08	0.010	0.22	2.9	0.00001	0.00004
4	0.17	0.03	0.009	0.17	2.4	0.00001	0.00005
5	0.27	0.11	0.028	0.22	3.6	<DL	0.00002
6	0.41	0.26	0.042	0.25	4.5	<DL	0.00005
7	0.66	0.09	0.011	0.19	2.1	<DL	0.00005
8	1.02	0.08	0.011	0.17	3.0	<DL	0.00006
9	1.65	0.12	0.011	0.39	9.5	0.00001	0.00016
10	2.52	1.06	0.150	0.14	4.4	<DL	0.00004
11	4.08	0.15	0.018	0.41	11.5	0.00002	0.00004
12	6.56	0.22	0.014	0.22	5.6	0.00001	0.00003
Sum with blanks		**3.82**	**0.34**	**5.37**	**73.1**	**0.00009**	**0.00075**

A – LH 924 – without DPF – Idle

ELPI Stages	Size class D50%	Fe	Ni	Zn	Ca	Rh	Pt
	[µm]	[µg/stage]	[µg/stage]	[µg/stage]	[µg/stage]	[µg/stage]	[µg/stage]
Backup stage	<0.03	1.5	0.030	1.36	5.7	<DL	0.00007
1	0.03	<DL	0.007	0.27	2.4	<DL	0.00008
2	0.06	<DL	0.007	0.21	2.2	<DL	0.00005
3	0.11	0.04	0.023	0.07	1.5	0.00008	0.00003
4	0.17	<DL	0.004	0.28	5.9	0.00001	0.00002
5	0.27	0.05	0.010	0.16	4.0	0.00001	0.00006
6	0.41	0.03	0.008	0.06	1.0	0.00001	0.00002
7	0.66	0.02	0.012	0.12	2.5	0.00004	0.00032
8	1.02	0.06	0.010	0.23	5.1	0.00001	<DL
9	1.65	0.08	0.009	0.19	3.4	<DL	0.00002
10	2.52	0.10	0.015	0.25	4.4	<DL	0.00003
11	4.08	0.32	0.014	0.33	5.8	0.00001	0.00001
12	6.56	0.22	0.014	0.18	2.8	<DL	<DL
Sum with blanks		**2.42**	**0.136**	**3.69**	**46.7**	**0.00016**	**0.00071**

Fe-mass size-specific for 13 ELPI-stages
Case A – without DPF – not corrected for blancs

Idle only
operation point 8



Case A: metal analysis corrected for blanks

blue: all sizes

red: < 60 nm

µg / Test	Fe	Ni	Zn	Ca
without DPF ISO 8178 < 60 nm	1.21 0.3	0.15 ND	1.87 1.43	45.3 15.8
with DPF ISO 8178 < 60 nm	0.03 < DL	0.05 0.005	0.22 0.04	25.6 5.2
without DPF Idle < 60 nm	0.92 0.83	0.02 0.016	0.78 0.49	26.2 3.15

Case B: metal analysis corrected for blanks

blue: all sizes

red: < 60 nm

mg/kWh – ISO 8178	Fe	Sr
Baseline w/o FBC	0.078	0.001
< 60 nm	0.023	0.000
Baseline with FBC	2.48	0.613
< 60 nm	1.34	0.333
with DPF and FBC	0.091	0.005
Penetration %	*3.6*	*0.8 %*
< 60nm	0.016	0.001
Penetration %	*1.22*	*0.4*

Filter-Ash of 3 DPF
analysed after 1000 operation hours

%	Filter A + DOC (Pt)	Filter B Pt-coated	Filter C
S	9.5	12.9	1.8
Ca	11	17	4.5
Zn	4.7 → 0.2 mg/kWh	4.9	1.2
Fe	0.3	0.24	1.33
Cu	0.14	0.05	0.11
Al	1.0	0.1	0.3
Cr	0.12	0.03	0.15
Ni	0.08	0.002	0.03
Pt	0.005 → 200 ng/kWh	0.0003	0.00001

Particle Mass converted to Particle Number

Assuming spherical particles

1 Particle 100 nm has a mass of 10^{-15} g = 1 Femtogramm

1 Particle 20 nm has a mass of 10^{-17} g

	1mg / kWh	0.1mg / kWh
100 nm	10^{12}/ kWh	10^{11}/ kWh
20 nm	10^{14}/ kWh	10^{13}/ kWh

Compare to : EURO VI : < 0.6 x10^{12} / kWh of > 23 nm

Conclusions

- Internal combustion engines emit metal oxide particles from engine wear and lubrication oil packages
- Most metal oxides are more toxic than EC (soot)
- Emission can be 0.1-1 mg/km → 10^8 #/cc → 10^{14} #/kWh
- Size around 20 nm, insoluble and toxic
- → **health concern is justified**

Measures:

- deploy highly efficient particle filter systems on all ICE
- diminish the metal content of the lubrication oil
- extend PN-measurement to particle sizes < 23 nm

→ Further research needed for SI and CNG engine metal oxide particle emissions and their toxicity